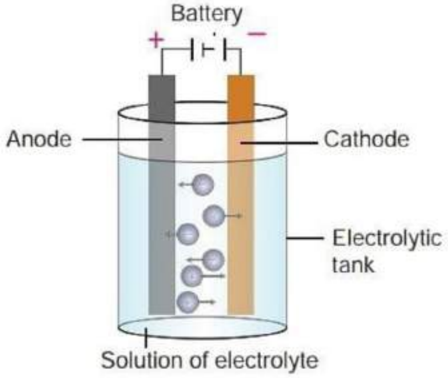
Chapter 3

Electrochemistry

Electrolytic Cells, Electrolysis & Products of Electrolysis

What is an Electrolytic Cell?

- An electrolytic cell can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction.
- Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds.
- For example, water can be subjected to electrolysis (with the help of an electrolytic cell) to form gaseous oxygen and gaseous hydrogen.
- This is done by using the flow of electrons (into the reaction environment) to overcome the activation energy barrier of the non-spontaneous redox reaction. The three primary components of electrolytic cells are:

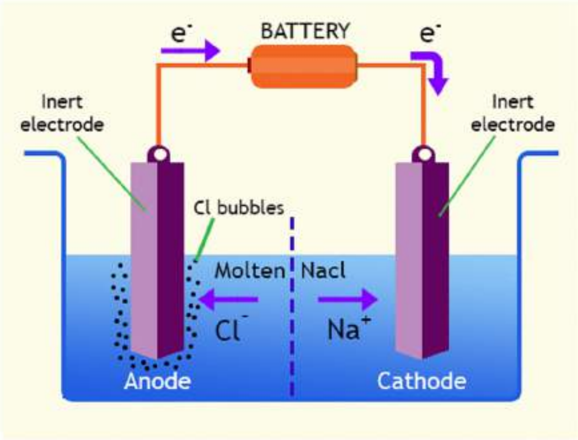


Components of Electrolytic Cell

- Cathode (which is negatively charged for electrolytic cells)
- Anode (which is positively charged for electrolytic cells)
- Electrolyte
- The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Commonly used electrolytes in electrolytic cells include water (containing dissolved ions) and molten sodium chloride.

Working of an Electrolytic Cell

- Molten sodium chloride (NaCl) can be subjected to electrolysis with the help of an electrolytic cell, as illustrated below.



- Here, two inert electrodes are dipped into molten sodium chloride (which contains dissociated Na+ cations and Cl– anions).
- The metal strip at which positive current enters is called an anode; the anode is positively charged in an electrolytic cell. On the other hand, the electrode at which the current leaves is called the cathode. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive Current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

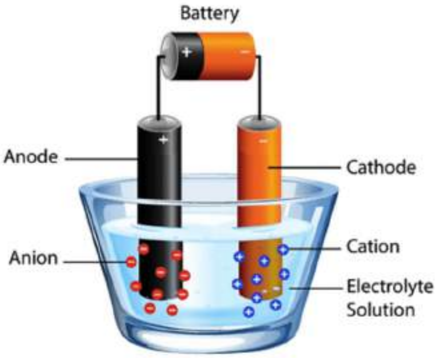
- When an electric current is passed into the circuit, the cathode becomes rich in electrons and develops a negative charge.
- The positively charged sodium cations are now attracted towards the negatively charged cathode.
- This results in the formation of metallic sodium at the cathode. Simultaneously, the chlorine atoms are attracted to the positively charged cathode.
- This results in the formation of chlorine gas (Cl2) at the anode (which is accompanied by the liberation of 2 electrons, finishing the circuit).
- The associated chemical equations and the overall cell reaction are provided below.

Reaction at Cathode: $Na^+ + e^- \rightarrow Na$
Reaction at Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
Cell Reaction: $2NaCl \rightarrow 2Na + Cl^-$

- Thus, molten sodium chloride can be subjected to electrolysis in an electrolytic cell to generate metallic sodium and chlorine gas as the products.

Electrolysis

The decomposition of electrolyte solution by passage of electric current, resulting in deposition of metals or liberation of gases at electrodes is known as electrolysis.



Electrolysis

Faraday's laws of electrolysis

(i) First law of electrolysis;

The amount of substance deposited or liberated at an electrode is directly proportional to the amount of charge passed (utilized) through the solution.
$w \propto Q$
W = weight liberated, Q = charge in coulomb
$w = ZQ$
Z = electrochemical equivalent
when $Q = 1$ coulomb, then $w = Z$
Thus, weight deposited by a 1-coulomb charge is called electrochemical equivalent.
Let 1-ampere current is passed till 't' seconds.
Then, $Q = It$ $w = ZIt$
1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at the corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulombs.

1 Coulomb will liberate $\frac{E}{96500}$ gm; By definition, $Z = \frac{E}{96500}$

$W = \frac{ItE}{96500}$

When gas is evolved at an electrode, then the above formula changes as,

$V = \frac{ItV_e}{96500}$

where V = volume of liberated gas, V_e = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulombs at STP.

(ii) Second law of electrolysis

When the same amount of charge is passed through different electrolyte solutions connected in series then the weight of substances deposited or dissolved at anode or cathode is in the ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

Electrolysis of Molten Sodium Chloride

$NaCl(molten) \rightarrow Na + Cl^-$

Reactions at anode (oxidation); cathode (reduction)

$2Cl^- \rightarrow Cl_2(g) + 2e^-$; $2Na + 2e^- \rightarrow 2Na(l)$

- In the electrolysis process, we have discussed above, we have taken molten salt as an electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, an aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depend on the ability of cation to get reduced and the ability of anion to get oxidized.
- The ability of an ion to get oxidized or reduced depends upon the size, mass, positive charge, negative charge etc.
- Thus it is not possible to predict qualitatively which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it.
- This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors responsible for an ion's ability to discharge.
- The value is referred to as standard potential, which is determined by keeping the concentration of ion as 1 M, the pressure of the gas at 1 atm,

and the measurement done at 25ºC. For a cation, the standard reduction potential (SRP) values are compared.

- The cation having a higher standard reduction potential value is discharged in preference to cation with a lower SRP value provided the ions are at a 1M concentration. For an anion, the standard oxidation potential (SOP) values are compared and an anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion.

Products of Electrolysis:

1. Products of electrolysis depend on the material being electrolyzed. In other words, the nature of electrolyte governs the process of electrolysis. The process is fast for a strong electrolyte whereas for a weak electrolyte an extra potential better known as overpotential is required.
Products of electrolysis depend on upon the value of this over potential too.
2. Products of electrolysis depend on the nature of electrodes too. That is, in the case of the inert electrode (say gold, platinum), it doesn't participate in the reaction whereas if the electrode used is reactive in nature it takes part in the reaction.
3. Various oxidising and reducing species present in the electrolytic cell do affect the products of electrolysis.
4. The products of electrolysis depend on standard electrode potentials of the different oxidizing and reducing species present in the electrolytic cell.
5. In the case of multiple reactions, the product of electrolysis depends on the standard electrode potential of various reactions taking place. For example, electrolysis of an aqueous solution of sodium chloride. Out of the multiple reduction reactions taking place, the reduction reaction which has the highest value of standard electrode potential takes place at the cathode. Similarly, out of the multiple oxidation reactions, the oxidation reaction which has the lowest value of standard electrode potential takes place at the anode.

The SRP Values at 25º C for some of the reduction half-reaction are given in the table below.

S. NO.	Reduction half cell reaction	E^o in volts at 25^0
1.	$F_2 + 2e^- \rightarrow\rightarrow 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \rightarrow Co^2+$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	+ 1.65

5.	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \rightarrow Au$	+ 1.50
7.	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
8.	$Cr_2O^{2-}{}_7 + 14\ H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \rightarrow Hg_2{}^2+$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \rightarrow CuI$	+ 0.86
14.	$Ag^+ + e^- \rightarrow Ag$	+ 0.799
15.	$Hg_2{}^{2+} + 2e^- \rightarrow 2Hg$	+ 0.79
16.	$Fe^{3+} + e^- \rightarrow Fe^2+$	+ 0.77
17.	$I_2 + 2e^- \rightarrow 2I^-$	+ 0.535
18.	$Cu^+ + e^- \rightarrow Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \rightarrow Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \rightarrow Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \rightarrow Cu+$	+ 0.15
23.	$Sn^{4+} + 2e^- \rightarrow Sn^2+$	+ 0.13
24.	$2H^+ + 2e^- \rightarrow H_2$	+ 0.00
25.	$Fe^{3+} + 3e^- \rightarrow Fe$	- 0.036
26.	$Pb^{2+} + 2e^- \rightarrow Pb$	- 0.126
27.	$Sn^{2+} + 2e^- \rightarrow Sn$	- 0.14
28.	$Agl + e^- \rightarrow Ag + I^-$	- 0.151
29.	$Ni^{2+} + 2e^- \rightarrow Ni$	- 0.25
30.	$Co^{2+} + 2e^- \rightarrow Co$	- 0.28
31.	$Cd^{2+} + 2e^- \rightarrow Cd$	- 0.403
32.	$Cr^{3+} + e^- \rightarrow Cr^2+$	- 0.41

