

# ELECTROCHEMISTRY

## Section – I (Electrolytic cell)

### 1. Electrolysis and Electrode Reactions :

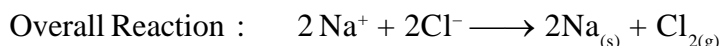
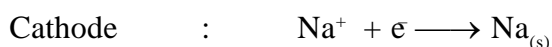
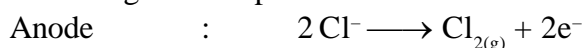
Electrolysis is a process in which chemical reactions occur at the electrodes, dipping in the electrolytes, when voltage is applied across them. The electrode that is charged positively is called anode and the electrode that is charged negatively is called cathode. The electrodes, like platinum, which only transfer electrons to and from the solutions are termed as “inert electrodes”. The “reactive electrodes” are those which enter chemically into the electrode reactions. During electrolysis, the reduction takes place at the cathode and oxidation takes place at the anode.

There can be many types of electrode reactions but general features are summarized below:

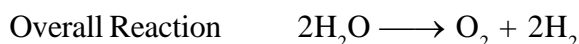
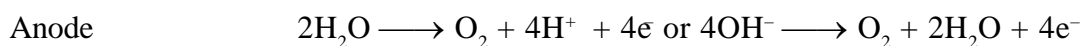
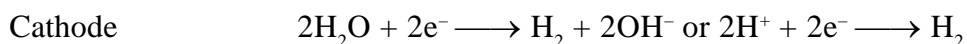
- (i) Current carrying ions are discharged at the electrodes.
- (ii) A negative ion which is difficult to get discharged at the anode, leads to the decomposition of  $H_2O$  and formation of  $O_2$ ,  $H^+$  and electron.
- (iii) A positive ion which is difficult to get discharged at cathode, leads to the decomposition of water, with the formation of  $H_2$ ,  $OH^-$  and absorption of electron.

Let us consider electrolysis of molten salts (e.g. NaCl) and then aqueous solution of salts.

Molten NaCl (an electrolyte) means free sodium ions ( $Na^+$ ) and chloride ions ( $Cl^-$ ), so it conducts current with the help of ions. As electric current is passed in the cell,  $Cl^-$  ions are attracted to anode (+ve electrode) and  $Na^+$  ions to cathode (–ve electrode). Both ions are discharged at respective electrode as follows:



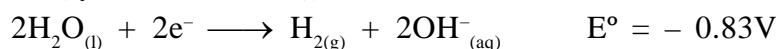
Let us now consider electrolysis of aqueous solution of salts (e.g.,  $Na_2SO_4$ ). In aqueous solution,  $Na^+$  ions and  $SO_4^{2-}$  ions are free to move for the conduction of electric current. When electric current is passed.  $Na^+$  ions are attracted to cathode and  $SO_4^{2-}$  ions to anode, but they are not discharged. The electrode reactions are as follows:



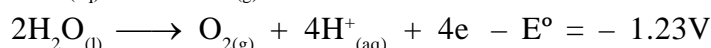
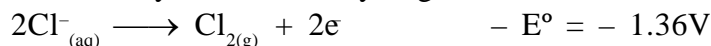
In this case,  $H_2$  is liberated at cathode and  $O_2$  at anode.

## Electrolysis of Sodium Chloride Solutions :

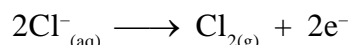
When you electrolyze an aqueous solution of sodium chloride, NaCl, the possible species involved in half-reactions are  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{H}_2\text{O}$ . The possible cathode half-reactions are



Under standard conditions, you expect  $\text{H}_2\text{O}$  to be reduced in preference to  $\text{Na}^+$ , which agrees with what you observe. Hydrogen is evolved at the cathode.

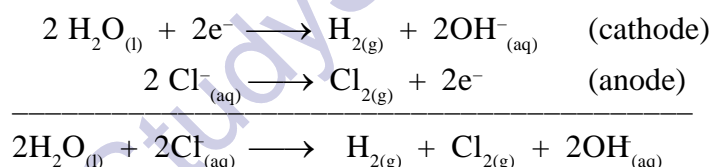


Under standard-state conditions, you might expect  $\text{H}_2\text{O}$  to be oxidized in preference to  $\text{Cl}^-$ . However, the potentials are close and over voltages at the electrodes could alter this conclusion. It is possible nevertheless to give a general statement about the product expected at the anode. Electrode potentials, as you have seen, depend on concentrations. It turns out that when the solution is concentrated enough in  $\text{Cl}^-$ ,  $\text{Cl}_2$  is the product; but in dilute solution,  $\text{O}_2$  is the product. To see this, you would simply apply the Nernst equation of the  $\text{Cl}^-|\text{Cl}_2$  half reaction.



Starting with very dilute NaCl solutions, you would find that the oxidation potential of  $\text{Cl}^-$  is very negative, so  $\text{H}_2\text{O}$  is reduced in preference to  $\text{Cl}^-$ . But as you increase the NaCl concentration, you would find that the oxidation potential of  $\text{Cl}^-$  increases until eventually  $\text{Cl}^-$  is oxidized in preference to  $\text{H}_2\text{O}$ . The product changes from  $\text{O}_2$  to  $\text{Cl}_2$ .

The half-reactions and cell reaction for the electrolysis of aqueous sodium chloride to chlorine and hydroxide ion are as follows:



Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is  $\text{Na}^+$ . When you evaporate the electrolyte solution at the cathode, you obtain sodium hydroxide NaOH.

### In General :

- (i) Of the two cations, that cation is liberated at the cathode which has higher reduction potential. Of the two anions, that anion will be discharged at the anode which has lower reduction potential.
- (ii) If electrode is active at cathode, metal goes on depositing on cathode and at anode metal is dissolved.
- (iii) It must be noted that it is not the SRP of a cation that decides its discharge, but its reduction potential. The SRP's should be used only when the concentration of ions are 1M. For concentrations other than 1M, the reduction potentials for each cation at the concentration is calculated and then the discharge of an ion can be predicted.
- (iv) The discharge of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  ions at anode does not commonly take place from aqueous solution.

## 2. Laws of Electrolysis :

The laws which govern the deposition of substances (in the form of ions) on electrodes with passage of electric current are called Faraday's laws of electrolysis.

- 1. Faraday's First Law :** The mass of an ion discharged during electrolysis is proportional to the quantity of electricity passed. Mathematically,  $W \propto Q$

Where

$W$  = Mass of ions liberated

$Q$  = Quantity of electricity passed in coulombs

But we know that  $Q = \text{Current in amperes (i)} \times \text{times in sec. (t)}$

$$\therefore W \propto i \times t \text{ or } W = Z \times i \times t$$

Where  $Z$  is a constant, known as electrochemical equivalent (ECE) of the ion deposited. When a current of 1 ampere is passed for 1 second (i.e.  $Q = 1$ ), then  $W = Z$

Thus electrochemical equivalent may be defined as the mass of the ion deposited by passing a current of one ampere for one second (i.e. by passing one coulomb of electricity). Its unit is  $\text{kg C}^{-1}$ .

1 F of charge = Charge on one mole of electron

$$= N_A \times e$$

$$= 6.023 \times 10^{23} \times 1.602 \times 10^{-19}$$

$$= 96514.8\text{C} \approx 96500\text{C}$$

= The charge which discharges  $E$  g of ion where  $E$  is equivalent weight of ion

Thus:  $F = N_A \times e$

Since 96500 C discharges  $E$  g of ion

$$\therefore 1\text{C discharge} = \frac{E}{96500} \text{ g of ion} = Z$$

Now substituting the value of  $Z$  in the reaction.

$$W = ZiT = \frac{EiT}{96500}$$

$$\text{or } \frac{W}{E} = \frac{it}{9650} = \frac{Q}{96500} = \frac{Q}{F}$$

- 2. Faraday's Second Law :** When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (equivalent weights). Suppose  $W_1$  and  $W_2$  are the weights of the elements deposited by passing a certain quantity of electricity through their salt solutions and  $E_1$  and  $E_2$  are their respective equivalent weights, then :

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \text{ or } \frac{Z_1it}{Z_2it} = \frac{E_1}{E_2} \quad (\because W=Zit)$$

$$\therefore \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Thus the electrochemical equivalent ( $Z$ ) of an element is directly proportional to its equivalent weight ( $E$ ), i.e.  $E \propto Z$  or  $E = FZ$

Where  $F$  is again a proportionality constant and has been found to be 96500 coulombs. It is called Faraday. Thus  $E = 96500 \times Z$

Therefore, when 96500 coulombs of electricity is passed through an electrolyte, one gram

equivalent of its ions is deposited at the respective electrode. This quantity of electricity which liberates one gram equivalent of each element is called one Faraday and is denoted by F.

$$\therefore 1 \text{ Faraday} = 96500 \text{ coulombs}$$

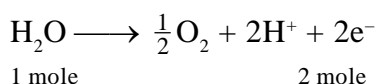
**Illustration 1.**

*How much electric charge is required to oxidise :*

- (a) 1 mole of  $\text{H}_2\text{O}$  to  $\text{O}_2$                       (b) 1 mole of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ?

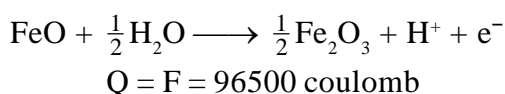
**Solution :**

- (a) The oxidation reaction is :



$$Q = 2F = 2 \times 96500 = 1.93 \times 10^5 \text{ C}$$

- (b) The oxidation reaction is

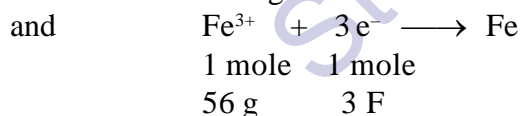
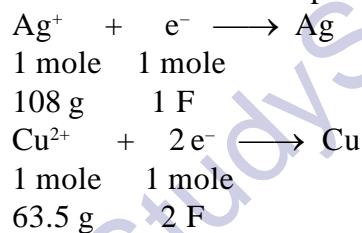


**Illustration 2.**

*Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing  $\text{AgNO}_3$ , second  $\text{CuSO}_4$  and third  $\text{FeCl}_3$  solution. How many gram of each metal will be deposited assuming only cathodic reaction in each cell.*

**Solution :**

The cathodic reaction in the cell are respectively,



Hence,  $\text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$

$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

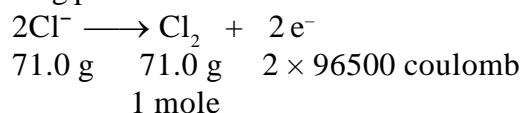
and  $\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$

**Illustration 3.**

*An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.*

**Solution :**

The reaction taking place at anode is



$$Q = i \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

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The amount of chlorine liberated by passing  $100 \times 5 \times 60 \times 60$  coulomb of electric charge.

