

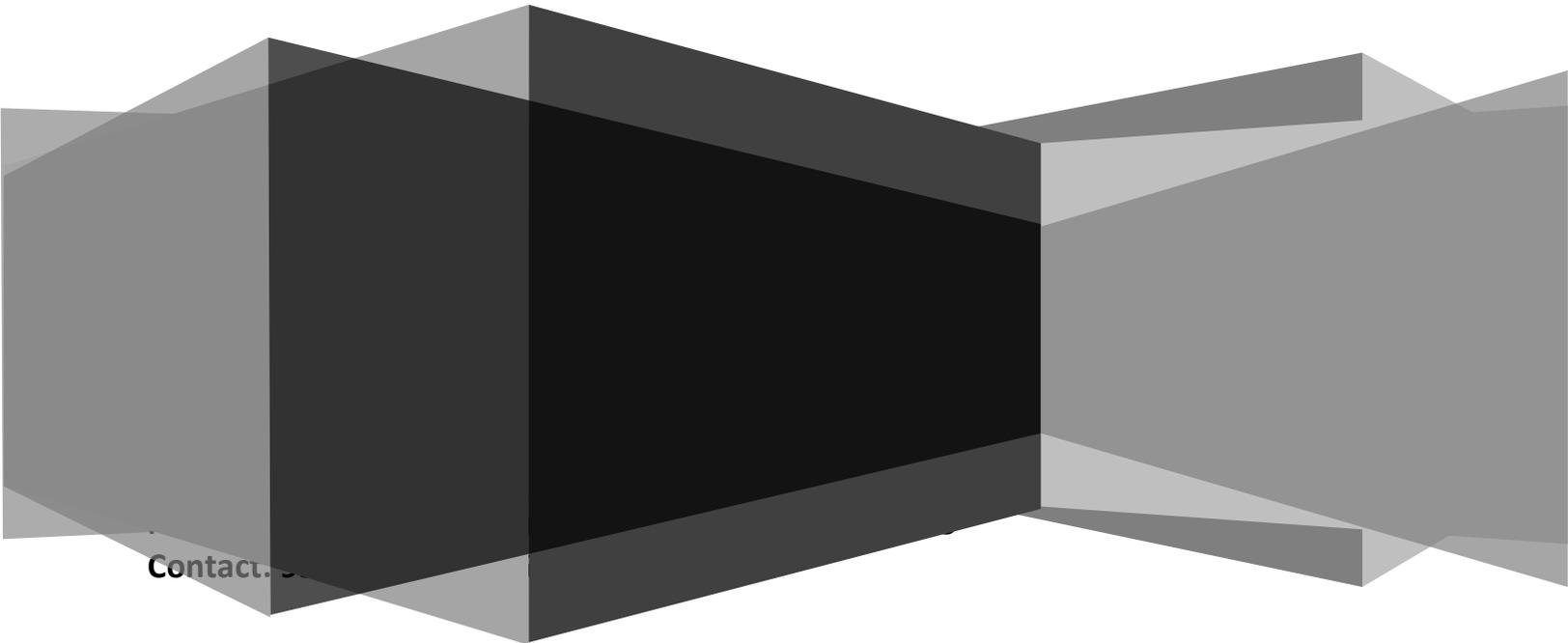
Marketed and Distributed by FaaDoEngineers.com

ELECTRO CHEMISTRY

GUPTA CLASSES

For any help contact:

9953168795, 9268789880

Contact: 

It is the branch of chemistry which deals with the relationship between electrical energy & chemical changes taking place in redox reaction.

Electrode potential

When an electrode is dipped in the solution of its ions it has a tendency to lose or gain electrons. This tendency of an electrode is known as electrode potential.

Tendency to gain electrons is known as *reduction potential* & tendency to lose electrons is known as *oxidation potential*.

Electrochemical series

A series of half cell reaction in which various half cell reactions are arranged in order of decreasing reduction potential is known as electrochemical series.

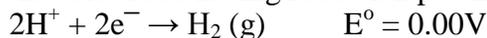
Information's conveyed by reduction potential

- (1) An element having lower value of reduction potential will be stronger reducing agent.
- (2) An element having higher value of reduction potential will stronger oxidizing agent.
- (3) A metal with lower value of reduction potential will displace a metal with higher value of reduction potential from its salt solution.
- (4) A metal with negative value of reduction potential will displace H_2 from acids.

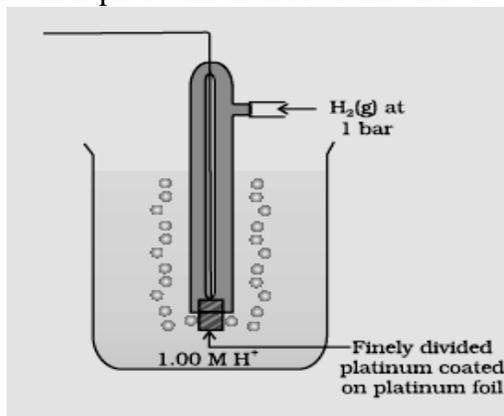
If concentration of the solution is 1 molar & temperature is 298K, the electrode potential is known as *standard electrode potential* (E°).

Normal hydrogen electrode (N.H.E.) or Standard hydrogen electrode

It is a reference electrode having reduction potential 0.00V.

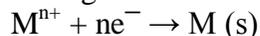


It consists of a platinum electrode coated with platinum black dipped in 1 molar acidic solution. Hydrogen gas under the pressure of 1atm is passed in the solution at 298 K.



