

ELECTROCHEMISTRY

Module – 13.1: Electrolytes, Non - electrolytes and Electrolysis

Introduction:

Electrochemistry is the field of chemistry which deals with the results in the generation of an electric current (electricity) or be caused by passing an electric current. Electron transfer reactions are oxidation-reduction or redox reactions. In other words ***"the study of interchange of chemical and electrical energy is Electrochemistry"***.

Electrochemistry can be divided in to two categories:

- a. Use of electrical energy to produce chemical changes which is known as Electrolysis,
- b. Conversion of chemical energy into electrical energy (by spontaneous redox reactions).

A substance which allows the passage of current to flow through it is called a conductor. For example copper wire, a solution of copper sulphate, Aluminium wire, Fused NaOH, etc., This substance may be a solid like a metal, a fused salt or an aqueous solution of a substance. Accordingly the electrical conductors are divided into two types. They are

1. Metallic conductors or electronic conductors (These are solids.)
2. Electrolytic conductors (These are solutions or fused substances)

Metallic conductors:

Metals are the best conductors. In them the passage of current is not accompanied by any movement of matter. Besides metals, alloys and some solids like graphite, some oxides also conduct electricity. In these substances the electrons move from a higher negative potential region to a lower positive potential region. No chemical reactions occur in such substances.

Ex: metallic wires like those of Cu., Al or Ag.,

Electrolytic Conductors:

In these conductors electricity is conducted due to the migration of ions or transport of ions to oppositely charged electrodes.

Ex: Fused salts like KCl, NaCl, Aqueous solutions like NaOH, KOH;

These substances are known as electrolytes". **A solution that contains ions and conducts electricity in the fused state or in the aqueous solution or as a solution in any other solvent is known as an electrolyte".** Chemical substances that do not permit the passage of current through them either in the fused state or in aqueous solution or in any other solution form is known as non-electrolytes.

Conduction of current through a metallic conductor and an electrolytic conductor may be distinguished briefly as follows:

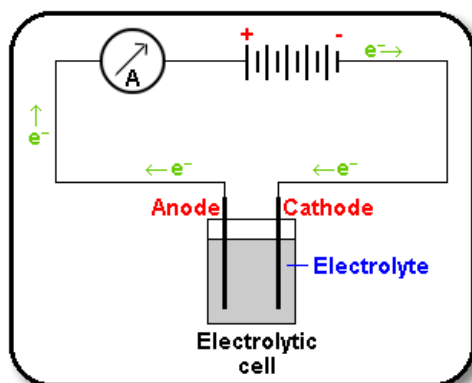
Metallic conduction	Electrolytic conduction
1. It occurs due to the flow of electrons	1. In the solution or in the fused state the current is conducted due to the movement of the ions.
2. This is only a physical change in the conductor	2. It involves a chemical change. This change occurs at the electrode.
3. No transfer of matter takes place	3. This involves transfer of matter in the form of ions.
4. Resistance increase with a raise in temperature.	4. It shows a decrease in resistance with a raise in temperature.

Electrolysis:

Electrolysis takes place in an electrolytic cell, the simplest form of which is shown below:

The components which make contact with the electrolyte are called **electrodes**. The electrode which is attached to the negative pole of the battery, and which supplies electrons to the electrolyte, is called the **Cathode**. Reduction takes place at the cathode.

The electrode which is attached to the positive pole of the battery, and which accepts electrons from the electrolyte, is called the **anode**. Oxidation takes place at the anode.



When a direct electric current is passed through an **electrolyte** (such as a molten salt or an aqueous solution of a salt, acid or base), chemical reactions take place at the contacts between the circuit and the solution. This process is called **electrolysis**.

Various reactions take place at the electrodes during electrolysis. In general, **reduction takes place at the cathode**, and **oxidation takes place at the anode**.

Some examples of electrolysis: Its products

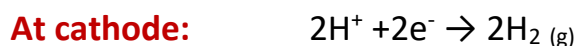
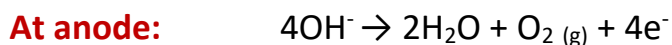
Electrolysis of water:

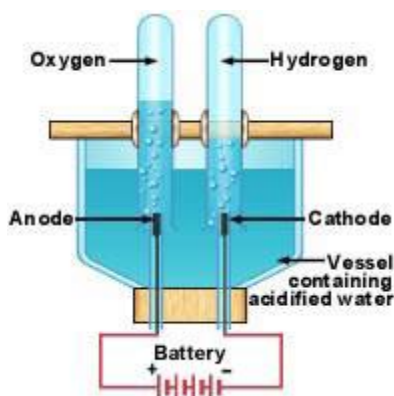
Water may be electrolysed in the apparatus shown below. Pure water is however a very poor conductor of electricity and one has to add dilute sulphuric acid in order to have a significant current flow.

Hydrogen gas is evolved at the cathode, and oxygen at the anode.

The ratio, by **volume** of hydrogen to oxygen, is exactly 2:1.

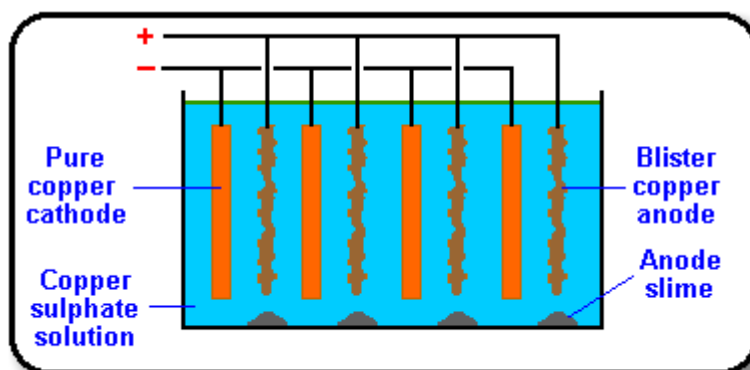
The overall reactions are



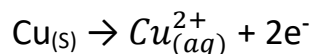


Electrorefining of copper:

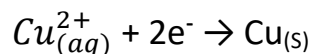
Impure Copper obtained by reduction of its ores is cast as slabs or ingots, called **blister copper**. In the **electrorefining** process, the blister ingots are used as anodes in an electrolytic cell. An acid solution of copper (II) sulphate is used as electrolyte. Initially, the cathode consists of thin sheets of pure copper



During electrolysis, copper passes into solution from the anodes, (leaving the impurities, normally containing silver, gold and platinum) as **an anode slime or anode mud**. The anode mud which sinks to the bottom of the cell. The anode reaction is



At the cathode, copper (II) ions are discharged. The pure copper sheet, cathode, becomes coated with a thick layer of very pure copper:



Assignment Questions:

1. Explain electrolysis with an example
2. Write a short note on metallic conductor

Example Set:

1. Metallic conduction is due to the movement of _____
- a. Ions
 - b. Atoms
 - c. Electrons
 - d. All

Solution: c)

2. Electrolytic conduction is due to migration of _____
- a. Protons
 - b. Electrons
 - c. Ions
 - d. All

Solution: c)

3. In electrolytic conduction the resistance of the electrolyte _____ with increase in temperature.
- a. increases
 - b. decreases
 - c. remains unchanged
 - d. becomes zero (at low temperature)

Solution: b)

4. An Electrolyte is defined as
- a. Solid state
 - b. Liquid state
 - c. Gaseous state
 - d. All states

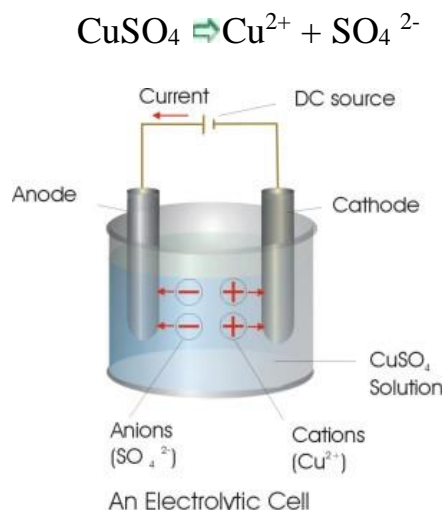
Solution: b)

5. What is electrolysis? Illustrate with a suitable example.

Solution: Chemical reactions take place at the contacts between the circuit and the solution is called electrolysis.

Let us take an example of electrolysis of aqueous copper sulphate solution using inert electrodes such as platinum electrodes.

In the aqueous solution copper sulphate dissociates into its respective ions, as shown below.



On passing electric current the copper ions (cations) move towards the cathode and get discharged. They are deposited as copper. Simultaneously the sulphate ions (anions) move towards the anode.

6. What is an electrolyte? Distinguish between metallic conduction and electrolytic conduction?

Solution: A solution that contains ions and conducts electricity in the fused state or in the aqueous solution or as a solution in any other solvent is known as an electrolyte.

Metallic conduction	Electrolytic conduction
1. It occurs due to the flow of electrons	1. In the solution or in the fused state the current is conducted due to the movement of the ions.
2. This is only a physical change in the conductor	2. It involves a chemical change. This change occurs at the electrode.
3. No transfer of matter takes place	3. This involves transfer of matter in the form of ions.

4. Resistance increase with a raise in temperature.	4. It shows a decrease in resistance with a raise in temperature.
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Problem Set:

1. In electrolysis, oxidation takes place at
 - a. anode
 - b. cathode
 - c. in the bulk of electrolyte
 - d. with anions and cations

Solution: a)

2. The reaction taking place at cathode is
 - a. Oxidation
 - b. Reduction
 - c. Neutralization
 - d. Hydrolysis

Solution: b)

3. During electrolysis of acidified H_2O , the ratio of volumes of H_2 and O_2 formed is
 - a. 2:1
 - b. 1:2
 - c. 1:3
 - d. 3:1

Solution: a)

4. In the electrolysis of CuSO_4 , the reaction $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ takes place at
 - a. Anode
 - b. Cathode
 - c. In solution
 - d. Both at the anode & cathode

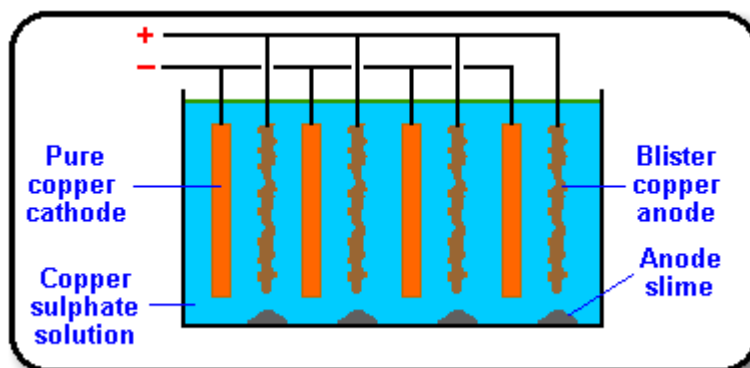
Solution: b)

5. Write a note on electrorefining of copper?

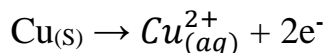
Solution:

Electrorefining of copper:

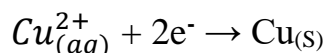
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During electrolysis, copper passes into solution from the anodes, (leaving the impurities, normally containing silver, gold and platinum) as **an anode slime or anode mud**. The anode mud which sinks to the bottom of the cell. The anode reaction is



At the cathode, copper (II) ions are discharged. The pure copper sheet, cathode, becomes coated with a thick layer of very pure copper:



6. What is the reason for the addition of dil. H_2SO_4 in electrolysis of pure water?

Solution:

Pure water is a very poor conductor of electricity and one has to add dilute sulphuric acid or an alkali in order to have a significant current flow.

ELECTROCHEMISTRY

Module – 13.2: Faraday's law of electrolysis and applications

Faraday's laws of electrolysis:

Michael Faraday, an English scientist, studied the quantitative relationships between electricity and the amount of substance deposited on the electrode. He summarized his result of the decomposition of electrolytes by electricity in the form of two laws, commonly known as Faraday's laws of electrolysis

1. Faraday's first law of electrolysis:

It states that ***“the weight of a chemical substance deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.”***

Let, W = Weight (in gm) of the substance deposited

Q = Quantity of electricity (in coulombs) passed, then mathematically,

$$W \propto Q$$

But we know that

Q = current (c) in amperes \times time (t) in seconds

$$\text{i.e., } Q = c \times t$$

$$W \propto c \times t$$

$$W = z \times c \times t$$

Where z is proportionality constant and known as electrochemical equivalent (e.c.e) of the substance. Its value depends upon the nature of the ion liberated. Now when C = 1 ampere and T = 1 second, *i.e.*, when a current of 1 ampere is passed through an electrolyte for one second, then

$$W = z \times 1 \times 1$$

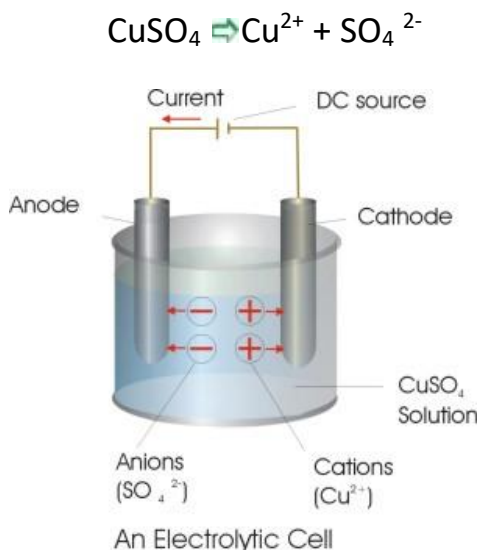
$$W = z$$

Hence electrochemical equivalent of a substance may be defined **as the amount of the substance deposited by passing a current of one ampere for one second (*i.e.*, by passing one coulomb of electricity)**. It is found that 1 gm equivalent of an ion is liberated by 96,500 coulombs nearly of electricity.

$$\text{Hence e.c.e (z) = Eq. Wt. /96,500}$$

Let us take an example of electrolysis of aqueous copper sulphate solution using inert electrodes such as platinum electrodes.

In the aqueous solution copper sulphate dissociates into its respective ions, as shown below.



On passing electric current the copper ions (cations) move towards the cathode and get discharged. They are deposited as copper. Simultaneously the sulphate ions (anions) move towards the anode.

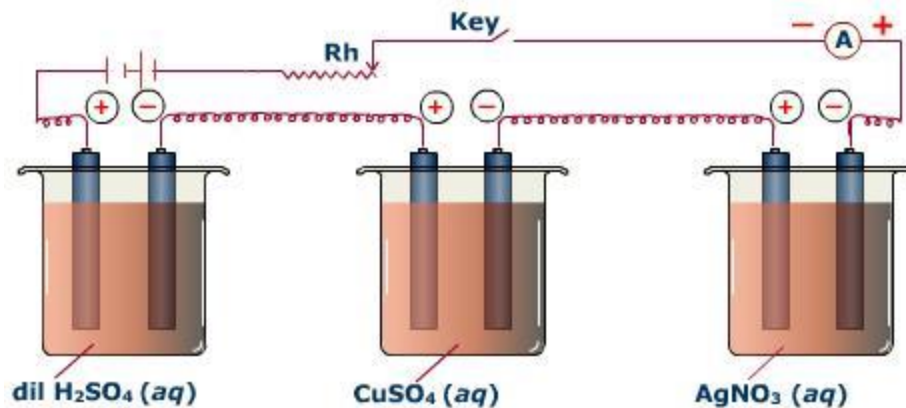
2. Faraday's second law of electrolysis:

It states that **“the weight of different substances produced, by the same quantity of electricity, is proportional to the equivalent of the substances.”** If W_1 and W_2 are the weights of two elements deposited by passing a certain quantity of electricity through their salt solutions. E_1 and E_2 are their respective equivalent weights, then

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

For example, when the same current is passed through the solutions of sulphuric acid (H_2SO_4), copper sulphate (CuSO_4) and silver nitrate (AgNO_3) for the same period of time, then according to the second law of Faraday's.

$$\frac{\text{Mass of copper deposited}}{\text{Mass of hydrogen gas liberated}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of hydrogen}}$$



Experimental set up for the verification of the Second Law of Electrolysis

Metal deposited \propto Eq. Wt. of the metal

In other words

$$\frac{\text{Wt. of metal } M_1 \text{ deposited}}{\text{Wt. of metal } M_2 \text{ deposited}} = \frac{\text{Eq. Wt of metal } M_1}{\text{Eq. Wt of metal } M_2}$$

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Where W_1 and W_2 are the weights of metal deposited at the respective electrodes and E_1 and E_2 are their respective equivalent weights.

