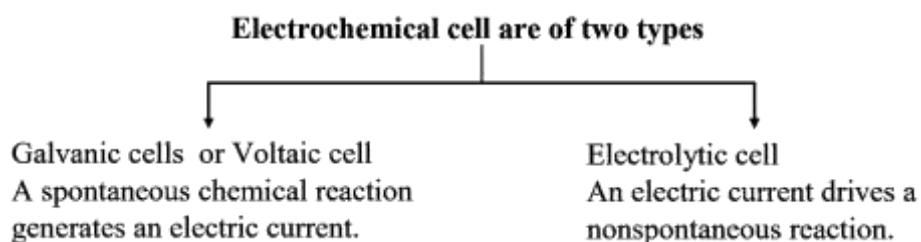## 1.   INTRODUCTION

Chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously.

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are eco friendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

ELECTROCHEMICAL CELL:

If a metal electrode is immersed in an aqueous solution containing cations of that metal, an equilibrium that leads to negative charge formation on the electrode is established. This configuration of electrode and solution is called a half-cell. Two half-cells can be combined to form an electrochemical cell. The equilibrium condition in an electrochemical cell is that the electrochemical potential, rather than the chemical potential, of a species is the same in all parts of the cell. The electrochemical potential can be changed through the application of an electrical potential external to the cell. This allows the direction of spontaneous change in the cell reaction to be reversed. Electrochemical cells can be used to determine the equilibrium constant for the cell reaction. Electrochemical cells can also be used to provide power, in which case they are called batteries. Electrochemical cells in which the reactants can be supplied continuously are called fuel cells.

Electrochemical cell are of two types

Galvanic cells or Voltaic cell
A spontaneous chemical reaction generates an electric current.

Electrolytic cell
An electric current drives a nonspontaneous reaction.

Thus the two types of cells are reverse of each other.

2. GALVANIC CELL OR VOLTAIC CELL:

A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

2.1 Constriction of galvanic cell:

Anode: Some metals (which are reactive) are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions. For example: Zn rod is placed in $ZnSO_4$ solution.
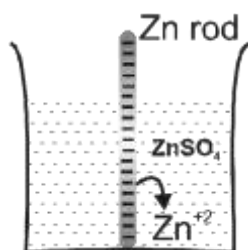
If a Zn electrode is partially immersed in an aqueous solution of $ZnSO_4$, an equilibrium is established between $Zn(s)$ and $Zn^{2+}(aq)$ as a small amount of the Zn goes into solution as $Zn^{2+}(aq)$ ions as depicted in above figure. $Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$

However, the electrons remain on the Zn electrode. Therefore, a negative charge builds up on the Zn electrode, and a corresponding positive charge builds up in the surrounding solution. This charging leads to a difference in the electrical potential between the electrode and the solution, which we call the half-cell potential or electrode potential. This particular electrode is known as anode.

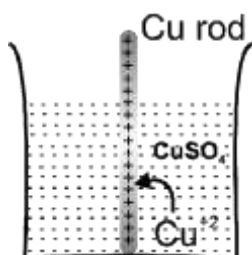On anode oxidation will take place. (release of electrons).

To act as source of electrons.

It is of negative polarity.

The electrode potential is represented by $E_{Zn(s)/Zn^{2+}(aq.)}$

Cathode:

Some metals (Cu, Ag, Au etc.,) are found to have the opposite tendency i.e., when placed in contact with their aqueous ions, the ions from the solution will get deposited on the metal rod.

The following equilibrium will be established: $Cu^{2+} + 2e^- \rightleftarrows Cu(s)$.

So rod will have deficiency of electron (positive charge). Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as half cell potential or electrode potential. This will be known as cathode.

At cathode reduction will take place. (gain of electrons will take place)

To act as sink of electron.

Positive polarity will be developed.

Their electrode potential can be represented by : $ECu^{2+}(aq.)/Cu(s)$

Anode: $\begin{cases} \text{Is where oxidation occurs} \\ \text{Is where electrons are produced} \\ \text{Has a negative sign} \end{cases}$ Cathode: $\begin{cases} \text{Is where reduction occurs} \\ \text{Is where electrons are consumed} \\ \text{Has a positive sign} \end{cases}$

Half-cell potentials cannot be measured directly. They are measured relative to one another rather than absolutely. To understand how this is done, it is useful to consider an **electrochemical cell**, which consists of two half-cells, such as the one shown figure. This particular cell is known as the **Daniell cell**, after its inventor. On the left, a Zn electrode is immersed in a solution of $ZnSO_4(aq)$. The solute is completely dissociated of CuSO4, which is completely dissociated to form $Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$. The two half-cells are connected by an ionic conductor known as a salt bridge. The salt bridge consists of an electrolyte such as KCl suspended in a gel. A salt bridge allows current to flow between the half-cells while preventing the mixing of the solutions. A metal wire fastened to each electrode allows the electron current to flow through the external part of the circuit.
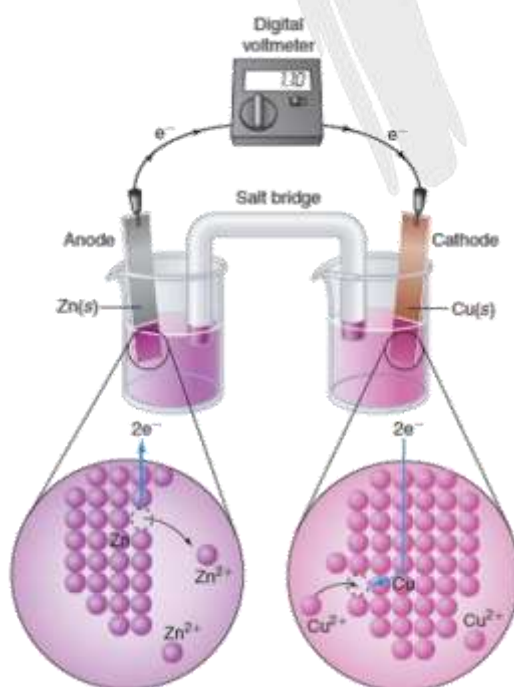
2.2 Salt bridge:

A **salt bridge** is a U-shaped inverted tube that contains a gel permeated with an inert electrolyte. Generally tube is filled with a paste of agar-agar powder with a natural electrolyte/generally not common to anodic/cathodic compartment with porous plugs at each mouth of tube. The ions of the inert electrolyte do not react with other ion in the solution and the ions are not oxidised or reduced at the electrodes.

The electrolyte in salt bridge should be such that speed of it's cation equals speed of it's anion in electrical field. For that charge and sign of the ions should be almost equal i.e. Mobility of cation = Mobility of anion

KCl is generally preferred but KNO_3 or NH_4NO_3 can also be used.

If $Ag^+, Hg_2^{2+}, Pb^{2+}, Tl^+$ ions are present in a cell then in salt bridge KCl is not used because there can be formation of precipitate of $AgCl, Hg_2Cl_2, PbCl_2$ or $TlCl$ at mouth of tube which will prevent the migration of ions and its functioning will stop.

Functions of Salt Bridge:

(i) It connects the solution of two half cell to complete the circuit.

(ii) It minimize the liquid junction potential. The potential difference between the junction of two liquids. **(Liquid-Liquid Junction Potential:** The potential difference which arises between two solutions (during the progress of reaction) when in contact with each other.)

(iii) It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.

"The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.

(iv) If the salt bridge is removed then voltage drops to zero.

(v) It prevents mechanical mixing of two electrolytic solution.

2.3 Shorthand Notation for Galvanic Cells

We require two half cells to produce an electrochemical cell, which can be represented by following few rules;

The anode half-cell is always written on the left followed on the right by cathode half cell.
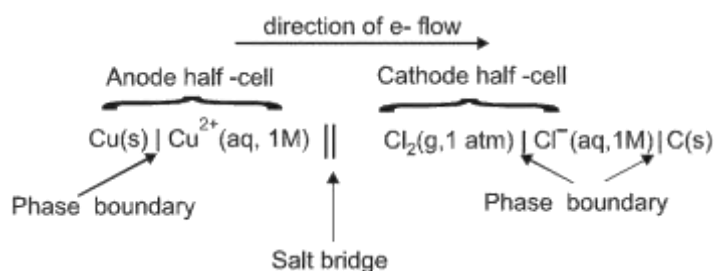
The separation of two phases (state of matter) is shown by a vertical line.