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

Volume of  $\text{Cl}_2$  liberated at NTP =  $9.3264 \times 22.4 = 208.91 \text{ L}$

### **Illustration 4.**

**What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?**

**Solution :**

Applying  $E = Z \times 96500$  (E for chlorine = 35.5),

$$35.5 = Z \times 96500$$

or 
$$Z = \frac{35.5}{96500}$$

Now, applying the formula

$$W = Z \times i \times t$$

Where  $W = 10\text{g}$ ,  $Z = \frac{35.5}{96500}$ ,  $t = 60 \times 60 = 3600$  second

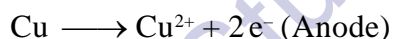
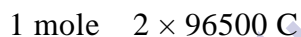
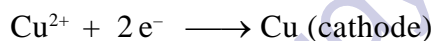
$$i = \frac{10 \times 96500}{35.5 \times 3600} = 7.55 \text{ ampere}$$

### **Illustration 5.**

**A current of 2.68 ampere is passed for one hour through an aqueous solution of copper sulphate using copper electrodes. Calculate the change in mass of cathode and that of the anode. (at. mass of copper = 63.5).**

**Solution :**

The electrode reactions are :



Thus, cathode increases in mass as copper is deposited on it and the anode decreases in mass as copper from it dissolved.

Charge passed through cell =  $2.68 \times 60 \times 60$  coulomb

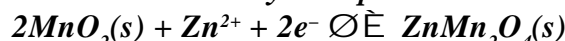
$$\text{Copper deposited or dissolved} = \frac{63.5}{2 \times 96500} \times 2.68 \times 60 \times 60 = 3.174 \text{ g}$$

Increase in mass of cathode = Decrease in mass of anode = 3.174 g

### **Illustration 6.**

**In a zinc manganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of  $\text{MnO}_2$ , carbon,  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  in aqueous base.**

**The cathodic reaction may be represented as**

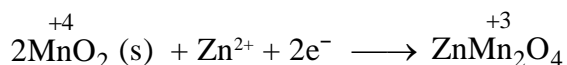


**Let there be 8 g  $\text{MnO}_2$  in the cathodic compartment. How many days will the dry cell continue to give a current of  $4 \times 10^{-3}$  ampere.**

**Solution :**

When  $\text{MnO}_2$  will be used up in cathodic process, the dry cell will stop to produce current .

Cathodic process :



$$\text{Equivalent mass of MnO}_2 = \frac{\text{Molecular mass}}{\text{Change in oxidation state}} = \frac{87}{1} = 87$$

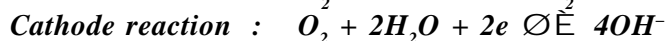
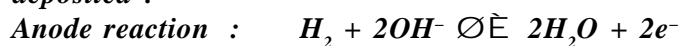
From first law of electrolysis,

$$W = \frac{ItE}{96500} \Rightarrow 8 = \frac{4 \times 10^{-3} \times t \times 87}{96500}$$

$$t = 2218390.8 \text{ second} = \frac{2218390.8}{3600 \times 24} = 25.675 \text{ day}$$

**Illustration 7.**

*In a fuel cell, hydrogen and oxygen react to produce electricity. In the process of hydrogen gas is oxidized at the anode and oxygen at the cathode. If 67.2 litre of H<sub>2</sub> 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 ?*



**Solution :**

From the given reactions, it is obvious that

22.4 litres of H<sub>2</sub> gas require 2 Faraday electricity

∴ 67.2 litres of H<sub>2</sub> will require = 6 Faraday electricity

$$Q = i \times t$$

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

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

$$w_{\text{cu}} = 31.75 \times 6 = 190.5 \text{ g}$$

## 1. Daily Practice Problem Sheet

- Q.1** Electrolysis of molten NaCl is carried out in the electrolytic tank by passing electricity, using Pt electrodes. Write cell representation & products formed at cathode & anode.
- Q.2** How many molecules of  $\text{Cl}_2$  would be deposited from molten NaCl in one minute by a current of 300 milliampere ?
- Q.3** Calculate the volume of  $\text{Cl}_2$  at NTP produced during electrolysis of  $\text{MgCl}_2$  which produces 6.50g Mg.
- Q.4** Determine products formed at cathode & anode and also write cell representation, if electrolysis of aqueous NaCl is carried out with :
- (i) conc. NaCl using Pt electrode.      (ii) dil. NaCl using Pt electrode.  
 (iii) conc. NaCl using Hg as cathode.      (iv) conc. NaCl using Ag electrode.
- Q.5** Calculate the quantity of electricity that will be required to liberate 710 g of  $\text{Cl}_2$  gas by electrolysing a conc. solution of NaCl. What weight of NaOH and what volume of  $\text{H}_2$  at  $27^\circ\text{C}$  and 1 atm pressure is obtained during this process ?
- Q.6** What is the effect on pH, when electrolysis of aqueous NaCl is carried out under following conditions :
- (i) conc. NaCl using Pt electrode.      (ii) dil. NaCl using Pt electrode.  
 (iii) conc. NaCl using Hg as cathode.      (iv) conc. NaCl using Ag electrode.
- Q.7** After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time, 600 mL of the 1 N solution was left which was found to be NaOH. During the same time 31.80 g Cu was deposited in copper voltameter in series with the electrolytic cell. Calculate the % of NaOH obtained.
- Q.8** Electrolysis of NaCl (aq) gives NaOH at cathode. Assuming 100 % current efficiency, determine the quantity of electricity required to convert 10 g NaCl into NaOH.
- Q.9** What will be the cell representation & products formed at cathode and anode when aqueous  $\text{RCOONa}$  is electrolysed using Pt electrode.
- Q.10** Find out the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of  $\text{CH}_3\text{COONa}$  at  $25^\circ\text{C}$  and 1 atm.
- Q.11** Write cell representation & products formed at cathode & anode, when aqueous  $\text{Na}_2\text{SO}_4$  is electrolysed using :
- (i) Pt electrode      (ii) Cu electrode
- Q.12** The same charge is passed through acidulated water and  $\text{SnCl}_2$  (aq). What volume of dry detonating gases at NTP are evolved from water when 1 g tin is deposited on electrode in other solution ?



## 2. Daily Practice Problem Sheet

- Q.1** Aqueous  $\text{H}_2\text{SO}_4$  is electrolysed by passing electric current using Pt electrodes. Find out products formed at cathode & anode and write cell representation, when electrolysis is done :  
 (i) using normal current density                      (ii) using high current density
- Q.2** Determine products formed at cathode & anode and also write cell representation,  
 (a) When electrolysis of aqueous  $\text{CuSO}_4$  is carried out using :  
       (i) Pt electrode                                      (ii) Ag as anode and Cu as cathode  
 (b) When electrolysis of aqueous  $\text{AgNO}_3$  is done using  
       (i) Pt electrode                                      (ii) Cu as anode & Ag as cathode
- Q.3** 500 mL of 1 M  $\text{CuSO}_4$  solution is electrolysed using Pt electrodes with a current of 1.93 ampere for a period of 600 seconds. Assuming that volume of solution does not change during electrolysis, calculate  $[\text{Cu}^{2+}]$ , and  $[\text{SO}_4^{2-}]$  after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes ?
- Q.4** Calculate the quantity of current required to liberate :  
 (i)  $\text{H}_2$  gas at STP at the rate of 1 cc per second  
 (ii)  $\text{O}_2$  gas at STP at the rate of 1 mm<sup>3</sup> per minute  
 (iii)  $\text{Cl}_2$  gas at STP at the rate of 1 dm<sup>3</sup> per hour
- Q.5** Cd amalgam is prepared by electrolysis of a solution of  $\text{CdCl}_2$  using a mercury cathode. Find how long should a current of 5 ampere is passed in order to prepare 12% Cd-Hg amalgam on a cathode of 5 g mercury ? Assuming current efficiency = 80 % .  
 [ Atomic weight of Cd = 112.40 ]
- Q.6** An oxide of metal (at. wt. 56) contains 30% oxygen by weight. The oxide was converted into chloride and then solution was electrolysed. Calculate the amount of metal that would be deposited at the cathode, if a current of 9.65 ampere was passed for a period of 30 minutes. What is the valency of metal ? What will be the formula of oxide ?
- Q.7** Current is passed through a cathode where the reaction is :  

$$5\text{e}^- + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
 All the permanganate present in 15.0 mL of solution has been reduced after a current of 0.600 A has passed for 603 second. What was the original concentration of permanganate ?
- Q.8**  $\text{H}_2\text{O}_2$  can be prepared by successive reactions ,  

$$2\text{NH}_4\text{HSO}_4 \longrightarrow \text{H}_2 + (\text{NH}_4)_2\text{S}_2\text{O}_8$$

$$(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \longrightarrow 2\text{NH}_4\text{HSO}_4 + \text{H}_2\text{O}_2$$
 The first reaction is an electrolytic reaction and second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 g pure  $\text{H}_2\text{O}_2$  per hr ? Assume current efficiency 50% .
- Q.9** Calculate the quantity of electricity in coulomb which liberates enough hydrogen at the cathode during electrolysis of acidified water so that it can fill a balloon of capacity 10 litre at a pressure of 1.5 atmosphere at 27°C. If the oxygen liberated is completely used in burning methane, calculate the volume of methane at STP which is burnt.
- Q.10** The density of copper is 8.94 g ml<sup>-1</sup>. Find out the number of coulomb needed to plate an area of 10 × 10 cm<sup>2</sup> to a thickness of 10<sup>-2</sup> cm using  $\text{CuSO}_4$  solution as electrolyte.
- Q.11** A current of 40 microampere is passed through a solution of  $\text{AgNO}_3$  for 32 minutes using Pt electrodes. A uniformly single atom thick layer of Ag is deposited covering 43% cathode surface. What is the total surface area of cathode if each Ag atom covers 5.4 × 10<sup>-16</sup> cm<sup>2</sup> ?