Now according to first law

$$W = z \times c \times t$$

Putting the values of W in (ii), we get

$$\frac{z_1 \times c \times t}{z_2 \times c \times t} = \frac{E_1}{E_2}$$

$$\frac{z_1}{z_2} = \frac{E_1}{E_2}$$

In other words, the electrochemical equivalent of an element is directly proportional to its equivalent weight, *i.e.*,

$$E \propto z$$

$$E = F \times z$$

Where F is proportionally constant and called as Faraday. The value of one Faraday is 96540 coulombs. Thus with the help of the above equation, we can determine the electrochemical equivalent of the metal as below.

$$z = \frac{E}{F}$$

Electrochemical equivalent of the metal (z)

$$= \frac{\text{Equivalent wt. of the metal}}{96500}$$

Definition of Faraday:

One Faraday may be defined as the quantity of electricity which can deposit one gram equivalent of the element(s) present in that electrolyte.

Applications of electrolysis:

The phenomenon of electrolysis has wide applications. The important ones are:

1. Determination of equivalent masses of elements:

According to second law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$\frac{W_A}{W_B} = \frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated. The equivalent masses of those non – metals which are evolved at anodes can also be determined by this method.

2. Electrometallurgy:

The metals like sodium, potassium, magnesium, calcium, aluminum etc. are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$\text{NaCl} + \text{CaCl}_2 + \text{KF}$	Na
$\text{CaCl}_2 + \text{CaF}_2$	Ca
$\text{Al}_2\text{O}_3 + \text{cryolite}$	Al
MgCl_2 (35%) + NaCl (50%) + CaCl_2 (15%)	Mg
NaOH	Na
$\text{KCl} + \text{CaCl}_2$	K

3. Manufacture of non – metals:

Non – metals like hydrogen, fluorine, chlorine are obtained by electrolysis

4. Electro – refining of metals:

The metals like copper, silver, gold, aluminum, tin etc., are refined by electrolysis

5. Manufacture of compounds:

Compounds like NaOH, KOH, Na_2CO_3 , KClO_3 , KMnO_4 etc., are manufactured by electrolysis

6. Electroplating:

The process of coating an inferior metal with a superior metal, by electrolysis is known as electroplating. The aims of electroplating are:

- To prevent the inferior metal from corrosion
- To make it more attractive in appearance

The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode – article in the form of a thin film.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$\text{CuSO}_4 + \text{dilute H}_2\text{SO}_4$

With silver	Ag	Object	$K[Ag(CN)_2]$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$K[Au(CN)_2]$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Assignment Questions:

1. State and explain Faraday's second law of electrolysis
2. How much copper will be deposited by a current of 2.4 amperes passing through a solution of copper sulphate for one hour and thirty eight minutes? (atomic weight of copper = 63) [Ans: 4.65 gm]
3. An electric current was passed through two voltmeter cells one containing copper sulphate (using copper electrodes) and the other containing silver nitrate solution (using silver electrodes). The increase in weight of cathodes in two cells was respectively 0.189 g and 0.648 g. Calculate the chemical equivalent of copper, taking that of silver as 108. [Ans: 31.5]

Example Set:

1. One Faraday is equal to ____ coulombs
 - a. 9650
 - b. 10,000
 - c. 19640
 - d. 96540

Solution: d)

2. The amount of electricity required to produce one mole of copper from copper sulphate solution will be ____ Faraday
 - a. 1
 - b. 1.33
 - c. 2
 - d. 2.33

Solution: c)

3. State Faraday's law of electrolysis

Solution:

Faraday's first law of electrolysis:

It states that **the weight of a chemical substance deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.**

Faraday's second law of electrolysis:

It states that **the weight of different substances produced, by the same quantity of electricity, is proportional to the equivalent of the substances.**

4. Give any four applications of Faraday's law of electrolysis

Solution:

a. Manufacture of non – metals:

Non – metals like hydrogen, fluorine, chlorine are obtained by electrolysis

b. Electro – refining of metals:

The metals like copper, silver, gold, aluminum, tin etc., are refined by electrolysis

c. Manufacture of compounds:

Compounds like NaOH, KOH, Na₂CO₃, KClO₃, KMnO₄ etc., are manufactured by electrolysis

d. Electroplating:

The process of coating an inferior metal with a superior metal, by electrolysis is known as electroplating. The aims of electroplating are:

- i. To prevent the inferior metal from corrosion
- ii. To make it more attractive in appearance

Problem Set:

1. Which equation represents the first law of electrolysis correctly?

- a. $wz = ct$
- b. $w = czt$
- c. $wc = zt$
- d. $c = wzt$

Solution: b)

2. when the same electricity is passed through the solution of different electrolytes in the series, the amount of elements deposited on the electrodes are in the ratio of their
- atomic numbers
 - atomic masses
 - molecular masses of the electrolyte
 - equivalent masses

Solution: d)

3. Calculate the time in seconds in which half gram of copper is liberated from copper sulphate solution, when a current of 0.50 ampere is passed (At. Wt. of copper = 63)

Solution:

$$W = 0.5 \text{ gm}$$

$$\text{At. Wt. of copper} = 63$$

$$c = 0.50 \text{ ampere}$$

$$z \text{ of copper} = \frac{\text{Eq.wt. of copper}}{96,500}$$

$$t = ?$$

$$= \frac{31.5}{96,500}$$

Now, applying the formula

$$W = z \times c \times t$$

$$t = \frac{W}{z \times c}$$

$$= \frac{0.5 \times 96500}{31.5 \times 0.50}$$

$$= 3063.5 \text{ seconds}$$

4. An electric current of 0.5 ampere was passed through acidulated water for 30 minutes. Calculate the volume of hydrogen produced at NTP. (z for hydrogen = 0.00001)

Solution:

Given,

$$c = 0.5 \text{ ampere}$$

$$t = 30 \times 60 = 1800 \text{ seconds}$$

$$z = 0.00001$$

$$W = ?$$

Now $W = z \times c \times t$

$$= 0.00001 \times 0.5 \times 1800$$

$$= 0.009 \text{ gm}$$

Now we know that 2 gm of hydrogen at NTP = 2.24 litres

$$0.009 \text{ gm of hydrogen at NTP} = \frac{22.4}{2} \times 0.009 \text{ L}$$

$$= 0.1008 \text{ litre}$$

5. Calculate the time required for a current of 0.10 amperes to deposit 160 mg. of copper from a solution of copper sulphate. [chemical equivalent of Cu = 32]

Solution:

Chemical equivalent (equivalent wt.) of Cu = 32

Thus 32 gm of Cu is deposited by = 96500 coulombs

$$160 \text{ mg. or } 0.16 \text{ gm of Cu will be deposited by} = \frac{96500}{32} \times 0.16 = 482.5 \text{ coulombs}$$

In other words, quantity of electricity (Q) = 482.5 coulombs

$$c = 0.10 \text{ amperes} \quad t = ?$$

Now since $Q = c \times t$

$$482.5 = 0.10 \times t$$

$$= \frac{482.5}{0.10}$$

$$= 4825 \text{ seconds}$$

6. 0.600 g of a metal was deposited during the electrolysis of its salt solution with a current of 0.10 amperes for $2\frac{1}{2}$ hours. Determine the equivalent weight and valency of the metal in the salt (Atomic weight of the metal is 64)

Solution:

Given $c = 0.10$ amperes

$$t = 150 \times 60 = 9000 \text{ seconds}$$

$$Q = c \times t$$

$$= 0.10 \times 9000 = 900 \text{ coulombs}$$

Now 900 coulombs of electricity deposits 0.600 gm of metal

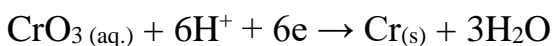
$$\begin{aligned} 96500 \text{ coulombs of electricity will deposit} &= \frac{0.600}{900} \times 96500 \\ &= 64.33 \end{aligned}$$

Hence the eq. wt. of the metal = 64.33

$$\text{Therefore valency of the metal} = \frac{\text{At. Wt.}}{\text{Eq. wt.}} = \frac{64}{64.33} = 1$$

Exercise questions:

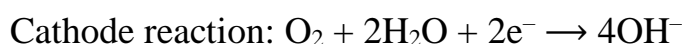
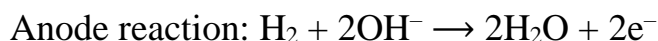
1. In electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold chloride and the second contains copper sulphate solution on passing current 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in amperes.
(At. Wt. of Au = 197 and At. Wt of Cu = 63.5)
2. How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm² with a 0.005 mm thick layer?
(Density of silver is 10.5 g / cm³.)
3. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited if the current flows for 10 hours
4. Calculate the quantity of electricity that will be required to liberate 710 g of Cl₂ gas by electrolyzing a conc. Solution of NaCl. What weight of NaOH and what volume of H₂ at 27⁰ C and 1 atm. pressure is obtained during this process?
5. How long would it take to deposit 100 g of Al from an electrolytic cell containing Al₂O₃ using a current of 125 ampere
6. An ammeter and copper voltmeter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 ampere. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter?
(At. Wt. of Cu = 63.54)
7. Chromium metal can be plated out from an acidic solution containing CrO₃ according to following equation. (At .Wt of Cr = 52)



Calculate:

- a. How many grams of chromium will be plated out by 24000 coulombs?
- b. How long will it take to plate out 1.5 g of Cr by using 12.5 amperes current?

8. An aqueous solution of NaCl on electrolysis give $\text{H}_{2(g)}$, $\text{Cl}_{2(g)}$ and NaOH according to the reaction $2\text{Cl}^-_{(aq)} + 2\text{H}_2\text{O} \rightarrow 2\text{OH}^-_{(aq)} + \text{H}_{2(g)} + \text{Cl}_{2(g)}$. A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 kg of Cl_2 , What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation).
9. In a fuel hydrogen and oxygen react to produce electricity. In the process hydrogen gas is oxidized at the anode and oxygen at the cathode. If 6.72 litre of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electro deposition of copper from copper (II) solution, how many grams of copper will be deposited?



10. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/ml, Sulphuric acid of density 1.294 g/ml is 39% by weight and that of 1.139 g/ml is 20% H_2SO_4 by weight. The battery holds 3.5 litres of the acid and the volume remained practically constant during the discharge

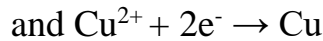
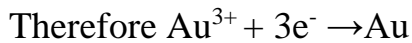
Calculate the number of ampere – hours for which the battery must have been used. The charging and discharging reactions are:



Solutions to exercise questions:

1. Equivalent of gold formed = Equivalent of Cu formed

$$\text{Therefore } \frac{\text{wt.of Au}}{\text{eq.wt.of Au}} = \frac{\text{wt.of Cu}}{\text{eq.wt.of Cu}}$$



$$\text{Therefore } \frac{9.85}{197/3} = \frac{W_{\text{Cu}}}{63.5/2}$$

$$W_{\text{Cu}} = \frac{9.85 \times 3 \times 63.5}{197 \times 2} = \frac{1876.425}{394} = 4.763 \text{ g}$$

$$\text{Also, } w = \frac{Eit}{96500}$$

$$\text{Therefore } 4.763 = \frac{63.5 \times i \times 5 \times 60 \times 60}{2 \times 96500}$$

$$\text{Therefore } i = \frac{4.763 \times 2 \times 96500}{63.5 \times 5 \times 60 \times 60}$$

$$= \frac{919259}{1143000}$$

$$= 0.804 \text{ ampere}$$

2. Volume of the surface (V) = area \times thickness

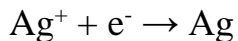
Given,

$$\text{Area} = 80 \text{ cm}^2, \text{ thickness} = 0.005 \text{ mm} = 0.0005 \text{ cm}$$

$$\text{Therefore } V = 80 \times 0.0005 = 0.04 \text{ cm}^3$$

$$\text{Mass of Ag (w)} = V \times \text{density}$$

$$= 0.04 \times 10.5 = 0.42 \text{ g}$$



$$\text{Therefore } W_{\text{Ag}} = \frac{Eit}{96500}$$

$$0.42 = \frac{108 \times 3 \times t}{96500}$$

$$\text{Therefore } t = \frac{0.42 \times 96500}{108 \times 3} = \frac{40530}{324} = 125.09 \text{ s}$$

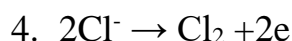
3. Watt = Ampere \times Volt

$$\text{Therefore Ampere (i)} = \frac{\text{Watt}}{\text{Volt}} = \frac{100}{110}$$

$$\text{Now, } w = \frac{Eit}{96500}$$

$$\text{Therefore } w_{\text{Cd}} = \frac{112.4 \times 100 \times 10 \times 60 \times 60}{2 \times 110 \times 96500}$$

$$= \frac{404640000}{21230000} = 19.06 \text{ g}$$



$$w = \frac{E.i.t}{96500} = \frac{E.Q}{96500}$$

$$Q = \frac{96500w}{E} = \frac{96500 \times 710}{35.5} = 20F$$

$$Q = 1930000 \text{ coulomb}$$

Therefore 1F gives 1g eq. or 40g NaOH

Therefore 20F gives 20g eq. or $40 \times 20\text{g NaOH} = 800\text{g NaOH}$

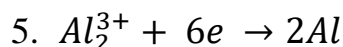
Therefore 1F gives 1g eq. or 1g H_2

Therefore 20F gives 20g eq. or 20g H_2

From $PV = \frac{w}{m} RT$

$$1 \times V = \frac{20}{2} \times 0.0821 \times 300$$

$$V_H = 246.3 \text{ litre}$$



$$E_{\text{Al}} = \frac{\text{At.wt}}{3} = \frac{27}{3} = 9$$

Now $w = \frac{E.i.t}{96500}$

$$100 = \frac{27 \times 125 \times t}{3 \times 96500}$$

$$t = 8577.77 \text{ second}$$

6. Current flown = 0.525 ampere as shown by ammeter

$$\text{Actual current flown (i)} = \frac{w}{E \times t} \times 96500 = \frac{0.6354 \times 96500}{(\frac{63.54}{2}) \times 60 \times 60} (\because t = 60 \times 60 \text{ sec})$$

$$i = 0.536 \text{ ampere}$$

$$\text{Thus error in (i)} = 0.536 - 0.525 = 0.011$$

$$\text{Therefore \% error in ammeter} = \frac{0.11 \times 100}{0.536} = 2.05\%$$

7. Eq. wt. of Cr = $\frac{\text{At.wt.}}{\text{No. of electrons lost or gained by one molecule of Cr}} = \frac{52}{6}$

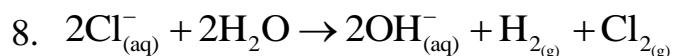
a. Therefore 96500 coulomb deposit = $\frac{52}{6} \times \frac{24000}{96500} \text{ g Cr} = 2.1554 \text{ g of Cr}$

b. Also given, $w_{\text{Cr}} = 1.5 \text{ g}$, $i = 12.5 \text{ ampere}$, $t = ?$, $E_{\text{Cr}} = \frac{52}{6}$

$$w = \frac{E.i.t}{96500}$$

$$1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500}$$

$$t = 1336.15 \text{ second}$$



$$i = \frac{62}{100} \times 25 = 15.4 \text{ amperes}$$

Weight of Cl_2 deposited = 1 kg or 1000 gm

We know that $\frac{W}{E} = \frac{Q}{F} = \frac{it}{F}$

$$\frac{1000}{35.5} = \frac{15.4 \times t}{96500}$$

$$t = 175300 \text{ sec. (or) } 48.69 \text{ hours}$$

Number of moles of Cl_2 thus produced

$$= \frac{1000}{71} = 14.08$$

Amount of OH^- released in the electrolysis = 2×14.08 moles = 28.16 moles

\therefore Molarity with respect of

$$\text{OH}^- = \frac{28.16 \text{ moles}}{20\text{l}} = 1.408 \text{ M}$$

9. For the given reactions, it is obvious that 22.4 litres of H_2 gas require 2 Faraday electricity.

\therefore 6.2 litres of H_2 will requires = 6 Faraday electricity

$$Q = C \times t$$

$$6 \times 96500 = C \times 15 \times 60$$

$$C = \frac{6 \times 96500}{15 \times 60} = 643.3 \text{ ampere}$$

Calculation of amount of Cu deposited by 6 F

$$\text{since } 1 \text{ F deposits} = \frac{63.5}{2} = 31.75 \text{ g of Cu}$$

$$6\text{F will deposits} = 31.75 \times 6 \text{ g} = 190.50 \text{ g of Cu}$$

10. When we add charging the discharging reaction, we get



$$\text{NH}_2\text{SO}_4 = \text{M}_{\text{H}_2\text{SO}_4} (\because 2\text{SO}_4^{2-} \text{ requires } 2e^-)$$

$$\therefore \text{Normality} = \text{Molarity}$$

Molarity of H_2SO_4 before electrolysis

$$= \frac{39 \times 1.2 \times 294 \times 1000}{98 \times 100} = 5.15$$

Molarity of H_2SO_4 after electrolysis

$$= \frac{20 \times 1.39 \times 1000}{98 \times 100} = 2.325$$

$$\text{Moles of } \text{H}_2\text{SO}_4 \text{ before electrolysis} = 5.15 \times 3.5 = 18.025$$

$$\text{Moles of } \text{H}_2\text{SO}_4 \text{ after electrolysis} = 2.325 \times 3.5 = 8.1375$$

$$\therefore \text{Moles (or equivalent) of } \text{H}_2\text{SO}_4 \text{ used} = 18.025 - 8.1375 = 9.8875$$

$$w = \frac{Eit}{96500} \quad \text{or} \quad i \times t = \frac{w \times 96500}{E} = 9.8875 \times 96500$$

$$= 954143.75 \quad ; \quad \text{or} \quad \mathbf{265.02 \text{ Amp.hr.}}$$

ELECTROCHEMISTRY

Module – 13.3: Conductance in Electrolytic Solutions

The electrolytic solutions obey ohm's law just as the metallic conductors do. According to this law the current flowing through an electrolyte (I) is inversely proportional to its resistance(R). Mathematically

$$I \propto \frac{1}{R} \quad (\text{or}) \quad I = \frac{V}{R}$$

Where V = potential applied (in volts)

I = current in amperes

R = the resistance in ohms

In electrochemistry, the term conductance (C) is used. It is the reciprocal of electrical resistance.