33.	$Fe^{2+} + 2e^- \rightarrow Fe$	- 0.44
34.	$Cr^{3+} + 3e^- \rightarrow Cr$	- 0.74
35.	$Zn^{2+} + 2e^- \rightarrow Zn$	- 0.762
36.	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	- 0.828
37.	$Mn^{2+} + 2e^- \rightarrow Mn$	- 1.18
38.	$Al^{3+} + 3e^- \rightarrow Al$	- 1.66
39.	$H_2 + 2e^- \rightarrow 2H^-$	- 2.25
40.	$Mg^{2+} + 2e^- \rightarrow Mg$	- 2.37
41.	$Na+ + e^- \rightarrow Na$	- 2.71
42.	$Ca^{2+} + e^- \rightarrow Ca$	- 2.87
43.	$Ba^{2+} + 2e^- \rightarrow Ba$	- 2.90
44.	$Cs^+ + e^- \rightarrow Cs$	- 2.92
45.	$K^+ + e^- \rightarrow K$	- 2.93
46.	$Li^+ + e^- \rightarrow Li$	- 3.03

- When a solution of an electrolyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of an ion in the solution.
- The value is referred to as potential, called reduction potential for cation and oxidation potential for the anion. The relation between reduction potential and standard reduction potential is given by the Nernst equation, as

$$E_{RP} = E_{RP}^{0} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

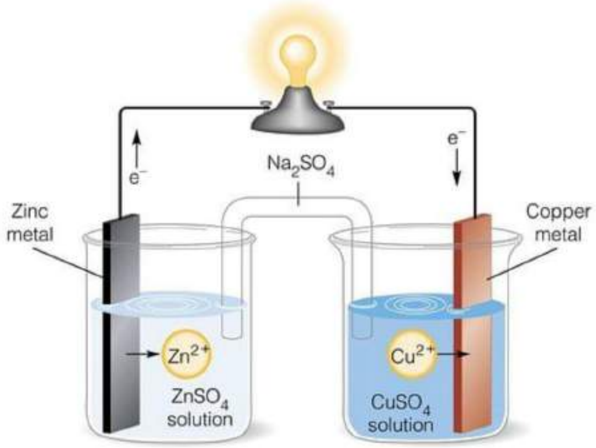
- Where E_{RP} = Reduction potential of cation and E^{o}_{RP} = Standard reduction potential of the cation.
- Thus, it is possible that a cation (A^+) with lower standard reduction potential getting discharged in preference to cation (B^+) having higher standard reduction potential because their concentration might be such that the reduction potential of A is higher than that of B^+.

- When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

Daniell Cell & Galvanic Cell

Daniell cell

It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current. It consists of two half-cells. The half-cells on the left contain a zinc metal electrode dipped in $ZnSO_4$ solution.

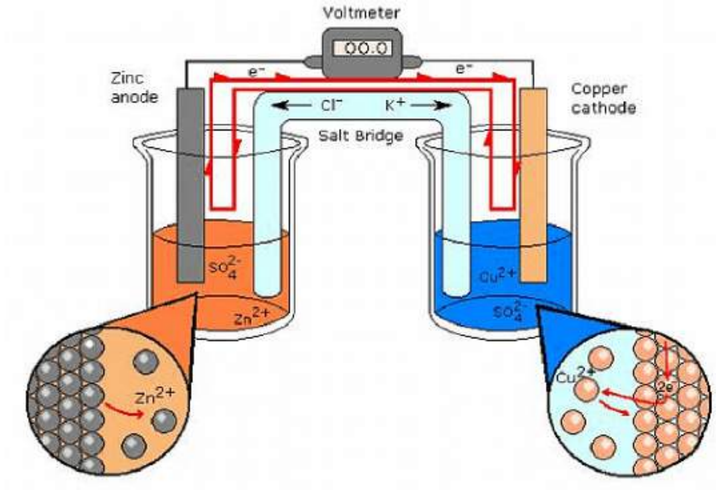


Daniell cell

The half-cell on the right consists of the copper metal electrode in a solution CuSO4. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.

When the zinc and copper electrodes are joined by a wire, the following observations are made:

- There is a flow of electric current through the external circuit.
- The zinc rod loses its mass while the copper rod gains in mass.
- The concentration of $ZnSO_4$ solution increases while the concentration of copper sulphate solution decreases.
- The solutions in both the compartments remain electrically neutral.



During the passage, if the electric current through the external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidized to zinc ions which go into the solution.

The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu2+ ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

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

Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at the copper electrode, reduction takes place; it is the cathode of the cell and is positively charged.

Thus, the above points can be summed up as:

- Voltaic or Galvanic cell consists of two half-cells. The reactions occurring in half-cells are called half-cell reactions. The half-cell in which oxidation taking place is called oxidation half-cell and the reaction taking place in it is called oxidation half-cell reaction. Similarly, the half-cell that occurs is called reduction half-cell and the reaction taking place in it is called reduction half-cell reaction.
- The electrode where oxidation occurs is called the anode and the electrode where reduction occurs is termed cathode.
- Electrons flow from anode to cathode in the external circuit.
- Chemical energy is converted into electrical energy.
- The net reaction is the sum of two half-cell reactions. The reaction is Daniell cell can be represented a

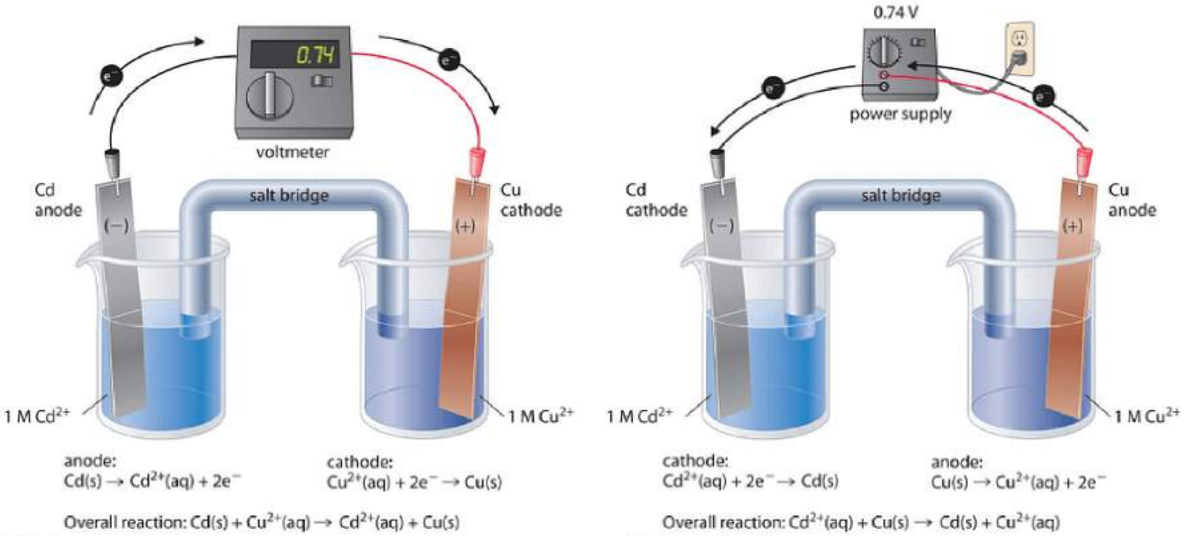
Oxidation half reaction	Reduction half reaction	Net reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Oxidation half reaction	Reduction half reaction	Net reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Electrode Signs

The signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells.

Electrolytic Cell	**Volatic or Galvanic Cell**
E.m.f. is applied to cell	**E.m.f. is generated by cell**



(a) Galvanic cell

(b) Electrolytic cell

Reversible and Irreversible Cells

	Electrolytic cell		**Voltaic or Galvanic cell**	
	Anode	**Cathode**	**Anode**	**Cathode**
Sign	+	-	-	+
Electron flow	Out	in	Out	in
Half-reaction	Oxidation	reduction	Oxidation	reduction

Daniell cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,
$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$
stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.
$Cu + Zn^{2+} \rightarrow Zn + Cu^{2+}$
Such a cell is termed a reversible cell. Thus, the following are the two main conditions of reversibility:

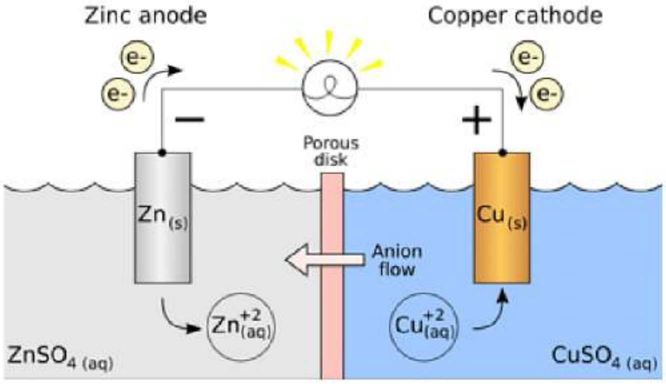
- The chemical reaction of the cell stops when an exactly equal opposing emf is applied.
- The chemical reaction of the cell is reversed and the current flows in the opposite direction when the opposing emf is slightly greater than that of the cell.
- Any other cell which does not obey the above two conditions is termed irreversible.
- A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is irreversible.
- Similarly, the cell Zn|H2S04(aq)|Ag is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,
- $Zn + 2^{H+} \rightarrow Zn^{2+} + H_2$ is not reversed but the cell reaction becomes $2Ag + 2H^+ \rightarrow 2Ag^+ + H_2$

Galvanic Cells

Among other cells, a galvanic cell is a type of electrochemical cell. It is used to supply electric current by making the transfer of electrons through a redox reaction. A galvanic cell is an exemplary idea of how energy can be harnessed using simple reactions between a few given elements. It is amazing to study how a galvanic cell can be set up and utilized to obtain energy.
Explaining in the most simple terms, a galvanic cell acts as a device in which simultaneous oxidation and reduction reactions take place. These reactions are used

to convert chemical energy into electrical energy, which can be utilized for any commercial purpose.