## Section-II (Electrochemical Cell)

### 3. Electrochemical Cell :

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

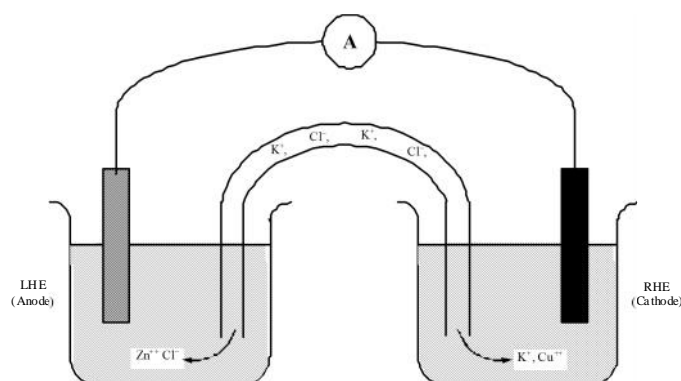
A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half-reaction take place.

A simple half-cell can be made from a metal strip that dips into a solution of its metal ion. An example is the zinc-zinc ion half-cell (often called simply a zinc electrode), which consists of a zinc metal strip dipping into a solution of a zinc salt. Another simple half-cell consists of a copper metal strip dipping into a solution of a copper salt (copper electrode).

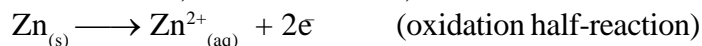
In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.

The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate out as copper, the solution builds up a negative charge. The half cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated . The voltage would drop, and the battery would run down quickly.



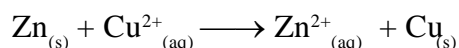
The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows.

The two half-cell reactions, as noted earlier, are



The first half-reaction, in which a species loses electrons, is the oxidation half-reaction. The electrode at which oxidation occurs is called the anode. The second half-reaction which a species gains electrons, is the reduction half-reaction. The electrode at which reduction occurs is called the cathode. These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.

Note that the sum of the two half-reaction



The net reaction that occurs in the voltaic cell, it is called the cell reaction.

Once you know which electrode is the anode and which is the cathode, you can determine the direction of electron flow in the external portion of the circuit. Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.

- Note :1.** The salt-bridge contains solution of strong ionic salts like NaCl, NaNO<sub>3</sub>, KNO<sub>3</sub>, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.
- 2.** It maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.

### Cell Notation :

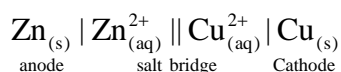
The efficiency of a cell depends on the tendency of LHE to lose electrons to RHE and the ability of RHE to receive electrons. Cell efficiency is measured in terms of emf (electromotive force), which is the difference in potentials of two electrodes due to which electrons flow from anode to cathode. EMF value of a cell is constant for given concentration of electrolyte, temperature and the pressure (in case of gases). Therefore, it depends on concentration, temperature and pressure.

EMF of a cell is measured in terms of the difference in electric potential (electrical pressure) between anode and cathode. Its unit is V(volt). The potential of half-cell is known as electrode potential, which is the tendency of an electrode to get oxidized or reduced. Thus, tendency to get oxidized is called oxidation potential and the tendency to get reduced is called reduction potential.

**Cell Notation :** A cell can be represented as :



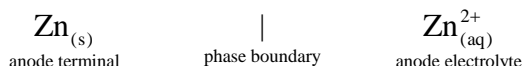
The anode or oxidation half-cell is always written on the left and the cathode or reduction half-cell is written on the right. The two electrodes are electrically connected by means of a salt bridge shown by two vertical bars.



The half-cell which has higher reduction potential, acts as cathode and the electrode with lower reduction potential or higher oxidation potential acts as anode.

## ELECTROCHEMISTRY

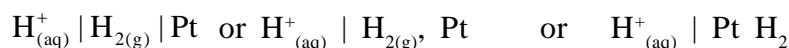
The cell terminals are at the extreme ends in this cell notation, and a single vertical bar indicates a phase boundary - say between a solid terminal and the electrode solution. For the anode of the same cell, you have



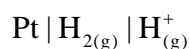
When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and as an electrode surface on which the half-reaction occurs. The platinum catalyzes the half-reaction but otherwise is not involved in it. Hydrogen bubbles over a platinum plate that is immersed in an acidic solution. The cathode half-reaction is



The notation for the hydrogen electrode, written as a cathode, is

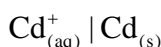
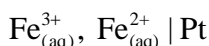


To write such an electrode as an anode, you simply reverse the notation:

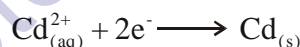
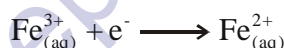


Here are several additional examples of this notation for electrodes (written as cathodes). A comma separates ions present in the same solution. We will write the cathode with oxidized species before reduced species, in the same order as in the half-reaction.

### Cathode



### Cathode Reaction

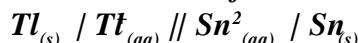


You can write the overall cell reaction from the cell notation by first writing the appropriate half-cell reactions, multiplying as necessary, and then summing so that the electrons cancel.

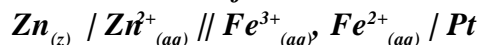
### Illustration 8.

#### Writing the cell Reaction from the Cell Notation

(a) Write the cell reaction for the voltaic cell



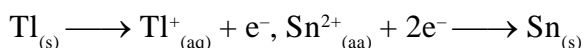
(b) Write the cell reaction for the voltaic cell



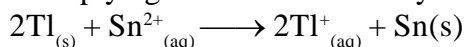
Problem strategy: The cell notation gives the species involved in each half-reaction. Complete the balance each half-reaction, then multiply by factors so that when you add the half-reactions, the electrons cancel. The result is the cell reaction.

#### Solution :

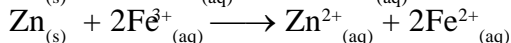
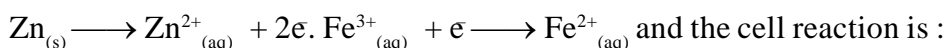
(a) The half-cell reactions are



Multiplying the anode reaction by 2 and then summing the half-cell reactions gives



(b) The half cell reactions are



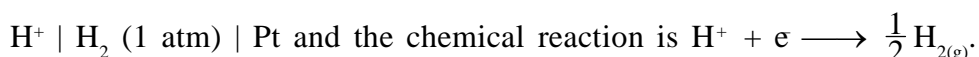
To fully specify the voltaic cell, it is necessary to give the concentrations of solutions or ions and the pressure of gases. In the cell notation, these are written within parentheses for each species.

For example :  $\text{Zn}_{(s)} \mid \text{Zn}^{2+} (1.0 \text{ M}) \parallel \text{H}^+ (1.0 \text{ M}) \mid \text{H}_2 (1.0 \text{ atm}) \mid \text{Pt}$

### Nature of Electrodes :

The various types of electrodes used and the chemical reactions which take place are:

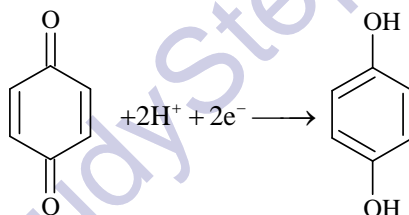
**Gas Electrodes :** Here the inert electrode is present in contact with the gas at 1 atm pressure (unless specified) and its ions in the solution e.g. Hydrogen gas electrode, etc. It is denoted as :



The nature of inert electrode should be such that, when the external voltage is changed even by small amount from the equilibrium value, the reaction will proceed one way or the other. Most suitable electrode is platinum with fine coat of platinum powder or platinum black.

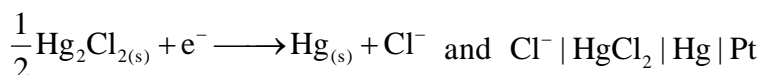
**Oxidation – Reduction Electrode :** Here the inert electrode (generally platinum) is dipping in the solution which contains ions of species having two oxidation states, e.g. platinum electrode dipping in solution containing stannous and stannic. It is denoted as  $\text{Sn}^{4+}, \text{Sn}^{2+} \mid \text{Pt}$  and chemical reaction is  $\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}$ . The solution can be a neutral species present in two oxidation stages e.g.  $\text{H}^+$ , Q,  $\text{QH}_2 \mid \text{Pt}$ .

Where  $\text{QH}_2$  is the hydroquinone an Q is quinone. It is commonly known as quinhydrone electrode. The chemical reaction is :



**Meta-Metal Ion Electrode :** Here the metal electrode dips in a solution containing its ions and the metal electrode takes part in chemical reaction. Reactivity of the metal should be intermediate otherwise the reactive metals will react with water and cannot act as electrodes. The example is the copper electrode dipping in copper sulphate solution. It is denoted as  $\text{M}^{n+} \mid \text{M}$  in general and in particular  $\text{Cu}^{2+} (\text{c}) \mid \text{Cu}$  and c is the concentration. The chemical reaction is  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}_{(s)}$ .

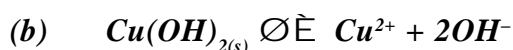
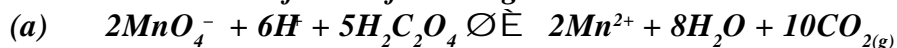
**Metal-Insoluble Salt Anion Electrode :** Here the metal electrode is in contact with its ions (generally the anion). The most common is the calomel electrode. This consists of mercury, mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ ) and saturated solution of KCl. But the concentration of  $\text{Cl}^-$  ions can be different. The chemical reaction taking place is :



Similarly lead amalgam lead sulphate electrode is depicted as  $\text{SO}_4^{2-} \mid \text{PbSO}_4 \mid \text{Pb}(\text{Hg})$  and the chemical reaction is  $\text{PbSO}_{4(s)} + 2\text{e}^- \longrightarrow \text{Pb}_{(s)} + \text{SO}_4^{2-}$

### Illustration 9.

Write cell electrode for the following reactions :



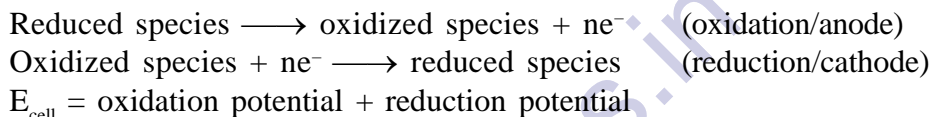
## ELECTROCHEMISTRY

**Solution :**

- (a) Half-cell reactions are
- $$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
- $$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{CO}_4$$
- $$\text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+ | \text{Pt} \text{ and } \text{Pt} | \text{CO}_2 | \text{H}^+$$
- (b) Half-cell reactions are
- $$\text{Cu}(\text{OH})_{2(s)} + 2\text{e}^- \longrightarrow \text{Cu} + 2\text{OH}^-$$
- $$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}_{(s)} \text{ and electrodes are}$$
- $$\text{Cu}^{2+} | \text{Cu} \text{ and } \text{Pt} | \text{Cu}(\text{OH})_2 | \text{OH}^-$$

## 4. Standard Cell EMF and Standard Electrode Potential :

A cell emf is a measure of the driving force of the cell reaction. This reaction occurs in the cell as separate half-reactions: an oxidation half-reaction and a reduction half-reaction. The general forms of these half-reactions are

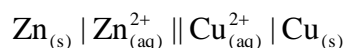


If you can construct a table of reduction potentials, you will have a list of strengths of oxidizing agents, in addition to having a way of calculating cell emf's.