$C = \frac{1}{R}$; C is expressed in ohm^{-1} or mhos(Ω^{-1}) or siemen (S) in SI system.

$$\text{i.e., } 1 \text{ S} = 1 \Omega^{-1}.$$

Specific resistance (P): The resistance of a conductor is directly proportional to its length (l) and inversely proportional to the area of cross section (a).

$$\text{i.e., } R \propto l \text{ and}$$

$$R \propto \frac{1}{a}$$

$\text{i.e., } R \propto \left(\frac{l}{a}\right)$ (or) $R = \rho \cdot \frac{l}{a}$ where 'ρ' is a constant for that particular conductor at a given temperature. 'ρ' is known as **resistivity** (or) **specific resistance**.

Definition of specific resistance: "The resistance of a conductor of length 1cm and 1cm^2 area of cross section, at a definite temperature".

Units of ρ : $\rho = R \left(\frac{a}{l} \right) = (\text{ohm}) \frac{(cm^2)}{(cm)} = [\text{ohm.cm}]$

(or)

$$(\text{ohm}) \frac{(m^2)}{(m)} = [\text{ohm.m}].$$

Specific conductance (k): The conductance of a solution taken in a cell in which the electrodes are at unit distance and have unit area of cross – section. And it is the reciprocal of specific resistance. It is denoted by **k**.

So $k = \frac{1}{\rho}$

Units of k: $k = \frac{1}{\rho} = \frac{1}{\text{ohm.cm}} = \text{ohm}^{-1} \text{cm}^{-1}$. (In CGS units)

(Or) $k = \frac{1}{\rho} = \frac{1}{\text{ohm.m}} = \text{ohm}^{-1} \text{m}^{-1}$. (In SI units)

Cell constant: The ratio of the length of the electrolytic conductor (l) and the area of cross – section, *i.e.*, cell constant = $\left(\frac{l}{a} \right)$

Unit of cell constant = $\frac{cm}{cm^2} = \text{cm}^{-1}$ (or) $\frac{m}{m^2} = m^{-1}$ (in SI units)

Equivalent conductivity (Λ_{eq}): In dealing with solutions of electrolytes, a quantity of great significance is the equivalent conductance (Λ). This is necessary to compare the electrical conductance of different electrolytes at a given temperature.

Definition: The conductivity of all the ions present in an electrolytic solution containing one gram – equivalent of a substance. It is represented by Λ .

If 'V' is the volume of the solution in cm^3 , containing one gram equivalent of the electrolyte, then

$$\Lambda = k \cdot V.$$

If the normality of the solution is 'c' g. equivalents per litre, then, the volume containing one gram equivalent of the solute is $[1000/c] \text{ cm}^3$.

$$\text{Hence } \Lambda = \left[k \times \frac{1000}{c} \right]$$

$$\text{Unit of } \Lambda = \left[(\text{ohm}^{-1} \cdot \text{cm}^{-1}) \frac{1}{(\text{g. mol. wt}) (\text{cm}^{-3})} \right]$$

$$= \{(\text{ohm}^{-1}) \cdot \text{cm}^2 \cdot (\text{g eq}^{-1})\}$$

$$\text{In SI system, } [\text{ohm}^{-1} \text{ m}^2 \cdot \text{Eq}^{-1}]$$

Molar conductance (μ): The conductivity of all the ions present in an electrolytic solution containing one gram molecular weight of a substance. It is represented by μ .

$$\text{Then } \mu = k \cdot V; \quad \text{and } \mu = \left[k = \frac{1000}{c} \right].$$

$$\text{Unit of: } \mu = \left[(\text{ohm}^{-1} \cdot \text{cm}^{-1}) \frac{1}{(\text{g mol. wt}) (\text{cm}^{-3})} \right]$$

$$= \text{ohm}^{-1} \text{ cm}^2 (\text{g. mol. Wt})^{-1}.$$

$$\text{In SI system } [\text{ohm}^{-1} \cdot \text{m}^2 \cdot (\text{g mol. wt})^{-1}]$$

Relation between Λ and μ :

The relation is given by $\Lambda = \frac{\mu}{(\text{No. of invidual charges that are carried by the ion})}$

$$= \left[\frac{\mu}{Z} \right]$$

Ex: For NaCl $\Rightarrow \Lambda_{\text{NaCl}} = \left[\frac{\mu_{\text{NaCl}}}{1} \right]$.

For $\text{CuSO}_4 \Rightarrow \Lambda_{\text{CuSO}_4} = \left[\frac{\mu_{\text{CuSO}_4}}{2} \right]$

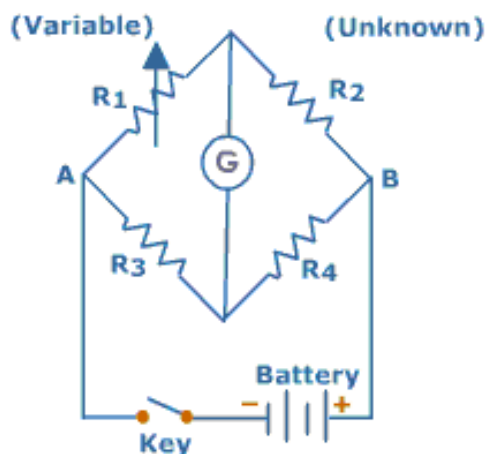
Degree of ionization or dissociation (α):

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty} = \frac{(\text{equivalent conductivity at a concentration})}{(\text{equivalent conductivity at infinite dilution})}$$

Arrhenius assumed this ratio to be equal to the degree of ionization of the electrolyte.

Measurement of electrolytic conductance:

Conductance of an electrolytic solution is measured, using Wheatstone bridge principle. The electrolyte is taken in conductivity cell. (See the next figure for the conductivity measurement). The cell is then kept instead of one resistance in the Wheatstone bridge.



R_1 = electrolytic cell

R_2 = Rheostat

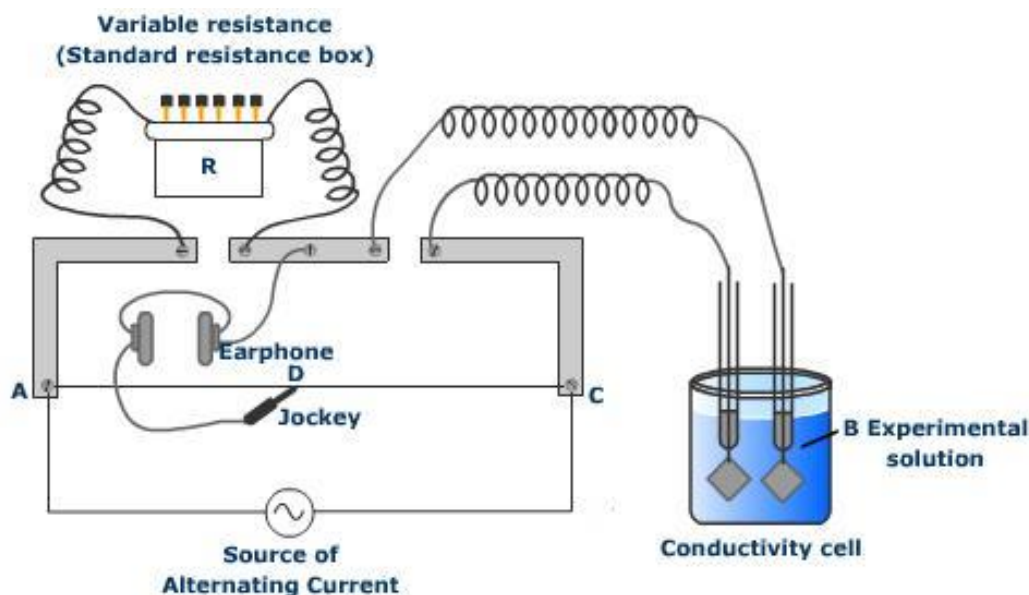
R_3, R_4 = Resistances

S = induction coil (source of A.C)

G = Null detector

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{According to Wheatstone bridge principle. The figure that is}$$

shown below explains the arrangement of the apparatus for the determination of the resistance of a given electrolyte.



J = Jackey;

H = Headphone;

T = Test solution;

R = Resistance box

I = Induction coil;

AB = Metre bridge wire

$$\text{Then } \frac{\text{Resistance, } R}{\text{Resistance of the electrolyte}} = \frac{\text{length AJ}}{\text{length BJ}} .$$

Then resistance of the electrolyte can be calculated, knowing R, AJ and BJ from the experiment.

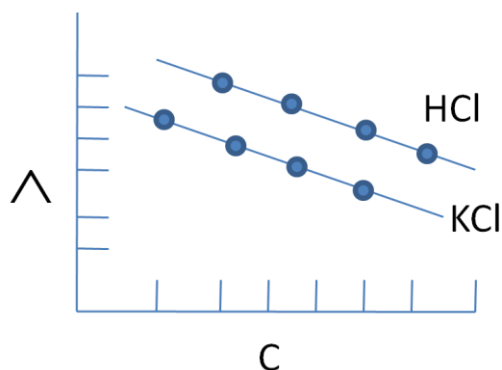
Strong and weak electrolytes:

The equivalent conductivity of an electrolyte varies with the nature of the electrolyte. A solution which contains larger number of ions as compared to another solution of the same concentration at the same temperature is called as a

strong electrolyte. Ex: KCl; HCl; NaOH. An electrolyte which has low degree of dissociation is known as a weak electrolyte. Ex: CH_3COOH ; NH_4OH ; HCN .

Effect of dilution on the equivalent conductivity:

The figure given here shows the variation of the equivalent conductivity of a typical strong electrolyte. For all electrolytes, the equivalent conductivity increases on dilution and reaches a limiting value. This limiting value is known equivalent conductivity at infinite dilution. It is represented by Λ_0 or Λ_∞ .



The equivalent conductivity of a strong electrolyte can be determined by the extrapolation method. Most of the procedures are based on the use of the formula $\Lambda = [\Lambda_\infty - b\sqrt{C}]$ where b = constant.

The value of Λ_∞ is inferred by extrapolation of the straight line to zero concentration.

But this method is not applicable to the weak electrolytes. For such electrolytes Kohlrausch's law is utilized.

Assignment Questions:

1. Define the terms specific, equivalent and molar conductances of an electrolyte?
Write the equations
2. Explain how molar conductivity varies with concentration of an electrolyte.

Example Set:

1. The unit of specific conductance is
 - a. $\text{Ohm}^{-1} \text{cm}^{-1}$
 - b. $\text{Ohm}^{-1} \text{m}^{-1}$
 - c. Siemens cm^{-1}
 - d. All

Solution: d)

2. What happens to the specific conductivity of an electrolytic solution, when the solution is diluted? It
- decreases
 - increases
 - remains constant
 - first decreases and then increases

Solution: a)

3. SI unit of specific conductance is
- $\text{Ohm}^{-1} \text{cm}^{-1}$
 - $\text{Ohm}^{-1} \text{m}^{-1}$
 - Ohm m^{-1}
 - Ohm cm^{-1}

Solution: b)

What is the principle used in calculation of resistance of unknown electrolyte?

Solution: Wheatstone bridge.

4. Define the terms
- Specific resistance
 - Specific conductance

Solution:

- Specific resistance:** “The resistance of a conductor of length 1cm and 1cm^2 area of cross section, at a definite temperature”.
- Specific conductance (k):** “The conductance of a solution taken in a cell in which the electrodes are at unit distance and have unit area of cross – section.” And it is the reciprocal of specific resistance. It is denoted by **k**.

Problem Set:

1. Cell constant has the unit
- cm
 - cm^{-1}

- c. cm^2
- d. cm sec^{-1}

Solution: b)

2. The specific conductance of a salt of 0.01 M conc. Is 1.061×10^{-4} . Then molar conductance will be
- a. 1.061×10^{-4}
 - b. 1.061
 - c. 10.61
 - d. 106.1

Solution: c)

3. Which of the solutions of NaCl will have the highest value of conductance
- a. 0.01 N
 - b. 0.001 N
 - c. 0.1 N
 - d. 1 N

Solution: d)

4. The specific conductance of a 0.02 M KCl solution at 25°C is $0.002768 \text{ mhos m}^{-1}$. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant

Solution:

We know that

Cell constant = specific conductance \times resistance

$$= 0.002768 \times 400 = 1.107200 \text{ m}^{-1}$$

5. 0.5 N solution of a salt occupying a volume between the platinum electrodes. 1.72 cm apart and of area 4.5 sq. cm has a resistance of 25 ohms. Calculate the equivalent conductivity of the solution

Solution:

Here, $R = 25$ ohms

$$\text{Therefore } C = \frac{1}{25} \text{ ohm}^{-1}$$

$$\text{Cell constant} = \frac{l}{a} = \frac{1.72}{4.5} = 0.38 \text{ cm}^{-1}$$

Now we know that

Specific conductance (k) = Observed conductance (C) \times Cell constant

$$= \left(\frac{1}{25} \times 0.38\right) \text{ ohm}^{-1} \cdot \text{cm}^{-1}.$$

$$= 0.0152 \text{ ohm}^{-1} \text{ cm}^{-1}$$

6. In a conductivity cell 0.01 N KCl solution gave a resistance of 225 ohms, while a 0.01 N solution of HCl gave a resistance of 77.1 ohms. Specific conductance of 0.01 N KCl is $0.00141 \text{ ohm}^{-1} \text{ cm}^{-1}$. Calculate the cell constant and equivalent conductance of HCl

Solution:

We know that

$$\text{Cell constant} = [\text{specific conductance of KCl} \times \text{Resistance of KCl}]$$

$$= 0.00141 \times 225 \text{ cm}^{-1}$$

$$= 0.31725 \text{ cm}^{-1}$$

$$\text{Specific conductance of 0.01 N HCl} = \frac{\text{cell constant}}{\text{resistance}}$$

$$= \frac{0.31725}{77.1}$$

$$= 0.0041 \text{ ohm}^{-1}$$

$$\text{Equivalent conductance of HCl, } \wedge_{eq} = \frac{\text{specific conductance} \times 1000}{0.01}$$

$$= \frac{0.0041 \times 1000}{0.01}$$

$$= 411.48$$

Exercise Questions:

- The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is
 - LiCl > NaCl > KCl
 - KCl > NaCl > LiCl
 - NaCl > KCl > LiCl
 - LiCl > KCl > NaCl

Solution: (b)

- The specific conductivity of M/50 KCl solution at 25°C is $0.2768 \Omega^{-1} \text{ m}^{-1}$. The resistance of this solution at 25°C, when measured with a particular cell was 250.2Ω . The resistance of 0.01 M CuSO₄ solution at 25°C measured with the same cell was 8331Ω . Calculate the molar conductivity of CuSO₄ solution

Solution:

Cell constant of the conductivity cell used

$$= \frac{\text{specific conductance of } \frac{M}{50} \text{ KCl solution}}{\text{conductance of } \frac{M}{50} \text{ KCl solution}} = \frac{0.2768 \Omega^{-1} \text{ m}^{-1}}{\left(\frac{1}{250.2}\right) \Omega^{-1}} = 69.26 \text{ m}^{-1}$$

Therefore specific conductance (k) of 0.01 M CuSO₄ solution

$$= \text{cell constant} \times \text{conductance of 0.01 M CuSO}_4 \text{ solution}$$

$$= 69.26 \text{ m}^{-1} \times \frac{1}{8333} \Omega^{-1} = 8.3135 \times 10^{-3} \Omega^{-1} \text{ m}^{-1}$$

$$\text{Concentration (C}_m\text{) of CuSO}_4 \text{ solution} = 0.01 \times 10^2 \text{ moles/m}^3$$

Therefore molar conductance of 0.01 M CuSO₄ solution

$$= \frac{k}{C_m} = \frac{8.3135 \times 10^{-3} \times \Omega^{-1} \times \text{m}^{-1}}{0.01 \times 10^3 \text{ moles/m}^3} = 9.3135 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$$

- When a certain cell was filled with 0.02 N KCl solution, the resistance was 350Ω when the same cell was filled with 0.01 N eq. solution of sodium acetate, the resistance was 1158Ω . If the specific conductance of 0.02 N KCl solution is

$27.7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. Calculate equivalent conductance of sodium acetate solution in $\text{ohm}^{-1} \text{ cm}^{-1} \text{ g equiv}^{-1}$.