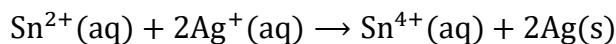The various materials present in the same phase are shown together using commas. The salt bridge is represented by a double slash (∥).

The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.

For a gas electrode, the gas is indicated after the electrode for anode and before the

electrode in case of cathode. (i.e PtH_2/H^+ or H^+/H_2Pt)

direction of e- flow

Anode half -cell   Cathode half -cell

$Cu(s)\,|\,Cu^{2+}(aq,\,1M)\;\|\; Cl_2(g,1\,atm)\,|\,Cl^-(aq,1M)\,|\,C(s)$
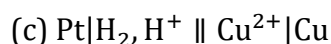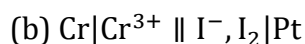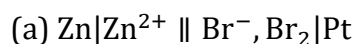
Phase boundary   Phase boundary

Salt bridge

Ex.1 Write short hand notation for the following reaction,

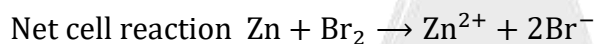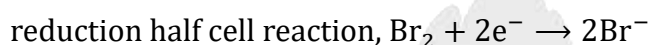$$Sn^{2+}(aq) + 2Ag^+(aq) \longrightarrow Sn^{4+}(aq) + 2Ag(s)$$

Sol. The cell consists of a platinum wire anode dipping into an Sn^{+2} solution and a silver cathode dipping into an Ag^+ solution therefore
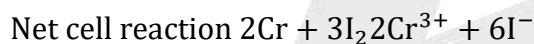
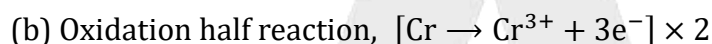$Pt\,(s)|Sn^{2+}(aq), Sn^{4+}(aq) \parallel Ag^+(aq)|Ag(s)$.
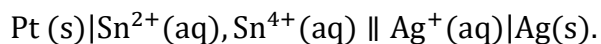
Ex.2 Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell ?
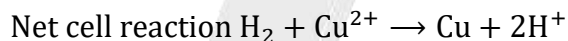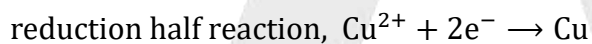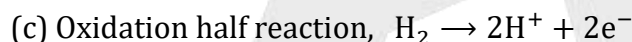
(a) $Zn|Zn^{2+} \parallel Br^-, Br_2|Pt$ (b) $Cr|Cr^{3+} \parallel I^-, I_2|Pt$

(c) $Pt|H_2, H^+ \parallel Cu^{2+}|Cu$ (d) $Cd|Cd^{2+} \parallel Cl^-, AgCl|Ag$

Sol. (a) Oxidation half cell reaction, $Zn \longrightarrow Zn^{2+} + 2e^-$

reduction half cell reaction, $Br_2 + 2e^- \longrightarrow 2Br^-$

Net cell reaction $Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^-$

(Positive terminal: cathode Pt)

(b) Oxidation half reaction, $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

reduction half reaction, $[I_2 + 2e^- \longrightarrow 2I^-] \times 3$

Net cell reaction $2Cr + 3I_2 \, 2Cr^{3+} + 6I^-$

(Positive terminal: cathode Pt)

(c) Oxidation half reaction, $H_2 \longrightarrow 2H^+ + 2e^-$

reduction half reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction $H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$

(Positive terminal: cathode Cu)

(d) Oxidation half reaction, $Cd \longrightarrow Cd^{2+} + 2e^-$

reduction half reaction, $[AgCl + e^- \, Ag + Cl^-] \times 2$

Net cell reaction $Cd + 2AgCl \, Cd^{2+} + 2Ag + 2Cl^-$
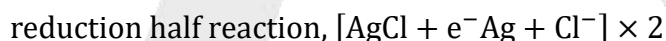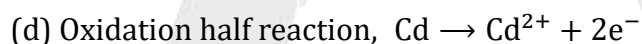
(Positive terminal: cathode Ag)

2.4   **Half cell potential/ Electrode Potential:**

The potential difference developed between metal electrode and its ions in solution in known as electrode potential.

The potential difference developed between metal electrodes and the solution in standard conditions (i.e. 1M concentration of its ions at 1 bar pressure and at a particular temperature) is known as standard electrode potential. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials Two types of oxidation potentials:

Standard Oxidation Potential(SOP) :	Reduction Potential (R.P.)
The electrode potential for oxidation half reaction	The electrode potential for half reduction half reaction
Greater is the SOP, greater will be tendency to get oxidized in standard conditions.	Greater is the R.P. greater will be tendency to get reduced in standard conditions.

	Type of Electrode	Half reaction	Representation
1.	Metal electrode (Zn electrode, Cu electrode etc.)	Reduction : $Zn^{2+} + 2e^- \rightarrow Zn(s)$ Oxidation : $Zn(s) \rightarrow Zn^{2+} + 2e^-$	$E^0_{Zn^{2+}/Zn(s)}$ (SRP) $E^0_{Zn(s/Zn^{2+}}$ (SOP)
2	Hydrogen peroxide electrode	Reduction : $2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$ Oxidation : $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	$E^0_{H_2O_2/H_2O}$(SRP) $E^0_{H_2O_2/O_2}$(SOP)
3.	Redox electrode	Reduction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$E^0_{MnO_4^-/Mn^{2+}}$(SRP)

2.3 Free energy changes for cell reaction:

The free energy change ΔG (a thermochemical quantity) and the cell potential E (an electrochemical quantity) both measure the driving force of a chemical reaction.

The values of ΔG and E are directly proportional and are related by the equation, $\Delta G = -nFE$

where n = Number of moles of electron transferred in the reaction.

F = Faraday constant = $96485C/mole^-$

2.4 Cell potential:

The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (emf) of the cell when no current is drawn through the cell.

The emf of the cell or cell potential can be calculated from the values of electrode potential of the two half cell constituting the cell. The following three method are in use:

(i) When oxidation potential of anode and reduction potential of cathode are taken into account:

E_{cell} = oxidation potential of anode + reduction potential of cathode
= E_{ox} (anode) + E_{red} (cathode)

In standard conditions

E^0_{cell} = SOP of anode + SRP of cathode

$E^0_{cell} = E^0_{ox}$ (anode) + E^0_{red} (cathode)

(ii) When reduction potential of both electrodes are taken into account:

E_{cell} = Reduction potential of cathode − Reduction potential of anode
= E_{red} (cathode) − E_{red} (anode)

In standard conditions

E_{cell}^0 = SRP of cathode + SRP of anode

$$E_{cell}^0 = E_{red}^0 \text{ (cathode)} - E_{red}^0 \text{ (anode)}$$

E_{cell}° is intensive property so on multiplying/Dividing cell reaction by any number, the E_{cell}° value would not change.

2.4.1 Measurement of Electrode Potential:

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode (Reference electrode) is assigned a zero potential at all temperatures corresponding to the reaction

$$2H^+(aq, 1M) + 2e^- \longrightarrow H_2(g, 1 \text{ bar}) \qquad E_{H^+/H_2}^0 = 0 \text{ V}$$

$$H_2(g, 1 \text{ bar}) \longrightarrow 2H^+(aq, 1M) + 2e^- \qquad E_{H_2/H^+}^0 = 0 \text{ V}$$
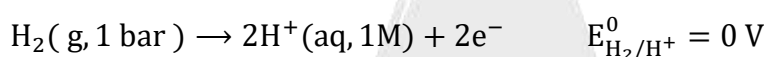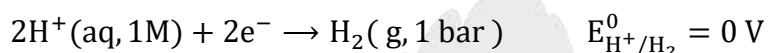
$$\Delta_f G^0[H^+(aq.)] = 0$$

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. To achieve equilibrium on a short timescale, this reaction $2H^+ + 2e^- \longrightarrow H_2$ is carried out over a **platinum black catalyst** electrode.

