Electromotive Force

For F.Y.B.Sc. Semester-II

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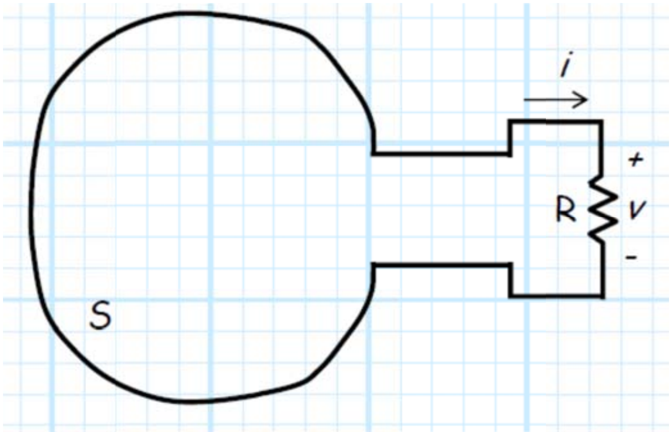
- We all know that energy cannot be produced or destroyed; it just converts into one form from another.
- Electrical energy plays a significant role in our routine life.
- The relationship between electrical energy and chemical energy has been studied a lot by number of scientists.
- Basically, redox reactions that are associated with production of electrical energy, was the basis of electrochemistry.
- For this chapter, we need to study the electromotive force that has been an important topic under electrochemistry.

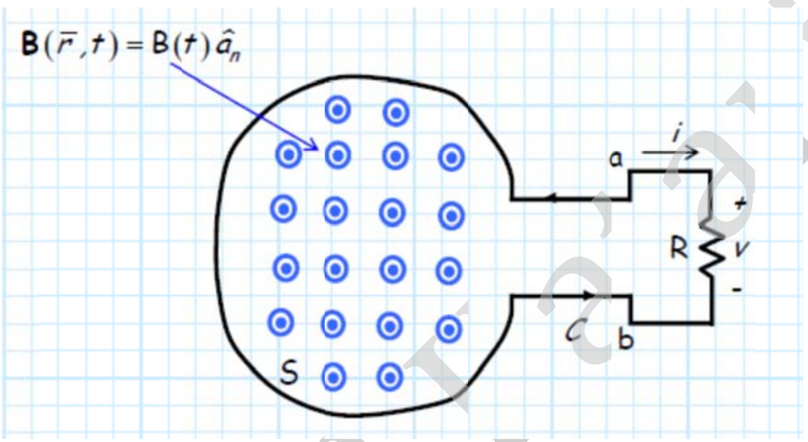
Introduction

- Electromotive force, also called emf (denoted ε measured in volts), is the voltage developed by any source of electrical energy such as a battery or dynamo.
- The word "force" in this case is not used to mean mechanical force, measured in newtons, but a potential, or energy per unit of charge, measured in volts.
- In electromagnetic induction, emf can be defined around a closed loop as the electromagnetic work that would be transferred to a unit of charge if it travels once around that loop.



- Since there is no voltage or current source in this circuit, both voltage v and current i are zero.
- Now consider the case where there is a time-varying magnetic flux density B (r ,t) within the loop only. In other words, the magnetic flux density outside the loop is zero (i.e., B (r ,t) = 0 outside of S).
- Say that this magnetic flux density is a constant with respect to position, and points in the direction normal to the surface S. In other words;