Solution:

Resistance of 0.02 N aq. KCl solution = 350Ω

Conductance of 0.02 N KCl solution = $\frac{1}{350} \text{ ohm}^{-1}$

Specific conductance of 0.02 N KCl solution = $27.7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$

Therefore cell constant = $\frac{27.7 \times 10^{-4}}{\frac{1}{350}} \text{ cm}^{-1} = 0.9695 \text{ cm}^{-1}$

Resistance of 0.01 N aq. Sodium acetate = 1158Ω

Therefore conductance of 0.01 N aq. Sodium acetate = $\frac{1}{1158} \text{ ohm}^{-1}$

Specific conductance (k) of 0.01 N aq. Sodium acetate

= cell constant \times (conductance of sodium acetate) = $0.9695 \text{ cm}^{-1} \times \frac{1}{1158} \text{ ohm}^{-1}$
 = $8.3722 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$

Therefore equivalent conductance of 0.01 N aq. Sodium acetate

$$= \frac{k \times 1000}{C} = \frac{8.3722 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.01 \text{ g.eq.}} = 83.72 \Omega^{-1} \text{ cm}^2 \text{ g eq}^{-1}$$

ELECTROCHEMISTRY

Module – 13.4: Kohlrausch Law

This is also popularly known as “**The Law of independent migration of ions**”. This can be defined as “**The equivalent conductance, at infinite dilution, of an electrolyte is composed of two independent quantities; one contributed by anion and the other by cation**”.

Mathematically $\Lambda_{\infty} = [\lambda_a^{\circ} + \lambda_c^{\circ}]$. Where λ_a° and λ_c° are the ionic equivalent conductivities of the anion and the cation respectively at infinite dilution.

At infinite dilution the dissociation of all electrolytes is complete. The interionic interactions disappear. Then each ion migrates independently. Each ion contributes a definite share to the total equivalent conductance of an electrolyte. The magnitude of this contribution depends only on its nature. It does not depend on the other type of ion which is present in the electrolyte.

Applications of Kohlrausch Law:

1. Determination of the equivalent conductance, of a weak electrolyte, at infinite dilution:

Kohlrausch law gives a different procedure for determining the Λ_{∞}° of a weak electrolyte. The determination of Λ_{∞} for the weak electrolyte, acetic acid, will explain the method of calculation.

- a. The equivalent conductances of sodium acetate (CH_3COONa); sodium chloride (NaCl) and Hydrochloric acid (HCl) are determined directly by the extrapolation method that is applicable to strong electrolytes. All three are strong electrolytes.
- b. According to Kohlrausch law, the equivalent conductance's can be written as

$$\Lambda_{\text{NaAc}} = \lambda_{\text{Na}^+} + \lambda_{\text{Ac}^-} \quad \text{_____} \quad (1)$$

$$\Lambda_{\text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} \quad \text{_____} \quad (2)$$

$$\Lambda_{\text{HCl}} = \lambda_{\text{H}^+} + \lambda_{\text{Ac}^-} \quad \text{-----} \quad (3)$$

From these three equations {eqn. (1) + (3) - (2)}, we can show that

$$\Lambda_{\text{CH}_3\text{COOH}} = \lambda_{\text{H}^+} + \lambda_{\text{Ac}^-} \quad \text{-----} \quad (4)$$

$$= \Lambda_{\text{NaAc}} + \Lambda_{\text{HCl}} - \Lambda_{\text{NaCl}} \quad \text{-----} \quad (5)$$

The equation (5) gives the value of $\Lambda_{\text{CH}_3\text{COOH}}$.

Similar method can be adopted for other weak electrolytes by selecting suitable strong electrolytes.

2. Calculating the degree of dissociation of a weak electrolyte:

The relation that is useful for the calculation is $\alpha = \frac{\Lambda_c}{\Lambda_\infty}$; In this relation Λ_∞ for the electrolyte is obtained by the use of Kohlrausch law.

3. The ionic product of water (K_w), at a given temperature can be calculated from the relations.

$$\Lambda_\infty = [\lambda_{\text{H}^+} + \lambda_{\text{OH}^-}] = 548.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1} \quad \text{-----} \quad (1)$$

$$\text{And } \Lambda_\infty = \frac{(1000)(k)}{c} = \frac{(1000)(5.51 \times 10^{-8})}{c} \quad \text{-----} \quad (2)$$

$$\begin{aligned} C = [\text{OH}^-] = [\text{H}^+] &= \frac{(1000)(5.51 \times 10^{-8})}{548.3} \\ &= 1.005 \times 10^{-7} \text{ M} \quad \text{-----} \quad (3) \end{aligned}$$

$$\begin{aligned} \therefore K_w = [\text{OH}^-] = [\text{H}^+] &= [1.005 \times 10^{-7} \text{ M}]^2 \\ &= 1.01 \times 10^{-14} \text{ M}^2 \end{aligned}$$

4. The other useful parameters that can be estimated by the use of Kohlrausch law are

- a. Ionic conductances λ_c or λ_a (i.e., conductance of cation and of anion respectively).

$\lambda_c = n_c \cdot \Lambda_\infty$ where n_c is called on the transport number of cation

$\lambda_a = n_a \cdot \Lambda_\infty$ where n_a = transport number of anion.

- b. The solubility product (K_{sp}) of a sparingly soluble salt also can be calculated.

Example Set:

1. At infinite dilution, each ion of an electrolyte contributes a characteristic ionic conductance towards equivalent conductance of electrolyte which is independent of the nature of other ion present in solution. This statement was is known as
- Kohlraush Law
 - Debye – Huckel theory
 - Arrhenius theory
 - Ohm's law

Solution: a)

2. Define is Kohlraush law.

Solution: This is also popularly known as “**The Law of independent migration of ions**”. This can be defined as “**The equivalent conductance, at infinite dilution, of an electrolyte is composed of two independent quantities; one contributed by anion and the other by cation**”.

Mathematically $\Lambda_\infty = [\lambda_a^o + \lambda_c^o]$. Where λ_a^o and λ_c^o are the ionic equivalent conductivities of the anion and the cation respectively at infinite dilution.

3. Give any two of Kohlrausch law.

Solution:

- We can determine the equivalent conductance, of a weak electrolyte, at infinite dilution
- We can calculate the degree of dissociation of a weak electrolyte

Problem Set:

1. How can you calculate ionic product of water (K_w), at a given temperature? Explain with an example.

Solution:

The ionic product of water (K_w), at a given temperature can be calculated from the relations.

$$\Lambda_{\infty} = [\lambda_{H^+} + \lambda_{OH^-}] = 548.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1} \quad \text{-----(1)}$$

$$\text{And } \Lambda_{\infty} = \frac{(1000) (k)}{c} = \frac{(1000) (5.51 \times 10^{-8})}{c} \quad \text{----- (2)}$$

$$\begin{aligned} C = [OH^-] = [H^+] &= \frac{(1000) (5.51 \times 10^{-8})}{548.3} \\ &= 1.005 \times 10^{-7} \text{ M} \quad \text{----- (3)} \end{aligned}$$

$$\begin{aligned} \therefore K_w &= [OH^-] = [H^+] = [1.005 \times 10^{-7} \text{ M}]^2 \\ &= 1.01 \times 10^{-14} \text{ M}^2 \end{aligned}$$

Exercise questions:

1. At 25°C the equivalent conductance of 0.1 M benzoic acid is 8.9 ohm⁻¹ cm² equiv⁻¹. The ionic conductances at infinite dilution of the hydrogen ion and benzoate ion are 349.8 and 32.3 ohm⁻¹ cm² respectively. Calculate the degree of dissociation of 0.1 M benzoic acid

Solution:

$$\begin{aligned} \text{Calculation of } \lambda_{C_6H_5COOH}^{\infty} (C_6H_5COOH) &= \lambda_{H^+}^{\infty} + \lambda_{C_6H_5COO^-}^{\infty} \\ &= 349.8 + 32.3 \\ &= 382.1 \end{aligned}$$

$$\text{Now we know that } \lambda_{C_6H_5COOH}^v (C_6H_5COOH) = 8.9 \text{ mhos. Cm}^2 \text{ eq}^{-1}$$

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

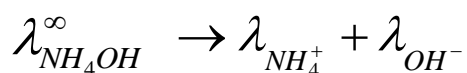
$$= \frac{8.9}{382.1}$$

$$= 0.023$$

2. The equivalent conductivities at infinite dilution of NH_4Cl , NaOH and NaCl are 125.6, 221.8 and 109.1 $\text{ohm}^{-1} \text{cm}^2$ respectively. Determine the percentage dissociation of N/100 solution of NH_4OH if the equivalent conductance of NH_4OH at this dilution is 9.33 $\text{ohm}^{-1} \text{cm}^2$

Solution:

Determination of equivalent conductance of NH_4OH at infinite dilution, $\lambda_{\text{NH}_4\text{OH}}^\infty$



This can be obtained by subtracting $\lambda^\infty(\text{NaCl})$ from the sum of $\lambda^\infty(\text{NH}_4\text{OH})$,
i.e.,

$$\Lambda_{\text{NH}_4\text{OH}}^\infty = \left[\Lambda_{\text{NH}_4\text{Cl}}^\infty + \Lambda_{\text{NaOH}}^\infty - \Lambda_{\text{NaCl}}^\infty \right]$$

$$= 125.6 + 221.8 - 109.1$$

$$= 238.3 \text{ ohm}^{-1} \text{cm}^2$$

$$\Lambda_{\text{NH}_4\text{OH}}^v = 9.33 \text{ ohm}^{-1} \text{cm}^2 \quad (\text{Given})$$

$$\text{Therefore degree of dissociation } (\alpha) = \frac{\Lambda_v}{\Lambda_\infty}$$

$$= \frac{9.33}{238.3} = 0.0392$$

$$\text{Therefore \% dissociation} = 0.0392 \times 100$$

$$= 3.92\%$$

ELECTROCHEMISTRY

Module – 13.5 & 13.6: Electrochemical Cells

Introduction:

Electrochemical cell:

“Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge to the external circuit.”

Electrochemical cells are of two types.

- a. Electrolytic cell
- b. Galvanic (or) voltaic cell

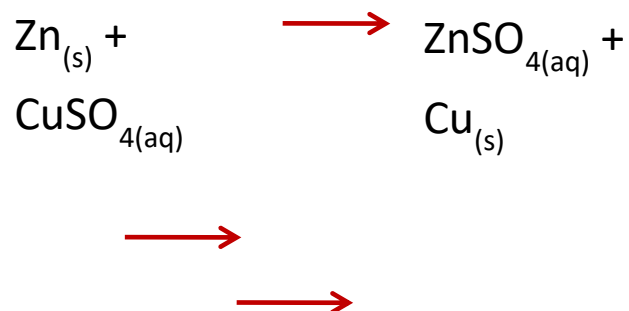
a. Electrolytic cell:

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done

b. Galvanic or voltaic cell:

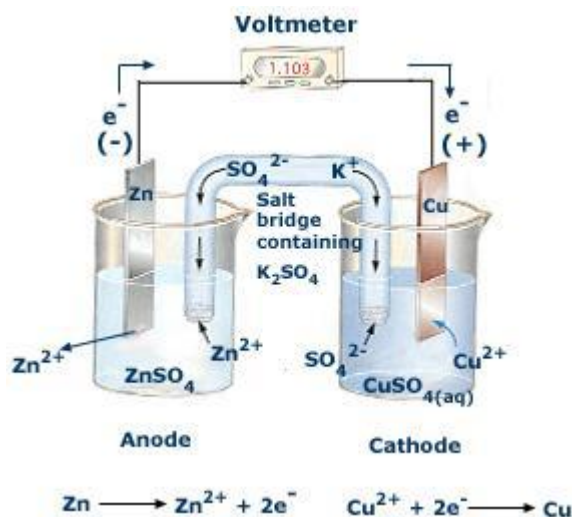
It is a device used to convert the chemical energy produced in a redox reaction into electrical energy.

Example: The redox reaction between Zn and CuSO_4 is



If a redox reaction is allowed to take place in such a way that the oxidation half reaction takes place in one beaker and the reduction half reaction in another

beaker, then electrons will flow from the former to the latter and a current will flow.



Salt bridge is an inverted U-tube filled with a strong electrolyte like KCl in Agar-Agar gel.

Anode (Negative terminal) is Zn (Oxidation takes place).



Cathode (positive terminal) is Cu (Reduction takes place).



Difference between electrochemical cell and electrolytic cell:

Galvanic Cell	Electrolytic Cell
It converts chemical energy into electrical energy	It converts electrical energy into chemical energy
It is based upon the redox reactions which are spontaneous	The redox reactions are non-spontaneous and take place only when energy is supplied
The electrolytes taken in the two beakers are different	Only one electrolyte is taken

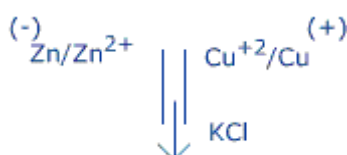
Anode (-ve) - Oxidation takes place	Anode (+ve) - Oxidation takes place
Cathode (+ve) - Reduction takes place.	Cathode (-ve) - Reduction takes place.

Representation of an electrochemical cell:

In general, the electrode at which reduction takes place is written on the RHS of the salt bridge and the electrode at which oxidation takes place is written on the LHS of the salt bridge. The salt bridge linking the aqueous solutions is represented by two vertical parallel lines having ions on both sides.

Left hand side	Right hand side
Anode	Cathode
(Oxidation)	(Reduction)

In the above system, Zn electrode is written on the LHS while the Cu electrode on the RHS of the salt bridge.



In general, of the two electrodes, the electrode having higher Standard Reduction Potential acts as a positive electrode.

Example: $\text{Zn} | \text{Zn}^{2+} (\text{C}_1) || \text{Cu}^{2+} (\text{C}_2) | \text{Cu}$

Metal/Metal ion (Conc.) $||$ Metal ion (Conc.) | Metal, C_1 and C_2 are the concentrations of Zinc and Copper ions respectively. $||$ - Represents the salt bridge.

Cell potential or EMF of a cell:

The difference between electrode potentials of two half cells is known as electromotive force or cell potential or cell voltage.

$$\text{EMF of galvanic cell} = [E_{\text{RHS}} - E_{\text{LHS}}]$$

Single electrode:

A metal rod dipped in the aqueous solution of its salt or a gaseous non – metal in contact with a solution containing its anion in the form of salt (or) acid (or) alkali functions as single electrode. Some examples are:

Metal electrodes:

1.	Zinc electrode	$Zn_{(aq)}^{++} \mid Zn$
2.	Copper electrode	$Cu_{(aq)}^{++} \mid Cu$
3.	Magnesium electrode	$Mg_{(aq)}^{++} \mid Mg$
4.	Silver electrode	$Ag_{(aq)}^{++} \mid Ag$
5.	Iron electrode	$Fe_{(aq)}^{++} \mid Fe$

Non – metal electrodes:

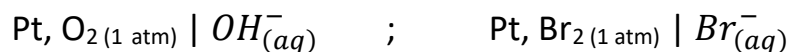
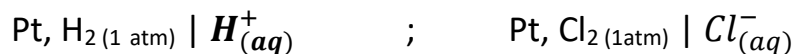
1.	Hydrogen electrode	$H_{(aq)}^{+} \mid H_2(g), Pt$
2.	Chlorine electrode	$Pt, Cl_{2(g)} \mid Cl_{(aq)}^{-}$
3.	Oxygen electrode	$Pt, O_{2(g)}^{-} \mid OH_{(aq)}^{-}$
4.	Bromine electrode	$Pt, Br_{2(g)}^{-} \mid Br_{(aq)}^{-}$

Generally the electrolyte in a single electrode is written in the form of the ions of the concerned metal or the non – metal while representing the half cell.