The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity. This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

At 298 K the emf of the cell, standard hydrogen electrode with second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential,

$$E_{cell}^0 = (E_{ox}^0)_{SHE} + (E_{red}^0)_{Elactrode}$$

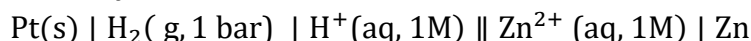$$E_{cell}^0 = 0 + (E_{red}^0)_{Electrode} = (E_{red}^0)_{Electrode}$$
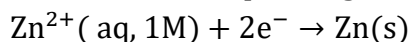
The measured emf of the cell:

Pt (s) | H_2 (g, 1 bar) | H^+(aq, 1M) ‖ Cu^{2+} (aq, 1M) | Cu

is 0.34 V and it is also the value for the standard electrode potential of the half - cell corresponding to the reaction:

Cu^{2+}(aq, 1M) $+ 2e^- \rightarrow Cu(s)$
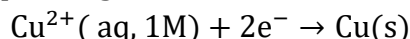
Similarly, the measured emf of the cell:

Pt(s) | H_2(g, 1 bar) | H^+(aq, 1M) ‖ Zn^{2+} (aq, 1M) | Zn

is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

Zn^{2+}(aq, 1M) $+ 2e^- \rightarrow Zn(s)$

The positive value of the standard electrode potential in the first case indicates that Cu^{2+} ions get reduced more easily than H + ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidize Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion. The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidise zinc (or zinc can reduce hydrogen ions).

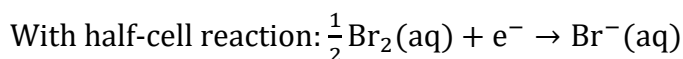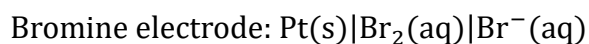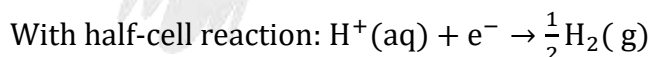In view of this convention, the half reaction for the Daniell cell in Fig. 3.1 can be written as:
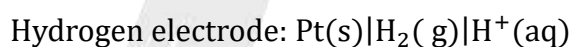
Left electrode : $Zn(s) \rightarrow Zn^{2+}(aq, 1M) + 2e^-$

Right electrode : Cu^{2+}(aq, 1M) $+ 2e^- \rightarrow Cu(s)$
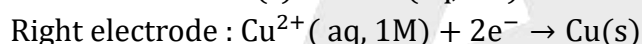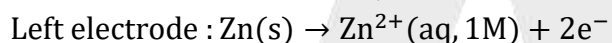
The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

emf of the cell $= E^0_{cell} = E^0_R - E^0_L$
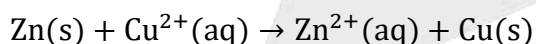
$= 0.34$ V $- (-0.76)$V $= 1.10$ V

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons.

For example, Pt is used in the following half - cells:

Hydrogen electrode: $Pt(s)|H_2(g)|H^+(aq)$

With half-cell reaction: $H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$

Bromine electrode: $Pt(s)|Br_2(aq)|Br^-(aq)$

With half-cell reaction: $\frac{1}{2}Br_2(aq) + e^- \rightarrow Br^-(aq)$

The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species. It can be seen that the standard electrode potential for fluorine is the highest in the Table indicating that fluorine gas (F_2) has the maximum tendency to get reduced

to fluoride ions (F) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution. It may be seen that as we go from top to bottom in Table the standard electrode potential decreases and with this, decreases the oxidizing power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Electrochemical cells are extensively used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

Electrode	Reaction	SRP (at 298 K)
* Li	$Li^+ + e^- \rightarrow Li(s)$	– 3.05 V
K	$K^+ + e^- \rightarrow K(s)$	– 2.93 V
Ba		
Ca	$Ca^{+2} + 2e^- \rightarrow Ca(s)$	– 2.87 V
Na	$Na^+ + e^- \rightarrow Na(s)$	– 2.71 V
Mg	$Mg^{+2} + 2e^- \rightarrow Mg(s)$	– 2.71 V
Al		
*Electrolytes (H_2O)	$H_2O(l) + e^- \rightarrow H_2 + OH^-$	– 0.828 V
Zn	$Zn^{+2} + 2e^- \rightarrow Zn(s)$	– 0.76 V
Cr	$Cr^{+3} + 3e^- \rightarrow Cr(s)$	– 0.74 V
*Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	– 0.44 V
Cd	$Cd^{+2} + 2e^- \rightarrow Cd(s)$	– 0.41 V
Co		
Ni	$Ni^{+2} + 2e^- \rightarrow Ni(s)$	– 0.24V
Sn	$Sn^{+2} + 2e^- \rightarrow Sn(s)$	– 0.14 V
Pb	$Pb^{+2} + 2e^- \rightarrow Pb(s)$	– 0.13 V
*H_2	$2H^+ + 2e^- \rightarrow H_2(g)$	– 0.00 V
Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	– 0.34 V
I_2		
Fe	$Fe^{3+} + e^- \rightarrow Fe$	– 0.77V
Hg	$Hg_2^{2+} + 2e^- \rightarrow Hg(l)$	– 0.79 V
Ag	$Ag^+ + e^- \rightarrow Ag$	– 0.80 V
Hg	$Hg^{2+} \rightarrow Hg(l)$	– 0.85 V
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	– 1.06 V

Left arrow label: Increasing strength of reducing agent

Right arrow label: Increasing strength of oxidising agent

Electrochemical Series :

* Electrolytes $O_2 + 2H^+ + 2e^- \rightarrow H_2O(\ell)$ 1.23 V
* $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$ 1.33 V
* $Cl_2 Cl_2 + 2e^- \rightarrow 2Cl^-$ 1.36 V
* $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 1.51 V
* $F_2 + 2e^- \rightarrow 2 F^-$ 2.87 V

Ex.3 Calculate E_{cell}^0 of (at 298 K), $Zn(s)/ZnSO_4(aq) \parallel CuSO_4(aq)/Cu(s)$ given that

$E_{Zn/Zn^2 (aq)}^0 = 0.76 \text{ V}, E_{Cu(s)/Cu^0 2 (aq)}^0 = -0.34 \text{ V}$

Sol. $E_{cell}^0 = (S.R.P)_{cathode} - (S.R.P)_{anode}$

$= 0.34 - (-0.76) = 1.1 \text{ V}$

Ex.4 Given the cell $AgAgCl(s)|NaCl(0.05M) \parallel AgNO_3(0.30M)|Ag$

(a) Write half reaction occurring at the anode.

(b) Write half reaction occurring at the cathode.

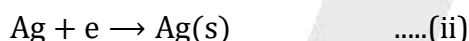(c) Write the net ionic equation of the reaction.

(d) calculate E_{cell}° at 25°C.

(e) Does the cell reaction go spontaneous as written ?

(Given $E_{AgCl,Cl}^\circ = +0.22 \text{ volt}$) ; $E_{Ag^+/Ag}^0 = +0.80 \text{ volt}$)

Sol. (a) LHS electrode is anode and half reaction is oxidation.

$Ag^+ + Cl^- \longrightarrow AgCl(s) + e^-$ .....(i)

(b) RHS electrode is cathode and half reaction is reduction.

$Ag + e \longrightarrow Ag(s)$ .....(ii)

(c) From equation (i) and (ii) cell reaction is : $Cl^-(0.05M) + Ag^+(0.30M) \longrightarrow AgCl(s)$

(d) $E_{cell}^\circ = E_{right}^\circ - E_{left}^\circ = (0.80 - 0.22 \text{ volt} = 0.58 \text{ volt}$
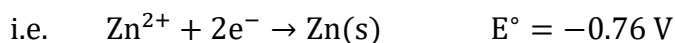
(e) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell eaction.

2.4.2 Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.