Working of Galvanic Cells



Working of Galvanic Cells

The working of a galvanic cell is quite simple. It involves a chemical reaction that makes the electric energy available as the end result. During a redox reaction, a galvanic cell utilizes the energy transfer between electrons to convert chemical energy into electric energy.

The galvanic cell utilizes the ability to separate the flow of electrons in the process of oxidization and reduction, causing a half-reaction and connecting each with a wire so that a path can be formed for the flow of electrons through such wire.

This flow of electrons is essentially called a current. Such current can be made to flow through a wire to complete a circuit and obtain its output in any device such as a television or a watch.

A galvanic cell can be made out of any two metals. These two metals can form the anode and the cathode if left in contact with each other. This combination allows the galvanic corrosion of that metal which is more anodic. A connecting circuit shall be required to allow this corrosion to take place.

Setup of a Galvanic Cell

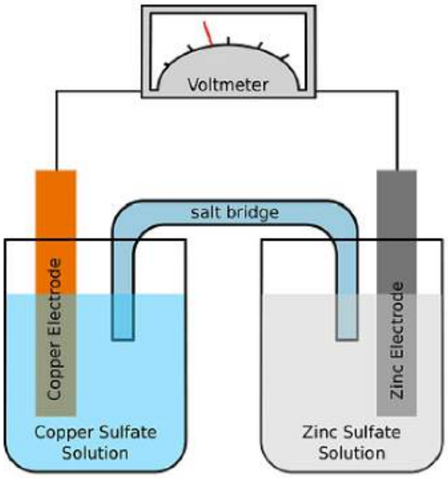
In order to create a galvanic cell, one would have to go through the following setup. The cell would ideally include two electrodes. One of these electrodes, the cathode, shall be a positively charged electrode while the other, shall be the anode, the negatively charged electrode.

These two electrodes shall form the two essential components of the galvanic cell. The chemical reaction related to reduction shall take place at the cathode while the oxidation half-reaction shall take place at the anode. As has already been said, any two metals can be used to create a chemical reaction.

Understanding the Galvanic Cell with an Example

Let us take an example where the two metals involved in the chemical reaction are zinc and copper. As the chemical reaction takes place, Zinc would end up losing two electrons. This will be taken up by copper to become elemental copper.

Since these two metals will be placed in two separate containers and would be connected by a conducting wire, an electric current would be formed, which would transfer all electrons from one metal to another.
At the same time, the two metals shall be immersed in a salt solution, say, Zinc sulphate and Copper sulphate in this case. In this case, the two solutions are not mixed together directly but can be joined using a bridge or a medium.
This medium shall be responsible for the transfer of ions but also make sure that the two solutions do not come to mix with each other.



Galvanic cell

Such a bridge helps in completing the circuit for carrying the electric charge and also makes sure that the solutions in the containers with the metals remain neutral and do not mix with each other.
As long as the salt bridge does not interfere with the redox reaction, under which oxidization and reduction are taking place, it does not matter which salt bridge is being used in the chemical reaction.

Some Important Terms

Some of the important terms brought into use in galvanic cells are listed below:
Phase boundaries: It refers to the two metals which act as cathode and anode.

Salt bridge: The connecting bridge or medium that allows a redox reaction to take place.
Oxidation and reduction: The chemical processes that allow the electric current to form and flow through a galvanic cell.

Electrochemical Cells, Galvanic Cells & Measurement of Electrode Potential

Key Concepts

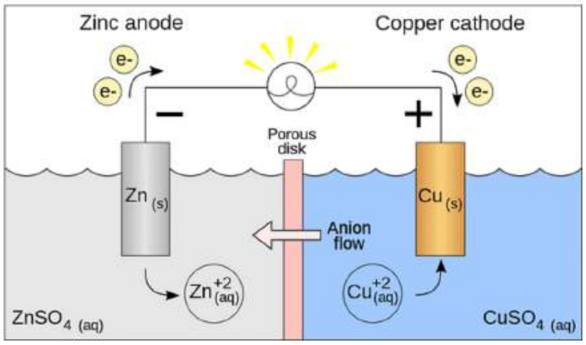
Electrochemical Cells

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).
An electrode and its electrolyte comprise an **Electrode Compartment.**
Electrochemical Cells can be classified as:
(i) **Electrolytic Cells:** Cells in which a non-spontaneous reaction is driven by an external source of current.
(ii) **Galvanic Cells:** Cells which produce electricity as a result of a spontaneous cell reaction.

Note: In a **galvanic cell**, cathode is positive with respect to anode.
In a **electrolytic cell**, anode is made positive with respect to cathode.

Galvanic Cell

This cell converts chemical energy into electrical energy.



Galvanic Cell

A galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as **voltaic cell.** It may be represented as shown in Fig. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.

Oxidation takes place at anode.
$Zn \rightarrow Zn^2 + 2e^-$ (loss of electron: oxidation)

Reduction takes place at cathode:
$Cu^2 + 2e^- \rightarrow Cu$(gain of electron ; reduction)

Overall process: $Zn(s) + Cu^{2+} \rightarrow Cu(s) + Zn^{2+}$
In galvanic cell like Daniell cell: electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+}; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

Representation of a cell (IUPAC Conventions):

Let us illustrate the convention taking the example of Daniel cell.
(i) Anodic half cell is written on left and cathodic half cell on right hand side.
$Zn(s)\ |ZnSO_4(sol)||CuSO_4(sol)|Cu(s)$
(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate slat bridge or any type of porous partition.
(iii) EMF (electromotive force) may be written on the righthand side of the cell.
(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.
$Zn|Zn^{2+}\ ||Cu^{2+}\ |Cu$
(v) Invert eletrodes are represented in the bracket
$Zn|ZnSO_4||H\ |H_2Pt$

Electrochemical cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore if the emf of the cell is E and nF is the amount of charge passed and ΔrG is the Gibbs energy of the reaction, then

$$\Delta_r G = -\ nFE_{(\mathrm{cell})}$$

It may be remembered that E(cell) is an intensive parameter but ΔrG is an extensive thermodynamic property and the value depends on n. Thus, if we write the reaction

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

$$\Delta_r G = -2FE_{\mathrm{(cell)}}$$

But when we write the reaction

$$2\ \mathrm{Zn(s)} + 2\,\mathrm{Cu^{2+}(aq)} \longrightarrow 2\ \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Cu(s)}$$

$$\Delta_r G = -4FE_{\mathrm{(cell)}}$$

If the concentration of all the reacting species is unity, then E(cell)
Thus, from the measurement of E^{-}_{Cell} we can obtain an important thermodynamic quantity, ΔrG^{-}, standard Gibbs energy of the reaction From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G^{\ominus} = -RT\ \ln\ K.$$

Relationship between ΔG and electrode potential:

Let n, Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,
Work done = Charge × Potential = nFE
From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion
ΔG = - nFE
Under standard state **Δ**Gº = - nFEº ....(1)
(i) From thermodynamics we know, DG = negative for spontaneous process. Thus from eq. (i) it is clear that the EMF should be ve for a cell process to be feasible or spontaneous.
(ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.

Standard free energy h, range of a cell may be calculated by electrode potential data. Substituting the value of Eº (i.e., standard reduction potential of cathode-standard reduction potential of anode) in eq. (i) we may get ΔGº.

Reactions	**ΔG**	**E**
Spontaneous	(-)	(+)
Non-spontaneous	(+)	(-)
Equilibrium	0	0

Measurement of Electrode Potential

Concept of electromotive force (EMF) of A Cell

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). EMF is called as cell potential. Unit of e.m.f. of cell is volt.
EMF of cell may be calculated as:
E_{cell} = reduction potential of cathode - Reduction potential of anode
Similarly, standard e.m.f. of the cell (E^{o}) may be calculated as
E^{o}_{cell} = Standard reduction potential of cathode - Standard reduction potential of anode.

Sign Convention of EMF

EMF of cell should be positive other wise it will not be feasible in the given direction.
$Zn|ZnSO_4||CuSO_4|Cu$, E = 1.10 volt (Feasible)
$Cu|CuSO_4||ZnSO_4|Zn$, E = - 1.10 volt (Not Feasible)

Salt Bridge

Two electrolyte solutions in galvanic cells are separated using salt bridge as represented in the Fig. Salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl, KNO_3, NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge.