Example: $Zn_{(aq)}^{++} \mid Zn$; $Cu_{(aq)}^{++} \mid Cu$; $Mg_{(aq)}^{++} \mid Mg$; $Ag_{(aq)}^{++} \mid Ag$; $Fe_{(aq)}^{++} \mid Fe$; $H_2 \mid H_{(aq)}^{+}$;

$Cl_2 \mid Cl_{(aq)}^{-}$; $O_2 \mid OH_{(aq)}^{-}$; $Br_2 \mid Br_{(aq)}^{-}$

In the case of non – metal electrodes, a platinum rod is placed in the concerned aqueous solution of the ion and along with it the concerned gas at atmospheric pressure is passed in to the solution. These are represented as



Standard electrode potential (E°):

It is potential developed when the pure metal is in contact with its ions at one molar concentration at 25°C or 298 K .

Example: When a Zn rod of any length is dipped in 1M ZnSO_4 solution, standard electrode is formed and the potential developed is called standard zinc electrode potential (E°_{Zn}). The standard zinc electrode is represented as $\text{Zn}/\text{Zn}^{+2} (1\text{M})$.

In case of a gas electrode, the standard electrode potential (E°) is defined as the potential developed at the interface of the gas and solution containing its own ions when an equilibrium is established between the gas at a pressure of 760 mm of Hg and the ions in solution of unit concentration.

When the H_2 gas at a pressure of 1atm is bubbled through HCl of 1 M std H_2 electrode is formed and the potential developed is called standard hydrogen electrode potential ($E^\circ_{\text{H}_2}$) whose magnitude is considered to be 0 .

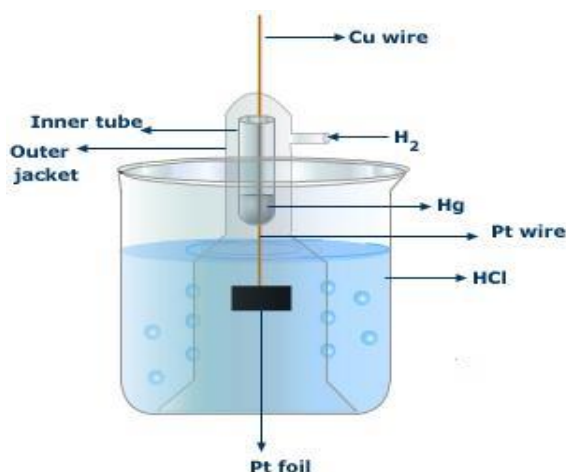
The standard H_2 electrode is represented as $\text{Pt, H}_2 / \text{H}^+(760 \text{ mm of Hg})/ (1\text{M})$

The magnitude of the standard electrode potential is independent of temperature since it depends only on the concentration of the ions.

Standard Hydrogen Electrode (SHE):

The absolute value of single electrode potential cannot be determined because the oxidation half reaction cannot take place without the reduction half. To overcome this difficulty the standard hydrogen electrode (SHE) is taken as the standard or reference.

Construction, Working and Limitations of Hydrogen Electrode:



This is a gas electrode. It consists of a thin rectangular platinum foil which is coated with fresh platinum black to increase the adsorption capacity of the metal. This is welded and the end of it is fused into the inner tube through the base. In the inner tube, little mercury is taken and a Cu wire is introduced to make the external electrical contact. The inner tube is enclosed in an outer jacket having an inlet tube for sending in H₂ gas and has a perforated wider base for the escape of excess of H₂. This unit is dipped in HCl taken in a beaker such that the metal foil remains in the solution.

Working:

When pure and dry H₂ gas is passed through the inlet tube, a part of the gas gets adsorbed and the excess bubbles out through the perforations. Between the H₂ gas absorbed on the surface of the metal and H⁺ of the solution, equilibrium is established and an electrical double layer of opposite charges is formed. The potential developed is called H₂ electrode potential.

In the above system, when the H₂ gas at a pressure of 1atm is bubbled through 1M HCl, the electrode (constructed) or formed is called STANDARD HYDROGEN ELECTRODE (SHE) or Normal H₂ electrode (NHE). This is represented as $\text{Pt}, \text{H}_2 (760 \text{ mm of Hg}) / \text{H}^+ (1\text{M})$

The standard H₂ electrode potential is defined as the potential that is developed between the H₂ gas adsorbed on the Pt metal and H⁺ of the solution when the H₂ gas at a pressure of 760 mm of Hg is in equilibrium with H⁺ of unit concentration. The magnitude of SHE potential is considered to be zero. It is used-

1. For the determination of electrode potential of metal electrode system.
2. For the determination of pH of the solution.

Limitations:

1. It is rather difficult to regulate the pressure of the H_2 gas to be at exactly 1atm throughout the experiment.
2. Excess of H_2 bubbling out carries little HCl with it and hence the H^+ concentration decreases. In such a system, it is difficult to maintain the concentration of HCl at 1M.
3. Platinum foil gets easily poisoned by the impurities present in the gas and HCl. In fact, the attainment of equilibrium is ensured by trial and error.
4. If the solution contains any oxidizing agent, the H_2 electrode cannot be used.

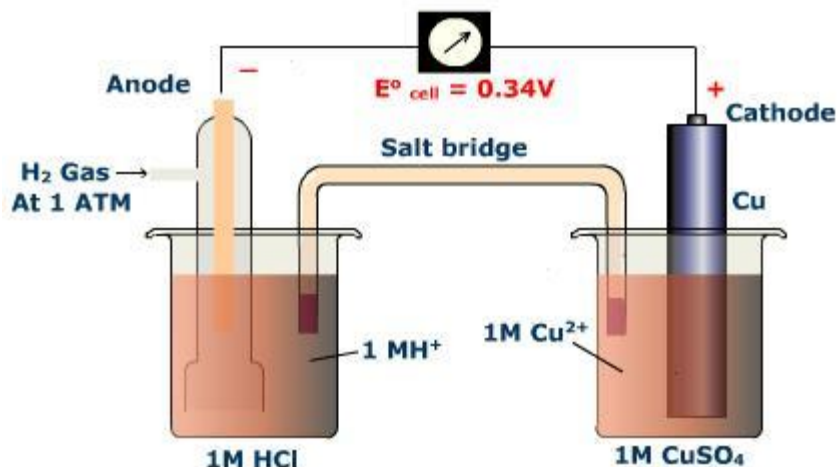
Measurement of electrode potentials:

The absolute value of a single electrode cannot be measured experimentally because a half-cell reaction cannot take place independently. One can measure only the difference between the electrode potentials of any two half-cell reactions. If the cell potential and the electrode potential for one of the half-cell reactions are known, the electrode potential of the other electrode can be calculated. Therefore, a standard hydrogen electrode is chosen and all other cell reactions are compared with this standard and a set of E° values are obtained.

Measurement of Electrode Potential of Cu^{2+}/Cu Electrode:

In order to obtain a cell reaction one must know the oxidized and reduced species to determine the cathode and anode in the cell. In a galvanic cell the cathode is the positive electrode while the anode is the negative electrode. When the electrodes of this cell are connected to the voltmeter, readings are obtained only when the terminal of opposite polarity are properly connected.

When a cell consisting of copper electrode immersed in 1 M $CuSO_4$ solution and standard hydrogen electrode are connected to a voltmeter, the emf of the cell is observed to be 0.34 V. Oxidation occurs at the Standard Hydrogen Electrode, which acts as the anode whereas reduction occurs at the copper electrode, which acts as the cathode.

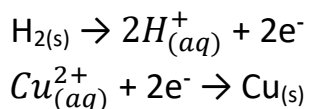


Determining standard electrode potential using standard hydrogen electrode

The Potential of the Cell:

(Pt), H_2 (g, 1 atm) H^+ (aq) (1 mol L^{-1}) Cu^{2+} (aq) (1 mol L^{-1}) Cu(s) at 298 K is called the standard electrode potential of cupric ion - copper electrode denotes as $E^0_{Cu^{2+} / Cu} = 0.34 V$

The two half-cell reactions are:



The EMF of the cell is:

$$E^0_{cell} = E^0_R - E^0_L$$

$$E^0_{cell} = E^0 (Cu^{2+} | Cu) - E^0 (H_2 | H^+)$$

$$0.34 = E^0 (Cu^{2+} | Cu) - 0$$

$$(or) E^0 (Cu^{2+} | Cu) = 0.34 V$$

Thus, the standard electrode potential of Cu is + 0.34 V.

We can conclude that in case, the electron accepting tendency of the electrode is more than that of a Standard Hydrogen Electrode, its standard reduction potential gets a positive sign and in case the electron accepting tendency of the metal

electrode is lesser than that of Standard Hydrogen Electrode., its standard reduction potential gets a negative sign. It must be remembered that according to latest convention standard potentials are taken as reduction potentials.

The electrode at which reduction occurs with respect to Standard Hydrogen Electrode has +ve reduction potential.

The electrode at which oxidation occurs with respect to Standard Hydrogen Electrode has -ve reduction potential.

Electrochemical series:

Different electrodes have different standard electrode potentials. The standard electrode potentials (E°) for some electrodes are negative, while for some others E° values are positive. The E° values of many electrodes have been measured and their standard reduction potentials are arranged in a sequential order. This arrangement of elements in order of increasing reduction potential values is called electrochemical series or activity series.

Standard reduction potentials at 298 K:

Electrode	Electrode reactions	E° volts
$\text{Li}^+ \text{Li}$	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	- 3.05
$\text{K}^+ \text{K}$	$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	- 2.93
$\text{Mg}^{2+} \text{Mg}$	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mg}(\text{s})$	- 2.37
$\text{Al}^{3+} \text{Al}$	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$	- 1.66
$\text{Zn}^{2+} \text{Zn}$	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	- 0.76
$\text{Fe}^{2+} \text{Fe}$	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	- 0.44
$\text{Cd}^{2+} \text{Cd}$	$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	- 0.40
$\text{Ni}^{2+} \text{Ni}$	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	- 0.25
$\text{Pb}^{2+} \text{Pb}$	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	- 0.13
$\text{Pt}, \text{H}^+ \text{H}$	$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{s})$	0.00
$\text{Cu}^{2+} \text{Cu}$	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+ 0.34
$\text{I}_2 \text{I}^-$	$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+ 0.54
$\text{Fe}^{3+} \text{Fe}^{2+}$	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Hg}_2^{2+} \text{Hg}$	$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+ 0.79
$\text{Ag}^+ \text{Ag}$	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.80
$\text{Br}_2 \text{Br}^-$	$\text{Br}_2(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.08
$\text{Pt}, \text{Cl}_2 \text{Cl}^-$	$\text{Cl}_2(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{s})$	+1.36
$\text{Au}^{3+} \text{Au}$	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+ 1.50

a* = increasing tendency for oxidation	b* = increasing tendency for reduction
to lose electrons	to gain electrons
as strong reducing agent	as strong oxidizing agent

The E° value of an electrode gives the relative tendency for the reduction reaction to occur at the electrode as compared to that of reduction of H^+ ion under standard conditions. Therefore, the electrodes with positive electrode potentials show greater tendency towards reduction than the tendency shown by H^+ for reduction. On the other hand, the electrodes with negative electrode potentials show lesser tendency towards reduction than the tendency of H^+ ions for reduction. This difference in the reduction tendencies of the two electrodes in a cell finds many applications in chemistry.

Characteristics of electrochemical series:

1. Reactive metals are placed on top (*e.g.*, Li) and they have a great tendency to get oxidized. Non-reactive metals like Ag and Au are placed at the bottom.
2. Any metal above hydrogen can displace it from dilute acids.

Example:



Any metal which is above another can displace that from its salt solutions

Example:



If two metals form a cell, the metal that is above undergoes oxidation and forms the anode while the one below forms the cathode.

Example:

Zn – Anode (+ 0.34V)

Cu – Cathode (-0.76V)

Application of electrochemical series (ECS):

1. Higher the SRP, greater is the tendency to accept e^- , higher is the tendency to get reduced and greater is the oxidizing power. Fluorine system (F_2/F^-) has the highest SRP and hence it possesses highest oxidizing power and this increases down the group.
2. Lower the SRP, lesser is the tendency to accept e^- , higher is the tendency to donate electrons, higher is the tendency to get oxidized and greater is the reducing power.
In the ECS, Lithium has the lowest SRP. Hence, it has the highest reducing power and this goes on decreasing down the series.
3. Higher the SRP, greater is the tendency to accept e^- to form anions, higher is the electro negative nature. In the ECS, Fluorine system has the highest SRP and hence it is most electro negative and this goes on increasing down the series.
4. Lower the SRP, lesser is the tendency to accept the electrons, greater is the tendency to donate the e^- to form cations and higher is the electro positive nature. In the ECS, Li system has the lowest SRP and is highly electro positive which goes on decreasing down the series.
5. A metal system occurring above H_2 , displaces H_2 from dilute acids, from water steam depending on its position and gets tarnished.
6. A metal system occurring below H_2 does not displace H_2 from dilute acids, water or steam does not get tarnished.

Assignment Questions:

1. What are galvanic cells? How are they represented? What is cell reaction and how is it written? Illustrate your answer
2. Give a brief note on standard hydrogen electrode
3. Define electro chemical series and give its applications

Example Set:

1. Standard electrode potential for the reaction $2H^+ + 2e^- \rightarrow H_{2(g)}$ is
 - a. Zero
 - b. + 1 V
 - c. - 1 V
 - d. + 100 V

Solution: a)

2. In a galvanic cell energy changes occurs as
- Chemical energy \rightarrow Electrical energy
 - Electrical energy \rightarrow Chemical energy
 - Chemical energy \rightarrow Internal energy
 - Internal energy \rightarrow Electrical energy

Solution: a)

3. In the cell $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$
- Copper gets reduced
 - Zinc ions gets oxidized
 - Zinc gets oxidized and copper ions gets reduced
 - Copper gets oxidized

Solution: c)

4. The cell $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ is represented by
- $\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Zn}^{2+} \mid \text{Zn}$
 - $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$
 - $\text{Cu}^{2+} \mid \text{Cu} \parallel \text{Zn} \mid \text{Zn}^{2+}$
 - $\text{Pt} \mid \text{Zn}^{2+} \parallel \text{Pt} \mid \text{Cu}^{2+}$

Solution: b)

5. Construct the cells in which following reactions are taking place
- $\text{Fe} + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}$
 - $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
 - $\text{Fe} + \text{SnCl}_2 \rightarrow \text{FeCl}_2 + \text{Sn}$
 - $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 \rightarrow \text{HCl}$

Solution:

Always remember that the metal which goes into solution in the form of its salt is undergoing oxidation and thus will act as negative electrode (*i.e.*, anode); while the other metal acts as positive electrode (*i.e.*, cathode).