(i) Obtain the reaction of the 3rd electrode with the help of some algebraic operations on reactions of the given electrodes.

(ii) Then calculate ΔG° of the 3rd reaction with the help of some algebaric operations of ΔG^0 of 1st and 2nd reactions.
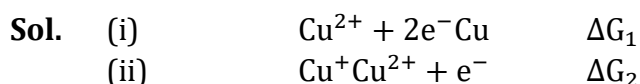
E_{cell}^0 is intensive property so if we multiply/divide electrode reaction by any number the E_{cell}^0 value would not changed

i.e. $Zn^{2+} + 2e^- \rightarrow Zn(s)$ $E^\circ = -0.76 \text{ V}$

Multiply by 2

$2Zn^{2+} + 4e^- \rightarrow 2Zn(s)$ $E^\circ = -0.76 \text{ V (remain same)}$

Ex.5   Given that $E^0_{Cu^{2+}/Cu} = 0.337$ V and $E^0_{Cu^+/Cu^{2+}} = -0.153$ V. Then calculate $E^0_{Cu^+/Cu}$.

Sol.   (i) $Cu^{2+} + 2e^- Cu$ ΔG_1

       (ii) $Cu^+ Cu^{2+} + e^-$ ΔG_2

       after adding $Cu^+ + e^- \rightarrow Cu$

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

                   $-2FE^0_1 - FE^0_2 = -FE^0_3$

                   $E_3 = 2E^0_1 + E^0_2$

                   $= 2 \times 0.337 - 0.153$

                   $= 0.674 - 0.153 = 0.521$ V

Ex. 6 $E^0_{Mn^{2+}/MnO_4^-} = -1.51$ V

         $E^0_{MnO_2/Mn^{+2}} = +1.23$ V

         $E^0_{MnO_4^-/MnO_2} = ?$ (All in acidic medium)

Sol. $4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e^- \;\; \Delta G_1$

       (i) $MnO_4^- + 8H^+ + 5e^- \rightarrow 4H_2O + Mn^{2+}$ $-\Delta G_1$

       $2e^- + MnO_2 + 4H^+ \rightarrow Mn^{2+} + 2H_2O$ ΔG_2

       (ii) $2H_2O + Mn^{2+} \rightarrow MnO_2 + 4H^+ + 2e^-$ $-\Delta G_2$

       (iii) $4H^+ + MnO_4^- + 3e^- \rightarrow MnO_2 + 2H_2O \;\; \Delta G_3$
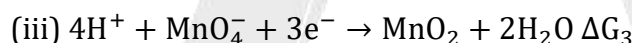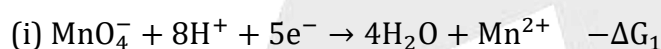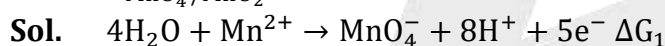
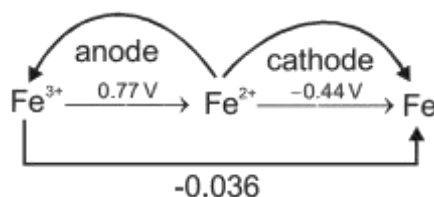   (i) $+$ (ii) $=$ (iii)

       $\Delta G_3 = -\Delta G_1 - \Delta G_2$

       $-3E_3\, F = 5E^0_1\, F + 2E^0_2\, F$

       $E = \dfrac{-[5E_1 + 2E_2]}{3} = \dfrac{-[5(-1.51)+2(1.23)]}{3} = \dfrac{-[-7.55+2.46]}{3} = \dfrac{+5.09}{3} = 1.69$ V

Ex.7   Will Fe^{2+} disproportionate or not

Sol.   This is known as **Latimer diagram**.

       S.R.P to right of the species greater than SRP of its left species will undergo disproportionation.

2.5   NERNST EQUATION:

Cell potentials depend on temperature and on the composition of the reaction mixtures. It depends upon the concentration of the solute and the partial pressure of the gas, if any. The dependence upon the concentration can be derived from thermodynamics. From thermodynamics

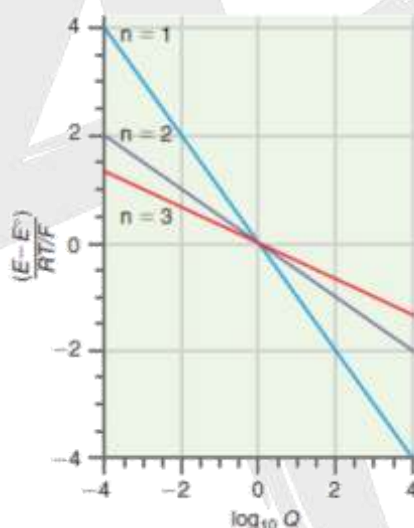$$\Delta G = \Delta G° + RTln\ Q$$
$$-nFE = -nFE° + 2.303RTlog\ Q$$
$$E = E° - \frac{2.303RT}{nF}log\ Q$$

Take $T = 298\ K, R = 8.314\ J/molK, F = 96500C$
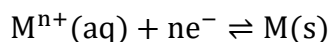
Now we get, $E = E° - \frac{0.059}{n}log\ Q$

Where n = number of transfered electron, Q = reaction quotient

- Nernst equation can be used to calculate cell potentials for non standard conditions also.

- Nernst equations can be applied to half cell reactions also.
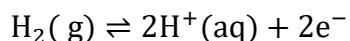

Applications of Nernst equation

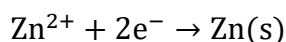### 2.5.1   Nernst Equation for Electrode Potential

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

$$E_{Red} = E_{red}^0 - \frac{RT}{nF}/n\left[\frac{M(s)}{M^{n+}}\right]$$

$$E_{Red} = E_{red}^0 - \frac{2.303RT}{nF}log\left[\frac{M(s)}{M^{n+}}\right]$$

at 298 K, $E_{Red} = E_{Red^n}^0 - \frac{0.059}{n}log\left[\frac{1}{M^{n+}}\right]$

Hydrogen Electrode

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

$$E = E^0 - \frac{0.0591}{2}\log\left[\frac{(H^+)^2}{P_{H_2}}\right]$$

Metal-metal soluble salt electrode.

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

$$E_{Red} = E^0_{Red^n} - \frac{2.303RT}{nF}\log\left(\frac{1}{Zn^{+2}}\right) \text{ at } 298 \text{ K}$$

$$E_{Red} = E^0_{red} - \frac{0.059}{2}\log\left(\frac{1}{Zn^{+2}}\right)$$

Gas - electrode Hydrogen electrode.

$$2H^+ + 2e^- \rightarrow H_2(g)$$
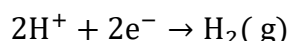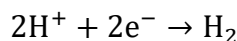
$$E_{Redn} = E^0_{Red^n} - \frac{0.059}{2}\log\left(\frac{P_{H_2}}{[H^+]^2}\right)$$

Redox electrode

$$4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e^-$$

$$E_{OX} = E^0_{ox} - \frac{0.059}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{+2}]}$$

Ex.8 Calculate R.P. of hydrogen electrode at 298 K which is prepared with the help of aq. solution of acetic acid with 0.1M concentration at 1 atm pressure $Ka = 1.8 \times 10^{-5}$.