Dependence of electrode potential on concentration of electrolyte & temperature (Nernst equation)

Let us consider following half cell reaction



According to Nernst equation

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}]}$$

As active mass of a solid is taken as 1,

$$\text{So } E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$\text{Or } E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

Where E = Electrode potential under given conditions

E° = Standard electrode potential

R = Gas constant

T = Temperature in K

F = 1 Faraday (96500 C)

n = number of electrons involved in the reaction

At 298K the expression is modified to give following expression

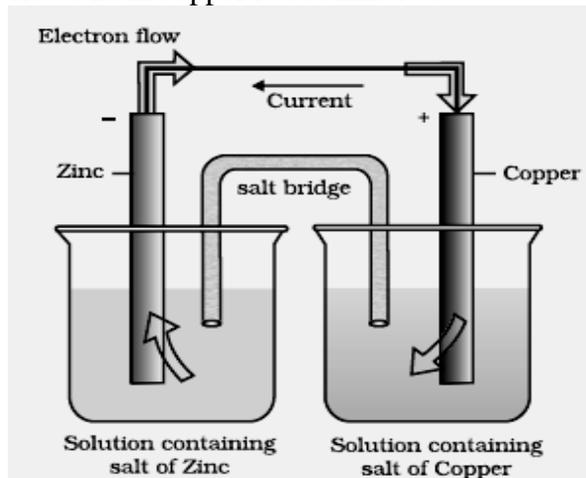
$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

Electrochemical cell or Galvanic cell or Voltaic cell

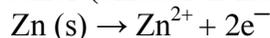
It is a chemical device in which redox reactions take place indirectly & chemical energy is converted into electrical energy which appears in the form of electric current.

Daniel cell: It is an example of galvanic cell.

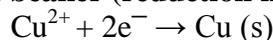
In the left beaker a zinc rod is dipped in 1 M $ZnSO_4$ solution & in the right beaker a copper rod is dipped in 1 M $CuSO_4$ solution. A salt bridge containing a strong electrolyte connects the two beakers. The two metal rods (electrodes) are connected through an ammeter, the electrons flow from zinc rod to copper rod and current flows from copper rod to zinc rod.



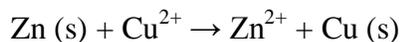
Reaction in left beaker (oxidation half cell reaction)



Reaction in right beaker (reduction half cell reaction)



Cell reaction



Marketed and Distributed by FaaDoEngineers.com

The electrode at which oxidation takes place is given a negative sign and is known as anode, in this cell zinc acts as anode.

The electrode at which reduction takes place is given a positive sign and is known as cathode, in this cell copper acts as cathode.

Representation of Daniel cell



Some examples of electrochemical cells

- (1) Zn (s)/ ZnSO₄ (1M)//AgNO₃ (1M)/Ag (s)
- (2) Cu (s)/ CuSO₄ (1M)// AgNO₃ (1M)/Ag (s)

Nature & Function of salt bridge

- (1) Salt in salt bridge should be a strong electrolytes.
- (2) It should be inert towards two solutions. KCl or NaCl cannot be used in salt bridge if any of the solution contains Ag⁺ ions.
- (3) The transport number of two ions given by electrolyte should be same. The transport number of an ion is the fraction of total current carried by an ion.
- (4) The two ions should have same ionic mobility i.e. same size.
- (5) The salt in salt bridge maintains the neutrality of two solutions.
- (6) It completes the inner circuit.

E.M.F. of a cell (Electromotive force of a cell) i.e. cell voltage.

It is the potential difference between two electrodes of a cell. When no current is drawn from the circuit i.e. circuit is open.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

If E°_{cell} has a positive value only then redox reaction will take place.

Difference between EMF and Potential difference.

EMF	POTENTIAL DIFFERENCE
1. EMF is the potential difference between the two electrodes of the cell when no current is flowing in the circuit (i.e., in an open circuit).	1. Potential difference is the difference between the electrode potentials of the two electrodes under any condition.
2. EMF can be measured by potentiometric method only so that the EMF sent by the potentiometer source is equal and opposite to that of the cell and there is no net current flowing in the circuit. It cannot be measured by a voltmeter which draws current.	2. Potential difference can be measured by a simple voltmeter.
3. EMF is the maximum voltage obtainable from the cell.	3. Potential difference is less than the maximum voltage obtainable from the cell (i.e. EMF of the cell).
4. EMF is responsible for the flow of steady current in the circuit.	4. Potential difference is not responsible for the flow of steady current in the circuit.

Prediction of a redox reaction

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

Contact: 9953168795, 9268789880

Marketed and Distributed by FaaDoEngineers.com

A cell corresponding to given redox reaction is constituted and e.m.f. of the cell is found out if the value comes to be positive the reaction will take place otherwise not.

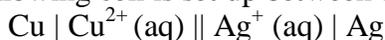
Assignments

1. For the cell shown below:



Calculate standard cell potential if standard state reduction electrode potentials for Cu^{2+}/Cu and Zn^{2+}/Zn are $+0.34\text{ V}$ and -0.76 V respectively.

2. Following cell is set up between copper and silver electrodes:



If its two half cells work under standard conditions, calculate the e.m.f. of the cell

$$[\text{Given } E^\circ \text{Cu}^{2+} | \text{Cu} (E^\circ_{\text{red}}) = +0.34 \text{ volt}$$

$$E^\circ \text{Ag}^+ | \text{Ag} (E^\circ_{\text{red}}) = +0.80 \text{ volt}]$$

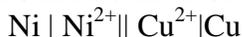
3. Write the cell reaction and calculate the standard E° of the cell:



$$\text{Given } E^\circ \text{Zn}^{2+} | \text{Zn} = -0.763 \text{ volt}$$

$$E^\circ \text{Cd}^{2+} | \text{Cd} = -0.403 \text{ volt}$$

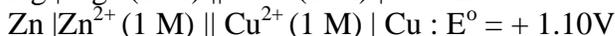
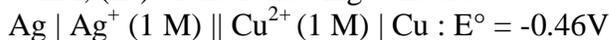
4. The standard EMF of the cell



Is 0.59 volt . The standard electrode potential (reduction potential) of copper electrode is 0.34 volt .