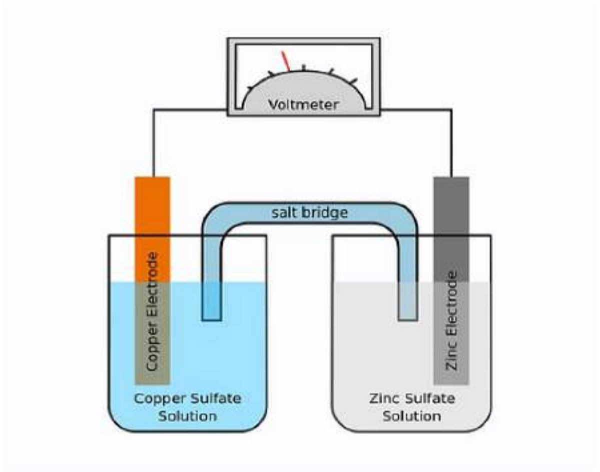


Fig: Salt bridgeSalt bridge contains high concentration of ions viz. K^+ and NO_3^- at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary; more over the K^+ and NO_3^- ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions completes the electrical circuit & permits the ions to migrate.

Faraday's Laws of Electrolysis

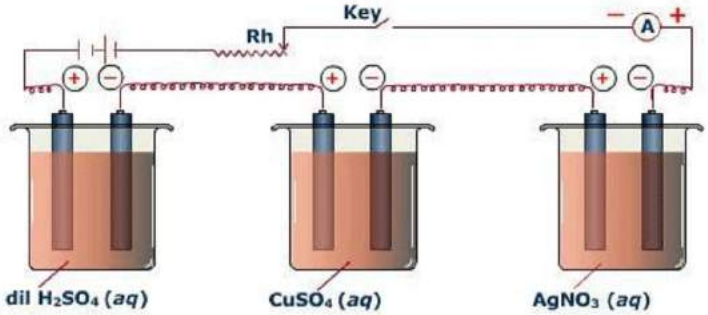


Fig: Electrolytic cell**Electrolytic cell:** The electrochemical cell which facilitates a chemical reaction through the induction of electrical energy is known as an electrolytic cell. This process of carrying out non-spontaneous reactions under the influence of electric energy is termed as electrolysis.

Michael Faraday conducted an extensive investigation on electrolysis of solutions and melts of electrolytes. He was the first scientist who described the quantitative aspects of Laws of Electrolysis. He proposed two laws to explain the quantitative aspects of electrolysis popularly known as Faraday's laws of electrolysis namely first law of electrolysis and the second law of electrolysis.

First Law of Electrolysis:

It is one of the primary laws of electrolysis. It states, during electrolysis, the amount of chemical reaction which occurs at any electrode under the influence of electrical energy is proportional to the quantity of electricity passed through the electrolyte.

Second Law of Electrolysis:

During electrolysis, when the same quantity of electricity passes through the electrolytic solution, a number of different substances liberated are proportional to their chemical equivalent weights (Equivalent weight is defined as the ratio of the atomic mass of metal and the number of electrons required for reducing the cation).

From these laws of electrolysis, we can deduce that the amount of electricity needed for oxidation- reduction depends on the stoichiometry of the electrode reaction. For example:
$Na^{+} + e^{-} \rightarrow Na$
As we can observe, one mole of the electron is required for the reduction of one mole of sodium ions. We know that charge on one electron is equal to 1.6021 × 10^{-19}C. Therefore, the charge on one mole of electrons is equal to:
$\mathbf{N_A \times 1.6021 \times 10^{-19} C = 6.02 \times 10^{23} mol^{-1} \times 1.6021 \times 10^{-19} C = 96487\ C\ mol^{-1}}$
This quantity of electricity is defined as one Faraday and is denoted by F.
Hence; one Faraday is defined as the charge carried per unit mole of electrons.
The product of an electrolytic reaction depends on the nature of the material being electrolyzed and the type of electrodes used.
In the case of an inert electrode such as platinum or gold, electrode does not participate in the chemical reaction and acts only as a source or sink for electrons. While, in the case of a reactive electrode, electrode participates in the reaction.
Hence, different products are obtained for electrolysis in the case of reactive and inert electrodes. Oxidizing and reducing species present in the electrolytic cell and their standard electrode potential too, affect the products of electrolysis.

Factors Affecting Products of Electrolysis:

1. Products of electrolysis depend on the material being electrolyzed. In other words, the nature of electrolyte governs the process of electrolysis. The process is fast for a strong electrolyte whereas for weak electrolyte an extra potential better known as over potential is required.
Products of electrolysis depend on upon the value of this over potential too.
2. Products of electrolysis depend on the nature of electrodes too. That is, in the case of the inert electrode (say gold, platinum), it doesn't participate in the reaction whereas if the electrode used is reactive in nature it takes part in the reaction.
3. Various oxidising and reducing species present in the electrolytic cell do affect the products of electrolysis.

4. The products of electrolysis depend on standard electrode potentials of the different oxidizing and reducing species present in the electrolytic cell.

5. In case of multiple reactions, product of electrolysis depends on the standard electrode potential of various reactions taking place. For example, electrolysis of aqueous solution of sodium chloride. Out of the multiple reduction reactions taking place, the reduction reaction which has highest value of standard electrode potential takes place at cathode. Similarly, out of the multiple oxidation reactions, the oxidation reaction which has the lowest value of standard electrode potential takes place at anode.

Nernst Equation, Equilibrium Constant from Nernst Equation, Half Cells

Nernst Equation

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

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$\Delta G = \Delta G^{\circ}$ RT ln Q ....(i)

where, ΔG and ΔG° are free energy and standard free energy change, 'Q' is reaction quotient.

$-\Delta G = nFE$ and $-\Delta G^{\circ} = nFE^{\circ}$

Thus from Eq. (i), we get $- nFE = - nFE^{\circ} + RT \ln Q$

At 25ºC, above equation may be written as $E = E^{\circ} - \frac{0.0591}{n} \log Q$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general, for a redox cell reaction involving the transference of n electrons

$aA + bB \rightarrow cC + dD$, the EMF can be calculated as:

$E_{Cell} = E^{\circ}_{Cell} - \frac{0.0591}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$

Thermodynamic Treatment of Nernest Equation

(i) Prediction and feasibility of spontaneity of a cell reaction.

Let us see whether the cell (Daniell) is feasible or not; i.e. whether Zinc will displace copper or not.

Zn | (s) | $ZnSO_4$(sol) || $CuSO_4$(sol) | Cu(s)

$E^0_{Zn^{2+}/Zn} = -0.76\text{volt}$; $E^0_{Cu^{2+}/Cu} = +0.34\text{volt}$

$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$

$= 0.34 - (-0.76) = +1.10$ volt

Since $E^0 = +ve$, hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

(ii) Determination of equilibrium constant form Nernst Equation: We know, that

$E = E^0 - \frac{0.0591}{n}\log Q$ ....(1)

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

From Eq. (i), we have

$0 = E^0 - \frac{0.0591}{n}\log K_{eq}$ or $K_{eq} = \text{anti}\log\left[\frac{nE^0}{0.0591}\right]$

(iii) Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E, then

$-\Delta G = nFE$ ....(i)

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P$ ....(ii)

From Eqs. (i) and (ii), we have

$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_P = DH - nFT\left[\frac{\partial E}{\partial T}\right]_P$

$\Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_P$

(iv) Entropy change inside the cell: We know that

$G = H - TS$ or $\Delta G = \Delta H - T\Delta S$ ....(i)

where ΔG = Free energy change; ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmholtz equation,

$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P$ ....(ii)

From Eqs. (i) and (ii), we have

$-T\Delta S = T\left[\frac{\partial \Delta G}{\partial T}\right]_P$ or $\Delta S = -\left[\frac{\partial \Delta G}{\partial T}\right]_P$

or $\Delta S = nF\left[\frac{\partial E}{\partial T}\right]_P$

where $\left[\frac{\partial E}{\partial T}\right]_P$ is called temperature coefficient of cell e.m.f.

Different types of half-cells and their reduction potential

(1) Gas - Ion Half Cell:

In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this cell, purified H_2 gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.

$H\,(aq)\;e^- \rightleftharpoons 1/2\,H_2$

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{1}\log\frac{(pH_2)^{1/2}}{[H^+]}$$

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M is contact with a solution containing M^n ions.

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

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

(3) Metal-Insoluble Salt-Anion Half Cell:

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg.-Silver-Silver Chloride Half Cell :
This half cell is represented as $Cl^-/AgCl/Ag$. The equilibrium reaction that occurs at the electrode is

$AgCl(s) + e^- \rightleftharpoons Ag^+(s) + Cl^-(aq)$

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - \frac{0.0591}{1}\log\left[Cl^-\right],\; E^0_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{(K_{sp})}{[Cl^-]}AgCl$$

(4) Oxidation-reduction Half Cell:

This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. Fe^2 - Fe^3 half cell.

