

ELECTROCHEMICAL CELL (GALVANIC CELL)

Definition: It is a system or device in which electricity is produced due to redox reaction. It constitutes two half cells, salt bridge and external circuit.

Principle: When metal strip is placed in its ionic solution, it acquires either a positive electric charge or a negative electric charge with respect to the solution. On the other hand, we may say either oxidation or reduction takes place at the metal strip. As a result, a potential is developed between the metal and its ionic solution. This potential difference is known as **electrode potential**. The electrode potential is termed as oxidation potential if oxidation takes place at the electrode and is termed as reduction potential if reduction takes place at the electrode. The magnitude of electrode potential depends on various parameters, i.e. nature of the electrode, concentration of ions and thermodynamic temperature. The metal strip/rod dipped in the electrolyte is known as a single electrode. The single electrode with its electrolyte is known as a half cell. The half cell in which oxidation takes place is known as oxidation half cell and that in which reduction takes place is known as reduction half cell. The combination of an oxidation half cell and a reduction half cell along with a salt bridge and external circuit constitute an electrochemical cell or galvanic cell.

The electrode potential at unit ionic concentration at 25°C (298K) and 1 atm pressure is known as **standard electrode potential**. It is denoted by $E^{\circ}_{\text{electrode}}$. As per IUPAC convention, standard reduction potential is known as standard electrode potential. The half cell in which oxidation takes place is known as **anode** and it is termed as **negative potential** with respect to the solution. Similarly, the half cell in which reduction takes place is known as **cathode** and it is termed as positive potential with respect to the solution.

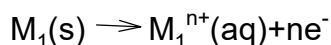
The potential difference between two electrodes of a galvanic cell is known as cell potential and it is measured in volts. The cell potential is the difference between electrode potentials (reduction potentials) of the cathode and anode. It is also known as cell electromotive force (emf) when no current is drawn through the cell. As per the convention, while representing a galvanic cell, the anode is placed at the left and the cathode is placed at the right side of the cell. A galvanic cell is symbolically represented by putting vertical lines between metal and electrolytic solutions and putting a double vertical line between two electrolytic solutions connected by a salt bridge.



Cell EMF: The emf is taken as positive by convention and is given by electrode potential of the half cell placed at right (oxidation half cell) minus electrode potential of the half cell placed at the left (reduction half cell).

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

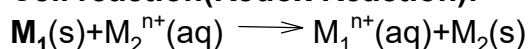
Half cell reaction at anode (oxidation):



Half cell reaction at cathode (reduction):



Cell reaction (Redox Reaction):



STANDARD CELL EMF: The emf value of a cell under standard conditions, 1 atm pressure, 298K and unit concentration of its ions (1 mole/dm³). It is denoted by E° .

A cell can be constructed by combination of two half cells (redox couple) by using two different metals with their ionic solutions along with a salt bridge and an external circuit. The values of the single electrode potentials (reduction potentials) of the redox couple is the determining factor which half cell acts as anode and which one would act as cathode in a galvanic cell.

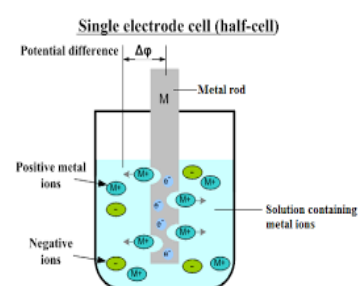


Fig-1

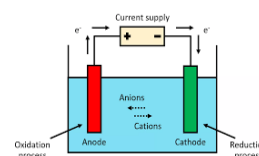


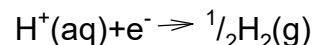
Fig-2

It is not possible to measure the absolute value of electrode potential of individual half cell, we are to take use of another reference standard hydrogen electrode as standard half cell. Its potential is assigned as zero volt at all temperatures.

STANDARD HYDROGEN ELECTRODE(SHE):

It consists of a platinum electrode coated with platinum black. The electrode is dipped in acidic solution and pure hydrogen gas is bubbled through it. It is represented by $\text{Pt(s)}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})$

The concentration of both reduced and oxidised forms of hydrogen is maintained at unity (1M), pressure of the hydrogen gas is one bar and temperature at 298 K (25°C). Its half reaction is as follows:



Its electrode potential is assigned as 0 volt at all temperatures

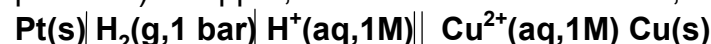
Measurement of Electrode potential (Reduction Potential):

The standard electrode potential of the half cell can be measured by constructing a cell by using standard hydrogen electrode as reference half cell as anode and the other half cell as cathode whose standard electrode potential is to be measured.