Calculate the standard electrode potential of nickel electrode.

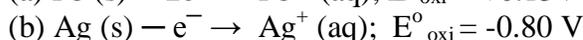
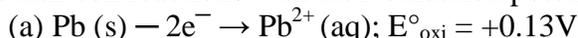
5. The e.m.f, (E°) of the following cells are



Calculate the e.m.f. of the cell

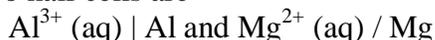


6. The half cell reactions with their oxidation potentials are



Write the cell reaction and calculate its emf-

7. Two half cells are



The reduction potentials of these half cells are -1.66 V and -2.36 V respectively. Calculate the cell potential. Write the cell reaction also.

8. Calculate E° for the cell



Given: $E^\circ \text{Al}^{3+} | \text{Al}$ and $E^\circ \text{Cu}^{2+} | \text{Cu}$ as -1.66V and 0.34 V respectively.

9. Calculate the EMF of the cell

(a) containing Nickel and Copper electrodes.

$$(\text{Given } E^\circ \text{Ni}^{2+} | \text{Ni} = -0.25\text{ V,}$$

$$E^\circ \text{Cu}^{2+} | \text{Cu} = +0.34\text{V})$$

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

Contact: 9953168795, 9268789880

Marketed and Distributed by FaaDoEngineers.com

(b) containing Zinc and Nickel electrodes

(Given $E^\circ \text{Zn}^{2+}/\text{Zn} = -0.76\text{V}$,

$E^\circ \text{Ni}^{2+}/\text{Ni} = -0.25\text{V}$

10. Predict reaction of 1 N sulphuric acid with the following metals: (i) Copper (ii) Lead (iii) Iron

Given, $E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34\text{ volt}$,

$E^\circ \text{Pb}^{2+}/\text{Pb} = -0.13\text{ volt}$ and

$E^\circ \text{Fe}^{2+}/\text{Fe} = -0.44\text{ volt}$

11. Can a solution of 1 M ZnSO_4 be stored in a vessel made of copper?

Given $E^\circ \text{Zn}^{2+}/\text{Zn} = +0.76\text{ volt}$ and

$E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34\text{ volt}$.

12. Can we store

(a) Copper sulphate solution in zinc vessel?

(b) Copper sulphate solution in silver vessel?

$E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34\text{V}$,

$E^\circ \text{Zn}^{2+}/\text{Zn} = -0.76\text{V}$,

$E^\circ \text{Ag}^+/\text{Ag} = 0.80\text{V}$

13. A copper wire is dipped in AgNO_3 solution kept in beaker A and a silver wire is dipped in a solution of copper sulphate kept in beaker B. If standard electrode potential for

$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ is $+0.34\text{ V}$ and for

$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ is $+0.80\text{ V}$,

Predict in which beaker the ions present will get reduced?

14. Why blue colour of copper sulphate solution gets discharged when zinc rod is dipped in it?

Given $E^\circ \text{Zn}^{2+}/\text{Zn} = +0.76\text{ volt}$ and

$E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34\text{ volt}$.

15. Can we use a copper vessel to store 1 M AgNO_3 solution?

Given $E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34\text{ volt}$ and

$E^\circ \text{Ag}^+/\text{Ag} = 0.80\text{V}$

16. Can chlorine gas be stored in a copper cylinder?

Given $E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34\text{ volt}$ and

$E^\circ \text{Cl}_2/\text{Cl}^- = 1.36\text{ V}$.

17. Using standard electrode potentials, predict the reaction, if any, that occurs between $\text{Fe}^{3+}(\text{aq})$ and I^- (aq)

$E^\circ \text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq}) = 0.77\text{V}$

$E^\circ \text{I}_2/2\text{I}^- (\text{aq}) = 0.54\text{V}$

18. Predict whether the following reaction would occur spontaneously at 298K:

$\text{Co}(\text{s}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + \text{Fe}(\text{s})$

Given $[\text{Co}^{2+}] = 1\text{ M}$ and $[\text{Fe}^{2+}] = 1\text{ M}$

$E^\circ \text{Co}^{2+}/\text{Co} = -0.28\text{V}$

$E^\circ \text{Fe}^{2+}/\text{Fe} = -0.44\text{V}$

19. Can a nickel spoon be used to stir a solution of silver nitrate? Support your answer with reason.

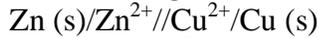
$E^\circ \text{Ni}^{2+}/\text{Ni} = -0.25\text{V}$

$E^\circ \text{Ag}^+/\text{Ag} = +0.80\text{V}$

Marketed and Distributed by FaaDoEngineers.com

Dependence of E cell on concentration of electrolytes i.e. Nernst equation for a cell

For the following cell



$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]}$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]}$$

$$E_{\text{cell}} = \left[E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} \right] - \left[E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]} \right]$$

$$= [E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}] - \frac{RT}{2F} \ln \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right]$$

$$= E^{\circ}_{\text{cell}} - \frac{RT}{2F} \ln \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right] = E^{\circ}_{\text{cell}} - \frac{2.303RT}{2F} \log \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right]$$