You can look at an oxidation half-reaction as the reverse of a corresponding reduction half-reaction. The oxidation potential for an oxidation half-reaction equals to negative of the reduction potential for the reverse half-reaction(which is a reduction).

Oxidation potential for a half-reaction = reduction potential for the reverse half-reaction.

This means that in practice you need to tabulate only oxidation potential or reduction potentials. The choice, by convention, is to tabulate reduction potentials. We call these electrode potentials, and we denote them by the symbol E (without the subscript cell, as in  $E_{\text{cell}}$ ).



The half-reaction are :  $\text{Zn}_{(s)} \longrightarrow \text{Zn}_{(\text{aq})}^{2+} + 2\text{e}^-$ ;  $\text{Cu}_{(\text{aq})}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}_{(s)}$

The first half-reaction is an oxidation. If you write  $E_{\text{Zn}}$  for the electrode potential corresponding to the reduction half-reaction  $\text{Zn}_{(\text{aq})}^{2+} \longrightarrow \text{Zn}_{(s)}$ , then  $-E_{\text{Zn}}$  is the potential for the oxidation half-reaction  $\text{Zn}_{(s)} \longrightarrow \text{Zn}_{(\text{aq})}^{2+} + 2\text{e}^-$ . The copper half-reaction is a reduction. Write  $E_{\text{Cu}}$  for the electrode potential.

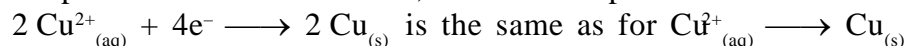
The cell emf is the sum of the potentials for the reduction and oxidation half-reactions. For the cell we have been describing, the emf is the sum of the reduction potential (electrode potential) for the copper half-cell and the oxidation potential (negative of the electrode potential) for the zinc half-cell.

$$E_{\text{cell}} = E_{\text{Cu}} + (-E_{\text{Zn}}) = E_{\text{Cu}} - E_{\text{Zn}}$$

Note that the cell emf equals the difference between the two electrode potentials. You can think of the electrode potential as the electric potential on the electrode, and you obtain the cell emf as a potential difference in which you subtract the anode potential from the cathode potential.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The electrode potential is an intensive property. This means that its value is independent of the amount of species in the reaction. Thus, the electrode potential for the half-reaction.



- Note :**
1. If  $E_{\text{cell}}$  is positive, then the cell reaction is spontaneous
  2. If in a cell reaction, more than one electron is involved, the standard electrode potential does not change but the standard free energy of the chemical reaction will be multiple of  $FE^0$ , i.e. then actual value of  $n$  should be used.

**Tabulating Standard Electrode Potential :** The emf of a voltaic cell depends on the concentrations of substances and the temperature of the cell. For purposes of tabulating electrochemical data, it is usual to choose thermodynamic standard-state conditions for voltaic cells. The standard emf,  $E^0_{\text{cell}}$ , is the emf of a voltaic cell operating under standard-state conditions (solute concentrations are each 1 M, gas pressures are each 1 atm, and the temperature has a specified value – usually 25°C). Note the superscript degree sign (0), which signifies standard-state conditions.

If you can derive a table of electrode potentials, you can calculate cell emf's from them. This provides a great advantage over tabulating cell emf's. From a small table of electrode potentials, you can obtain the emf's of all the cells that you could construct from pairs of electrodes. For instance, a table of 40 electrode potentials would give the emf's of nearly 800 voltaic cells.

However, it is not possible to measure the potential of a single electrode; only emf's of cells can be measured. What you can do is measure the emf's of cells constructed from various electrodes connected in turn to one particular electrode, which you choose as a reference. You arbitrarily assign this reference electrode a potential equal to zero and obtain the potentials for the other electrodes by measuring the emf's. By convention, the reference chosen for comparing electrode potentials is the standard hydrogen electrode.

The standard electrode potential,  $E^0$ , is the electrode potential when the concentrations of solutes are 1 M, the gas pressures are 1 atm, and the temperature has a specified value (usually 25°C). The superscript degree sign (0) signifies standard state conditions.

To understand how standard electrode potentials are obtained, look at how you would find the standard electrode potential,  $E^0$ , for the zinc electrode. You connect a standard zinc electrode to a standard hydrogen electrode. When you measure the emf of the cell with a voltmeter, you obtain 0.76V, with the zinc electrode acting as the anode.

Now write the cell emf in terms of the electrode potentials.

The cell is  $\text{Zn}_{(\text{s})} | \text{Zn}^{2+}_{(\text{aq})} || \text{H}^{+}_{(\text{aq})} | \text{H}_{2(\text{g})} | \text{Pt}$  and the half-reactions with corresponding half-cell potentials (oxidation or reduction potentials) are :  $\text{Zn}_{(\text{s})} \longrightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-}$  ;  $-E^0_{\text{Zn}}$

The cell emf is the sum of the half-cell potentials.  $E_{\text{cell}} = E^0_{\text{H}_2} + (-E^0_{\text{Zn}})$

Substitute 0.76V for the cell emf and 0.00V for the standard hydrogen electrode potential.

This gives  $E^0_{\text{Zn}} = -0.76\text{V}$ .

Proceeding in this way, you can obtain the electrode potential for a series of half-cell reactions. Table given below lists standard electrode potentials for selected half-cells at 25°C.



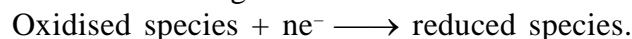
## ELECTROCHEMISTRY

Cathode (Reduction) Half Reaction	Standard Potential E(V)
$\text{Li}^+_{(\text{aq})} + \text{e}^- \longrightarrow \text{Li}_{(\text{s})}$	- 3.04
$\text{Na}^+_{(\text{aq})} + \text{e}^- \longrightarrow \text{Na}_{(\text{s})}$	- 2.71
$\text{Mg}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Mg}_{(\text{s})}$	- 2.38
$\text{Al}^{3+}_{(\text{aq})} + 3\text{e}^- \longrightarrow \text{Al}_{(\text{s})}$	- 1.66
$2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \longrightarrow \text{H}_{2(\text{g})} + 2\text{OH}^-_{(\text{aq})}$	- 0.83
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Zn}_{(\text{s})}$	- 0.76
$\text{Cr}^{3+}_{(\text{aq})} + 3\text{e}^- \longrightarrow \text{Cr}_{(\text{s})}$	- 0.74
$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Fe}_{(\text{s})}$	- 0.41
$\text{Cd}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Cd}_{(\text{s})}$	- 0.40
$\text{Ni}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Ni}_{(\text{s})}$	- 0.23
$\text{Sn}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Sn}_{(\text{s})}$	- 0.14
$\text{Pb}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Pb}_{(\text{s})}$	- 0.13
$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Fe}_{(\text{s})}$	- 0.04
$2\text{H}^+_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{H}_{2(\text{g})}$	0.00
$\text{Sn}^{4+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Sn}^{2+}_{(\text{aq})}$	0.15
$\text{Cu}^{2+}_{(\text{aq})} + \text{e}^- \longrightarrow \text{Cu}^+_{(\text{aq})}$	0.16
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Cu}_{(\text{s})}$	0.34
$\text{IO}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \longrightarrow \text{I}^-_{(\text{aq})} + 2\text{OH}^-_{(\text{aq})}$	0.49
$\text{Cu}^+_{(\text{aq})} + \text{e}^- \longrightarrow \text{Cu}_{(\text{s})}$	0.52
$\text{I}_{2(\text{s})} + 2\text{e}^- \longrightarrow 2\text{I}^-_{(\text{aq})}$	0.54
$\text{Fe}^{3+}_{(\text{aq})} + \text{e}^- \longrightarrow \text{Fe}^{2+}_{(\text{aq})}$	0.77
$\text{Hg}^{2+}_{2(\text{aq})} + 2\text{e}^- \longrightarrow \text{Hg}_{(\text{aq})}$	0.80
$\text{Ag}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{Ag}_{(\text{l})}$	0.80
$\text{Ag}^+_{(\text{aq})} + \text{e}^- \longrightarrow \text{Ag}_{(\text{l})}$	0.85
$\text{ClO}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \longrightarrow \text{Cl}^-_{(\text{aq})} + 2\text{OH}^-_{(\text{aq})}$	0.90
$\text{Hg}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Hg}_{(\text{aq})}$	0.90
$\text{NO}^{3-}_{(\text{aq})} + 4\text{H}^+_{(\text{aq})} + 3\text{e}^- \longrightarrow \text{NO}_{(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$	0.96
$\text{Br}_{2(\text{l})} + 2\text{e}^- \longrightarrow 2\text{Br}^-_{(\text{aq})}$	1.07
$\text{O}_{2(\text{g})} + 4\text{H}^+_{(\text{aq})} + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}_{(\text{aq})}$	1.23
$\text{Cr}_2\text{O}^{2-}_{7(\text{aq})} + 8\text{H}^+_{(\text{aq})} + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}_{(\text{aq})} + 7\text{H}_2\text{O}_{(\text{l})}$	1.33
$\text{Cl}_{2(\text{g})} + 2\text{e}^- \longrightarrow 2\text{Cl}^-_{(\text{aq})}$	1.36
$\text{MnO}^-_{4(\text{aq})} + 8\text{H}^+_{(\text{aq})} + 6\text{e}^- \longrightarrow \text{Mn}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\text{l})}$	1.49
$\text{H}_2\text{O}_{2(\text{aq})} + 2\text{H}^+_{(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}_{(\text{l})}$	1.78
$\text{S}_2\text{O}^{2-}_{6(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{SO}^{2-}_{4(\text{aq})}$	2.01
$\text{F}_{2(\text{g})} + 2\text{e}^- \longrightarrow 2\text{F}^-_{(\text{aq})}$	2.87



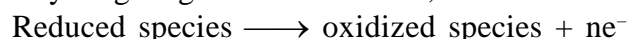
## Strength of Oxidising and Reducing Agents :

Standard electrode potentials are useful in determining the strengths of oxidizing and reducing agents under standard-state conditions. Because electrode potentials are reduction potentials those reduction half-reactions in the table with the larger (that is more positive) electrode potentials have the greater tendency to go left to right as written. A reduction half-reaction has the general form.