$Fe^{3+}\,(aq) + e^- \rightleftharpoons Fe^{2+}\,(aq)$

$$E_{Fe^{3+}/Fe^{2+}} = E^0_{Fe^{3+}/Fe^{2+}} - \frac{0.0591}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Concentration cell

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

(i) Electrode Gas concentration cell:

Pt, $H_2(P_1)\ |H^+\ (C)|H_2(P_2)$, Pt

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell Process: $1/2H_2(p_1) \rightarrow H\ (c)\ e^-$ (Anode process)

$$\frac{H^+(c) + e^- \longrightarrow \tfrac{1}{2} H_2(p_2)}{\tfrac{1}{2} H_2(p_1) \rightleftharpoons \tfrac{1}{2} H_2(p_2)}$$

$$E = -\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$$

$$\text{or } E = -\left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right],$$

$$\text{At } 25^{\circ}C,\ E = -\frac{0.059}{2F}\log\left[\frac{p_2}{p_1}\right]$$

For spontanity of such cell reaction $p_1 > p_2$

(2) Electrolyte concentration cells:

$Zn(s)\ |ZnSO_4(C_1)\ ||ZnSO_4(C_2)\ |\ Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,

$Zn(s) \rightarrow Zn^2\ (C_1) + 2e^-$ (Anodic process)

$$\frac{Zn^{2+}(C_2) + 2e^- \longrightarrow Zn(s)}{Zn^{2+}(C_2) \rightleftharpoons Zn^{2+}(C_1)} \quad \text{(Over all process)}$$

From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

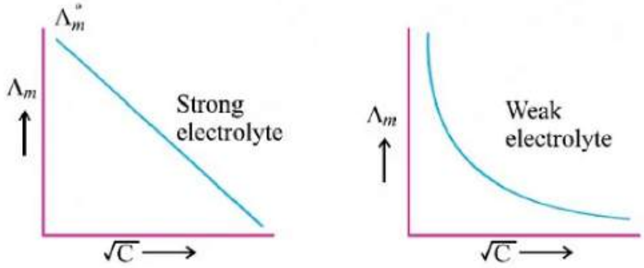
For spontanity of such cell reaction, $C_2 > C_1$.

Kohlrausch's Law

Kohlrausch's Law of Independent Migration of Ions:

Kohlrausch determine $\wedge_0$ values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in $\wedge_0$ value in each case remains the same

$\wedge^{0}_{m}$ (KCl) - $\wedge^{0}_{m}$ (KF) = $\wedge^{0}_{m}$ (NaCl) - $\wedge^{0}_{m}$ (NaF)
He also determined $\wedge^{0}$ values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in $\wedge_{0}$ values is each case remains the same.
$\wedge^{0}_{m}$ (KF) - $\wedge^{0}_{m}$ (NaF) = $\wedge^{0}_{m}$ (KCl) - $\wedge^{0}_{m}$ (NaCl)
This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.



Variation with Strong and Weak electrolytes
At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,
$\wedge^{0}_{m} = \lambda_{+}^{o} + \lambda_{-}^{o}$
Where λ^{0} is the contribution of the cation is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ^{0} is the molar ionic conductance of cation and λ_{-}^{o} is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

Uses of Kohlrausch's law

- Calculation of molar conductivity at infinite dilution for weak electrolytes
- Calculation of degree of dissociation.
- Calculation of dissociation constant for a weak electrolyte
- Calculation of solubility of sparingly soluble salt.

Application of Kohlrausch's law:

(1) **Determination of $\wedge^0_m$ of a weak electrolyte:** In order to calculate $\wedge^0_m$ of a weak electrolyte say CH_3COOH, we determine experimentally $\wedge^0_m$ values of the following three strong electrolytes:

(a) A strong electrolyte containing same cation as in the test electrolyte, say HCl

(b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa

(c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\wedge^0_m$ of CH_3COOH is the given as:

$\wedge^0_m (CH_3COOH) = \wedge^0_m (HCl) + \wedge^0_m (CH_3COONa) - \wedge^0_m (NaCl)$

Proof:

$\wedge^0_m (HCl) = \lambda^0_{H^+} + \lambda^0_{Cl^-}$ ....(i)

$\wedge^0_m (CH_3COONa) = \lambda_{CH_3COO^-} + \lambda_{Na^+}$ ....(ii)

$\wedge^0_m (NaCl) = \lambda_{Na^+} + \lambda_{Cl^-}$ ....(iii)

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$\wedge^0_m (HCl) + \wedge^0_{(CH_3COONa)} - \wedge^0_{(NaCl)} = \lambda^0_{H^+} + \lambda^0_{(CH_3COO^-)} = \wedge^0_{(CH_3COOH)}$

(2) Determination of degree of dissociation (α):

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\wedge_m}{\wedge^0_m}$$

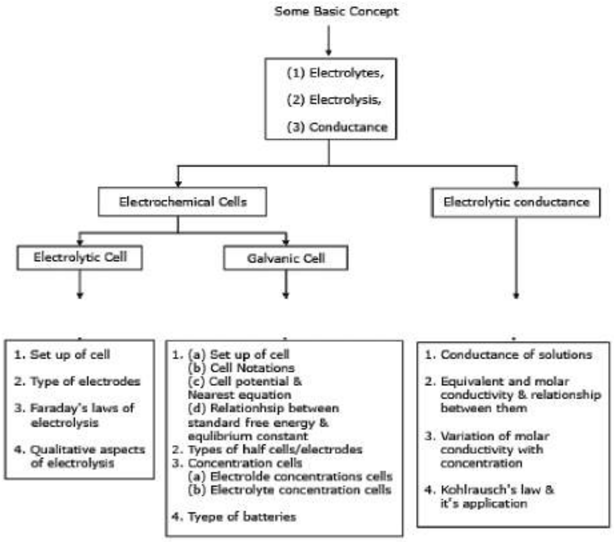
(3) Determination of solubility of sparingly soluble salt:

The specific conductivity of a saturated solution of the est electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\wedge^0_m$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\wedge^0_m = \frac{1000\,\kappa}{C}$$

Where C is the molarity of solution and hence the solubility.

ATLAS



Electroplating

Electroplating is the process through which one metal is plated to another metal through hydrolysis. It is usually done for decorative purposes along with prevention

of corrosion of metals

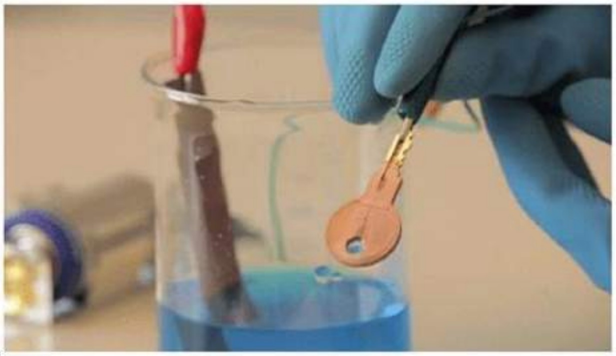


Fig: Electroplating

Electroplating is the process through which one metal is plated to another metal through hydrolysis. It is usually done for decorative purposes along with prevention of corrosion of metals. There are certain specific types of electroplating like copper plating, chromium plating and silver plating.

The manufacturers get the benefit of electroplating since they can easily use inexpensive metals like zinc and steel for the majority of the product and then electroplate different metals on outside for appearance, protection and achieving the other desired properties for the product. The surface can be plastic or even a metal.

The process of electroplating includes using an electrolytic cell which consists of applying a negative charge to the metal and dipping it in a solution containing metal salt i.e. electrolytes which is full of positively charged metal ions.

Attraction between the two metals occurs owing to the positive and the negative charges.

The process of electroplating was first discovered by Luigi Brugnatelli in 1805. He electroplated the gold by using the electrode position process.

CHOOSING THE ELECTROLYTES AND PREPARING THE SURFACE:

Determining the right electrolyte for electroplating is important to maintain the quality of plating. Some of the electrolytes used are acids, metal salts, bases or molten salts. While choosing the correct type of electrolyte, it is important to keep certain things in the mind. They are corrosion, brightness, reflectivity, resistance, hardness, ductility, mechanical strength and wear resistance.

The surface is prepared before starting to plate another metal on it is to make sure that the surface is clean and free from the contaminants which can interfere in the bonding. Due to contamination, lack of adhesion happens along with no deposition. The surface is prepared in three steps by cleaning it with solvents, treatment (surface modification where there is hardening of parts and application of metal layers) and rinsing.

USES OF ELECTROPLATING:

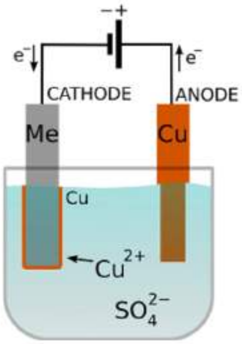


Fig: Process of electroplating

- It can make a relatively cheap metal like copper look expensive by coating copper with a thin layer of gold or silver.
- Electroplating can be used to make things rust resistant.
- Chromium plating improves the wear and appearance of the objects.

- Zinc or the tin coatings are used for making anything corrosion resistant.
- Electroplating can also be done for increasing the thickness of any item.
- Electroplating is mostly used in automobile industries, electronics, airplanes, toys and jewellery.