At 298K

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right]$$

For Zn (s)/Zn²⁺//Ag⁺/Ag

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Ag}^{+}(\text{aq})]^2} \right]$$

Dependence of hydrogen electrode on pH of solution

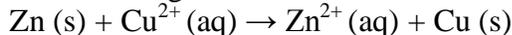
$$E_{\text{H}^+/\text{H}_2} = E^{\circ}_{\text{H}^+/\text{H}_2} - \frac{0.0591}{1} \log \left[\frac{1}{[\text{H}^+]} \right]$$

$$= 0 - 0.0591[-\log(\text{H}^+)] \quad -\log[\text{H}^+] = \text{pH}$$

$$= 0.0591 \times \text{pH}$$

Equilibrium constant and Nernst equation

For the following cell reaction



The Nernst equation is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{2F} \log \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right]$$

With time concentration of Zn²⁺ ion goes on increasing & concentration of Cu²⁺ goes on decreasing, so E_{cell} goes on decreasing and a state is reached when E_{cell} becomes equal to zero, this is the state of equilibrium.

$$E_{\text{cell}} = 0 = E^{\circ}_{\text{cell}} - \frac{2.303RT}{2F} \log \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right]$$

$$E^{\circ}_{\text{cell}} = \frac{2.303RT}{2F} \log \left[\frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} \right]$$

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

Contact: 9953168795, 9268789880

$$\text{As } \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]} = K_c$$

$$\text{So } E^\circ_{\text{cell}} = \frac{2.303RT}{2F} \log K_c$$

At 298K

$$E^\circ_{\text{cell}} = \frac{0.0591}{2} \log K_c$$

Electrochemical cell & Gibbs energy of the reaction

$$E^\circ_{\text{cell}} = \frac{2.303RT}{nF} \log K_c$$

$$nFE^\circ = 2.303RT \log K_c$$

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

$$\text{So } \Delta G^\circ = -2.303 RT \log K_c$$

Assignments

1. The standard electrode potential for Daniel cell is 1.1V, calculate the standard Gibbs energy for the reaction.
2. Calculate the equilibrium constant for the reaction
 $\text{Cu (s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag (s)}$ $E_{\text{ocell}} = 0.46 \text{ V}$.
3. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10?
4. Calculate emf of the cell in which following reactions take place
 $\text{Ni (s)} + 2\text{Ag}^+(0.002\text{M}) \rightarrow \text{Ni}^{2+}(0.160\text{M}) + 2\text{Ag (s)}$
Given $E^\circ_{\text{cell}} = 1.05\text{V}$
5. In the following cell
 $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$ has $E^\circ_{\text{cell}} = 0.236\text{V}$ at 298K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Conductance of electrolytic solutions

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A}$$

Where R = Resistance of conductor

A = Area of cross section

l = length of conductor

ρ = Specific resistance or resistivity

Specific resistance may be defined as the resistance offered by a conductor of unit length length having area of cross section (unit length)², i.e. ohm cm or ohm m.

Conductance (G) is reciprocal of resistance

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

Where κ = specific conductance or conductivity. It is the conductance offered by a conductor of unit length having area of cross section (unit length)², i.e. ohm⁻¹ cm⁻¹ (S cm⁻¹) or ohm⁻¹ m⁻¹ (S m⁻¹).

Cell constant:

$$\text{Cell constant} = \frac{l}{A} = \frac{\rho}{G} = \rho \times R$$

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

Contact: 9953168795, 9268789880

Marketed and Distributed by FaaDoEngineers.com

$$K = \frac{\text{Cell constant}}{R}$$

Molar conductance at a given dilution

It is the total conductance offered by all the ions given by 1 mole of an electrolyte dissolved in given volume of solution (Λ_m)

$\Lambda_m = K \times V$, where V is the solution containing 1 gm mole of electrolyte.

If K is in $S \text{ cm}^{-1}$ and M is the molarity of solution, then

$$V = \frac{1000}{M}$$

$$\text{So } \Lambda_m = K \times \frac{1000}{M} \text{ S cm}^2 \text{mole}^{-1}$$

If K is in S/m then

$$V = 10^{-3}/M$$

$$\text{So } \Lambda_m = K \times 10^{-3}/M \text{ S m}^2/\text{mole}$$

Molar conductivity at infinite dilution

It is the total conductance offered by all the ions obtained by dissolving 1gm mole of electrolyte in large excess of water. (Λ_m^0)

Degree of dissociation of a weak electrolyte at a given dilution (α)

$$\alpha = \Lambda_m / \Lambda_m^0$$

Assignments

1. Resistance of a conductivity cell filled with 0.1 mole/L, KCl solution is 100Ω . If the resistance of the same cell filled with 0.02 mole/L KCl solution is 520Ω . Calculate the conductivity & molar conductivity of 0.02 mole/L KCl solution. The conductivity of 0.1 mole/L KCl solution is 1.29 S/m .
2. The electrical resistance of a column of 0.05 mole /L NaOH solution of diameter 1 cm & length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity & molar conductivity.