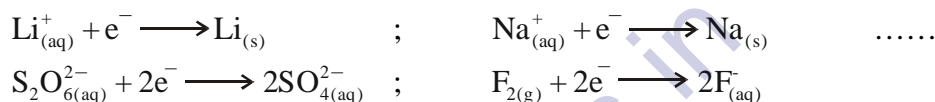
The oxidized species acts as an oxidizing agent. Consequently, the strongest oxidizing agents in a table of standard electrode potentials are the oxidized species corresponding to half-reactions with the largest (most positive)  $E^0$  values.

Those reduction half-reactions with lower (that is, more negative) electrode potentials have a greater tendency to go right to left. That is,



The reduced species acts as a reducing agent. Consequently, the strongest reducing agents in a table of standard electrode potentials are the reduced species corresponding to half-reactions with the smallest (most negative)  $E^0$  values.

The first two and last two entries in the table are as follows :



The strongest oxidizing agents are the species on the left side in the last two entries in the table. The strongest reducing agents are the species on the right side in the first two entries in the table.

## Standard EMF of a cell ( $E^0$ )

$E^0$  = difference in potentials of two half-cells

$E^0 = \{\text{standard oxidation potential of anode} - \text{standard oxidation potential of cathode}\}$

$$E^0_{\text{cell}} = (E^0_{\text{oxidation}})_{\text{anode}} - (E^0_{\text{oxidation}})_{\text{cathode}}$$

**OR**

$E^0 = \{\text{standard reduction potential of a cathode} - \text{standard reduction potential of anode}\}$

$$E^0_{\text{cell}} = (E^0_{\text{reduction}})_{\text{cathode}} - (E^0_{\text{reduction}})_{\text{anode}}$$

### Illustration 10.

*Electrode potential of the metals in their respective solution are provided. Arrange the metals in their increasing order of reducing power.*

$K^+/K = -2.93\text{V}$ ,  $\text{Ag}^+/\text{Ag} = +0.80\text{V}$ ,  $\text{Hg}^+/\text{Hg} = +0.79\text{V}$ ,  $\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$

$\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$

### Solution :

We know that the reducing power of a metal depends upon its tendency to lose electrons. Thus lower the reduction potential, more the tendency to get oxidized and thus more will be the reducing power. Hence increasing order of reducing power is:



## ELECTROCHEMISTRY

### Illustration 11.

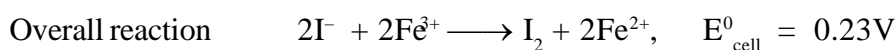
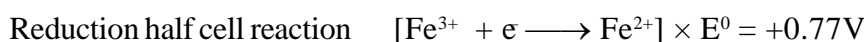
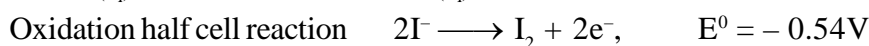
Using the standard electrode potentials predict the reaction, if any, that occurs between the following :

- |                                                                                                                              |                                                                           |
|------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|
| (a) $Fe^{3+}_{(aq)}$ and $I^{-}_{(aq)}$<br>(c) $Fe^{3+}_{(aq)}$ and $Br^{-}_{(aq)}$<br>(e) $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$ | (b) $Ag^{+}_{(aq)}$ and $Cu_{(s)}$<br>(d) $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$ |
|------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|

**Given :**  $E^0_{Fe^{3+}/Fe^{2+}} = +0.77V$ ,  $E_{I_2/I^{-}} = +0.54V$   $E^0_{Ag^{+}/Ag} = +0.80V$ ,  $E^0_{Cu^{2+}/Cu} = +0.34V$   
 $E^0_{Br_2/Br^{-}} = +1.08V$

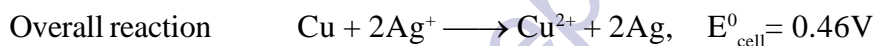
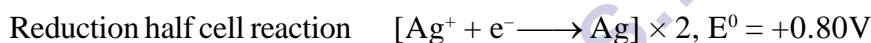
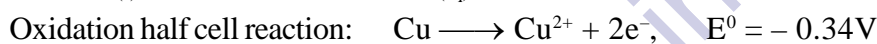
**Solution :**

- (a) Here  $I^{-}_{(aq)}$  loses electrons and  $Fe^{3+}_{(aq)}$  gains electrons. Thus



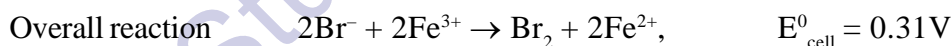
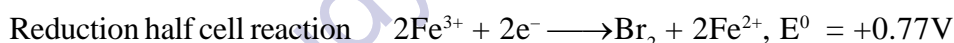
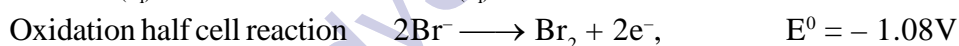
Since  $E^0_{cell}$  is +ve, the reaction is spontaneous i.e., the reaction does take place.

- (b) Here  $Cu_{(s)}$  loses electrons and  $Ag^{+}_{(aq)}$  gains electrons. Thus



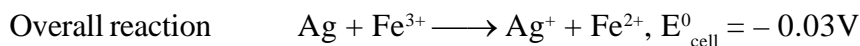
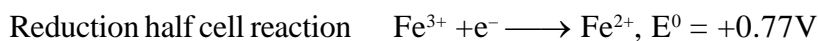
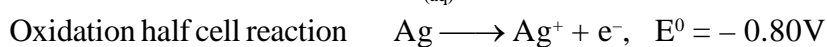
Since  $E^0_{cell}$  is +ve, the reaction is spontaneous

- (c) Here  $Br^{-}_{(aq)}$  loses electrons and  $Fe^{3+}_{(aq)}$  gains electrons. Thus



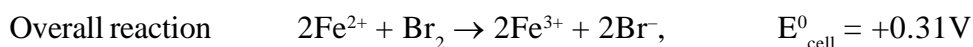
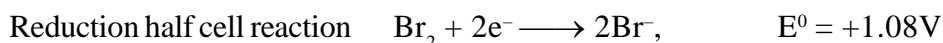
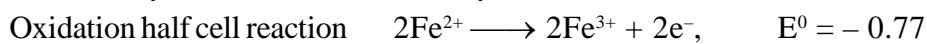
Since  $E^0_{cell}$  is -ve, the reaction is non-spontaneous, i.e., reaction does not take place.

- (d) Here  $Ag$  loses electrons and  $Fe^{3+}_{(aq)}$  gains electrons. Thus



Since  $E^0_{cell}$  is -ve, the reaction is non-spontaneous, i.e., reaction does not take place.

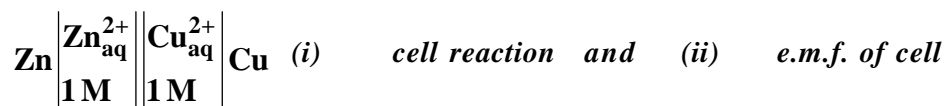
- (e) Here  $Fe^{2+}_{(aq)}$  loses electrons and  $Br_{2(aq)}$  gains electrons. Thus



Since  $E^0_{cell}$  is +ve, the reaction is spontaneous, i.e., the reaction does not take place.

**Illustration 12.**

Calculate the values for cell



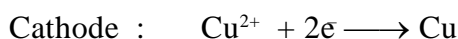
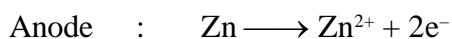
**Given :**  $E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.35\text{V}$ ;  $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$

**Solution :**

(i)  $E^0_{\text{OP}}$  for  $\text{Cu}/\text{Cu}^{2+} = -0.35\text{V}$

$E^0_{\text{OP}}$  for  $\text{Zn}/\text{Zn}^{2+} = +0.76\text{V}$

More is  $E^0_{\text{OP}}$ , more is tendency to show oxidation and thus Zn will oxidize and  $\text{Cu}^{2+}$  will reduce.



(ii) Also,  $E^0_{\text{cell}} = E^0_{\text{OP}_{\text{Zn}/\text{Zn}^{2+}}} + E^0_{\text{RP}_{\text{Cu}^{2+}/\text{Cu}}} = 0.76 + 0.35 = 1.11\text{V}$

## 5. Dependence of emf of a Cell on Concentration :

The emf of a cell depends on the concentration of ions and on gas pressures. For that reason, cell emf's provide a way to measure ion concentration. The pH meter, for example, depends on the variation of cell emf with hydrogen ion concentration. You can relate cell emf's for various concentrations of ions and various gas pressures to standard electrode potentials by means of an equation first derived by the German Walther Nernst (1864 – 1941).

### Nernst Equation

Recall that the free-energy change ,

$$\Delta G = \Delta G^0 + RT \ln Q$$

Here Q is the thermodynamic reaction quotient. The reaction quotient has the form of the equilibrium constant, except that the concentrations and gas pressures are those that exist in a reaction mixture at a given instant. You can apply this equal to a voltaic cell. In that case, the concentrations and gas pressures are those that exist in the cell at a particular instant. If you substitute,  $\Delta G = -nFE_{\text{cell}}$  and  $\Delta G^0 = -nFE^0_{\text{cell}}$  into this equation, you obtain.

$$-nFE_{\text{cell}} = -nFE^0_{\text{cell}} + RT \ln Q$$

The result rearranges to give the Nernst equation, an equation relating the cell emf to its standard emf and the reaction quotient.

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln Q \quad \text{or} \quad E_{\text{cell}} = E^0_{\text{cell}} - \frac{2.303RT}{nF} \log Q$$

If you substitute 298K (25°C) for the temperature in the Nernst equation and put in values for R and F, you get (using common logarithms).

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0592}{n} \log Q \quad (\text{values in volts at } 25^\circ\text{C})$$

## ELECTROCHEMISTRY

You can show from the Nernst equation that the cell emf,  $E_{\text{cell}}$ , decreases as the cell reaction proceeds. As the reaction occurs in the voltaic cell, the concentrations of products increase and the concentrations of reactants decrease. Therefore,  $Q$  and  $\log Q$  increase. The second term in the Nernst equation,  $(0.0592/n) \log Q$ , increases, so that the difference  $E_{\text{cell}}^0 - (0.0592/n) \log Q$  decreases. Thus, the cell emf,  $E_{\text{cell}}$ , becomes smaller. Eventually the cell emf goes to zero, and the cell reaction comes to equilibrium.