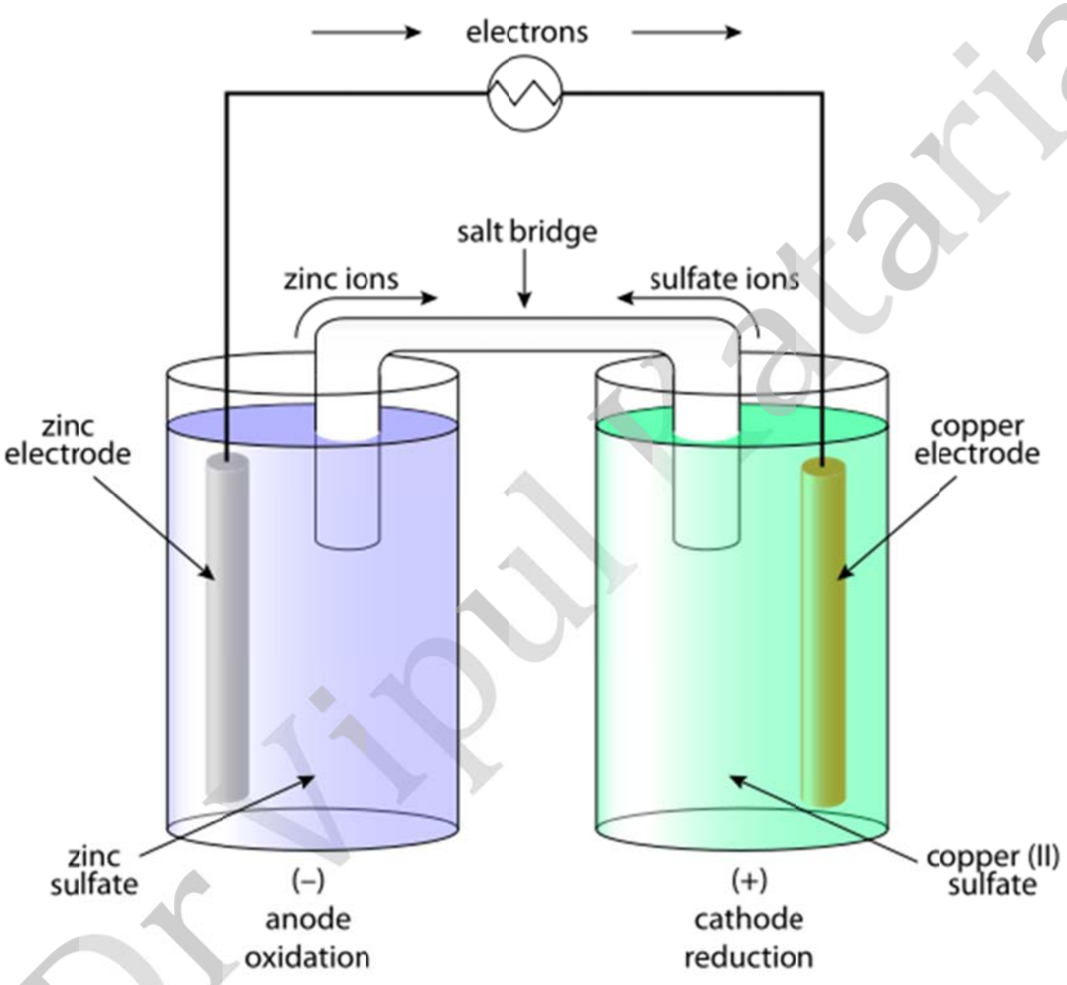
$$B(\boldsymbol{r},t) = B\,(t)a_n$$



- According to Faraday's law (The induced electromotive force in any closed circuit is equal to the negative of the time rate of change of the magnetic flux through the circuit.)
- Definition: Electromotive force is the difference in potential between the electrodes of cell. The unit of EMF is volt.
- Electrochemical cell converts chemical energy into electrical energy.
- The metal strip dipped in an electrochemical cell or non-metal like graphite on whose surface the oxidation or reduction reaction takes place is called an electrode.
- In an electrochemical cell, electrons flow from anode to cathode in an external circuit, and electric energy that is developed due to chemical reaction flows from cathode to anode.
- The potential of electrical energy is called the cell potential and denoted by E_{cell}.
- The potential of electrochemical cell can be measured by potentiometer.

Galvanic Cell (Electrochemical cell)

- A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell.
- It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.



- The cell consists of two electrolyte solutions in which two electrodes of different metal are dipped.
- The Zn electrode dipped in $ZnSO_4$ solution whilst Cu electrode dipped in $CuSO_4$ solution.
- The Zn electrode represents anode. The anode is the electrode at which oxidation occurs. The oxidation includes liberation of electrons that make the electrode negative.

- The Cu electrode represents cathode. The cathode is the electrode at which reduction occurs. The reduction includes consumption of electrons that make the electrode positive.
- As the diagram indicates, the Zn metal rod is dipped in ZnSO4 solution whilst Cu metal rod is dipped in CuSO4 solution.
- The metal electrodes are joined by galvanometer or ammeter.
- Both the solutions are joined by salt bridge filled up with KCl (Potassium Chloride).
- As the circuit get closed, chemical reaction get started and current also flows that can be measured in galvanometer.
- The Zn metal losses two electrons and get converted into Zn^{2+}.
- The two electrons are gained by Cu^{2+} and get converted into Cu.

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Reduction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

- The liberated electrons due to oxidation of Zn transfers to Cu electrode via galvanometer.
- The flow of electrons is from anode to cathode.
- The flow of current is from cathode to anode (reverse of electrons).
- The overall reaction can be designated as under.