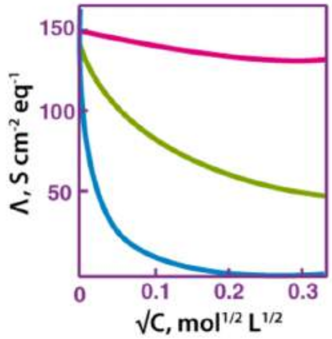
Variation of Conductivity & Molar Conductivity with Concentration

What is Specific Conductivity?

Specific conductivity or conductivity of an electrolytic solution at any given concentration is the conductance of unit volume of solution. It is the conductance when kept between two platinum electrodes with a unit area of cross-section.
The electrodes are at a distance of unit length.
Conductivity decreases with a decrease in concentration as the number of ions per unit volume that carry the current in a solution decrease on dilution.
The molar conductivity of a solution at a given concentration is the conductance of volume V of the solution containing one mole of electrolyte kept between two electrodes with an area of cross section A and distance of unit length.
$\Lambda_m = K/c$
Here, c = concentration in moles per volume, K = specific conductivity and Λ_m = molar conductivity. As the solution contains only one mole of electrolyte, the above equation can be modified as:
$\Lambda_m = KV$

Change in Molar Conductivity:

Molar conductivity increases with a decrease in concentration. This happens because the total volume, V, of the solution containing one mole of electrolyte also increases. Upon dilution, the concentration decreases.
Furthermore, when the concentration approaches zero, the molar conductivity of the solution is known as limiting molar conductivity, Ë°m. Variation of molar conductivity with concentration is different for both, strong and weak electrolytes.



Variation of Molar Conductivity with Concentration

Variation of Molar Conductivity with Concentration of Strong Electrolytes:

For strong electrolytes, the molar conductivity increases slowly with the dilution. The plot of the molar conductivity and c1/2 is a straight line having y-intercept equal to Ë°m. The value of limiting molar conductivity, Ë°m can be determined from the graph or with the help of Kohlrausch law.
For strong electrolytes, the molar conductivity increases slowly with the dilution. Thus, the plot of the molar conductivity and c1/2 is a straight line having y-intercept equal to Ë°m. The general equation for the plot is:
$\Lambda_m = \text{Ë°m} - Ac_1/2$
Where −A is a constant equal to the slope of the line. Furthermore, the value of "A" for a given solvent depends on the type of electrolyte at a particular temperature. Hence, it differs from solution to solution.

Variation of Molar Conductivity with Concentration for Weak Electrolytes:

For weak electrolytes, the graph plotted between molar conductivity and $c_1/2$ (where c is the concentration) is not a straight line. This is because weak electrolytes have lower molar conductivities and lower degree of dissociation at higher concentrations which increases steeply at lower concentrations. Hence, we use the Kohlrausch law of independent migration of ions for determining to limit molar conductivity, Ëm° of weak electrolytes.

Batteries & Primary Batteries

What is a Battery?

You can get a galvanic cell by combining two different electrodes together. However, you cannot use all the galvanic cells as practical cells or batteries. Usually, we use the term battery for a combination of a few cells that are similar in nature. A practical battery must have the following characteristics:

- It must be light in weight and compact in size.
- The cell or a battery must be able to give a constant voltage. Moreover, the voltage of the battery or the cell must not vary during use.

Types of Batteries:

The batteries or the practical cells of the commercial values are mainly of two types. These are:

- **Primary cell/battery**
- **Secondary cell/battery.**

Primary Batteries

The primary cells produce electricity by the virtue of a chemical reaction. Here the reaction occurs only in one direction. We can not reverse this phenomenon. As a result, these cells become dead over a period of time. You cannot reuse or recharge a primary cell. Some of the examples of primary cells are Daniell cell, Dry cell, and Mercury cell.

Daniell Cell:

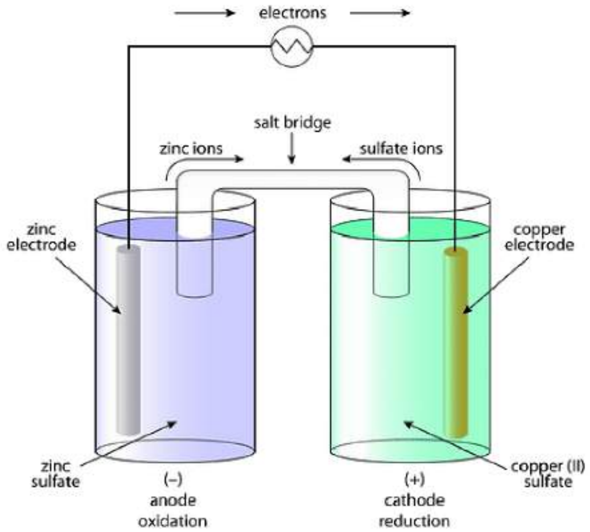


Fig: Daniell cell

The Daniell cell has a copper vessel that contains a concentrated solution of copper sulphate. A porous pot containing dilute sulphuric acid is placed in the copper vessel containing copper sulphate solution. A zinc rod is dipped into dilute sulphuric acid. The zinc electrode acts as an anode, while the copper container acts as a cathode.
The reactions taking place in the cell are:
At anode: $Zn(s) \rightarrow Zn_2+(aq) + 2e^-$
At cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Net cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$
The cell may be represented as,
$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$
(anode)   (cathode)

Daniell cell gives an emf of 1.1 V.

Dry Cell:

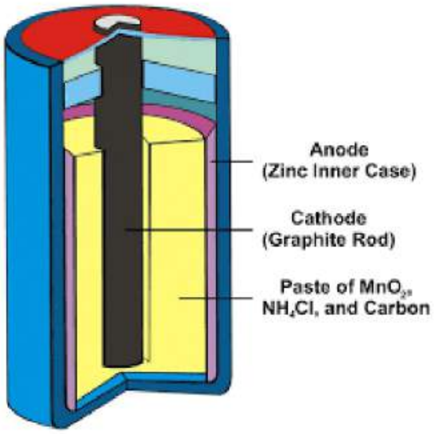


Fig: Dry cellA compact form of the LeClanche cell is the dry cell. It comprises of an outer container made of inc, which acts as an anode. The zinc content of the cell is lined from inside with porous insulating paper. The cathode is a carbon rod having a brass cap.

There is a space between the cathode and the anode which is filled with a mixture of $_{\mathrm{MnO}}2$ along with a thick paste of ammonium chloride, (NH_4Cl), zinc chloride ($ZnCl_2$), and charcoal. The lining of the porous paper prevents direct contact between the zinc container and the paste. It acts as a salt bridge. The cell is sealed from the top with pitch or wax.

Reactions during discharge

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

The Zn2+ ions migrate towards the carbon electrode (cathode). The reaction at the cathode is,

At cathode: $MnO_2 + NH^{4+} + e^- \rightarrow MnO\ (OH) + NH_3MnO_2$

It acts as a depolarizer. The state of manganese is reduced from + 4 to + 3 in cathodic reaction. The ammonia molecules formed at the cathode react with Zn^{2+} ions coming from the anode, to form a complex ion $Zn(NH_3)_4{}^{2+}$. The complication of Zn^{2+} by NH_3 molecules lowers the concentration of free Zn^{2+} and results in an increase in the voltage of the cell. A dry cell has a potential of about 1.5 V.

Are dry cells really dry?

In reality, the dry cells aren't really dry. They have a wet paste of NH_4Cl and $ZnCl_2$. In reality, a dry cell will function only as long as the paste in the cell is moist. Moreover, you cannot recharge a dry cell. So, naturally, the dry cells do not have an indefinite life. This is because the NH_4Cl paste is acidic in nature and it goes on corroding the zinc container even when it isn't in use.

Mercury cell

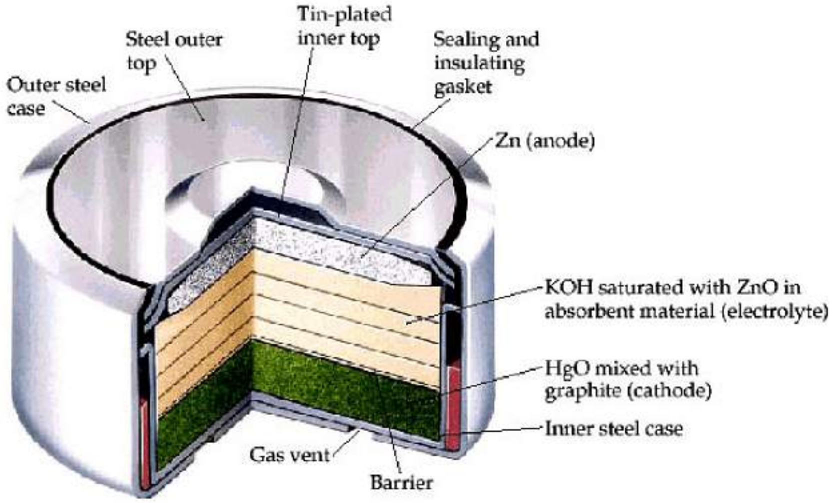


Fig: Mercury cell

Mercury cell is recently introduced in the market. It offers a rather more stable voltage. The emf of the Mercury Cell is 1.35 V. Usually, the mercury cell is costlier. This is the reason, why they are used only in sophisticated instruments such as cameras, hearing aids, and watches, etc. Amalgamated zinc plate coated with a steel top plate acts as an anode in Mercury cell.