For Galvanic Cell :  $\text{Zn}_{(s)} \mid \text{Zn}^{2+} (x_1) \parallel \text{Cu}^{2+} (x_2) \mid \text{Cu}_{(s)}$

Let us assume Zn to be anode and Cu to be cathode, though this can be correct only when the emf of the cell is positive.

Thus,  $E_{\text{cell}} = E_{\text{C}} - E_{\text{A}}$

For cathode  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}_{(s)}$

For anode  $\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}_{(s)}$

Therefore  $E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 = \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]}$

$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^0 - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]}$

Putting these values in (1), we get

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

## Electromotive Force

Potential difference is the difference in electric potential (electrical pressure) between two points. You measure this quantity in volts. The volt, V, is the SI unit of potential difference. The electrical work expended in moving a charge through a conductor is

Electrical work = charge  $\times$  potential difference

Corresponding SI units for the terms in this equation are

Joules = coulombs  $\times$  volts

The Faraday constant,  $F$  is the magnitude of charge on one mole of electrons; it equals  $9.65 \times 10^4 \text{ C}$  (96,500 coulombs). The faraday is a unit of charge equal to  $9.65 \times 10^4 \text{ C}$ . In moving this quantity of charge (one faraday of charge) from one electrode to another, the numerical value of the work done by a voltaic cell is the product of the faraday constant  $F$  times the potential difference between the electrodes. The work  $w$  is the negative of this, because the voltaic cell loses energy as it does work on the surroundings.

$$w = -F \times \text{potential difference.}$$

In the normal operation of a voltaic cell, the potential difference (voltage) across the electrodes is less than the maximum possible voltage of the cell. One reason for this is that it takes energy or work to drive a current through the cell itself. The decrease in cell voltage as current is drawn reflects this energy expenditure within the cell; and the greater the current, the lower the voltage. Thus, the cell voltage has its maximum value only when no current flows. The situation is analogous to measuring the difference between the pressure of water in a faucet and that of the outside atmosphere. The maximum potential difference between the electrodes of a voltaic cell is referred to as the electromotive force (emf) of the cell, or  $E_{\text{cell}}^0$ .

We can now write an expression for the maximum work obtainable from a voltaic cell. Let  $n$  be the number of electrons transferred in the overall cell equation. The maximum electrical work of a voltaic cell for molar amounts of reactants (according to the cell

equation as written) is :

$$W_{\max} = nFE_{\text{cell}}^0$$

Here  $E_{\text{cell}}^0$  is the cell emf, and F is the Faraday constant,  $9.65 \times 10^4 \text{C}$

**Illustration 13.**

**Calculate the standard e.m.f. of the reaction**  $\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}_{(s)}$   $E_3^0 = ?$

**Given**  $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$   $E_1^0 = 0.771\text{V}$        $\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}_{(s)}$   $E_2^0 = -0.44\text{V}$

**Solution :**

With the help of calculation of free energy

$$\Delta G_1^0 = -nFE^0 = -(1)(F)(0.771\text{V}) = -0.771F$$

$$\Delta G_2^0 = -(2)(F)(0.44) = -0.88F$$

$$\Delta G_3^0 = -(3)(F)(E^0) = -3FE^0$$

The free energy change for the unknown process can be obtained as

$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-3FE^0 = -0.771F + 0.88F = 0.109F$$

$$\text{or } E^0 = -\frac{0.109}{3} = -0.036\text{V}$$

**Illustration 14.**

**The standard electrode potentials of the electrode  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Ag}^+/\text{Ag}$  are 0.34V and 0.7991V respectively. What would be the concentration of  $\text{Ag}^+$  in a solution containing 0.06M of  $\text{Cu}^{2+}$  ion such that both the metals can be deposited together. Assume that activity coefficients are unity and both silver and copper do not dissolve among themselves.**

**Solution :**

The individual reactions are :



The electrode potentials given by Nernst equation

$$E(\text{Cu}^{2+} | \text{Cu}) = E^0 = \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.037 - \frac{(0.0591)}{2} \log \frac{1}{0.06} = 0.037 - 0.036 = 0.301$$

$$E(\text{Ag}^+ | \text{Ag}) = 0.7991 - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]}$$

Two metals will be deposited together when the electrode potentials are equal i.e.

$$0.301 = 0.7991 - 0.0591 \log \frac{1}{[\text{Ag}^+]} \quad \text{i.e. } \log \frac{1}{[\text{Ag}^+]} = \frac{0.7991 - 0.301}{0.0591} = 8.428$$

$$\frac{1}{[\text{Ag}^+]} = 10^{8.428}$$

$$\text{or } [\text{Ag}^+] = 10^{-8.428} = 0.37 \times 10^{-8} \text{ mol dm}^{-3}$$

## 6. Thermodynamics of the Cells :

The e.m.f. of the cell is related to free energy by equation (1) i.e.

$$\Delta G = -nFE \quad \text{.....(1)}$$

Now  $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$

So  $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -nF\left(\frac{\partial E}{\partial T}\right)_P = -\Delta S$

or  $\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P \quad \text{.....(2)}$

The enthalpy of the cell reaction will be

$$\Delta H = \Delta G + T\Delta S$$

$$= -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_P \quad \text{.....(3)}$$

The thermodynamic quantities of the cell reaction can be calculated by equations (1), (2) and (3) provided one knows the emf of cell and its dependence on temperature.

The heat effects in the system can be calculated as follows. If the process is irreversible (i.e. by mixing the reactants together), heat flow to the system can be given by the reaction,  $\Delta H = Q_p$ . If the process is reversible the heat flow to system is given by  $Q_p = T\Delta S$ .

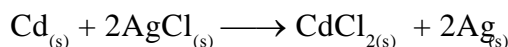
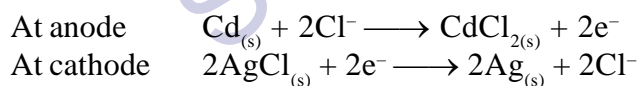
### Illustration 15.

*Consider the cell  $\text{Cd} / \text{CdCl}_2 \cdot 2\text{H}_2\text{O} / \text{AgCl}_{(s)} / \text{Hg}$*

*The emf of the cell at  $15^\circ\text{C}$  is  $0.67531\text{V}$  and temperature coefficient of emf is  $0.00065\text{V deg}^{-1}$ . Calculate the value of  $\Delta H$  at  $15^\circ\text{C}$  and heat flow if the process is carried reversibly.*

### Solution :

The cell reaction is



The number of electrons involved are two

So,  $\Delta G = -nFE$

$$= -(2) (96500\text{C}) (0.67531\text{V})$$

$$= -130.335\text{kJ}$$

$$\Delta S = (2) (96500\text{C}) (-0.00065\text{V deg}^{-1})$$

$$= -125.45\text{ J deg}^{-1}$$

$$\Delta H = \Delta G + T\Delta S$$

$$= (-130.335\text{ kJ}) + (288\text{ K}) (-125.45\text{ JK}^{-1}) (10^{-3}\text{ kJ J}^{-1})$$

$$= -166.465\text{kJ}$$

$$Q_p = (288\text{K}) (-125.45\text{ JK}^{-1}\text{ mol}^{-1}) = 36.$$

### Condition of Equilibrium : ( $E_{\text{cell}} = 0.0\text{V}$ )

When  $E_{\text{cell}} = 0.0\text{ V}$ , i.e., no potential difference is obtained between the terminals of cell (battery), the cell reaction in such a state is said to be in equilibrium. So in such cases,

When  $E_{\text{cell}} = Q = K_{\text{eq}}$  = equilibrium constant.

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log Q \qquad 0.0 = E_{\text{cell}}^0 - \frac{0.059}{n} \log K_{\text{eq}}$$

$$E_{\text{cell}}^0 = \frac{0.059}{n} \log K_{\text{eq}}$$

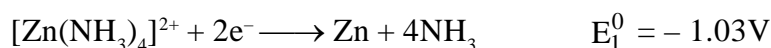
**Illustration 16.**

*Calculate the equilibrium constant for the reaction ,*

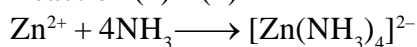


$$E^0(\text{Zn}^{2+}/\text{Zn}) = -0.763 \text{ and } E^0[\text{Zn}(\text{NH}_3)_4]^{2+}/\text{Zn} + \text{NH}_3 = 1.03 \text{ V}$$

**Solution :** The electrode reactions for the given electrodes, can be written as



Reaction (1) – (2)



$$\text{The standard emf of this reaction} = E_1^0 - E_2^0 = -0.763 \text{ V} - (-1.03) = 0.267 \text{ V}$$

$$\text{According to Nernst equation } E = E^0 - \frac{RT}{2F} \ln \frac{a_{[\text{Zn}(\text{NH}_3)_4]^{2+}}}{a_{\text{Zn}^{2+}} \cdot a}$$

$$\text{If the process is equilibrium, } E = 0 \text{ at } 25^\circ\text{C} \quad \frac{0.0591}{2} \log K = 0.267$$

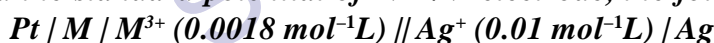
$$\log K = \frac{(0.267)(2)}{(0.059)} = 9.036$$

$$K = 10^{-0.36} 10^9 = 1.09 \times 10^9$$

**The equilibrium constant is also called the “Stability Constant” of the complex. If the reaction is written in a reverse manner, it will be “instability constant”.**

**Illustration 17.**

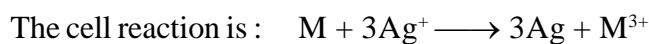
*To find the standard potential of  $M^{3+}/M$  electrode, the following cell is constituted.*



*The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the*

*half reaction ,  $M^{3+} + 3e^- \rightleftharpoons M$   $E_{\text{Ag}^+/\text{Ag}}^0 = 0.80 \text{ volt}$ .*

**Solution :**



Applying Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{3} \log \frac{[M^{3+}]}{[\text{Ag}^+]^3}$$

$$0.42 = E_{\text{cell}}^0 - \frac{0.0591}{3} \log \frac{(0.0018)}{(0.01)^3}$$

$$= E_{\text{cell}}^0 - 0.064$$

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$E_{\text{anode}}^0 = E_{\text{cathode}}^0 - E_{\text{cell}}^0$$

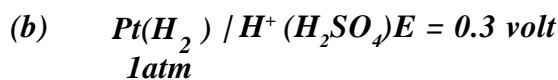
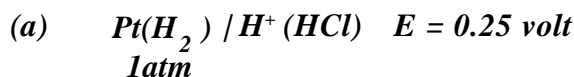
$$= (0.80 - 0.484) = 0.32 \text{ volt}$$



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### Illustration 19.