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

- The Zn electrode refers to anode whilst Cu electrode refers to cathode.

Half Cell

- A half-cell consists of a solid metal (called an electrode) that is submerged in a solution; the solution contains cations of the electrode metal and anions to balance the charge of the cations.
- For example, in a Daniel cell, Zn rod submerged in $ZnSO_4$ solution.
- The half-cell can be represented using vertical line between an electrode and electrolyte solution.

- For Example:

1. Zn/Zn^{2+}
2. Cu/Cu^{2+}
3. $Pt/H_2/H^+$

Reversible and irreversible cells

- The reversible cell can be characterized by following aspects.
- If we connect the electrochemical cell to external electric source of same EMF then there will not be any chemical reaction. In other words, the chemical reaction of the cell stops when an exactly equal opposing EMF is applied.
- If the external EMF is decreased to small extent then the reaction within the cell would proceed in forward direction that will produce current.
- If the external EMF is increased to small extent then the reaction within the cell would proceed in backward direction. In other words, the chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing EMF is slightly greater than that of the cell.
- The Daniel cell is an example of reversible cell.
- In Daniel cell, the anode is represented by Zn which is submerged in $ZnSO_4$ solution.
- Cathode is represented by Cu which is submerged in $CuSO_4$ solution.
- The cell is represented as below.

$$Zn/ZnSO_4//CuSO_4/Cu$$

- The emf of cell is 1.1 v.
- If an external emf is 1.1 v then no reaction will take place hence the value for current will be zero.
- If the external emf is little less than reaction would be proceed in forward direction and current would obtained. The reaction will be as follows.

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

- If external emf is higher than 1.1 v than reaction would be proceed in backward direction and the reaction will be as follows.

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

- In an irreversible cell, if an external emf is provided the original state cannot be obtained as small amount of substance undergo precipitation or is converted into heat.
- For example:

$$Zn/H_2SO_4/Ag$$

- The expected reaction is as follows.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

- But if small amount of external emf is provided the reaction occurs is as follows.

$$2Ag + H_2SO_4 \rightarrow Ag_2SO_4 + H_2$$

- In such cell where the reaction involves gaseous product.
- In such cases reaction does not shift to reverse direction.
- In some cells, the precipitation occurs hence reaction does not shift into reverse direction.

Convention Signs and Representation of Cell

- According to IUPAC, the electrode at which reduction occurs when connected to standard hydrogen electrode (SHE) is denoted by positive sign (Cathode).
- The electrode at which oxidation occurs when connected to standard hydrogen electrode (SHE) is denoted by negative sign (Anode).
- The electrode at which oxidation takes place is anode.
- The electrode at which reduction takes place is cathode.
- The anode is written on the left side and cathode is written on right side.
- The double vertical line shows that the solution is separated by salt bridge.
- The single vertical line shows boundary between electrode and another phase.
- Sometimes colon (:) is used in place of single vertical line.
- The prefixes are used to designate the states.

Types of Reversible Electrode

- A metallic or non-metallic strip on whose surface a reaction (either oxidation or reduction) occurs is known as electrode.
- The following are types of electrodes.

a. Electrode reversible with respect to cations

- This type of electrode consists of metal in contact with a solution of its own cations. For example: Ag electrode in $AgNO_3$, Cu electrode in $CuSO_4$, Zn electrode in $ZnSO_4$.
- In such electrodes metal ions undergo reduction at the electrode.
- The reaction is $M \rightarrow M^{n+} + ne^-$

b. Electrodes reversible with respect to anions

- This type of electrode consists of metal in contact with sparingly soluble salt and solution of a soluble salt having common anion.
- For example: $Ag_{(s)}/AgCl/KCl_{(aq)}$

c. Gas Electrode

- In this type of electrode gas is adsorbed on the platinum strip and dipped in the electrolyte and the ions associated with the gas are in contact with the solution.
- For example: $Pt/H_{2(g)1\ atm}/HCl_{(M)}$

d. Metal insoluble salt

- It consists of a metal, its insoluble salt and insoluble salt of another metal having a common anion and a solution of any soluble salt of the later having same cation.
- For example: $Pb/PbC_2O;CaC_2O, CaCl_{2(aq)}$

e. Inert electrode

- It consists of an inert electrode like gold or platinum immersed in a mixed solution containing both oxidised and reduced form of a molecule or ion.
- For Example: $Pt/Fe^{2+}, Fe^{3+}$ and $Pt/ Sn^{2+}, Sn^{4+}$

Types of Electrochemical Cells

- Electrochemical cells are of two types as follow.