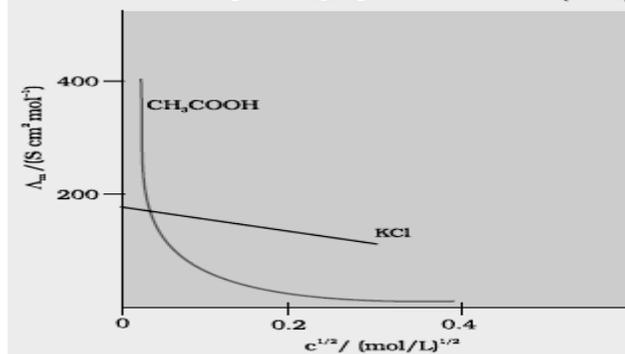
Effect of dilution on molar conductivity of the solution of an electrolyte

(a) Strong electrolytes

Strong electrolytes have high molar conductance even in concentrated solution. The molar conductance increases on dilution although increase is small. The effect of dilution on the molar conductance of strong electrolyte is given by Debye Huckel-Onsager equation.

$$\Lambda_m = \Lambda_m^0 - b\sqrt{C}$$

C = conc. of electrolyte, b = constant depending upon nature of solvent, electrolyte and temperature.



Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

Contact: 9953168795, 9268789880

The molar conductance at infinite dilution may be found out by extra polating the curve. In concentrated solution as the electrolyte is completely ionized, so even in concentrated solution these electrolytes have higher molar conductance. In concentrated solution inter ionic distance is small, so inter ionic interactions are strong so ions have low mobility. On dilution the inter ionic distance increases, so inter ionic interactions become weaker & so ionic mobility increases and molar conductance increases.

(b) **Weak electrolytes:** They have low conductance in concentrated solution as they have small degree of dissociation, with increase in dilution degree of dissociation increases, so conductance increases. There is large increase in molar conductance on dilution and the molar conductance at infinite dilution can not be found out by extra polating the curve.

Kohlrausch law of independent migration of ions

“Each ion makes a definite contribution towards the total conductance irrespective of the nature of other ion associated with it”.

$$\Lambda_m^{\circ} AB = \lambda^{\circ} A^{+} + \lambda^{\circ} B^{-}$$

Where $\lambda^{\circ} A^{+}$ = ionic conductance at A^{+} at infinite dilution and $\lambda^{\circ} B^{-}$ is ionic conductance of B^{-} at infinite dilution.

This law may be used to find out

(1) **The molar conductance of a weak electrolyte at infinite dilution.** The molar conductance of a weak electrolyte may be found out by considering the molar conductance at infinite dilution of strong electrolytes having corresponding ions. E.g. the molar conductance of acetic acid a weak electrolyte may be found out by knowing the molar conductance at infinite dilution of HCl, CH_3COONa and $NaCl$.

$$\Lambda_m^{\circ} HCl = \lambda^{\circ} H^{+} + \lambda^{\circ} Cl^{-} \dots\dots(1)$$

$$\Lambda_m^{\circ} CH_3COONa = \lambda^{\circ} Na^{+} + \lambda^{\circ} CH_3COO^{-} \dots\dots(2)$$

$$\Lambda_m^{\circ} NaCl = \lambda^{\circ} Na^{+} + \lambda^{\circ} Cl^{-} \dots\dots(3)$$

By adding equations (1) & (2) and subtracting (3) we can find out the molar conductance of acetic acid at infinite dilution

$$\Lambda_m^{\circ} CH_3COOH = \lambda^{\circ} H^{+} + \lambda^{\circ} CH_3COO^{-}$$

Assignments

(1) The molar conductivities at infinite dilution of $NaCl$, HCl and CH_3COONa are 126.4, 426.1 and 91.0 $S\ cm^2\ mole^{-1}$ respectively. What will be that of acetic acid?

(2) Molar conductivities at infinite dilution $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 457.6, 240.6 and 129.8 $S\ cm^2\ mole^{-1}$ respectively. Find out molar conductance of NH_4OH at infinite dilution.

(2) **Calculation of degree of dissociation of a weak electrolyte & dissociation constant.**

Degree of dissociation of a weak electrolyte at a given dilution (α)

$$\alpha = \Lambda_m / \Lambda_m^{\circ}$$

Assignments

(1) The conductivity of 0.001 M acetic acid is $4.95 \times 10^{-5}\ S/cm$. Calculate its dissociation constant. Given for acetic acid Λ_m° is $390.5\ S\ cm^2\ mole^{-1}$?

(2) At 291K the molar conductivities at infinite dilution of NH_4Cl , $NaOH$ and $NaCl$ are 129.8, 271.4 and 108.9 $S\ cm^2$ respectively. If molar conductivity of centimolar solution of NH_4OH is $9.33\ S\ cm^2$, what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation of NH_4OH .

(3) Calculation of solubility of a sparingly soluble salt.

$$\Lambda_m^{\circ} = K \times \frac{1000}{\text{Molarity}} = K \times \frac{1000}{\text{Solubility}}$$

$$\text{Solubility} = K \times \frac{1000}{\Lambda_m^{\circ}}$$

Assignment

(1) The conductivity of a saturated solution of AgCl at 288 K is found to be 1.382×10^{-6} S/cm. Find its solubility. Given ionic conductance of Ag^+ and Cl^- at infinite dilution are 61.9 and 76.3 S $\text{cm}^2 \text{mole}^{-1}$?