Calculate the pH of the following half cells solutions.



**Solution :**

(a)  $H_2 \longrightarrow 2H^+ + 2e^-$

$$E_{H_2/H^+} = E_{H_2/H^+}^0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$$

$$= 0.0 - 0.0591 \log \frac{[H^+]}{1}$$

$$0.25 = 0.0591 \text{ pH}$$

$$\text{pH} = \frac{0.25}{0.0591} = 4.23$$

(b)  $E_{H_2/H^+} = E_{H_2/H^+}^0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$

$$= 0.0 - 0.0591 \log \frac{[H^+]}{1}$$

$$0.3 = 0.0591 \text{ pH}$$

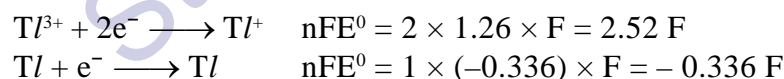
$$\text{pH} = \frac{0.3}{0.0591} = 5.076$$

### Illustration 20.

What is the standard potential of the  $Tl^{3+}/Tl$  electrode?



**Solution :**

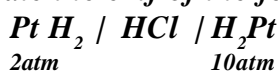


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addition  $Tl^{3+} + 3e^- \longrightarrow Tl \quad E^0 = \frac{2.52F - 0.336F}{nF} = \frac{2.184}{3} = 0.728 \text{ volt}$

### Illustration 21.

Calculate the emf of the following cell at 25 °C.



**Solution :**

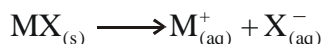
$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{2}{10}$$

$$= \frac{0.0591}{2} \log \frac{2}{10}$$

$$= -0.0206 \text{ volt}$$

## 7. Solubility Product :

The solubility product of sparingly soluble salt MX can be discussed in terms of the equilibrium of the kind



Since the activity of the pure solid is always unity, the equilibrium constant of the solubility product can be written.

$$K_{sp} = a_{M^{+}} a_{X^{-}} \quad \dots\dots(1)$$

When the solubility of the salt is very small, the solution is ideal and thus  $a_i = c_i$  of ions. The equation (1) can be written as

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{M^{+}} a_{X^{-}}}{a_{MX}}$$

Under equilibrium conditions the emf of the cell will be zero i.e.,  $E = 0$  and also the activity of pure solid is unity. Further  $K_{sp} = a_{M^{+}} \cdot a_{X^{-}}$ , the above equation at 25 °C can be written as :

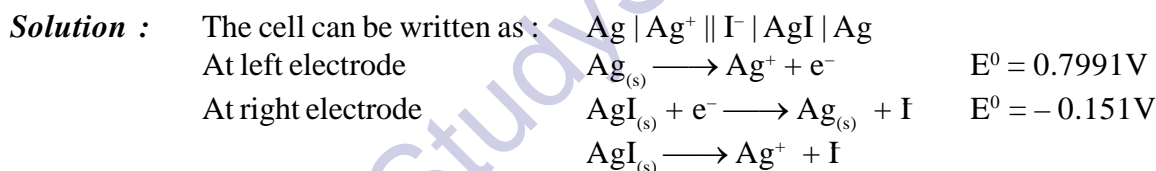
$$\log K_{sp} = \frac{E^0 \cdot n}{0.0591} \quad \dots\dots(2)$$

The solubility product thus can be calculated from the standard emf of one cell, formed in such a way that the final reaction is the type given above.

### Illustration 22.

**Calculate the  $K_{sp}$  of AgI by forming proper cell.**

**Given**  $E_{I^{-}/Ag(s)/Ag}^0 = -0.151V$  and  $E_{Ag^{+}/Ag}^0 = 0.7991V$



The standard emf of the cell is  $E^0 = E_R^0 - E_L^0 = -0.151 - 0.7991$   
 $= -0.9501V$

Using relation (1) at 25°C

$$\log K_{sp} = -\frac{(0.9501)(1)}{0.059} = -16.1 \quad K_{sp} = 10^{-16.1} = 7.94 \times 10^{-17}$$

## 8. Concentration Cells :

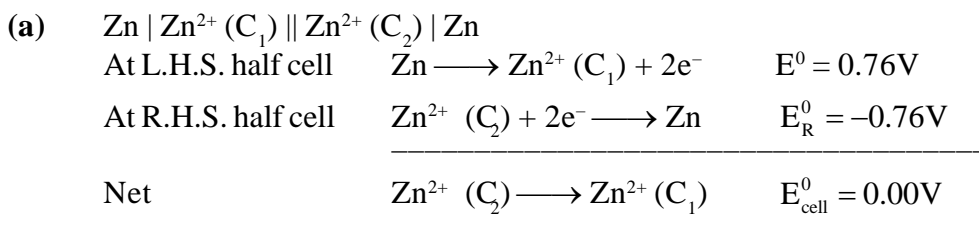
In concentration cell, the two electrodes are of the same material and they are dipping in the solutions of their respective ions at different concentrations. The two solutions are separated by salt bridge. The electrode dipping in a solution of higher concentration of positive ions is positive and the electrode dipping in lower concentration of positive ions is negative. The overall cell reaction is nothing but a transference of material from higher activity to lower activity. The emf of the cell is given by :

$$E = -\frac{RT}{nF} \ln \frac{a_1}{a_2}$$

## ELECTROCHEMISTRY

where  $a_1$  and  $a_2$  are the activities of the ion in two solutions. The term  $E^0$  cancels out because both the electrodes are same and will have the same standard electrode potential at unit activity. The  $E$  is positive if  $a_2 > a_1$  and negative if  $a_1 > a_2$ .

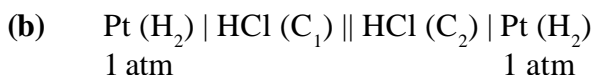
### Concentration Cell in which Electrodes is Reversible with Respect to Cation



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \left( \frac{C_1}{C_2} \right)$$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

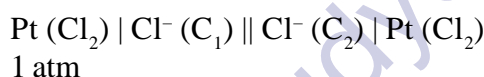
Cell reaction is spontaneous in forward direction if  $(C_2 > C_1)$



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \left( \frac{C_1}{C_2} \right)$$

$$E_{\text{cell}} = 0.0591 \log \frac{C_2}{C_1}$$

### Concentration Cell in which Electrode is Reversible with Respect to Anion



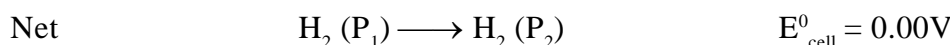
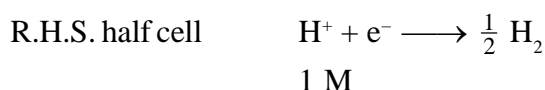
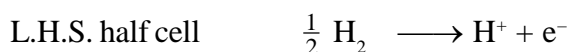
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \left( \frac{C_2}{C_1} \right)$$

For such cases, cell reaction is spontaneous in forward reaction if  $C_1 > C_2$ .

### Concentration Cell having Electrodes at Different Concentration Dipped into Same Electrolyte



Two half cells are joined by two salt – bridges since they have common electrolyte



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \left( \frac{p_2}{p_1} \right)$$

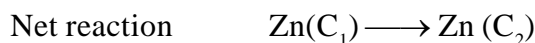
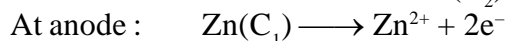
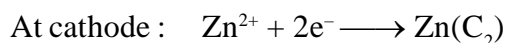
$$E_{\text{cell}} = 0.591 \log \frac{p_1}{p_2}$$

Cell reaction is spontaneous in forward direction if,  $p_1 (\text{L.H.S.}) > p_2 (\text{R.H.S.})$

**Illustration 23.**

Calculate the emf of the cell  $\text{Zn-Hg } (C_1)/\text{Zn}^{2+} (\text{aq}) \mid \text{Zn} - \text{Hg } (C_2)$  at  $25^\circ\text{C}$ , if the concentration of the zinc amalgam are  $C_1 = 2 \text{ gm per } 100 \text{ gm of Hg}$  and  $C_2 = 1 \text{ gm per } 100 \text{ gm of Hg}$ .

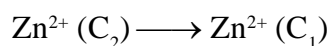
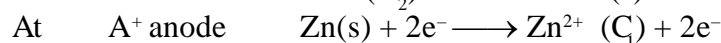
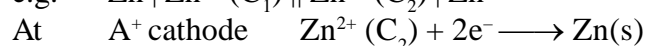
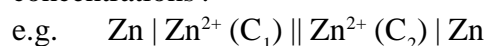
**Solution :**



$$\therefore E = \frac{0.059}{2} \log \frac{C_2}{C_1} = -0.295 \log \left( \frac{1}{2} \right) = 8.8 \times 10^{-3} \text{ V}$$

**Electrolyte Concentration Cells :**

Two electrodes of the same metal are dipping in solutions of metal ions of different concentrations :



$$\therefore E_{\text{cell}} = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

For the process to be spontaneous, emf should be +ve. Hence,  $C_2 > C_1$ .

## 9. Some Commercial Cells :

The commercial cells are actually portable source of electrical energy. These cells are also known as Batteries. There are mainly two types of commercial cells :

**(a) Primary Cells :**

These cells cannot be used for longer period of time because they are not chargeable. Some common examples of primary cells are:

(i) Dry cell

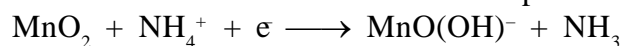
(ii) Mercury Cell

**(i) Dry Cell :**

It is used in torches, toys and in other electronic devices. Leclanche cell is the compact form of the dry cell.

In this cell zinc cylinder acts as an anode. The cylinder is filled with the paste of  $\text{NH}_4\text{Cl}$  and little amount of  $\text{ZnCl}_2$  in the form of paste in water. A graphite rod surrounded by a black paste of  $\text{MnO}_2$  and carbon powder acts as a cathode.

The cathodic reaction of the cell is represented as



It gives voltage of approximately 1.2 to 1.5V

Since, the  $\text{NH}_4\text{Cl}$  in slightly aqueous medium is acidic, it will corrode the Zn and the cell stops its functioning. Due to the corrosion and the consumption of Zn in the process, this cell cannot be reused.

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### (ii) Mercury Cell :

It consists of Zn anode and  $\text{HgO}_{(s)}$  as a cathode. The electrolyte of this cell is a paste of KOH and ZnO.