1. Chemical cell

- In chemical cell, the emf produced due to chemical reaction (redox reaction).
- There are two types of chemical cells: (a) chemical cell without transference (b) chemical cell with transference.
- In chemical cell without transference, the two electrodes are dipped in same electrolyte solution.
- In chemical cell with transference, the two electrodes are dipped in different electrolyte solutions and joined with liquid junction (salt bridge).

2. Concentration cell

- In concentration cell the emf produced due to difference in concentration between two half cells.
- Concentration cells are of two types: (a) electrolyte concentration cells (b) electrode concentration cells.
- Electrolyte concentration cells may involve cells with or without transference whilst electrode concentration cells are cells without transference.

Standard Electrode Potential

- The emf produce by the half cell (single electrode) is its potential.
- The emf is dependent upon constituents opposing the electrode, activities of solutions and temperature.
- If the activity (different term than concentration) of a substance is unity (one) than the substance is called in its standard states.
- In a reversible cell, if the substances are in their standard states (unit activity) then emf can be represented as E^0 (standard).
- If the reaction takes place with passage of n faradays then free energy can be represented as follows.

$$-\Delta G^0 = nE^0F \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..[1]$$

If the reaction is as follows

$$aA + bB \rightleftharpoons cC + dD$$

According to law of mass action the equilibrium constant will be given by

$$k = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [2]$$

If the reaction is at equilibrium then the change in free energy is zero.

But when the substances are at arbitrary activities then change in free energy can be given by

$$-\Delta G = RTLn\ K = RT\ Ln\ \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [3]$$

Now if the reactants are at arbitrary activities then

$$-\Delta G = nEF \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [4]$$

Now we know that

$$\Delta G = \Delta G^0 + RT\ Ln\ K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [5]$$

Now put value of equations 1, 2, and 4 in equation 5

$$-nEF = nE^0F + RT\ Ln\ \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [6]$$

Now divide equation 6 with –nf

$$E = E^0 - RT\ Ln\ \frac{Oxidised\ state}{Reducing\ state} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [7]$$

If the activities are unity then the emf of cell will be its standard electrode potential.

‘It may be defined as the potential of electrode when the activities of reactants and products are unity’.

Electrolytic Cell

- In this kind of cell, electrical energy gets transformed into chemical energy.
- Redox reaction does not take place spontaneously.

- Electrode that is connected to positive terminal is cathode and to negative terminal is anode.
- Both the electrodes remain in same vessel.
- Salt bridge is not required.

EMF Series

- When the potential (emf) of an electrode is measured with reference to standard hydrogen electrode is known as the electromotive force of that electrode.
- If the values of oxidation potentials of different half cells are arranged in their decreasing order the series obtained is called EMF series.
- A negative potential indicates a tendency greater than that of hydrogen to pass in the solution in the form of ions.
- This means with more negative potentials will displace those having more positive potential from their solutions.
- This series indicates the relative activity of metals.
- The more reactive metal with more negative oxidation potentials appear higher up in the series.
- This series provides a very good method of studying displacement reactions.
- Thus the metal placed higher up in series can displace the metal below it.
- For example: rusting of iron is an electrochemical phenomenon. Plating iron with zinc (higher up in series than iron) will protect iron from rusting.

Electrode	E^0 Volts	Electrode	E^0 Volts
Li^+, Li	-2.959	Co^{2+}, Co	-0.28
Rb^+, Rb	-2.926	Ni^{2+}, Ni	-0.23
K^+, K	-2.924	Sn^{2+}, Sn	-0.136
Ca^{3+}, Ca	-2.76	Pb^{2+}, Pb	-0.12
Na^+, Na	-2.715	H^+, H_2(Pt)	0.00
Al^{3+}, Al	-1.33	Sb^{3+}, Sb	+1.10
Zn^{2+}, Zn	-0.762	Cu^{2+}, Cu	+0.344
Fe^{2+}, Fe	-0.441	Ag^+, Ag	+0.798
Ti^+, Ti	-0.336	Au^{3+}, Au	+1.36

Relation between G, H, S, and K

According to well-known Gibbs-Helmholtz equation, the change in free energy can be given by

$$-\Delta G = \Delta H - T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p \text{……………………………………………[1]}$$

Now we know that $-\Delta G = nEF$……………………………………[2]

$$+nEF = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_p \text{……………………………………..[3]}$$

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p \text{………………………………………………..[4]}$$

From equation 1 and 4 it is possible to determine various thermodynamic quantities like enthalpy, change in free energy, and change in entropy by measuring emf of the cell and its temperature co-efficient.