(4) Calculation of ionic product of water.

$$\Lambda_m^{\circ} = K \times \frac{1000}{\text{Molarity}}$$

$$\text{Molarity} = [\text{H}^+] = [\text{OH}^-] = K \times \frac{1000}{\Lambda_m^{\circ}}$$

$$\lambda^{\circ}\text{H}^+ = 349.8 \text{ S cm}^2 \text{mole}^{-1}$$

$$\lambda^{\circ}\text{OH}^- = 198.5 \text{ S cm}^2 \text{mole}^{-1}$$

according to Kohlraush's law

$$\Lambda_m^{\circ} \text{H}_2\text{O} = \lambda^{\circ}\text{H}^+ + \lambda^{\circ}\text{OH}^-$$

$$= 349.8 + 198.5 = 548.3 \text{ S cm}^2 \text{mole}^{-1}$$

The specific conductance of pure water at 298K is 5.54×10^{-8} S/cm.

$$\text{Molarity} = \frac{5.54 \times 10^{-8} \times 1000}{548.3} = 1.01 \times 10^{-7} \text{ g ions/L}$$

$$K_w = [\text{H}^+] [\text{OH}^-]$$

$$= (1.01 \times 10^{-7}) \times (1.01 \times 10^{-7})$$

$$= 1.02 \times 10^{-14}$$

Electrolytic cell & Electrolysis

When electricity is passed through the solution of an electrolyte or electrolyte in molten state then ions move towards oppositely charged electrodes and are liberated there by losing or gaining electrons.

Such a cell is known as electrolytic cell and the *decomposition of electrolytes with the passage of electricity is known as electrolysis.*

Faradays laws of electrolysis

(1) 1st Law: The amount of a substance deposited at an electrode is directly proportional to quantity of charge passed.

$w \propto Q$, where w = amount of substance deposited on an electrode

Q = quantity of charge in Coulombs.

$Q = I \times t$, where I = current strength in amperes and t = time in seconds

$w = z \times I \times t$, z = electrochemical equivalent, it is the amount of substance deposited by a current of 1 amp for 1 sec. i.e. 1 Coulomb.

Faraday : It is the total charge present over 1 mole of electrons. It is nearly equal to 96500 C. It is the charge required to deposit 1 g equivalent of a substance.

$$z = \frac{E}{96500}, \text{ } z = \text{electrochemical equivalent and } E = \text{equivalent weight.}$$

Marketed and Distributed by FaaDoEngineers.com

(2) 2nd Law: When same quantity of charge is passed through the solution of different electrolytes, the amounts of substances liberated at different electrodes are in the ratio of their equivalent weight.

$$\frac{\text{w.t. of A}}{\text{w.t. of B}} = \frac{\text{E. wt. of A}}{\text{E. wt. of B}}$$

Assignments

(1) How much charge is required for the following reduction?

(i) 1 mole of Al^{3+} to Al

(ii) 1 mole of Cu^{2+} to Cu

(iii) 1 mole MnO_4^- to Mn^{2+}

(2) How many Coulombs are required for the following oxidation

(i) 1 mole of H_2O to O_2

(ii) 1 mole FeO to Fe_2O_3

(3) How much copper will be deposited on the cathode of an electrolytic cell containing copper sulphate solution by the passage of a current of 2 amp for 30 minutes? (At. mass of copper = 63.5)

(4) Ag is electro deposited on a metallic vessel of surface area 800 cm² by passing a current of 0.2 amp for 3 hours. Calculate the thickness of Ag deposited. Given the density of Ag is 10.47 gm/cc and Atomic mass of Ag is 107.92 amu.

(5) Two electrolytic cells containing silver nitrate and copper sulphate solution are connected in series. A steady current of 2.5 amp was passed through them till 1.078 gm of Ag was deposited. How long did the current flow? What weight of copper will be deposited? (At. Mass of Ag = 107.8, Cu = 63.5)

Products of electrolysis

Products of electrolysis depend upon the electrolyte and nature of electrodes. If the electrode is inert like platinum, then it does not take part in electrode reaction and if electrode is reactive then it will take part in electrode reaction.

In presence of inert electrode

(1) Electrolysis of NaCl

Electrolysis of molten NaCl: NaCl ionizes to give Na^+ ion and Cl^- ion.

Cathode — $\text{Na}^+ + 1e^- \rightarrow \text{Na (s)}$

Anode — $\text{Cl}^- \rightarrow \text{Cl} + 1e^-$ (primary change)

$2\text{Cl} \rightarrow \text{Cl}_2$ (secondary change)

Sodium metal is deposited at cathode and chlorine gas is liberated at anode.

Electrolysis of aqueous solution of NaCl

Following reactions may take place at cathode

(1) $\text{Na}^+ (\text{aq}) + 1e^- \rightarrow \text{Na (s)}$ $E^\circ = -2.71 \text{ V}$

(2) $2\text{H}_2\text{O (l)} + 2e^- \rightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$ $E^\circ = -0.83 \text{ V}$

As the reduction potential of water is more than sodium, so second reaction takes place at cathode i.e. H_2 (g) is liberated at cathode. Reactions at anode

(1) $2\text{Cl}^- \rightarrow \text{Cl}_2 (\text{g}) + 2e^-$ $E^\circ = +1.36 \text{ V}$

(2) $\text{H}_2\text{O (l)} \rightarrow 2\text{H}^+ + 1/2\text{O}_2 + 2e^-$ $E^\circ = +1.23 \text{ V}$

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

Contact: 9953168795, 9268789880

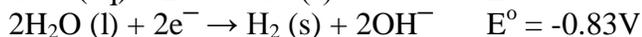
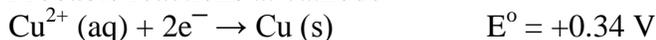
Marketed and Distributed by FaaDoEngineers.com

As reduction potential of reaction first is greater than second so second reaction should take place at anode but as the discharge potential of reaction first is less than second, so first reaction takes place at anode and chlorine gas is liberated at anode.