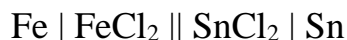
i. In this Fe is oxidized and thus will act as anode. Hence the cell will be represented as below.



ii. In this Zn is oxidized to ZnSO_4 , hence the cell will be



iii. In this Fe is oxidized to FeCl_2 , hence the cell will be



iv. In this H_2 is oxidized, hence the cell reaction will be



6. Calculate the e.m.f of the following cell

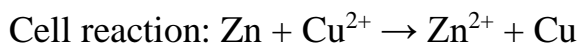


The reduction potentials of zinc and copper electrodes are -0.7623 volt and +0.337 volt respectively. Also write the cell reaction

Solution:

In the above cell, Zn is converted to Zn^{2+} , *i.e.*, it is oxidized while Cu^{2+} is reduced. In other words, Zn is acting as anode while Cu as cathode. In terms of reduction potential, EMF of a cell is given by the relation

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ &= 0.337 - (-0.7623) \\ &= 1.0993 \text{ volt} \end{aligned}$$



Problem Set:

1. In the $\text{Cu} \mid \text{Zn}$ cell

- Reduction occurs at copper cathode
- Oxidation occurs at copper at copper cathode
- Reduction occurs at the anode
- Chemical energy is converted to light energy

Solution: a)

2. In a galvanic cell which is wrong statement?
- Anode has negative polarity
 - Cathode has positive polarity
 - Reduction takes place at anode
 - Reduction takes place at cathode

Solution: c)

3. The standard reduction electrode potential values of the elements A, B and C are + 0.68, – 2.5 and – 0.5 V respectively. The order of their reducing power is
- $A > B > C$
 - $A > C > B$
 - $C > B > A$
 - $B > C > A$

Solution: d)

4. In a cell containing zinc electrode and standard hydrogen electrode (SHE), the zinc electrode acts as
- Anode
 - Cathode
 - Neither cathode nor anode
 - Both anode and cathode

Solution: a)

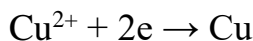
5. Write the cell reaction for the following cells.
- $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$
 - $\text{Fe} \mid \text{Fe}^{2+} \parallel \text{H}_2\text{SO}_4 \mid \text{H}_2 \mid \text{Pt}$
 - $\text{Pt} \mid \text{H}_2 \mid \text{HCl} \parallel \text{Cl}_2 \mid \text{Pt}$

Solution:

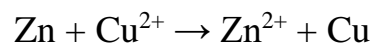
- i. The reaction of oxidation half – cell is

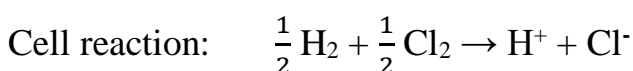
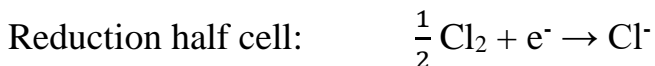
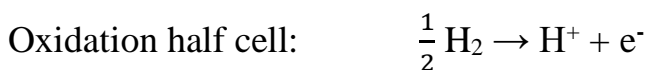
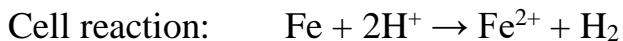
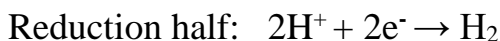


The reaction of reduction half – cell is

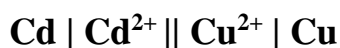


Thus the cell reaction is obtained on adding the two half – cell reactions.





6. Calculate the EMF of the cell



at 25°C. The standard reduction potentials of cadmium and copper electrodes are - 0.40 and + 0.34 volt respectively.

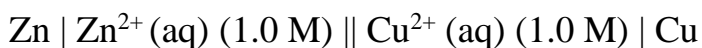
Solution:

$$E^0_{\text{cell}} = E^0_{\text{right}} - E^0_{\text{left}}$$

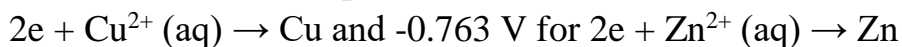
$$= 0.340 - (-0.40)$$

$$= 0.74 \text{ volt}$$

7. Consider the cell



The standard reaction potentials are: +0.35 V for



i. Write down the cell reaction

ii. Calculate the emf of the cell

iii. Is the cell reaction spontaneous or not?

Solution:

i. The two half – cell reactions can be written as below

Oxidation half reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Reduction half reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

Thus the cell reaction will be: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

ii. EMF of the cell (E^0_{cell}) = $E^0_{\text{cathode}} - E^0_{\text{anode}}$

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{right}} - E^0_{\text{left}} \\ &= 0.350 - (-0.763) \\ &= 0.350 + 0.763 \text{ volts} \\ &= 1.113 \text{ volt} \end{aligned}$$

iii. Since emf of the cell is positive, the reaction takes place spontaneously

Exercise Questions:

1. Calculate the e.m.f of the cell $\text{Zn} | \text{Zn}^{2+}(\text{aq}) || \text{Cd}^{2+}(\text{aq}) | \text{Cd}$. If the standard potentials are -0.77 V for $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}$ and -0.40 V for $\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}$

Solution:

$$E^0_{\text{Zn}^{2+}(\text{aq}) | \text{Zn}} = -0.77 \text{ V}$$

$$E^0_{\text{Cd}^{2+}(\text{aq}) | \text{Cd}} = -0.4 \text{ V}$$

$$E^0_{\text{cell}} = E^0_{\text{Cd}} - E^0_{\text{Zn}}$$

$$E^0_{\text{cell}} = -0.4 \text{ V} - (-0.77 \text{ V})$$

$$E^0_{\text{cell}} = 0.37 \text{ V}$$

2. Calculate the emf of a cell in which the following reactions takes place at different electrodes

$$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}; E^0 = -0.76 \text{ V}$$

$$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}; E^0 = 0.79 \text{ V}$$

Solution:

$$E_0 \text{ of } \text{Zn}^{2+} | \text{Zn} = -0.76 \text{ V}$$

$$E_0 \text{ of } \text{Ag}^+ | \text{Ag} = 0.79 \text{ V}$$

$$E_{\text{cell}} = E^0_{\text{Ag}} - E^0_{\text{Zn}}$$

$$= 0.79 - (-0.76)$$

$$\text{EMF of cell} = 1.55 \text{ V}$$

3. Standard reduction potential of $\text{Cd} | \text{Cd}^{2+}$ and $\text{Pb} | \text{Pb}^{2+}$ electrodes are -0.408 volt and - 0.126 volt respectively. State whether the following cell set up is feasible or not. Give reason.

Solution:

In the given cell



We require reduction potential of $\text{Pb} | \text{Pb}^{2+}$ and $\text{Cd}^{2+} | \text{Cd}$.

Here we are given

Reduction potential of $\text{Pb} | \text{Pb}^{2+} = 0.126$ Volt

And reduction potential of $\text{Cd} | \text{Cd}^{2+} = - 0.408$ Volt

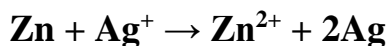
Therefore reduction potential of $\text{Cd}^{2+} | \text{Cd} = + 0.408$ Volt

Now since

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ &= 0.409 - (- 0.126) \\ &= 0.534 \text{ Volt} \end{aligned}$$

Since the EMF of the cell is positive, the set up of the cell is possible.

4. Calculate the standard EMF of cell which involves the following cell reaction



Given that $E^0_{\text{Zn}}, \text{Zn}^{2+} = 0.76$ volt and $E^0_{\text{Ag}}, \text{Ag}^+ = -0.80$ volt

Solution:

The cell reactions may be split into two half reactions as



Thus, we need oxidation potential of zinc electrode and reduction potential of silver electrode. But we are given

$$E^0_{\text{Zn}}, \text{Zn}^{2+}, \text{i.e. } E^0_{\text{Zn}/\text{Zn}^{2+}} = 0.76 \text{ Volt}$$

Thus 0.76 volt represents the oxidation potential of zinc

$$\text{and } E^0_{\text{Ag}}, \text{Ag}^+, \text{i.e. } E^0_{\text{Ag}/\text{Ag}^+} = -0.80 \text{ volt}$$

Thus -0.80 volt represents the oxidation potential of silver

Thus reduction potential of Ag electrode = - Oxi. Potential of Ag electrode

$$= - (-0.80)$$

$$= 0.80 \text{ Volt}$$

Similarly, reduction potential of Zn electrode = - 0.76

Thus standard EMF of the cell,

$$E^0_{\text{cell}} = E^0_{\text{right}} - E^0_{\text{left}}$$

$$= 0.80 - (-0.76)$$

$$= 1.56 \text{ volt}$$

Alternatively,

$$E^0_{\text{cell}} = [\text{standard oxi. Poten. of Zn electrode}] + [\text{standard reduc. Poten. of Ag electrode}]$$

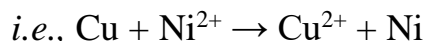
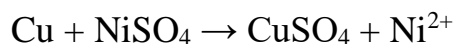
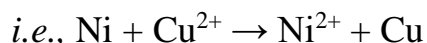
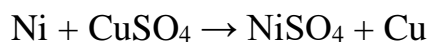
$$= 0.76 + 0.80$$

$$= 1.56 \text{ volt}$$

5. A cell is prepared by dipping a copper rod in 1 M CuSO_4 solution and a nickel in 1 M NiSO_4 solution. The standard reduction potentials of copper and nickel electrodes are 0.32 volt and -0.28 volt respectively.
- What will be cell reaction?
 - What will be the standard EMF of the cell?
 - Which electrode will be positive?
 - How will the cell be represented?

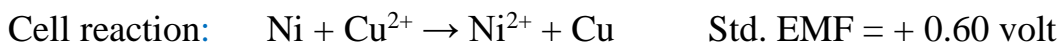
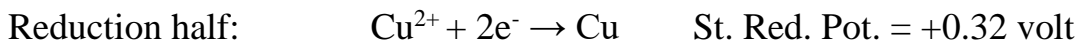
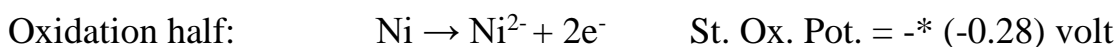
Solution:

- a. Theoretically two reactions are possible in the cell.



Of the above possible reactions, the correct reaction is that which gives positive EMF. So let us calculate the EMF of the two reactions.

The two half – reactions of (i) reaction are



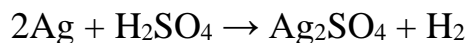
The positive EMF of the reaction indicates its feasibility. Hence this is the correct cell reaction. In the (ii) case the EMF will come out to be - 0.60 volt which indicates it's non – feasibility.

- b. Standard EMF of the cell as calculated above = 0.60 volt
- c. Since oxidation is taking place (electrons are produced) at the nickel, electrode, it acts as anode or negative electrode and hence copper will act as cathode or positive electrode.
- d. The cell reaction can thus be represented as
- $$\text{Ni} \mid \text{NiSO}_4 (1 \text{ M}) \parallel (\text{CuSO}_4 (1 \text{ M}) \mid \text{Cu})$$
6. The standard reduction potential of silver and zinc are 0.80 and – 0.76 volt respectively. Predict, whether silver and zinc both or either or none react with 1 sulphuric acid evolving hydrogen gas

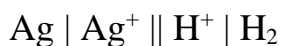
Solution:

To predict reaction between Ag and H₂SO₄

If they react, the possible reaction is



The cell in which above reactions are taking place may be represented as



$$\text{Therefore } E^0_{\text{cell}} = E^0_{\text{H}^+/\text{H}_2} - E^0_{\text{Ag}/\text{Ag}^+}$$

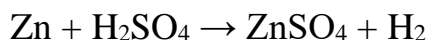
$$= 0 - 0.80$$

$$= -0.80 \text{ volt}$$

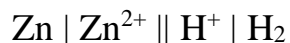
Since EMF of the reaction comes out to be negative, the reaction is not feasible

To predict reaction between zinc and sulphuric acid

If they react; the possible reaction is



By convention, the cell reaction will be represented by



$$\text{Therefore } E^0_{\text{cell}} = E^0_{\text{H}^+/\text{H}_2} - E^0_{\text{Zn}/\text{Zn}^{2+}}$$

$$= 0 - (-0.76)$$

$$= +0.76 \text{ volt}$$

The positive EMF shows the feasibility of the reaction.

ELECTROCHEMISTRY

Module – 13.7: EMF of the cell & Nernst equation

Gibb's Free Energy:

When a cell reaction takes place electrical energy is produced which results in decrease in the free energy of the system.

Decrease in free energy of the system = Electrical work

In an electro chemical cell,

Electric work done = [Quantity of current produced x EMF of the cell].

Produced for one mole of electrons, the quantity of current is equal to 1F (96500 coulomb)

Therefore for n moles of electrons, it is nF.

Hence Electric work done = nFE_{cell}

So, change in free energy = $-\Delta G = nFE_{\text{cell}}$

For a standard cell

$$-\Delta G^0 = nFE_{\text{cell}}$$

For equilibrium establishment in a redox reaction. The decrease in the free energy is given by

$$\Delta G = -n F E_{\text{cell}}^0 = RT \ln K_C$$

Where K_c = equilibrium reaction.

$$E_{\text{cell}}^0 = \frac{RT}{nF} \ln K_C$$

$$\text{(Or)} \quad -\Delta G^0 = nF \times \frac{RT}{nF} \ln K_C$$

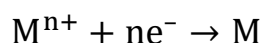
$$= RT \ln K_c$$

$$\Delta G^0 = - 2.303 RT \log K_c$$

Nernst Equation:

This equation tells us the effect of temperature and concentration of the electrolyte on electrode potential

For the reduction reaction,



$$E = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

Where E^0 = standard reduction potential of the electrode.

$[M]$ and $[M^{n+}]$ = conc. of the respect species.

$$(\text{or}) \quad E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

$[M]$ = Concentration of the metal say M

$[M^{n+}]$ = Concentration of oxidized state of the metal.

E = Electrode potential at concentration M^{n+} .

E^0 = Standard electrode potential of (M^{n+} / M)

R = Gas constant

T = Temperature in K

F = 1 Faraday (96500 coulombs)

n = Number of electrons involved in the electrode reaction.

For pure solids or liquids or gases at one atmosphere the concentration is taken as unity.

$$\therefore [M] = 1$$

$$i.e., E = E^0 - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$\text{or } E = E^0 - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}]}$$

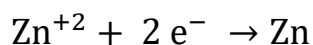
$$R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}, F = 96500 \text{ coulombs}$$

$$\text{At } T = 298 \text{ K}$$

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad \left[\because \frac{RT}{F} \text{ at } 25^\circ\text{C} = 0.0591 \right]$$

Example:

For the Zn - ZnSO₄ electrode

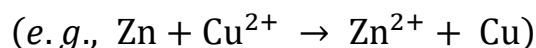
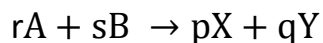


$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

Nernst Equation for EMF of a Cell:

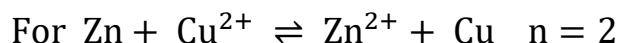
Effect of temperature and concentration on the E.M.F. of a cell

For a cell represented as reaction



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[X]^p [Y]^q}{[A]^r [B]^s}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log \frac{[X]^p [Y]^q}{[A]^r [B]^s}$$



$$E = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}] [\text{Cu}]}{[\text{Zn}] [\text{Cu}^{2+}]}$$

$$[\text{Zn}] = [\text{Cu}] = 1 \quad (\because \text{they are solids})$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Equilibrium Constant (K_c) From Nernst Equation:

In the following cell,

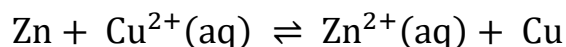


Electrons flow from the Zn to the Cu rod.

1. Zn from the Zn rod dissolves as Zn^{2+}
2. Cu^{2+} from CuSO_4 deposits on the Cu plate.
3. SO_4^{2-} moves through the salt bridge from CuSO_4 solution.

The concentration of CuSO_4 decreases while that of ZnSO_4 increases. As electrode potential depends upon concentration, a stage comes where both the electrode potentials are equal. Current stops flowing and the cell is said to have attained equilibrium.

Example:



The concentration of Cu^{2+} and Zn^{2+} at this stage is the equilibrium concentrations.

$$K_c = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \text{ when } E_{\text{cell}} = 0$$

$$0 = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log K_c \text{ at } 298 \text{ K}$$

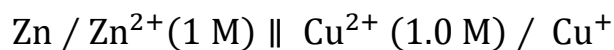
$$\log K_c = \frac{nE_{\text{cell}}^0}{0.0591}$$

Significance of K_c :

It tells us about the extent to which the reaction has been completed. K_c for Zn – Cu cell at 298K is 2×10^7 which shows that the reaction has nearly gone to completion.

Assignment Questions:

1. What is Nernst equation? Calculate the EMF of the galvanic cell using Nernst equation.



$$E_{\text{Zn}/\text{Zn}^{2+}}^0 = -0.766 \text{ V}; \quad E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.327 \text{ V}$$

2. Derive equilibrium constant (K_c) relation from Nernst equation.
3. How could you calculate the EMF of a cell by using Nernst equation?

Example Set:

1. The effect of change in ion concentration of the electrolyte on the value of E_{cell} , is given by
 - a. Le chatelier principle
 - b. Faraday's law
 - c. Nernst equation
 - d. Einstein's relationship

Solution: c)

2. The equation $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[\text{Products}]}{[\text{reactants}]}$ is called

- a. Gibbs free energy relation
- b. Gibbs – Helmholtz equation
- c. Nernst equation
- d. van der Waals equation

Solution: c)

3. any electrode at which a reduction half reaction shows a lesser tendency to occur than does $2 \text{H}^+ (1 \text{ M}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}, 1 \text{ atm})$ has an E^0 value of

- a. 0
- b. + ve sign
- c. – ve sign
- d. Infinity.