Sol. $[H^+] = \sqrt{Ka \times c} = \sqrt{1.8 \times 10^{-5} \times 10^{-1}} = \sqrt{1.8 \times 10^{-6}}$

$2H^+ + 2e^- \rightarrow H_2$

$E_{Redn} = E^0_{red} - \frac{0.059}{2}\log\frac{P_{H_2}}{[H^+]^2}$ $\left(E^0_{Redn} = 0\right)$

$E_{Redn} = -\frac{0.059}{2}\log\left(\frac{1}{1.8 \times 10^{-6}}\right) = -\frac{0.059}{2}[6 - \log(1.8)]$

$E_{Redn} = -\frac{0.059}{2} \times 5.74 = -0.169 \text{ V}$

Ex.9 Which is stronger oxidizing agent

(i) $K_2Cr_2O_7$ in solution in which

$[Cr_2O_7^{2-}] = 0.1M, [Cr^{3+}] = 10^{-2}M$ and $[H^+] = 10^{-1}M$

(ii) $KMnO_4$ in a solution in which

$[MnO_4^-] = 10^{-1}M, [Mn^{2+}] = 10^{-2}M, [H^+] = 10^{-2}M$

$E^0_{Cr_2O_7^{2-}/Cr^{+3}} = 1.33 \text{ V} E^0_{MnO_4^-/Mn^{+2}} = 1.51 \text{ V}$

Sol. (i) $14H^+ + Cr_2O_7^{2-} 2Cr^{+3} + 7H_2O + 6e^-$

$E_{Redn} = 1.33 - \frac{0.059}{6}\log\left[\frac{10^{-4} \times 10}{10^{-14}}\right] = 1.33 - \frac{0.059}{6} \times 11$
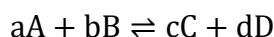
$E_{Redn} = 1.33 - \frac{0.649}{6} = 1.330 - 0.108 = 1.222 \text{ V}$

(ii) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$E_{Redn} = 1.51 - \frac{0.059}{5}\log\left[\frac{10^{-2}}{10^{-16} \times 10^{-1}}\right] = 1.51 - 0.059 \times 3 = 1.51 - 0.18 = 1.33 \text{ V}$

E_{Redn} **is more so, good oxidising agent**

2.5.2 Nernst Equation for cell Potential:

$aA + bB \rightleftharpoons cC + dD$

$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q$

n - no. of electrons which gets cancelled out while making cell reaction.

Equilibrium in electrochemical cell

$\Delta G^0 = -n n F E^o_{cell}$

$\Delta G = -nFE_{cell}$

From thermodynamics

$\Delta G = \Delta G^0 + RT/nQ$

at chemical equilibrium $\Delta G = 0$

$E_{cell} = 0$ cell will be of no use

so, $\Delta G^0 = -RT/nK_{eq}$

at equilibrium $-nFE^o_{cell} = -2.303RT\log(K_{eq})$

$\log K_{eq} = \frac{nF}{2.303RT} E^o_{cell}$

at 298 K and R = 8.314 J/molK

$\log K_{eq} = \frac{n}{0.059} E^o_{cell}$

Ex.10 Calculate E_{cell} of $Pt(s) \begin{vmatrix} Cl_2(g) \\ 0.1 \ atm \end{vmatrix} \begin{vmatrix} Cl^-(aq) \\ 10^{-2}M \end{vmatrix} \begin{vmatrix} Cr_2O_7^{2-}, Cr^{+3} \ (in \ H_2SO_4) = 0.05M \\ 0.01 \ M \qquad \qquad 0.1 \ M \end{vmatrix} Pt$

given that $E^0_{C_2O_7^2/Cr^{+3}} = 1.33$ V

$E^0 Cl^- \mid Cl_2 = -1.36$ V

Sol.　$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

$[2Cl^- \rightarrow Cl_2 + 2e] \times 3$

$14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$
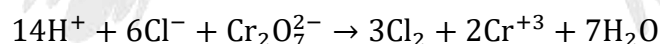
$E^0_{cell} = 1.33 - (+1.36) = -0.03$

$E_{cell} = -0.03 - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2 [P_{Cl_2}]^3}{[H^+]^{14}[Cl^-]^6 [Cr_2O_7^{2-}]} = -0.03 - \frac{0.059 \times 23}{6}$

$E_{cell} = -0.26$ V

Example problem 11.5

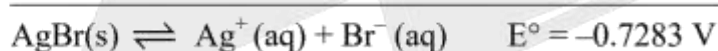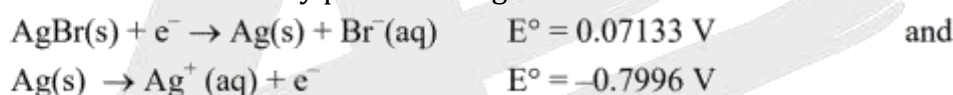For the Daniell cell $E° = 1.10$ V. calculate K for the reaction at 298.15 K

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$.
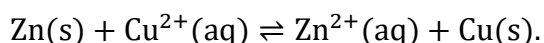
Solution.

$\ln K = \dfrac{nF}{RT} E° = \dfrac{2 \times 96485 \, C mol^{-1} \times 1.10 \, V}{8.314 \, J \, K^{-1} \, mol^{-1} \times 298.15 \, K} = 85.63$

$K = 1.55 \times 10^{37}$

Note that the equilibrium constant calculated in Example Problem 11.5 is so large that it could not have been measured by determining the activities of $a_{Zn^{2+}}$ and $a_{Cu^{2+}}$ by spectroscopic methods. This would require a measurement technique that is accurate over more than 30 orders of magnitude in the activity. By contrast, the equilibrium constant in an electrochemical cell can be determined with high accuracy using only a voltmeter.

A further example of the use of electrochemical measurements to determine equilibrium constants is the solubility constant for a weakly soluble salt. If the overall reaction corresponding to dissolution can be generated by combining half-cell potentials, then the solubility constant can be calculated from the potentials. For example, the following half-cell reaction can be combined to calculate the solubility product of AgBr.

$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$ $E° = 0.07133$ V   and

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E° = -0.7996$ V

$\overline{}$

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ $E° = -0.7283$ V

In $K_{SP} = \dfrac{nF}{RT} E° = \dfrac{1 \times 96485 \, C \, mol^{-1} \times (-0.7283 \, V)}{8.314 \, J \, K^{-1} \, mol^{-1} \times 298.15 K} = -28.35$
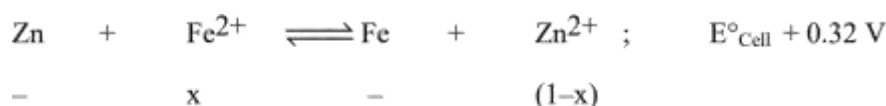
The value of the solubility constant is $K_{SP} = 4.88 \times 10^{-13}$.

Ex.11 The $E°_{cell}$ for the reaction $Fe + Zn^{2+} \rightleftharpoons Zn + Fe^{2+}$, is -0.32 volt at 25°C. What will be the equilibrium concentration of Fe^{2+}, when a piece of iron is placed in a $1M Zn^{2+}$ solution ?

Sol. We have the Nernst equation at equilibrium at 25°C

$E° = \dfrac{0.0591}{n} \log K$ .....(i)

Since E° Cell for the given reaction is negative, therefore, the reverse reaction is feasible for which $E°_{cell}$ will be +0.32 V, Thus for

$Zn \quad + \quad Fe^{2+} \rightleftharpoons Fe \quad + \quad Zn^{2+} \; ; \quad E°_{Cell} + 0.32$ V

$\quad\quad - \quad\quad\quad x \quad\quad\quad - \quad\quad\quad (1-x)$

Now , $E° = \dfrac{0.0591}{n} \log \dfrac{[Zn^{2+}]}{[Fe^{2+}]}$ or $0.32 = \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Fe^{2+}]}$

$\log \dfrac{[Zn^{2+}]}{[Fe^{2+}]} = -10.829$ Taking antilog,

$[Fe^{2+}] = 1.483 \times 10^{-11}$ M

Work done by a cell:

(i) Let ' n ' faraday charge be taken out of a cell of EMF 'E'; then work done by the cell will be calculated as : work = Charge × Potential = nFE

(ii) Work done by cell = Decrease in free energy

so $-\Delta G = nFE$

Ex.12 Calculate the maximum work that can be obtained from the Daniel cell given below -

Zn(s)|Zn^{2+}(aq) ‖ Cu^{2+}(aq)|Cu(s). Given that $E^o_{Zn^{2+}/Zn} = -0.76$ V and $E^o_{Cu^{2+}/Cu} = +0.34$ V.