(2) Electrolysis of CuSO_4 solution

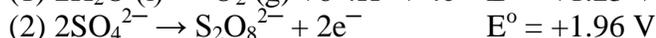
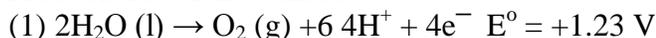
(a) Using inert electrode (Pt):

Probable reactions at cathode



As reduction potential of Cu is more so Cu is deposited at cathode

Probable reaction at anode

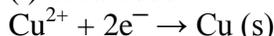


As reduction potential of reaction (1) is less than , reaction (2). So reaction (1) takes place at anode i.e. oxygen is liberated at anode.

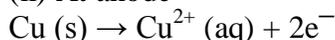
(b) Using Cu electrode

Following reactions take place

(i) at cathode



(ii) At anode



BATTERIES

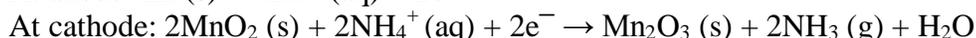
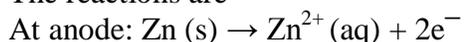
(1) *Primary batteries or primary cells*: The cells which cannot be recharged are known as primary cells.

(a) **Ordinary dry cell**:

Cylindrical zinc container acts as anode, a graphite rod

placed in the centre acts as cathode. Graphite rod is surrounded by powdered MnO_2 and carbon. The space between anode and cathode are filled with a paste of $\text{NH}_4\text{Cl} + \text{ZnCl}_2$.

The reactions are

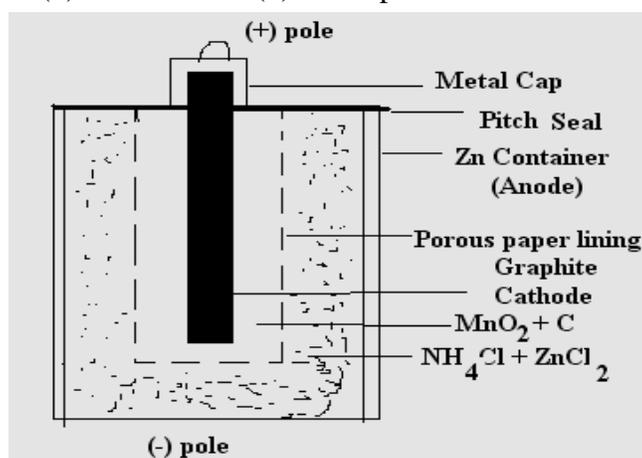


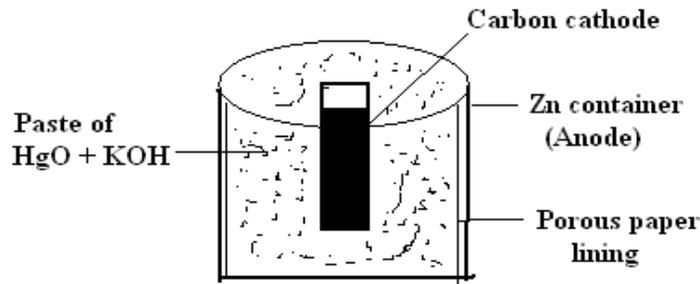
This cell gives a voltage 1.25 to 1.50 V.

In this cell one of the products NH_3 combines with ZnCl_2 to give $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$, so the reaction becomes irreversible and the cell cannot be recharged.

(b) **Mercury cell (Ruben-Mallory cell)**

Zn container acts as anode, graphite rod acts as cathode and a paste of mercuric oxide with KOH acts as electrolyte. A porous paper lining separates electrolyte from zinc anode.





At anode: $\text{Zn (s)} + 2\text{OH}^- \rightarrow \text{ZnO (s)} + \text{H}_2\text{O (l)} + 2\text{e}^-$
 At cathode: $\text{HgO (s)} + \text{H}_2\text{O (l)} + 2\text{e}^- \rightarrow \text{Hg (l)} + 2\text{OH}^-$
 This cell gives a constant potential of 1.35V.

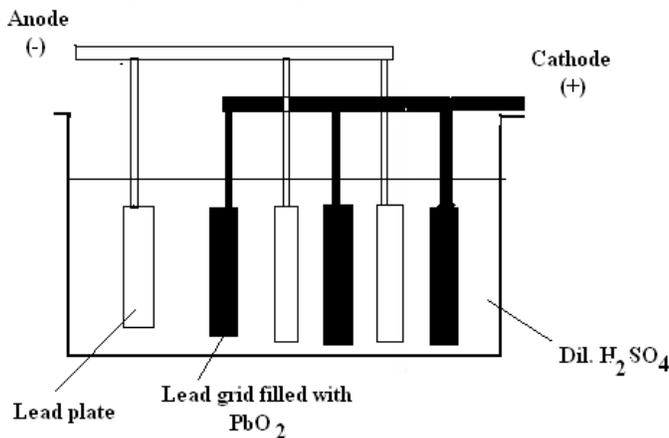
(2) Secondary Batteries or secondary cells

These cells can be recharged

(a) Lead storage battery: Each cell consists of the lead anode and a grid of lead packed with PbO_2 as cathode. The electrodes are arranged alternately separated by thin wooden or fibre glass sheets, the electrolyte is dilute H_2SO_4 which is 38% by mass i.e. having a density of 1.30 gm/cc.