Solution: c)

4. If $\frac{2.303 RT}{F} = 0.059 \text{ V}$ activities of solids are constant than any of the cell.



- a. $E = E^0 - 0.059 \log \frac{a_2}{a_1}$
- b. $E = E^0 - 0.059 \log \frac{a_1}{a_2}$
- c. $E = E^0 - \frac{0.059}{2} \log \frac{a_1}{a_2}$
- d. $E = E^0 - \frac{0.059}{2} \log \frac{a_2}{a_1}$

Solution: c)

5. In the manufacture of Al, Al_2O_3 is dissolved in Na_3AlF_6 at 300 K and electrolyzed between Al and carbon electrodes. The net reaction is



Write the reaction at each electrode. Calculate the minimum voltage required between the electrodes if the Gibbs energy change for the above reaction is $-1370 \text{ kJ mol}^{-1}$.

Solution:

(No. of electrons involved in change = 12)

$$-\Delta G^0 = nFE_{\text{cell}}^0$$

$$1370 \times 10^3 = 12 \times 96500 \times E_{\text{cell}}^0$$

$$E_{\text{cell}}^0 = 1.1830 \text{ V}$$

Problem set:

1. In the cell $\text{Zn}/\text{Zn}^{+2} // \text{Cu}^{+2}/\text{Cu}$; If the concentrations of Zn^{+2} and Cu^{+2} ions is doubled, the emf of the cell.
- Doubles
 - Reduces half
 - Remains same
 - Becomes zero

Solution: c)

2. Which is correct representation for Nernst equation for an electrode?

a. $E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$

- b. $E = E^0 - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$
- c. $E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Products}]}{[\text{Reactants}]}$
- d. All

Solution: d)

3. Given, the standard electrode potentials;



The standard electrode potential E^0 for $\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{2+}$ is

- a. -0.476 volt
- b. -0.404 volt
- c. 0.440 volt
- d. 0.772 volt

Solution: d)

4. Relation between standard free energy change and standard cell potential is

- a. $\Delta G^0 = -nF E_{\text{cell}}$
- b. $\Delta G^0 = \frac{-nF}{E_{\text{cell}}}$
- c. $\Delta G^0 = \Delta H^0 - T \times \frac{nF}{E_{\text{cell}}}$
- d. $\Delta G^0 = -\log \frac{nF}{E_{\text{cell}}}$

Solution: a)

5. Construct a cell in which the disproportionation reaction.

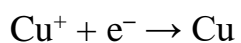


Takes place. Calculate the equilibrium constant for the reaction. If $\text{Cu}^{2+} / \text{Cu}$ and Cu^+ / Cu are 0.153 V and 0.518 V respectively.

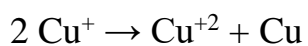
Solution:



$$E_{\text{Oxidation of half reaction}} = -0.153 \text{ V}$$



$$E_{\text{Reduction half reaction}} = 0.518 \text{ V}$$



$$E_{\text{cell}} = E_{\text{RP}} + E_{\text{OP}}$$

$$= (0.518 \text{ v}) + (-0.153 \text{ v})$$

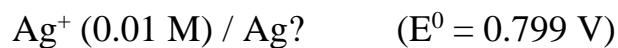
$$= 0.365 \text{ v}$$

$$\log K_c = \frac{n E_{\text{cell}}}{0.059}$$

$$= \frac{(1) (0.365)}{0.059}$$

$$K_C = 1.54 \times 10^6$$

6. Calculate the electrode potential of the single electrode.



Solution:

$$E = E^0 - \frac{0.059}{n} \log \frac{1}{c}$$

$$= 0.799 - \frac{0.059}{1} \log \frac{1}{10^{-2}}$$

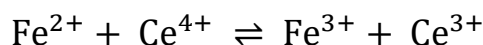
$$= 0.799 - 2 (0.059)$$

$$= 0.799 - 0.118$$

$$E = 0.681 \text{ V}$$

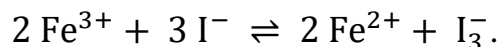
Exercise Questions:

- Two students use same stock solution of ZnSO_4 and a solution of CuSO_4 . The emf of one cell is 0.03 V higher than the other. The conc. of CuSO_4 in the cell with higher emf value is 0.5 M. Find out the conc. of CuSO_4 in the other cell $\left(\frac{2.303 RT}{F} = 0.06\right)$.
- Calculate the equilibrium constant for the reaction.



Given, $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.44 \text{ V}$ and $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.68 \text{ V}$

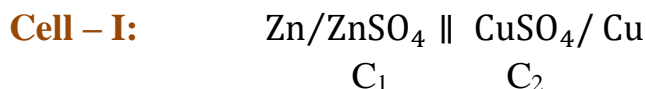
- Calculate the equilibrium constant for the reaction,



The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- couples.

Solutions:

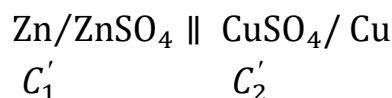
- Given,



$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.06}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.06}{2} \log \frac{[C_2]}{[C_1]} \quad \text{_____ (1)}$$

Cell – II:



$$E'_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.06}{2} \log \frac{C_2'}{C_1'}$$

If $E_{\text{cell}} > E'_{\text{cell}}$, then $E_{\text{cell}} - E'_{\text{cell}} = 0.03 \text{ V}$ and $C_2 = 0.5 \text{ M}$

\therefore By equations (1) and (2)

$$0.03 = \frac{0.06}{2} \log \frac{0.5}{C_2'}$$

$$C_2' = 0.05 \text{ M}$$

$$2. \quad E_{\text{cell}}^0 = \frac{0.059}{1} \log_{10} K_c$$

$$E_{\text{cell}}^0 = E_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}}^0 + E_{\text{RP}_{\text{Ce}^{4+}/\text{Ce}^{3+}}}^0 = -0.68 + 1.44 = 0.76 \text{ V}$$

$$\therefore \log_{10} K_c = \frac{0.76}{0.059} = 12.8814$$

$$\therefore K_c = 7.6 \times 10^{12}$$

3. For the change $2 \text{Fe}^{3+} + 3 \text{I}^- \rightleftharpoons 2 \text{Fe}^{2+} + \text{I}_3^-$, at equilibrium, $E = 0$

$$E = E^0 - \frac{0.059}{2} \log_{10} K_c \quad \text{or} \quad E^0 = \frac{0.059}{2} \log_{10} K_c$$

$$\text{Also} \quad E_{\text{cell}}^0 = E_{\text{RP}_{\text{Fe}^{3+}/\text{Fe}^{2+}}}^0 + E_{\text{OP}_{\text{I}^-/\text{I}_3^-}}^0 = 0.77 - 0.54 = 0.23 \text{ V}$$

$$\text{Thus,} \quad 0.23 = \frac{0.059}{2} \log_{10} K_c$$

$$\therefore K_c = 6.26 \times 10^7$$

ELECTROCHEMISTRY

Module – 13.8 & 13.9: Primary, Secondary and Fuel Cells

For an electrochemical cell to be used as a commercial cell it must

1. Be compact, light and rugged.
2. Voltage should not drop during use.

Battery:

A number of cells connected in series forms a battery.

Primary cells:

In these the redox reactions occur only once and cannot be used again.

Example: Dry cells, Mercury cells.

Secondary cells:

These can be recharged by passing current and can be used again and again.

Example: Lead storage cell, Ni – Cd storage cell.

Fuel cell:

Energy produced by combustion of fuels like H_2 , CO , CH_4 can be directly converted to electric energy.

Primary Cells:

Dry Cells:

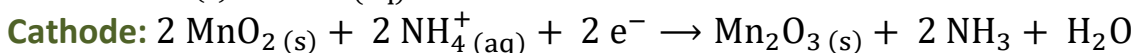
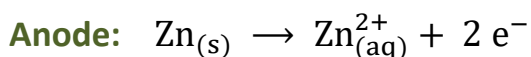
It is the compact form of the Leclanche cell.

Anode: Cylindrical Zn container.

Cathode: Central Graphite rod.

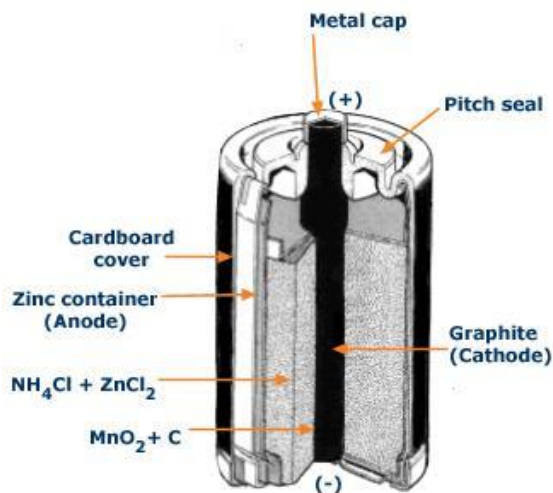
The space in between the electrodes is filled with NH_4Cl and $ZnCl_2$. The graphite rod is surrounded by MnO_2 and carbon.

Reactions:



Voltage: 1.25 V to 1.5 V

It does not have a long life because the acidic NH_4Cl corrodes the Zinc container.

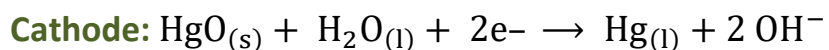
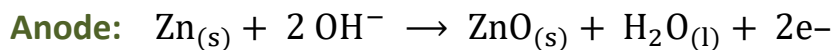


The Dry cell

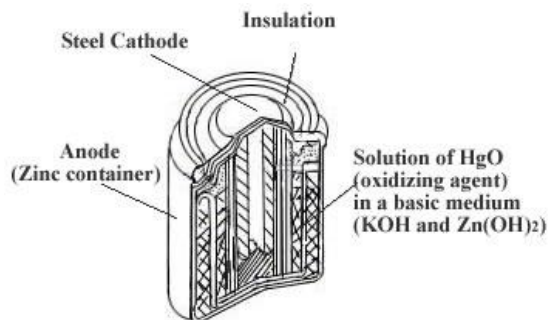
Mercury Cell: Used in small electric devices like hearing aids and watches.

Anode: Zinc container
 Cathode: Carbon rod
 Electrolyte: Moist HgO mixed with KOH .

Reactions:



The cell shows a constant potential of 1.35 V throughout as it does not involve any ion whose concentration changes.



Mercury dry cell battery

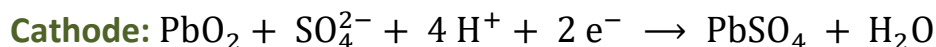
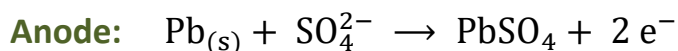
Secondary Cell:

Lead storage battery:

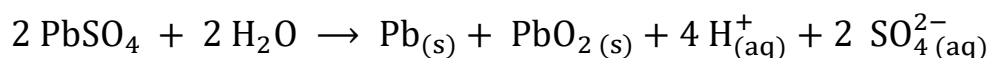
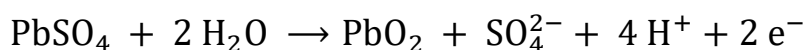
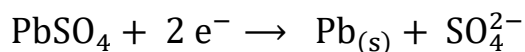
Anode:	Lead
Cathode:	PbO ₂
Electrolyte:	dilute H ₂ SO ₄ .

The electrodes are arranged alternately, separated by thin wooden or fiber glass sheet.

Electrode reaction (during discharging)



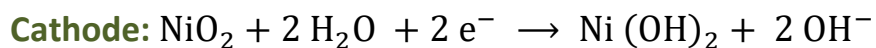
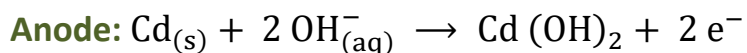
During charging, reverse reactions take place



Nickel – Cadmium storage cell: Used mainly in calculators.

Anode:	Cadmium
Cathode:	NiO ₂

Reactions:

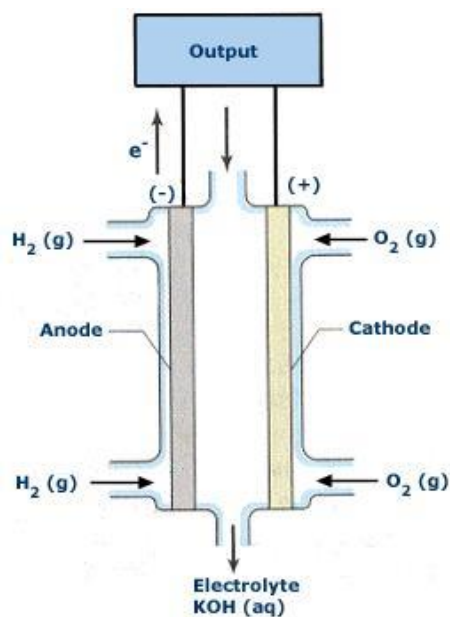
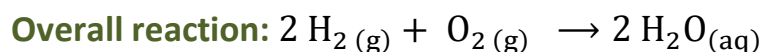
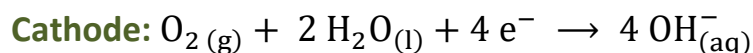


Fuel Cell:

These are devices which convert the energy produced during the combustion of fuels like H_2 , CO and CH_4 directly into electrical energy. The most successful fuel cell is the H_2 - O_2 fuel cell. It was used in the Apollo space programme and the water produced used as drinking water for the astronauts.

Working:

H_2 and O_2 are bubbled through a porous carbon rod into concentrated NaOH . Catalysts are present in the electrodes.



Fuel cell

Advantages:

1. More efficient than conventional cells because the energy of the fuel is converted directly into electric energy. Efficiency = 60 – 70%.
2. They are free from pollution.

Assignment Questions:

1. What are primary and secondary cells? Explain with examples.
2. What are fuel cells? Explain with examples.

Example Set:

1. A depolarizer used in dry cell is
 - a. Ammonium chloride
 - b. Manganese dioxide
 - c. Potassium oxide
 - d. Sodium phosphate

Solution: b)

2. The cell that cannot be recharged
 - a. Fuel cell
 - b. Solar cell
 - c. Primary cell
 - d. Secondary cell

Solution: c)

3. Fuel cell works on the basis of
 - a. Heat of formation
 - b. Heat of combustion
 - c. Heat of solution
 - d. Heat of neutralization

Solution: b)

4. In which of the following cells chemical energy of H_2 and O_2 is converted directly into electrical energy?
 - a. Mercury cell

- b. Daniel cell
- c. Lead storage cell
- d. Fuel cell

Solution: d)

5. Describe anyone dry cell.

Solution:

Dry Cells:

It is the compact form of the Leclanche cell.

Anode: Cylindrical Zn container.

Cathode: Central Graphite rod.

The space in between the electrodes is filled with NH_4Cl and ZnCl_2 . The graphite rod is surrounded by MnO_2 and carbon.

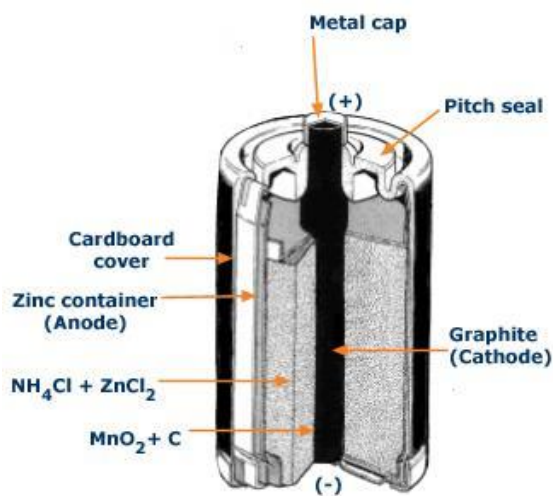
Reactions:

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

Cathode: $2\text{MnO}_{2(s)} + 2\text{NH}_4^+_{(aq)} + 2e^- \rightarrow \text{Mn}_2\text{O}_{3(s)} + 2\text{NH}_3 + \text{H}_2\text{O}$

Voltage: 1.25 V to 1.5 V

It does not have a long life because the acidic NH_4Cl corrodes the Zinc container.



The Dry cell

6. Write a short note on lead storage battery.

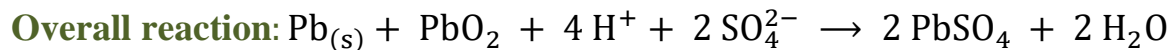
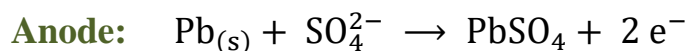
Solution:

Lead storage battery:

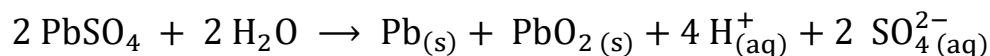
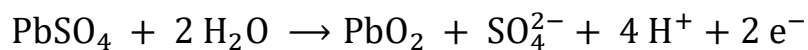
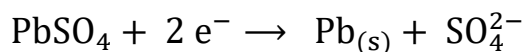
Anode:	Lead
Cathode:	PbO ₂
Electrolyte:	dilute H ₂ SO ₄ .