Sol.   Cell reaction is: $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$ Here n = 2

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} \text{ (On the basis of reduction potential)}$$
$$= +0.34 - (0.76) = 1.10 \text{ V}$$

We know that: $W_{max} = \Delta G^o = -nFE°$

$$= -(2 \text{ mol}) \times (96500 \text{Cmol}) \times (1.10 \text{ V}) = -212300$$

C.V. $= -212300$ J

Or $W_{max} = -212300$ J

2.6   CONCENTRATION CELLS :

A concentration cell consists of two electrodes of the same material, each electrode dipping in a solution of its own ions and the solution being at different concentrations.

The two solutions are separated by a salt bridge.

e.g. Ag (s)|Ag^+ (a_1) ‖ Ag^+ (a_2)|Ag (s) ($a_1 < a_2$)a_1, a_2 are concentrations of each half cell At LHS electrode Anode: $Ag(s) \longrightarrow Ag^+(a_1) + e^-$

At RHS electrode Cathode : $Ag^+ (a_2) + e^- \longrightarrow Ag(s)$

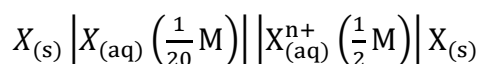The net cell reaction is: $Ag^+(a_2) \longrightarrow Ag^+(a_1)$

The nernst eq. is

$$E_{cell} = -\frac{0.059}{n}\log\frac{a_1}{a_2} \text{ (Here n = 1, Temp, 298 K)}$$

• Likewise, the e.m.f. of the cell consisting of two hydrogen electrodes operating at different pressure P_1 and $P_2(P_1 > P_2)$ and dipping into a solution HCl is:
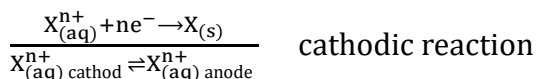
$$E_{cell} = \frac{0.059}{2}\log\frac{P_1}{P_2}(\text{ at 298 K})$$

Q. If for the concentration cell.

$$X_{(s)} \left| X_{(aq)} \left(\frac{1}{20}M\right) \right| \left| X_{(aq)}^{n+} \left(\frac{1}{2}M\right) \right| X_{(s)}$$

$E_{cell} = 0.029$ V at 298 K calculate n.

Sol. $X_{(s)} \longrightarrow X^{n+}_{(aq)} + ne^-$ anodic reaction

$$\frac{X_{(aq)}^{n+} + ne^- \rightarrow X_{(s)}}{X_{(aq)\ cathod}^{n+} \rightleftharpoons X_{(aq)\ anode}^{n+}} \quad \text{cathodic reaction}$$

$$0.029 = 0 - \frac{0.059}{n} \log \frac{[X^{+n}]_{anode}}{[X^{+n}]_{cathode}}$$

$$\because 0.029 = 0 - \frac{0.059}{n} \log \frac{\left(\frac{1}{20}\right)}{\left(\frac{1}{2}\right)}$$

$$0.029 = -\frac{0.059}{n} \log \frac{1}{10}$$

$$0.029 = -\frac{0.059}{n} \log 10^{-1}$$

$$0.029 = \frac{0.059}{n}$$

$$\therefore n = 2$$

Q. A hydrogen electrode is immersed in a solution pH $= 0$(HCl). By how much will the reuction potential change if an equivalent amount of NaOH is added to this solution, so that solution, so that solution becomes neutral $\left(P_{H_2} = 1 \text{ atm}\right) T = 298$ K

Sol. $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

$$E_{RP} = E_{SRP}^\circ - \frac{0.0591}{n} \log \left(\frac{(P_{H_2})}{[H^+_{(aq)}]}\right)$$

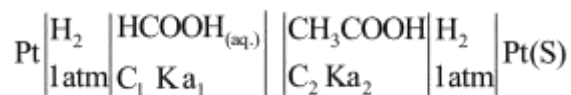$$E_{RP} = 0 - \frac{0.059}{1} \log \left(\frac{1}{1^2}\right)$$

$$E_{RP_1} = 0 - \frac{0.059}{1} \log \left(\frac{1}{1^2}\right) = 0$$

$$E_{RP_1} = 0$$

$$E_{RP_{firal}} = 0 - \frac{0.059}{2} \log \frac{1}{(10^{-7})^2} = \frac{0.059}{2} \times 14 \text{ V} = 0.4137 \text{ V}$$

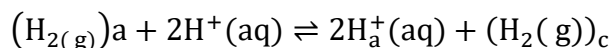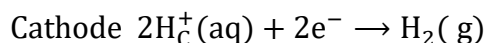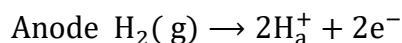Change in reduction potential $[0.4137 - 0] = 0.4137$

Q. Calculate E_{cell} of:

$$Pt\left|\begin{matrix}H_2\\1\,atm\end{matrix}\right.\left|\begin{matrix}HCOOH_{(aq.)}\\C_1\ Ka_1\end{matrix}\right.\left|\left|\begin{matrix}CH_3COOH\\C_2\ Ka_2\end{matrix}\right.\right|\left.\begin{matrix}H_2\\1\,atm\end{matrix}\right|Pt(S)$$

Prove that $E_{cell} = -\dfrac{0.059}{2}\log\dfrac{C_1 Ka_1}{C_2 Ka_2}$

Sol. $HCOOH \rightleftharpoons HCOO^- + H^+$

$C_1(1-\alpha_1)\ c_1\alpha_1\ c_1\alpha_1$

Anode $H_2(g) \longrightarrow 2H_a^+ + 2e^-$

Cathode $2H_C^+(aq) + 2e^- \longrightarrow H_2(g)$

$(H_{2(g)})a + 2H^+(aq) \rightleftharpoons 2H_a^+(aq) + (H_2(g))_c$

$\therefore\ E_{cell} = 0 - \dfrac{0.059}{2}\log\dfrac{[H^+]_a^2[P_{H_2}]_c}{[H^+]_C^2[P_{H_2}]_a}$ $(P_{H_2})_c = (P_{H_2})_a = 1\ atm$

$\because\ [H^+]_a = \sqrt{c_1 Ka_1}$

$[H^+]_c = \sqrt{c_2 Ka_2}$

$\therefore\ E_{cell} = -\dfrac{0.059}{2}\log\dfrac{c_1 Ka_1}{c_2 Ka_2}$

2.6 METAL -METAL INSOLUBLE - ION ELECTRODE:

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt.
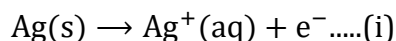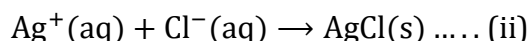
(i) Construction:
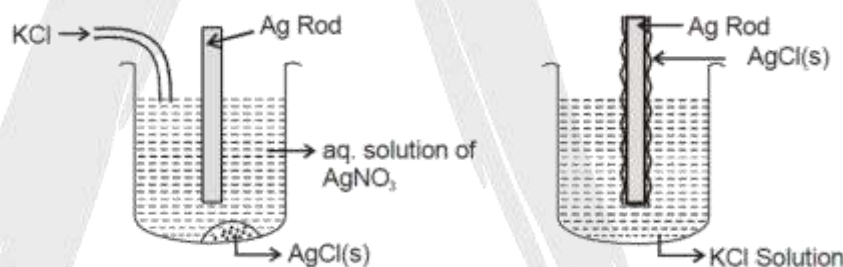
(ii) Half cell reaction:
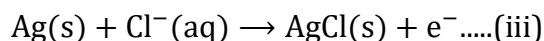
(a) If it act as Anode: At anode oxidation take place.

If it is normal silver electrode than.

$\qquad Ag(s) \longrightarrow Ag^+(aq) + e^- \dots..(i)$

But solution have Cl.(aq) ion so Ag + (aq)&Cl.(aq) Form PPT of AgCl(s)

$\qquad Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) \dots.. (ii)$

Overall half cell reaction at anode [from eq. (i) & (ii)].

$\qquad Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^- \dots..(iii)$

(b) If it act as cathode: At cathode reduction take place.

If it is normal silver electrode than.