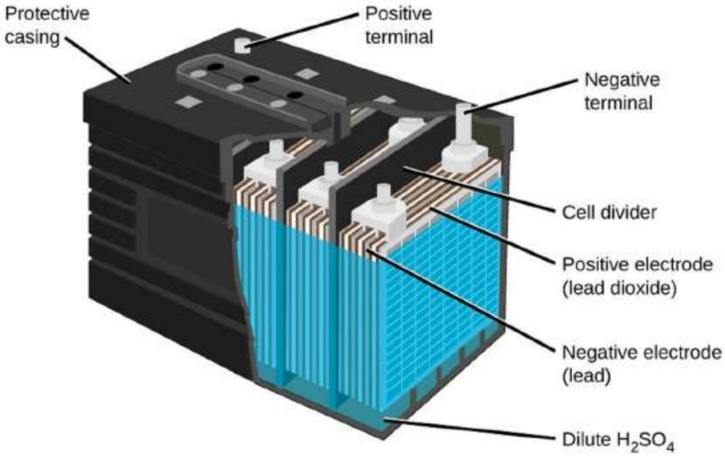
A paste of Hg, HgO, and carbon powder acts as the cathode. It is placed in contact with the outer steel case. The electrolyte is a paste of KOH saturated with $Zn(OH)_2$. An inert porous material carries this paste. The two electrodes are separated by an insulation seal of neoprene rubber. The reactions during discharge are,
At anode: $Zn(Hg) + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$
At cathode: $HgO + H2O + 2e^- \rightarrow Hg + 2OH^-$
Overall reaction: $Zn(Hg) + HgO(s) \rightarrow Zn(OH)_2 + Hg(l)$

Secondary Batteries (Lead-Acid Battery)

Lead-Acid Battery Construction:

The lead-acid battery is the most commonly used type of storage battery and is well-known for its application in automobiles. The battery is made up of several cells, each of which consists of lead plates immersed in an electrolyte of dilute sulfuric

acid. The voltage per cell is typically 2 V to 2.2 V. For a 6 V battery, three cells are connected in series, and for a 12 V battery, six cells are series-connected.
The construction of a lead-acid automobile type battery is illustrated in Figure 1.
The electrodes are lead-antimony alloy plates with a pattern of recesses so that they are in the form of grids.



Plates:

Lead oxide (termed active material) is pressed into the recesses of the plates. Each electrode consists of several plates connected in parallel with porous rubber separators in between, as illustrated in Figure 1 (b). This arrangement and the shape of the plates give the largest possible electrode surface area within the size limitations of the battery.

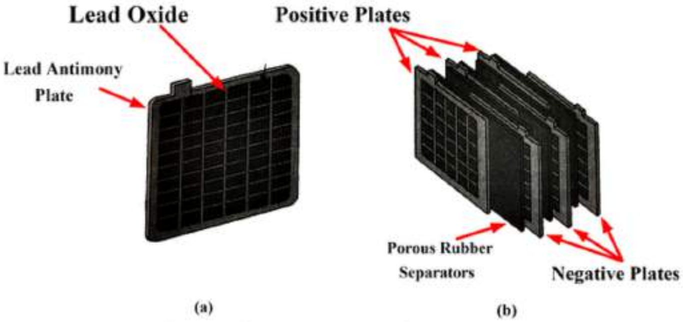


Fig 1: Lead-Acid Battery Plates Arrangement

Rubber Case:

The complete 12 V battery, illustrated in Fig. 1, has an outer case of hard rubber. The case is divided into six sections for the six separate cells. Projections are provided on the inside at the bottom of the case to support the plates.
These projections ensure that the lower edges of the plates are normally well above

the level of an active material that falls to the bottom of a cell. Such material can short out the positive and negative plates and render a cell useless.

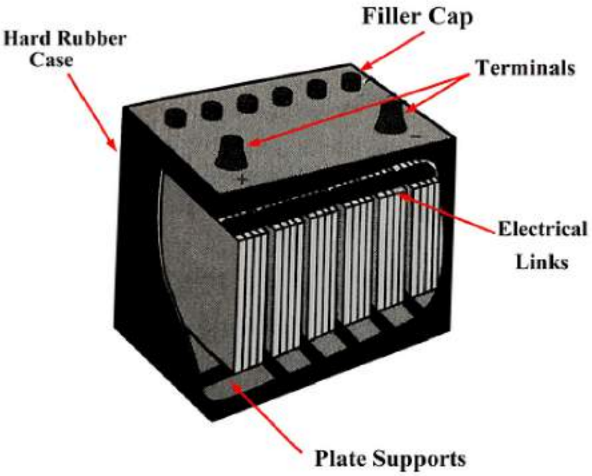


Fig 1 (c): **Complete Lead Acid Battery**

Filler Cap:

Every cell has a threaded filler cap with a small hole in its centre. The filler caps provide access for adding electrolyte, and the holes allow gases to be vented to the atmosphere.

Fig: Filler cap

Electrical Links:

Thick electrical links connect the cells in series, and hefty battery terminals are provided. Because the battery may be required to supply a very heavy current, it is important that the resistance of all electrical connections be very low to minimize voltage drops. A current of 250 A is not unusual for a battery driving an automobile starter.

Lead-Acid Battery Working:

When the lead-acid cell is charged, the lead oxide on the positive plates changes to lead peroxide, and that on the negative plates becomes a spongy or porous lead. In this condition, the positive plates are brown in color, and the negative plates are gray.

Lead-Acid Battery Discharging:

When the battery is discharging (i.e., supplying a current), atoms from the spongy lead on the negative plates combine with sulfate molecules to form lead sulfate and hydrogen. As always, electrons are left behind on the negative plates so that they maintain a negative potential.
The hydrogen released in the electrolyte combines with the lead peroxide on the positive plate, removing electrons from the plate to keep a positive potential. The combination of lead peroxide and hydrogen at the positive electrode produces water and lead sulfate.
The water dilutes the electrolyte, making it a weaker solution, and the lead sulfate that is produced at both positive and negative plates tends to fill the pores of the active material. Both these effects (dilution of the electrolyte and formation of lead sulfate) render each cell less efficient and eventually cause the battery output voltage to fall.

Lead-Acid Battery Recharging:

When the battery is recharged, a current (conventional direction) is made to flow into the positive electrode of each cell.
This current causes the lead sulfate at the negative electrode to recombine with hydrogen ions, thus re-forming sulfuric acid in the electrolyte and Spongy lead on the negative plates.
Also, the lead sulfate on the positive electrodes recombines with water to regenerate lead peroxide on the positive plates and sulfuric acid in the electrolyte.
The final result of charging the cell is that the electrodes are re-formed and the electrolyte is returned to its original strength.
With proper care a lead—acid battery is capable of sustaining a great many cycles of charge and discharge, giving satisfactory service for several years.

Ampere-Hour Rating of Lead-Acid Battery:

Typical ampere-hour ratings for 12 V lead-acid automobile batteries range from 100 Ah to 300 Ah. This is usually specified for an 8 h discharge time, and it defines the amount of energy that can be drawn from the battery until the voltage drops to about 1.7 V per cell.

For a 240 Ah rating, the battery could be expected to supply 30 A for an 8h period (see Figure 2). With greater load currents, the discharge time is obviously shorter. However, the ampere-hour rating is also likely to be reduced for a shorter discharge time because the battery is less efficient when supplying larger currents. Another method of rating a lead-acid battery is to define what its terminal voltage will be after about 5 s of supplying perhaps 250 A. This corresponds to the kind of load that a battery experiences in starting an automobile. It is important to avoid battery overloads that may demand excessive currents. Drawing a larger current than the battery is designed to supply may cause severe damage.

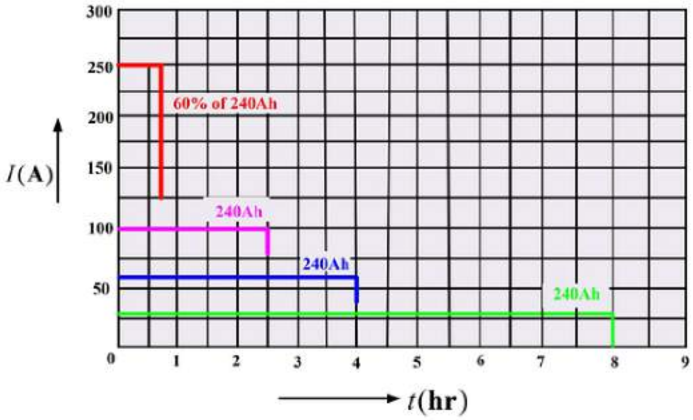


Fig 2: Ampere Hour Rating for a Lead-Acid Battery

The rating of a battery is typically stated for temperatures around 25°C, and this must be revised for operation at lower temperatures. Because the chemical reactions occur more slowly at reduced temperatures, the available output current and voltage are less than at 25°C. Around -18°C a fully charged battery may be capable of delivering only 60% of its normal ampere-hour rating.
As the cell is discharged and the electrolyte becomes weaker, freezing of the electrolyte becomes more likely. A fully charged cell is less susceptible to freezing, but even a fully charged cell may fail when its temperature falls to about -21°C.