The electrodes are arranged alternately, separated by thin wooden or fiber glass sheet.

Electrode reaction (during discharging)



During charging, reverse reactions take place



7. Give any two advantages of fuel cells.

Solution:

Advantages:

1. More efficient than conventional cells because the energy of the fuel is converted directly into electric energy. Efficiency = 60 – 70%.
2. They are free from pollution.

Problem Set:

1. In the dry cell Leclanche cell, the reaction which takes place at the zinc anode is

- a. $\text{Zn}^{2+} + 2 \text{e}^{-} \rightarrow \text{Zn (s)}$
- b. $\text{Zn (s)} \rightarrow \text{Zn}^{2+} + 2 \text{e}^{-}$
- c. $\text{Mn}^{2+} + 2 \text{e}^{-} \rightarrow \text{Mn (s)}$
- d. $\text{Mn (s)} \rightarrow \text{Mn}^{2+} + 2 \text{e}^{-}$

Solution: b)

2. Fuel cells convert

- a. Electrical energy into chemical energy
- b. Mechanical energy into chemical energy
- c. Chemical energy into electrical energy
- d. Electrical energy into heat

Solution: c)

3. Lead storage battery contains

- a. Lead as anode
- b. Pb plates coated with PbO_2 act as cathode
- c. Electrolyte is dil H_2SO_4
- d. All the above

Solution: d)

4. Which of the following cells is used by Astronauts in Apollo space programme?

- a. Mercury
- b. Daniel
- c. Secondary
- d. $\text{H}_2 - \text{O}_2$ cell.

Solution: d)

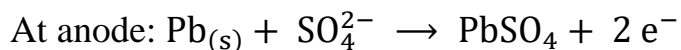
Exercise Questions:

1. Can the batteries used in the torchlights be recharged after their discharge? Give reason.
2. Write the chemistry of recharging the lead storage battery.
3. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

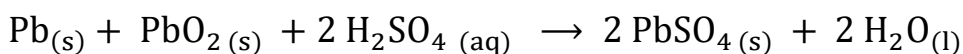
Solutions:

1. No. the cell reaction is not completely reversible.
2. A lead storage battery consists of a lead anode, a grid of lead packed with lead oxide (PbO_2) as the cathode, and a 38% solution of sulphuric acid (H_2SO_4) as an electrolyte.

When the battery is in use, the following cell reactions take place:



The overall cell reaction is given by,



When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, $\text{PbSO}_{4(s)}$ present at the anode and cathode is converted into $\text{Pb}_{(s)}$ and $\text{PbO}_{2(s)}$ respectively.

3. Methane and methanol can be used as fuels in fuel cells.

ELECTROCHEMISTRY

Module – 13.10: Corrosion

The process of slowly eating away of the metals due to attack of the atmospheric gases on the surface of metals; forming oxides, carbonates, sulphides is called corrosion (*e.g.*, tarnishing of Ag, development of a green coating on Cu (or) bronze etc). In corrosion, a metal loses electrons to oxygen and is oxidized.

Corrosion of iron is called ***Rusting of iron*** due to corrosion.

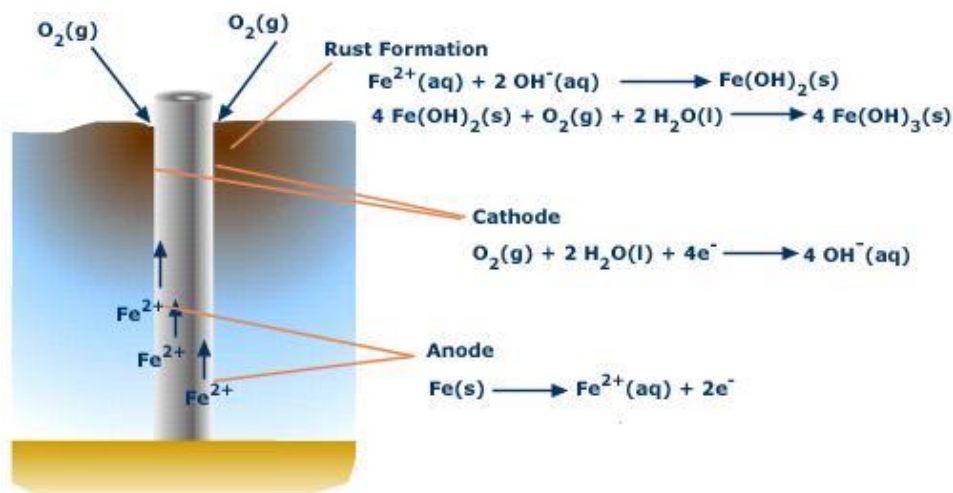
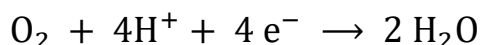
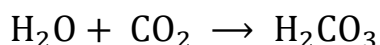
Rust is $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

Rusting is an ***electrochemical process***.

Theory of rusting:

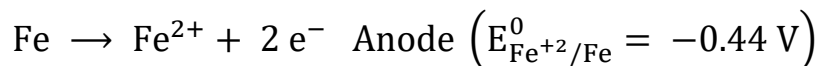
The chemistry of corrosion is quite complex. It is considered essentially as an electrochemical change.

1. Water present on the metal surface dissolves CO_2 and O_2 from the air.

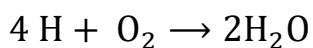
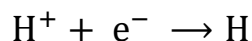


Corrosion of iron

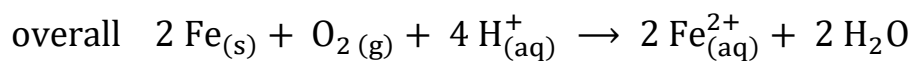
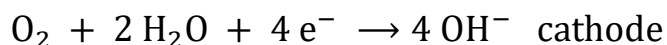
2. Fe in contact with dissolved CO₂ and O₂ undergoes oxidation.



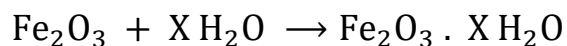
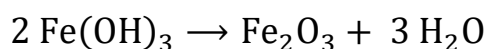
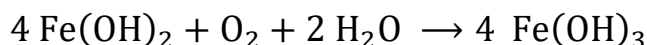
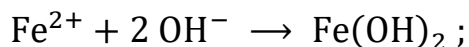
3. Electrons lost by Fe are taken by H⁺



The dissolved O₂ can take electrons directly also



4. Fe²⁺ reacts with dissolved O₂ and water



Rust (Hydrated ferric oxide)

Factors which Promote Corrosion:

1. Reactivity of metal
2. Presence of impurities
3. Presence of air, moisture, gases like SO₂ and CO₂
4. Presence of electrolytes

Prevention of Rusting:

Prevention of corrosion is of prime importance. Anti corrosion measures saves loss of lives through accidents and money with extended life of materials.

Barrier protection:

The metal surface is not allowed to come in contact with moisture, O_2 and CO_2 .

- i. Coating the metal surface with paint. This prevents the access to moist air. It the paint is defective, corrosion takes place.
- ii. Applying oil or grease.
- iii. Electroplating with non-corroding metals like Ni, Cr, Al, Sn, Zn.
- iv. Coating with alkaline earth phosphate (anti rust) solution.

Sacrificial protection:

Covering the surface with a more electro positive metal than Fe. The more electro positive metal loses electrons and as long as this coating is present Fe is protected.

Example:

Galvanization – Covering the iron objects with zinc. Zinc (Reduction potential = -0.76 V) corrosion thermodynamically takes place more readily than iron.

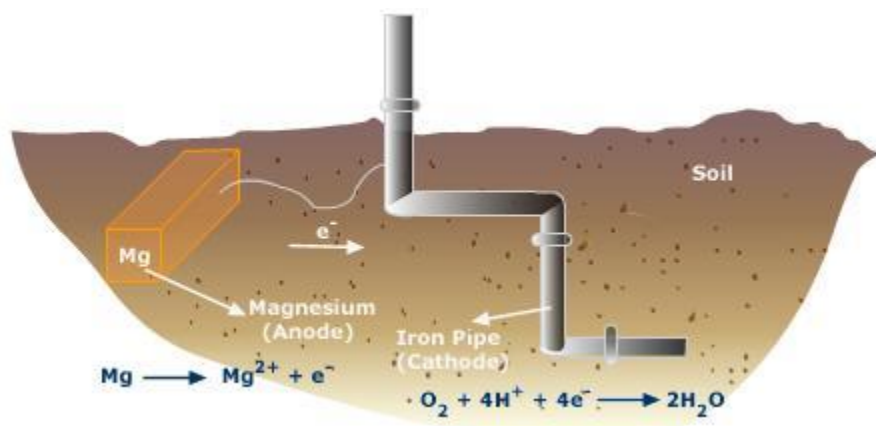
The zinc also forms a protective coating of $ZnCO_3$. $Zn(OH)_2$.

Electrical protection (Cathodic protection):

The iron object is connected to a more active metal (a metal with more negative electrode potential) either directly or through a wire. Fe acts as the cathode. The more reactive metal is the anode. It loses electrons and gradually disappears.

Example: $Mg = -2.363\text{ V}$

Fe can be connected to Mg, Zn or Al, which are called the sacrificial anodes. Used for protecting underground pipes from rusting.



Electrical protection of underground iron pipes

Assignment Questions:

1. What is corrosion? How is it prevented?
2. What are the factors promoting corrosion?
3. Write a note on theory of corrosion.

Example Set:

1. The factors that play a vital role in corrosion process
 - a. Impurities
 - b. Reactivity of metal
 - c. Air, moisture
 - d. All the above

Solution: d)

2. Which of the following can be used for cathode protection
 - a. Al
 - b. Cd
 - c. Cu
 - d. Au

Solution: a)

3. In galvanization, _____ is used to cover the metal.

- a. Ag
- b. Zn
- c. Cu
- d. Al

Solution: b)

4. Write a short note on electrical protection.

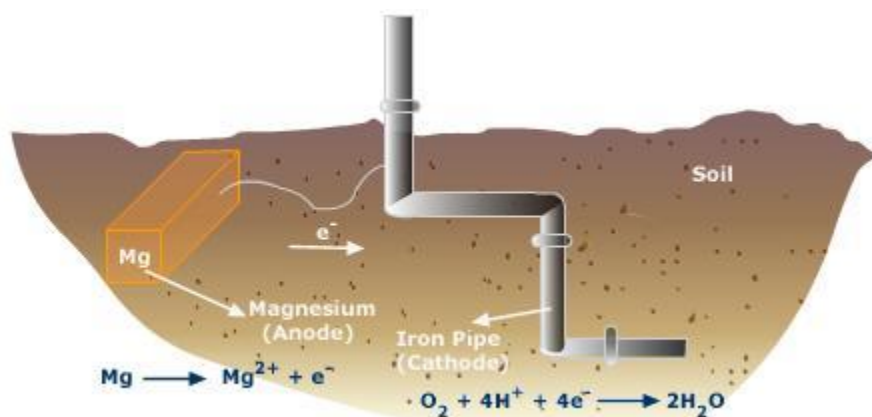
Solution:

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Electrical protection of underground iron pipes

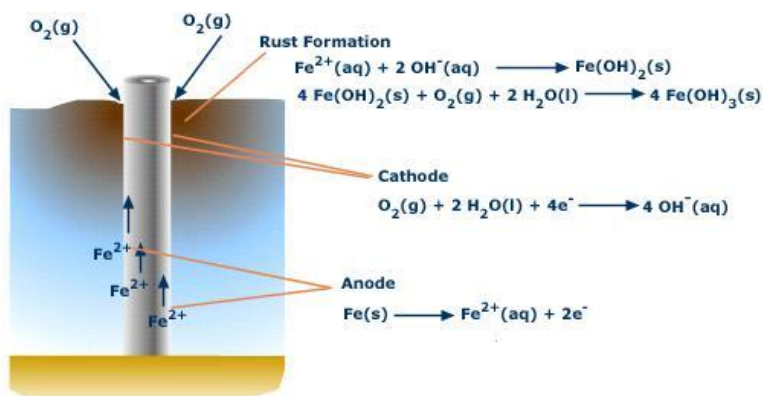
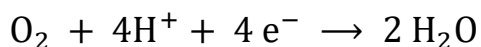
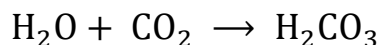
5. Explain briefly about the theory of rusting.

Solution:

Theory of rusting:

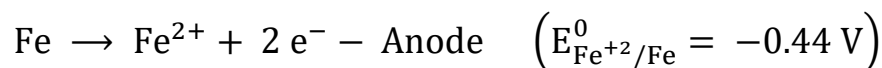
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1. Water present on the metal surface dissolves CO_2 and O_2 from the air.

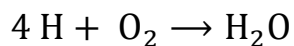
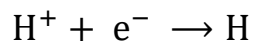


Corrosion of iron

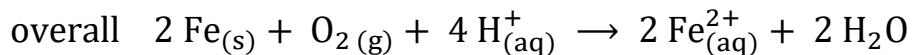
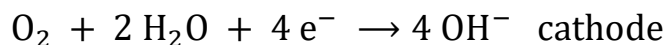
2. Fe in contact with dissolved CO_2 and O_2 undergoes oxidation.



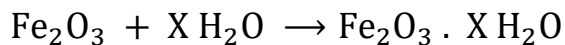
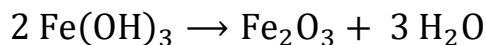
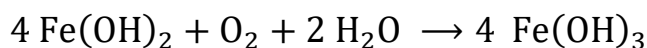
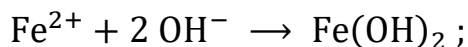
3. Electrons lost by Fe are taken by H^+



The dissolved O_2 can take electrons directly also



4. Fe^{2+} reacts with dissolved O_2 and water



Rust (Hydrated ferric oxide)

Problem Set:

1. The technique of protecting a metal from corrosion by connecting it to a more active second metal is called
 - a. Cathodic protection
 - b. Anodic protection
 - c. Galvanization
 - d. Annealing

Solution: a)

2. In barrier protection, which of the following methods is used?
 - a. Applying oil or grease
 - b. Treating with anti rust solution
 - c. Electroplating

- d. All the above

Solution: d)

3. Corrosion of a metal involves

- a. Physical changes
- b. Chemical reactions
- c. Both a) and b)
- d. Neither a) nor b)

Solution: b)

4. Define Sacrificial protection

Solution:

Sacrificial protection:

Covering the surface with a more electro positive metal than Fe. The more electro positive metal loses electrons and as long as this coating is present Fe is protected.

Example: Galvanization – Covering the iron objects with zinc. Zinc (Reduction potential = -0.76 V) corrosion thermodynamically takes place more readily than iron. The zinc also forms a protective coating of ZnCO_3 . Zn(OH)_2 .

5. Define Barrier protection.

Solution:

Barrier protection:

The metal surface is not allowed to come in contact with moisture, O_2 and CO_2 .

- i. Coating the metal surface with paint. This prevents the access to moist air.
It the paint is defective, corrosion takes place.
- ii. Applying oil or grease.

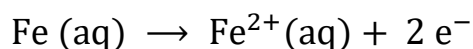
- iii. Electroplating with non-corroding metals like Ni, Cr, Al, Sn, Zn.
- iv. Coating with alkaline earth phosphate (anti rust) solution.

Exercise Questions:

1. Iron rod is immersed in NaCl solution such that its leach is exposed to air and the other half immersed in NaCl solution. Which part is corroded and why?
2. Which of the following is corroded faster? Iron pole in sea water or iron pole on the beach.
3. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Solutions:

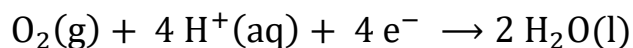
1. Immersed part is corroded due to less oxygenation of the surface of the metal. It is in contact with dissolved CO₂ and O₂
2. Iron pole in the sea water because of high salt concentration. *i.e.*, an electrolyte and dissolved gases. Iron is a reactive metal.
3. In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,



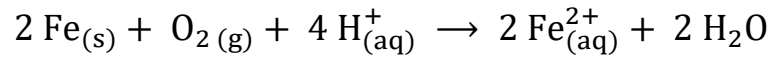
Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of H⁺ ions, the electrons reduce oxygen. This spot behaves as the cathode. These H⁺ ions come either from H₂CO₃, which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides present in the atmosphere, in water.

The reaction corresponding at the cathode is given by,



The overall reaction is:



Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) *i.e.*, rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.