If the emf is standard then $-\Delta G^0 = nE^0F$…………………………………[5]

Now we know that

$$\left(\frac{\partial(\Delta G^0)}{\partial T}\right)_p = nF\left(\frac{\partial E^0}{\partial T}\right)_p \text{…………………………………..[6]}$$

Now put the value of $\left(\frac{\partial(\Delta G^0)}{\partial T}\right)_p = \Delta S^0$

$$\Delta S^0 = nF\left(\frac{\partial E^0}{\partial T}\right)_p \text{…………………………………..[7]}$$

Now we know that $\Delta H^0 = \Delta G^0 + T\Delta S^0$……….[8]

Now put the value of equation 5 and 7 into 8

$$\Delta H^0 = -nE^0F + nFT\left(\frac{\partial E^0}{\partial T}\right)_p \text{………………………[9]}$$

From equation 9 it is clear that by measuring the standard emf of cell at different temperature we can calculate various thermodynamic quantities.

If the standard emf of any cell is known than the equilibrium constant can be measured using following equation

$$-\Delta G = RTLn\,K = NE^0F$$

$$Ln\,K = \frac{nE^0F}{RT} \quad or \quad Log\,K = \frac{nE^0F}{2.303RT} \quad or \quad Log\,K = \frac{nE^0}{0.0591}\ at\ 25°\ C$$

Nernst Equation and its applications

In 1889, Walter Nernst derived a mathematical expression which helps to calculate the electrode potential (E) on the basis of standard electrode potential (E^0) and temperature. The mathematical expression is known as Nernst equation.

$$E = E^0 - \frac{2.303RT}{nF}\,Log\,K \quad or\ E = E^0 - \frac{2.303RT}{nF}\,Log\,\frac{Oxidised\ state}{Reduced\ state}$$

Where E = Electrode potential

E^0= Standard electrode potential

n = no. of electrons

T = absolute temperature in kelvin

F = Faraday of electricity

K = Equilibrium constant

R = Gas constant

The emf of any half-cell can be calculated as follows

(1) Zn electrode in contact with Zn2+ ions using Nernst equation emf can be calculated as follows

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

$$E_{Zn/Zn^{2+}} = E^0_{zn/Zn^{2+}} - \frac{RT}{nF}\,Ln\frac{a_{Zn^{2+}}}{a_{Zn}}$$

Now, in standard state the value of active mass is unity so $a_{zn} = 1$

$$E_{Zn/Zn^{2+}} = E^0_{zn/Zn^{2+}} - 2.303\frac{RT}{nF}\,Log\,a_{Zn^{2+}}$$

Now at 25° C,

$$E_{Zn/Zn^{2+}} = E^0_{zn/Zn^{2+}} - \frac{0.0591}{2} \, Log \, a_{Zn^{2+}}$$

(2) For Ag metal in contact with Ag^+ ions

$Ag \rightarrow Ag^+ + e^-$

$$E_{Ag/Ag^+} = E^0_{Ag/Ag^+} - \frac{RT}{nF} \, Ln \, a_{Ag^+}$$

$$E_{Ag/Ag^+} = E^0_{Ag/Ag^+} - \frac{0.0591}{1} \, Log \, a_{Ag^+}$$

(3) Gas electrode

When H_2 gas is passed through a solution containing H^+ ions the H_2 ionises as follows

$\frac{1}{2}H_{2(g)} \rightarrow H^+ + e^-$

$$E_{H_2/H^+} = E^0_{H_2/H^+} - \frac{0.0591}{1} \, Log \, H^+$$

Now E^0 for Hydrogen is zero and –Log H^+ is pH.

$$E_{H_2/H^+} = 0.0591 \, pH$$

(4) Inert electrode

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$$E_{Fe^{2+}/Fe^{3+}} = E^0_{Fe^{2+}/Fe^{3+}} - \frac{RT}{nF} \, Ln \, \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$E_{Fe^{2+}/Fe^{3+}} = E^0_{Fe^{2+}/Fe^{3+}} - 0.0591 \, Log \, \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

In general equation for any metal in contact with its salt can be represented as follows.

M → $M^+ + e^-$

$$E_{M/M^+} = E^0_{M/M^+} - \frac{RT}{nF} \, Log \, a_{M^{+n}}$$

$$E_{M/M^+} = E^0_{M/M^+} - \frac{0.0591}{n} \, Log \, a_{M^{+n}}$$

I have work hard preparing this material……

You also work hard preparing from this material!!!!

Best Luck….