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \ldots\ldots (i)$$

$$AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)\ldots\ldots(ii)$$
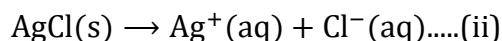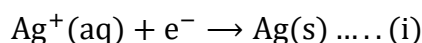
Overall half cell reaction at cathode [from eq. (i) & (ii)].

$$AgCl(s) + e. \longrightarrow Ag(s) + Cl^-(aq) \ldots\ldots(iii)$$

(iii) Cell representation:

(a)   (aq)   ‖   (aq)
(b)   Metal will be at the end.
(c)   Metal insoluble salt will be in middle.
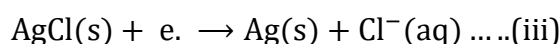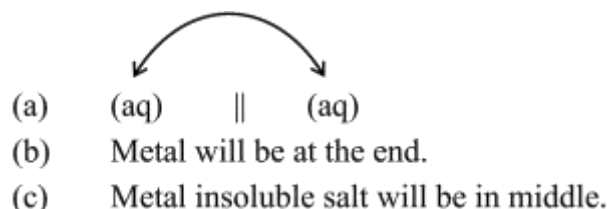
Abode: $Ag(s)|AgCl(s)|Cl^-(aq) \parallel$ _____

Cathode: $\dfrac{E^\circ_{Ag(s)|AgCl|Cl^-(aq)}}{E^\circ_{Cl^-(aq)|AgCl(s)|Ag(s)}} \parallel Cl^-(aq)|AgCl(s)|Ag(s)$

(iv) Relation between $E^\circ_{Cl^-(aq)|AgCl(s)|Ag(s)}$ **& K_{sp} of AgCl**

If a cell is constructed using metal-metal soluble salt and metal-metal unsoluble salt electrode.

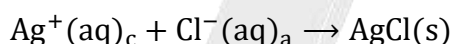Given $E^0_{Ag^+|Ag} = 0.80\text{ V}, \; E^0_{Cl^-|AgC|Ag} = 0.22\text{ V}$

$\qquad$ Anode $\qquad\qquad$ Cathode
$Ag|AgCl|Cl^-(aq) \quad \parallel \quad Ag^+(aq) \mid Ag$

Anode : $\quad Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^- \quad$ (Metal-metal insoluble salt)
Cathode: $\quad Ag^+ + e^- \longrightarrow Ag \qquad\qquad\qquad$ (Metal-metal soluble salt)

Overall cell reaction:

$$Ag^+(aq)_c + Cl^-(aq)_a \longrightarrow AgCl(s)$$

At equilibrium the concentratuion of $[Ag^+]_a = [Ag^+]_c$

So that at equilibrium $E_{cell} = 0$

But $E_{cell} = E^0_{cell} - \dfrac{0.059}{1}\log\dfrac{[AgCl(s)]}{[Ag^+]_c[Cl^-]_a}$

At equilibrium

$$0 = E^0_{cell} - \dfrac{0.059}{1}\log\dfrac{1}{[Ag^+]_c[Cl^-]_a}$$

Now for AgCl

$$AgCl(s) \longrightarrow Ag^+(aq)_a + Cl^-(aq)_a$$
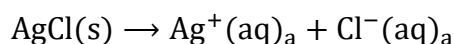
$$K_{sp} = [Ag^+]_a[Cl^-]_a$$

So, $\quad [Cl^-]_a = \dfrac{K_{sp}(AgCl)}{[Ag^+]_a}$

$$0 = E^0_{cell} - \dfrac{0.059}{1}\log\dfrac{[Ag^+]_a}{[Ag^+]_a \times K_{sp}}\text{[At equilibrium the concentratuion of }[Ag^+]_a = [Ag^+]_c]$$

$$E^0_{cell} = \dfrac{0.059}{1}\log\dfrac{1}{K_{sp}}$$

$$E^0_{cell} = -\frac{0.059}{1}\log\frac{1}{K_{sp}}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{Anode}$$

$$= E^0_{Ag^+/Ag} - E^0_{Cl^-/agCl/Ag}$$

So, $$E^0_{Ag^+|Ag} - E^0_{Cl^-|AgCl|Ag} = \frac{0.059}{1}\log\frac{1}{K_{sp}}$$

$$E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \frac{0.059}{1}\log K_{sp}$$

Some other example:

$$Pb|PbSO_4|SO_4{}^{2-} \parallel Pb^{2+} | Pb$$
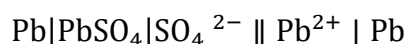
White ppt.

$$E^0_{SO_4^{2-}|PbSO_4|Pb} = E^0_{Pb^{2+}|Pb} + \frac{0.059}{2}\log Ksp$$

Ex. Calculate Ksp of AgI with the help of following cell.

$$Ag|AgI(s)|0.05MKI(aq)||0.05MAgNO_3 | Ag(s)$$

Sol. First methode: If $E^0_{cell} = 0$

Anode : $Ag \longrightarrow Ag^+_a + e^-$
Cathode : $Ag^+_c + e^- \longrightarrow Ag$
   $Ag^+_c \rightleftharpoons Ag^+_a$
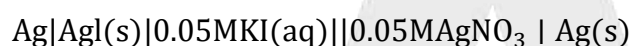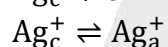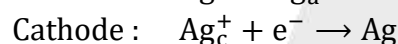
According to nernst equation.

$$E_{cell} = E^0_{cell} - \frac{0.059}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$$

$$0.7884 = 0 - \frac{0.059}{1}\log\frac{[Ag^+]_a}{0.05}$$

$$-\frac{0.7884}{0.059} = \log[Ag^+]_a - \log(5\times10^{-2})$$

$$\log[Ag^+]_a = -1.3 - \frac{0.7884}{0.059}$$

$$[Ag^+]_a = 2.17\times10^{-15}$$

$$K_{sp} = [Ag^+]_a[I^-]_a$$

$$K_{sp} = 2.17\times10^{-15}\times0.05 = 1\times10^{-16}.$$

Second Methode: if $E^0_{cell} \neq 0$

$$E_{cell} = E^0_{cell} - \frac{0.059}{1}\log\frac{1}{[Ag^+]_c[I^-]_a}$$

$$E_{cell} = -\quad -\frac{0.059}{1}\log K_{sp} - \frac{0.059}{1}\log\frac{1}{[Ag^+]_c[I^-]_a}$$

So $$E_{cell} = -\frac{0.059}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}\frac{I^-_a}{[I^-]_a}$$

$$E^0_{cell} = -\frac{0.059}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$$

$$\begin{array}{l} \text{But} \quad E^0_{cell} = -\frac{0.059}{1}\log K_{sp} \\[2mm] E^0_{cell} = -\frac{0.059}{1}\log[Ag^+]_c[I^-]_a \end{array}$$
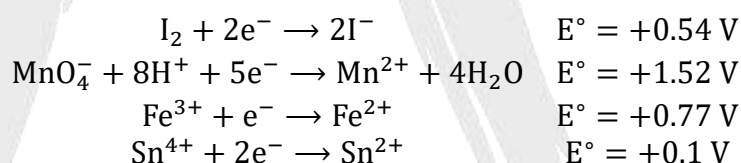
(4)   Calomel Electrode:

- A calomel cell consists of a platinum electrode dipping into mercury in contact with calomel (dimercury) (1) chloride, Hg_2Cl_2) and potassium chloride solution.

- Usually the solution is saturated with potassium chloride.