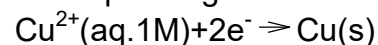
$$E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0 = E_{\text{cathode}}^0 - E_{\text{Anode}}^0 = E_{\text{cathode}}^0 - 0 = E_{\text{Cathode}}^0$$

$$E_{\text{cell}}^0 = E_{\text{Cathode}}^0$$

In order to measure standard electrode potential (reduction potential) of copper, we have to construct a cell,



The measured emf of above cell is found to be 0.34 Volt corresponding to the half cell reaction,

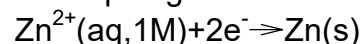


which is absolute value of standard electrode potential (reduction potential) for copper electrode.

Similarly, for measuring standard electrode potential (reduction potential) for Zinc, we have to construct a cell,



The measured emf of the above cell is found to be -0.76 volt corresponding to the half cell reaction,



which is the absolute value of standard electrode potential (reduction potential) for Zinc electrode. The positive value of electrode potential indicates that the metal ions get reduced more easily than H^+ ions. Similarly, the negative value of the electrode potential indicates that the hydrogen ion can oxidize the Zinc electrode.

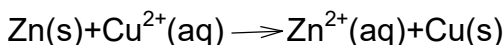
DANIELL CELL

It is a typical example of galvanic cell (fig-3.1). It consists of two half cells, one containing Zinc electrode dipped in 1M solution of zinc sulphate (ZnSO_4) and other containing copper electrode dipped in 1M solution of copper sulphate (CuSO_4).

At Zinc electrode oxidation takes place, $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$. It acts as anode.

At Copper electrode, reduction takes place, $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$. It acts as cathode

The overall cell reactions are as is the sum of two reactions,



The emf of the cell, $E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0 = 0.34 - (-0.76) = 1.10$ volt

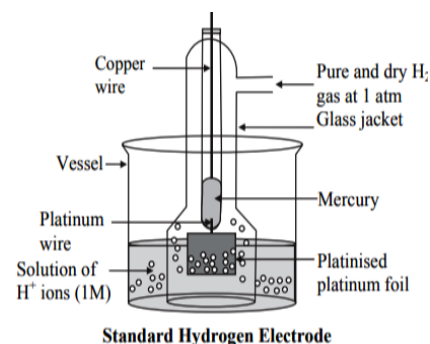


Fig.3

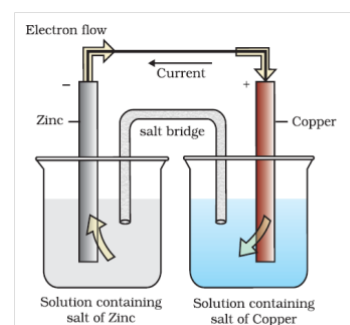


Fig. 3.1: Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

ELECTRO CHEMICAL SERIES

The value of the standard electrode potential is very important information. If the standard electrode potential is greater than zero, then its reduced forms are more stable compared to hydrogen gas. If the electrode potential is negative, then hydrogen gas is more stable than reduced form of species. The electrochemical series are a list of elements which are arranged in the decreasing order of their standard electrode potentials along with their half cell reactions. The following table depicts the electrochemical series.

<div style="display: flex; flex-direction: column; align-items: center;"> <div style="color: red; font-weight: bold; margin-bottom: 10px;">Stronger oxidizing agent</div> <div style="width: 20px; height: 100%; background: linear-gradient(to top, red, orange); border: 1px solid red; margin: 0 auto;"></div> <div style="color: red; font-weight: bold; margin-top: 10px;">↑</div> </div>	$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87	<div style="display: flex; flex-direction: column; align-items: center;"> <div style="color: blue; font-weight: bold; margin-bottom: 10px;">Weaker reducing agent</div> <div style="width: 20px; height: 100%; background: linear-gradient(to bottom, lightblue, blue); border: 1px solid blue; margin: 0 auto;"></div> <div style="color: blue; font-weight: bold; margin-top: 10px;">↓</div> </div>
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23	
	$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09	
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15	
	$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26	
	$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45	
	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76	
$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83		
$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66		
$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37		
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71		
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04		
<div style="display: flex; flex-direction: column; align-items: center;"> <div style="color: blue; font-weight: bold; margin-bottom: 10px;">Stronger reducing agent</div> <div style="width: 20px; height: 100%; background: linear-gradient(to bottom, lightblue, blue); border: 1px solid blue; margin: 0 auto;"></div> <div style="color: blue; font-weight: bold; margin-top: 10px;">↓</div> </div>			

It is observed that the standard electrode potential of fluorine is the highest means it has the maximum tendency to get reduced to Fluorine ions (F^-), the fluorine gas is the strongest oxidising agent and fluorine ion is weakest reducing agent. Similarly, Lithium has the lowest electrode potential means that Lithium atom is the strongest reducing agent where as lithium ion is the weakest oxidising agent. It is evident from the above table that there is a decrease of oxidising power of the species on the left and increase in reducing power of the species on the right hand side of the half cell reactions.

electrochemical cells are extensively used for determining pH of the solutions, solubility product, equilibrium constant and other thermodynamic properties.