Reactions at anode $\text{Pb (s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
 At cathode $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$
 During recharging following reactions take place
 At anode $\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb (s)} + \text{SO}_4^{2-}(\text{aq})$
 At cathode: $\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+ + 2\text{e}^-$

Each cell gives a voltage of 2V,



(b) Nickel cadmium storage cell (Ni cad cell)

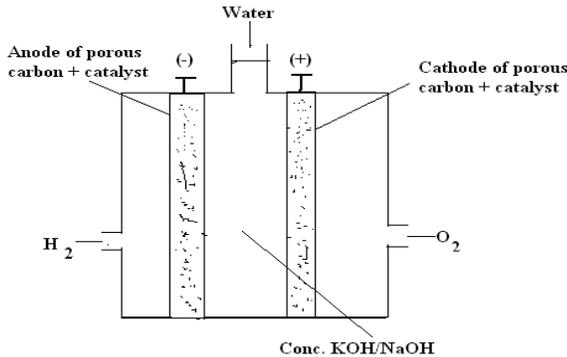
Anode is cadmium and a metal grid containing NiO_2 acts as cathode and electrolyte is KOH solution, this cell gives a voltage of 1.4V.

At anode: $\text{Cd (s)} + 2\text{OH}^- (\text{aq}) \rightarrow \text{Cd(OH)}_2 (\text{s}) + 2\text{e}^-$
 At cathode: $\text{NiO}_2 (\text{s}) + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Ni(OH)}_2 (\text{s}) + 2\text{OH}^-$

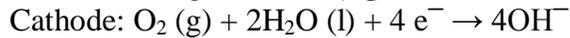
(c) FUEL CELLS: these cells energy produced by combustion of fuels like hydrogen, methane etc. directly into electrical energy. One of this type of cells is hydrogen-oxygen fuel cell which was used as a primary source of electrical energy in Appolo moon flights.

Marketed and Distributed by FaaDoEngineers.com

It contains porous carbon electrodes containing suitable catalyst which is finely divided platinum and palladium. Concentrated solution of KOH or NaOH is placed between two electrodes and it acts as electrolyte. Hydrogen and oxygen gases are bubbled through the porous electrodes into alkali solution.



Cell reactions are



This cell gives a voltage of 0.9 V, and chosen 60-70%.

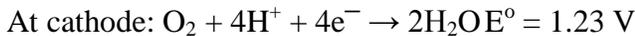
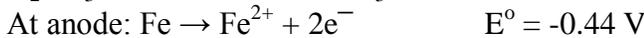
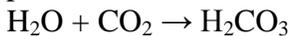
$$\text{Thermodynamic efficiency of fuel cell } (\eta) = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$$

CORROSION

When metals are exposed to atmosphere they react with moisture and other gases present in the atmosphere to give compounds of metals. This process is known as Corrosion. Corrosion of iron is known as rusting of iron. The formula of the rust is $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

Theory of corrosion (electrochemical theory)

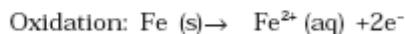
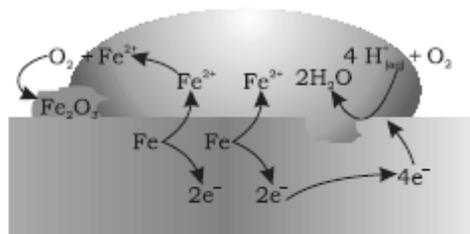
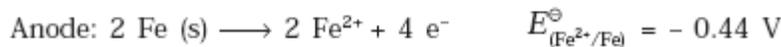
The metal surface is not completely smooth, it may have small pits in which water droplets are collected. CO_2 from the atmosphere dissolved in water to give carbonic acid which acts as electrolyte. One end of the pit behaves as anode and the other as cathode.



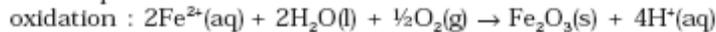
The ferrous ion is further converted into Fe_2O_3 and rust.



(Rust)



Atmospheric



Factors which promote corrosion

- (1) Reactivity of metal
- (2) Presence of impurities

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85

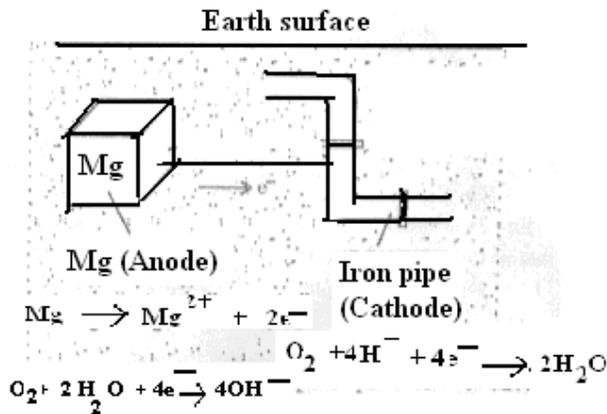
Contact: 9953168795, 9268789880

Marketed and Distributed by FaaDoEngineers.com

- (3) Presence of air & moisture
- (4) Strains in the metal
- (5) Presence of electrolytes

Prevention of corrosion

- (1) Barrier protection (surface protection): A barrier is put between surface of metal and atmosphere, this is done by
 - (a) Coating metal with paint, oil or grease.
 - (b) Iron surface is coated with less reactive metals like nickel, chromium or tin
 - (c) By coating iron surface with phosphates or other chemicals which form a tough film over the surface of iron.
- (2) Sacrificial protection (Galvanisation): Iron metal is coated with more reactive metals like Zn. The more reactive metal becomes anode and is protected from oxidation.
- (3) Electrical protection (Cathodic protection): under ground iron pipes are protected by this method. The iron pipes are connected to a more reactive metal like magnesium or Zinc directly or through a wire and is made cathode. These metals become anode and are oxidized and iron is not oxidized i.e. not rusted.



Marketed and Distributed by FaaDoEngineers.com

Nishant Gupta, D-122, Prashant vihar, Rohini, Delhi-85
Contact: 9953168795, 9268789880