Example 1: A lead-acid battery has a rating of 300 Ah.

1. Determine how long the battery might be employed to supply 25 A.
2. If the battery rating is reduced to 100 Ah when supplying large currents, calculate how long it could be expected to supply 250 A.
3. Under very cold conditions the battery supplies only 60% of its normal rating. Find the length of time that it might continue to supply 250 A to the starter motor of

an automobile.

Ans:

a. From the following equation,
Ah Rating=I×t
Therefore

$$t = \frac{Ah}{I} = \frac{300}{25} = 12h$$

b. Time to supply 250 A current

$$t = \frac{Ah}{I} = \frac{100}{250} = 0.4h = 24\,\text{min}$$

c. Time to supply 250 A at 60 % rating
Ah Rating = 60% of 100Ah = 60Ah

$$t = \frac{Ah}{I} = \frac{60}{250} = 0.24h = 14.4\,\text{min}$$

Lead-Acid Battery Charging

When a battery is to be charged, a dc charging voltage must be applied to its terminals. The polarity of the charging voltage must be such that it causes current to flow into the battery, in opposition to the normal direction of the discharge current. This means that the positive output terminal of the battery charger must be connected to the positive terminal of the battery, and the charger negative terminal must be connected to the battery negative terminal. The arrangement is shown in Figure 3. The battery charger normally has a voltmeter and ammeter to monitor the charging voltage and current, and a control to adjust the rate of charge.

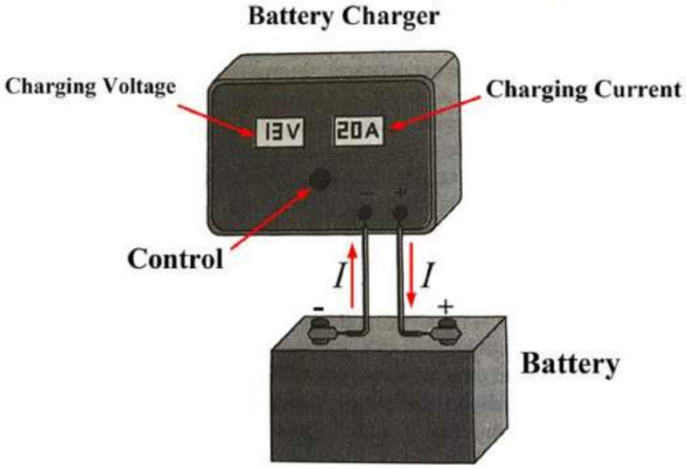


Fig 3: Lead-Acid Battery and Battery

Charger Arrangement

The output voltage of a battery charger must be greater than the battery voltage in order to cause current to flow into the battery positive terminal. The charging current depends on the difference between the battery voltage and the charging voltage and on the internal resistance of the battery.

A very large charging current is to be avoided because it could cause the battery to overheat, possibly resulting in warping of the lead plates. The maximum safe charging current is frequently taken as the maximum output current from the battery when discharging at its 8 h rate.

Example 2: A battery with a rating of 300 Ah is to be charged.

1. Determine a safe maximum charging current.

2. If the internal resistance of the battery is 0.008 Ω and its (discharged) terminal voltage is 11.5 V, calculate the initial output voltage level for the battery charger.

Ans:

a. Safe rate of charge at the 8h discharge rate:

$$I = \frac{Ah}{t} = \frac{300}{8} = 37.5A$$

b. Charging current:

$$I = \frac{\text{Charger Voltage} - Battery\,Voltage}{r_1}$$

Therefore,

Charger Voltage = $(I \times r_1)$ + Battery Voltage

= $(37.5 \times 0.008) + 11.5 = 11.8$V

Lead-Acid Battery Specific Gravity:

When a lead-acid battery is in a nearly discharged condition, the electrolyte is in its weakest state. Conversely, the electrolyte is at its strongest (or greatest density) when the battery is fully charged. The density of electrolyte related to the density of water is termed its specific gravity.

The specific gravity of the electrolyte (measured by means of a hydrometer) is used as an indication of the state of charge of a lead-acid battery. Electrolyte with a specific gravity of 1100 to 1150 is 1.1 to 1.15 times as dense as water. At 1100 to 1150 the cell is completely discharged. When the specific gravity is 1280 to 1300, the cell may be assumed to be fully charged.

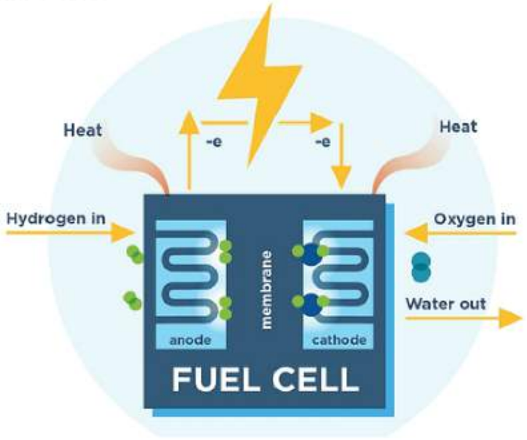
Care of Lead-Acid Batteries:

1. The level of the electrolyte in each cell should be checked regularly, and distilled water added as necessary to keep the top of the plates covered by about 1 cm of liquid.
2. Battery terminals should be kept clean and lightly coated with petroleum jelly to avoid corrosion.
3. In cold weather, batteries should always be maintained in a nearly fully charged condition to avoid freezing.
4. Lead-acid batteries should never be allowed to remain for a long period in a discharged state because lead sulfate could harden and permanently clog the pores of the electrodes.
5. Before storing it for a long time the battery should be completely charged, then the electrolyte should be drained so that the battery is stored dry.

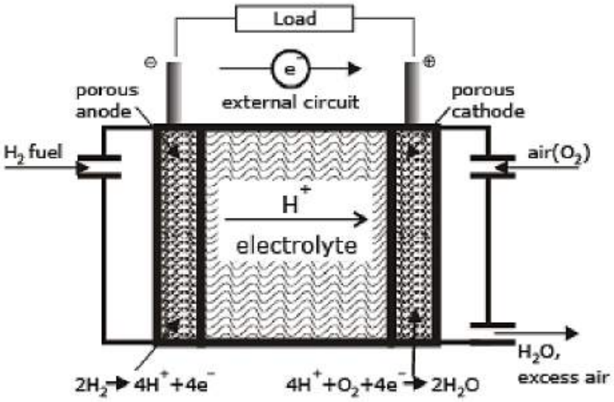
Fuel Cells & Corrosion

Fuel Cells

An advantage of voltaic cells is that they are small and portable, but their size is also a limitation. The amount of electric current produced is limited by the number of reagents contained in the cell.



When one of the reactants is completely consumed, the cell will no longer generate a current. Fuel cells avoid this limitation because the reactants (fuel and oxidant) can be supplied continuously to the cell from an external reservoir.
In a Hydrogen - Oxygen fuel cell figure, hydrogen is pumped onto the anode of the cell, and O_2 (or air) is directed to the cathode where the following reactions occur.
Cathode, reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$, $E^º = 1.23$ V
Anode, Oxidation: $H_2(g) \rightarrow 2H\,(aq) + 2e^-$, $E^º = 0V$



Schematic diagram of a modern hydrogen-oxygen fuel cell. Commonly used electrolytes are NaOH solution, phosphoric acid, or solid oxides. A major limitation of any oxygen-consuming fuel cell is the slow rate of the reduction of this element at a cathode. The best cathode surfaces are usually made of platinum, which is a major cost factor in fuel cell design.

Corrosion

Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M + e^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a **depolarizer.**
In a scene, corrosion can be viewed as the spontaneous return of metals to their ores: the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.
The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and form metal, but a thin film of adsorbed moisture can be sufficient. A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
and the cathodic steps can be any of
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
$H^+ + e^- \rightarrow \frac{1}{2}H_2(g)$
$M^{2+} + 2e^- \rightarrow M(s)$
where M is a metal. Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that

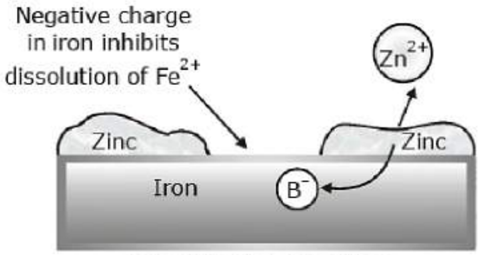
are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

Control of Corrosion

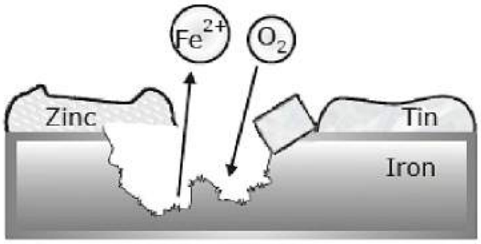
Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads.
A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction $M \rightarrow M^{2+} + 2e^-$ to take place.

Sacrificial coatings

One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behing electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.



Sacrificial coating



Noble coating

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

Cathodic Protection

A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as cathodic protection. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a price of zinc or aluminum buried in the ground nearby.