- The cell has an e.m.f of 0.246 V at 28°C

Standrad (normal) calomel electrode when $[Cl^-] = 1\,M = 1\,N$

At Anode	At Cathode
$2Hg(l) \rightarrow Hg_2^{2+}(aq) +$	$Hg_2^{2+} + 2e^- \rightarrow$
$\underline{Hg_2^{2+}(aq) + 2Cl^- \rightarrow}$	$\underline{Hg_2Cl_2 \rightarrow Hg_2^{2+}(aq) + 2Cl^-}$
$2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$	$Hg_2Cl_2(s) + 2e^- \rightarrow Hg(l) + 2Cl^-$

- Cell representation
$Pt(s) \mid Hg(l) \mid Hg_2Cl_2(s) \mid Cl^-(aq) \parallel$ cathode
$E^0_{Pt\,Hg\mid Hg_2Cl_2 + Cl^-} = SOP$

$E_{Cl^-/Hg_2Cl_2/Hg} = E^0_{Cl^-/Hg_2Cl_2/Hg} - \dfrac{RT}{F}\ln[Cl^-]$

- Cell representation
(Anode) $\parallel Cl^-(aq) \mid Hg_2Cl_2 \mid Hg(l) \mid Pt(s)$
$E^0_{Cl^-\mid Hg_2Cl_2\mid Hg(l)} = SRP$
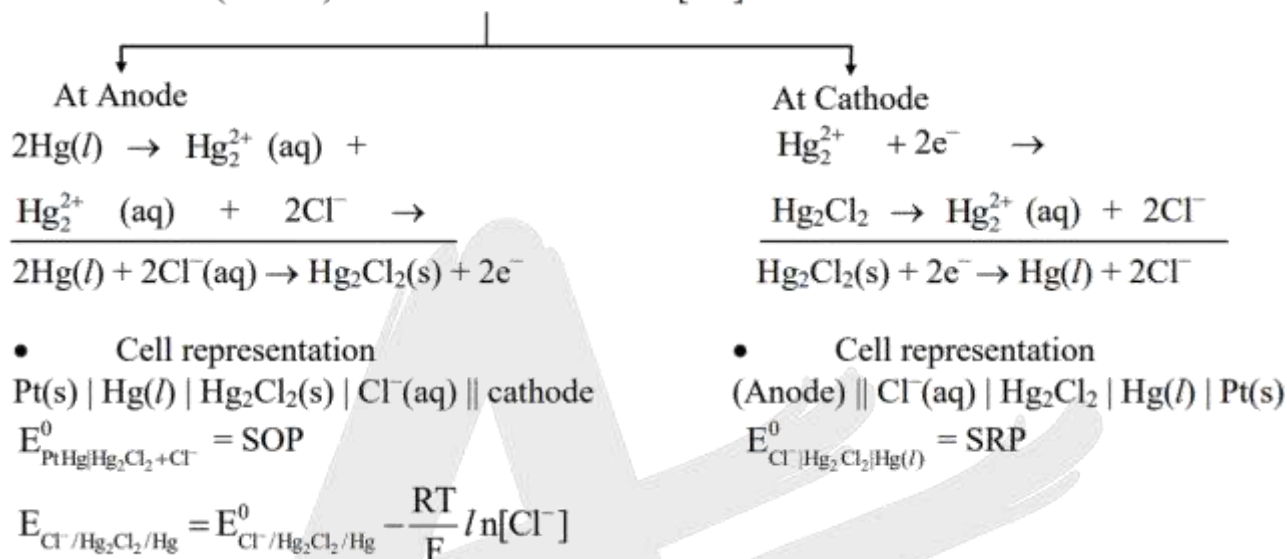
DO YOURSELF–1

1.   Colour of KI solution containing starch turns blue when Cl_2 water is added. Explain.

2.   E° of some oxidants are given as :

$$I_2 + 2e^- \longrightarrow 2I^- \qquad\qquad E° = +0.54\,V$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad E° = +1.52\,V$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad\qquad E° = +0.77\,V$$
$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+} \qquad\qquad E° = +0.1\,V$$

(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below.

(i) $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$

(ii) $2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$

(iii) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$

(iv) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

3. Given the standard electrode potentials;

    $K^+/K = -2.93\ V, Ag^+/Ag = 0.80\ V, Hg^{2+}/Hg = 0.79\ V, Mg^{2+}/Mg = -2.37\ V, Cr^{3+}/Cr = -0.74\ V.$

    Arrange these metals in their increasing order of reducing power.

4. Answer of following:

    (i) In a cell, anode is represented by -ve sign and cathode by +ve sign. What is the type of the cell?

    (ii) Write the reaction taking place at anode in the following cell:

    $$Pt, H_2(1\ atm)\ |\ HCl(1M)Cl_2, Pt.$$

    (iii) With the help of the following possible reactions, arrange Mg, Zn, Cu and Ag in decreasing order of their reduction potentials.

    $$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$
    $$Mg + Zn^{2+} \longrightarrow Mg^{2+} + Zn$$
    $$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

    (iv) Cl_2 can displace I_2 from KI solution but I_2 does not displace.

    (v) The E° (standard oxidation potentials) values of the elements A, B, C and D are + $0.76, -0.34, +0.25$ and -0.85 volt respectively. Arrange these in decreasing order of reactivity.

5. A cell is prepared by dipping a copper rod in $1M CuSO_4$ solution and a nickel rod in 1M $NiSO_4$. The standard reduction potentials of copper and nickel electrodes are $+0.34\ V$ and $0.25\ V$ respectively.

    (i) Which electrode will work as anode and which as cathode?

    (ii) What will be the cell reaction?

    (iii) How is the cell represented?

    (iv) Calculate the EMF of the cell.

6. Predict whether the following reaction can occur under standard conditions or not.

    $$Sn^{2+}(aq) + Br_2(\ell) \longrightarrow Sn^{4+}(aq) + 2Br^-(aq)$$

    Given $E°_{Sn4+Sn2+} = +0.15, E°_{Br2Br-} = 1.06\ V.$

    $$Co^{3+} + e^- \longrightarrow Co^{2+} E° = +1.82\ V$$

    $$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-; E° = -1.23\ V.$$

7. Given that, $Co^{3+} + e^- \longrightarrow Co^{2+} E° = +1.82\ V$

    $$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-; E° = -1.23\ V.$$

    Explain why Co^{3+} is not stable in aqueous solutions.

8. The measured e.m.f. at 25°C for the cell reaction,

    $Zn(s) + Cu^{2+}(1.0M) \longrightarrow Cu(s) + Zn^{2+}(0.1M)$

    is 1.3 volt Calculate E° for the cell reaction.

9. Calculate ΔG° for the reaction : Cu^{2+} (aq) +Fe(s) $\rightleftharpoons$ Fe^{2+} (aq) +Cu(s). Given that

    $E°_{Cu+/Cu} = +0.34$ V, $E°_{Fe°+2/Fe} = -0.44$ V

10. Calculate the equilibrium constant for the reaction at 298 K

    $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

    Given $E°_{Zn^{2+}/Zn} = -0.76$ V and $E°_{Cu^{2+}/Cu} = +0.34$ V

11. Calculate the cell e.m.f. and ΔG for the cell reaction at 298 K for the cell.

    $Zn(s)|Zn^{2+}(0.0004M) \parallel Cd^{2+}(0.2M)|Cd(s)$

    Given $E°_{Zn^{2+}/Zn} = -0.763$ V; $E°_{Cd^{+2}/Cd} = -0.403$ V at 298 K.

    $F = 96500 Cmol^{-1}$.

2.6   CALCULATION OF THERMODYNAMICS FUNCTION OF CELL REACTION:

(1) $\Delta G° = -nF^0_{cell}$

    $\Delta G° = -nF_{cell}$

(2) $G = H - TS$ (But: $H = E + PV$)

    $\therefore G = (E + PV) - TS$

    $dG = dE + PdV + VdP - TdS - SdT$

(a) From 1st law of thermodynamics

    $dE = dq + dW$

    $\quad = dq - pdV$

    $dq = dE + pdV$

(b) From 2nd law of thermodynmics

    $dS = \dfrac{dq}{T}$

    $dq = TdS$

    Using 1st law and 2nd law of thermodynamics

    $\qquad dG = (dE + PdV) + Vdp - TdS - SdT \Rightarrow dG = Vdp - SdT$

    If a cell reaction is taking place at constant pressure (which is generally the case).

    $dG = Vdp - SdT$

at constant pressure

So, $Vdp = 0$

And $dG = -SdT$

$\therefore S = -\left[\dfrac{dG}{dT}\right]_p$ (At constant pressure)

$\Delta S = -\left[\dfrac{d(\Delta G)}{dT}\right]_p$ (At constant pressure)

$\Delta G = -nRE_{cell}$

$\Delta S = -\left(\dfrac{d}{dT}(E_{cell})\right)_p (-nF)$