The anodic reaction of the cell:  $\text{Zn(Hg)} + 2\text{OH}^- \longrightarrow \text{ZnO}_{(s)} + \text{H}_2\text{O} + 2\text{e}^-$

And the cathodic reaction is  $\text{HgO}_{(s)} + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Hg}_{(l)} + 2\text{OH}^-$

The voltage of the mercury cell is 1.35V. The cell shows constancy in its potential throughout its life. This cell is used in small electrical circuits e.g., watches, hearing aids etc.

### (b) Secondary Cells :

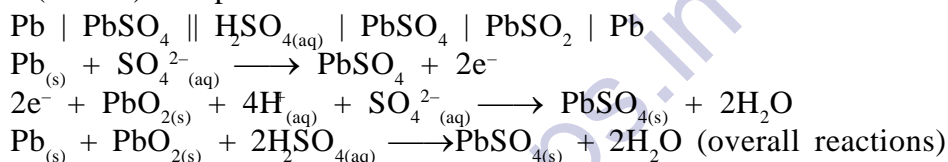
They are rechargeable by passing direct current in them, and, therefore, they can be used again and again. These cell are also known as accumulators or storage cells.

Most common accumulators are Lead Accumulators and Nickel Cadmium Accumulators.

**Lead Accumulators :** In lead accumulators three to six voltaic cells are connected in series to get 6 to 12 volt.

The anode of this cell is made of spongy lead and cathode is a grid of lead packed with  $\text{PbO}_2$ . The electrolyte used in the cell is 38%  $\text{H}_2\text{SO}_4$  by weight having a density of 1.30 g/ml. When the Pb plates are placed for sometimes, a deposit of  $\text{PbSO}_4$  is formed on them.

The cell (voltaic) is represented as :



It is clear from the net cell reaction that  $\text{H}_2\text{SO}_4$  is consumed during the operation of the cell and its density regularly decreases. When the density of the  $\text{H}_2\text{SO}_4$  solution falls below 1.2g/ml, the recharging of the battery is required.

**Recharging of the Cell :** When D.C. passed directly in this battery, the reactions of its voltaic cells are reversed and this will slowly increase the density of the  $\text{H}_2\text{SO}_4$  solution. The recharging reaction is represented as :



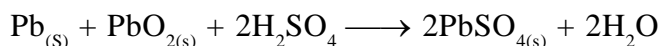
**The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.**

#### Illustration 24.

*If a completely charged lead storage cell is found to have 1.6 litre of 6 M  $\text{H}_2\text{SO}_4$  3.5 ampere of current is consumed for 6 hours, what is the concentration of sulphuric acid and moles of sulphuric acid ?*

#### Solution :

The overall reaction is :



$$\therefore \text{Moles of electron used} = \frac{3.5 \times 6 \times 60 \times 60}{96500} = 0.783$$

This equals moles of  $\text{H}_2\text{SO}_4$  used.

$$\therefore \text{Moles of } \text{H}_2\text{SO}_4, \text{ left} = 9.6 - 0.783 = 8.817$$

$$\therefore \text{Molarity of } \text{H}_2\text{SO}_4 \text{ left} = \frac{8.817}{1.6} = 5.51$$

### 3. Daily Practice Problem Sheet

**Q.1** A galvanic cell is constructed with 2 metals P and Q . Electrolysis used in the galvanic cell are sulphates of the metals . If  $E^0_{P^{+m}|P} = a$  and  $E^0_{O^{+n}|O} = b$  and  $a > b$  then find out :

- |            |                               |            |                                                          |
|------------|-------------------------------|------------|----------------------------------------------------------|
| <b>(a)</b> | Anode of the cell             | <b>(b)</b> | Cathode of the cell                                      |
| <b>(c)</b> | Reaction at anode             | <b>(d)</b> | Reaction at cathode                                      |
| <b>(e)</b> | Redox change                  | <b>(f)</b> | Nernst equation for both half cell and for complete cell |
| <b>(g)</b> | Direction of flow of electron | <b>(h)</b> | Direction of flow of current                             |

**Q.2** Calculate e.m.f. of the half cell given below :

- |            |                                              |                             |            |                                               |                             |
|------------|----------------------------------------------|-----------------------------|------------|-----------------------------------------------|-----------------------------|
| <b>(a)</b> | Fe   FeSO <sub>4</sub><br>0.1M               | E° <sub>OP</sub> = 0.44 V   | <b>(b)</b> | Zn   ZnSO <sub>4</sub><br>0.2 M               | E° <sub>OP</sub> = 0.76 V   |
| <b>(c)</b> | Cu   Cu(NO <sub>3</sub> ) <sub>2</sub><br>2M | E° <sub>OP</sub> = - 0.34 V | <b>(d)</b> | Ag   Ag <sup>+</sup><br>0.5 M                 | E° <sub>RP</sub> = 0.8 V    |
| <b>(e)</b> | Co <sup>+2</sup>   Co<br>0.01 M              | E° <sub>OP</sub> = 0.28 V   | <b>(f)</b> | Cd   Cd <sup>+2</sup><br>0.05 M               | E° <sub>RP</sub> = -0.4 V   |
| <b>(g)</b> | Ni <sup>+2</sup>   Ni<br>0.12 M              | E° <sub>RP</sub> = -0.24 V  | <b>(h)</b> | Hg   Hg <sub>2</sub> <sup>+2</sup><br>0.015 M | E° <sub>OP</sub> = -0.792 V |
| <b>(i)</b> | Pb   PbSO <sub>4</sub><br>0.004 M            | E° <sub>OP</sub> = -0.126 V | <b>(j)</b> | SnCl <sub>2</sub>   Sn<br>0.006 M             | E° <sub>OP</sub> = -0.136 V |

**Q.3** The standard electrode potential of  $\text{Cu}|\text{Cu}^{2+}$  is -0.34 volt. At what concentration of  $\text{Cu}^{2+}$  ions, will this electrode potential be zero ?

**Q.4** A zinc electrode is dipped in a 0.1 M solution at 25°C. Assuming that salt is dissociated to 20 % at this dilution, calculate the electrode potential .  $E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$

**Q.5**  $K_{sp}$  of  $\text{Cu}(\text{OH})_2$  is  $1.0 \times 10^{-19}$ . Calculate the reduction potential at pH = 8 for the couple  $\text{Cu}^{2+}/\text{Cu}$ . Given:  $E^\circ_{\text{RP}}$  of  $\text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$ .

**Q.6** Using oxidation potential and reduction potential of various metals in Q.2 determine anode and cathode of the cell,  $E^\circ_{\text{cell}}$ ,  $E_{\text{cell}}$  when galvanic cell is composed of

- (1) Zn- Fe      (2) Ag - Cu      (3) Cd - Co      (4) Hg - Sn  
(5) Pb - Ni      (6) Zn - Cu      (7) Pb - Ag      (8) Hg - Ag

**Q.7** The potential for the reaction,  $\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$  is 1.23 V in 0.1 N strong acid solution. Calculate the potential of this couple in aqueous solution of : (i) pH = 10 (ii) pH = 14

**Q.8** Standard reduction potential of Cu and Ag are 0.34 and 0.8 respectively. A galvenic cell is constructed using Cu-Ag . Determine :

- (i) Anode and cathode of the cell
- (ii)  $E^\circ_{\text{cell}}$
- (iii) Cell potential when concentration of  $\text{Cu}^{+2}$  and  $\text{Ag}^+$  are  $3 \times 10^{-2} \text{ M}$  and  $1.73 \times 10^{-3} \text{ M}$  respectively

**Q.9** Calculate the values for cell,  $\text{Zn} | \text{Zn}^{2+}(\text{aq.}) || \text{Cu}^{2+}(\text{aq.}) | \text{Cu}$

- (i) Cell reaction
- (ii) E.m.f. of cell if  $\text{Zn}^{2+}$  and  $\text{Cu}^{+2}$  are 1 M each
- (iii) The minimum concentration of  $\text{Cu}^{2+}$  at which the cell reaction,  
$$\text{Zn} + \text{Cu}^{2+} (\text{aq.}) \longrightarrow \text{Zn}^{+2} (\text{aq.}) + \text{Cu}$$
will be spontaneous if  $\text{Zn}^{2+}$  is 1 M
- (iv) Does the displacement of  $\text{Cu}^{2+} (\text{aq.})$  by Zn goes to completion.

### ELECTROCHEMISTRY

- Q.10** Consider the reaction,  $2\text{Ag}^+ + \text{Cd} \longrightarrow 2\text{Ag} + \text{Cd}^{2+}$ . The standard reduction potential of  $\text{Ag}^+/\text{Ag}$  and  $\text{Cd}^{2+}/\text{Cd}$  couples are +0.80 and -0.40 volt respectively.
- (a) What is the standard cell e.m.f.,  $E^\circ$  ?
- (b) Will the total e.m.f. of the reaction be more +ve or -ve, if conc. of  $\text{Cd}^{2+}$  is 0.10 M rather than 1 M ?
- Q.11** A graph is plotted between  $E_{\text{cell}}$  and  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ . The curve was linear with intercept on  $E_{\text{cell}}$  axis equal to 1.10 V. Calculate  $E_{\text{cell}}$  for  $\text{Zn} \left| \text{Zn}^{2+} \right| \left| \text{Cu}^{2+} \right| \text{Cu}$ .
- Q.12** Which of the following hydrogen gas ion electrodes are in standard state ? Also calculate their electrode potential if they are not in standard state .
- |                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>(1) <math>\text{Pt} (\text{H}_2) \mid \text{H}_2\text{SO}_4</math><br/>1 atm      0.5 M</p> <p>(3) <math>\text{Pt} (\text{H}_2) \mid \text{H}_2\text{O}</math><br/><math>10^{-14}</math> atm</p> <p>(5) <math>\text{CH}_3\text{COONH}_4 \mid \text{Pt}(\text{H}_2)</math><br/><math>10^{-3}</math> M      <math>10^{-14}</math> atm</p> <p>(7) <math>\text{Mg} (\text{OH})_2 \mid \text{Pt}(\text{H}_2)</math><br/>(sat. sol.)      10 atm</p> | <p>(2) <math>\text{CH}_3\text{COOH} \mid \text{Pt}(\text{H}_2)</math><br/>0.1 M      0.1 atm</p> <p>(4) <math>\text{Pt} (\text{H}_2) \mid \text{HCOOH} + \text{HCOONa}</math><br/><math>10^{-5}</math> atm      1 M      1 M</p> <p>(6) <math>\text{NH}_4\text{OH} \mid \text{Pt}(\text{H}_2)</math><br/><math>10^{-3}</math> M</p> <p>(8) <math>\text{H}_2\text{SO}_4 + \text{HCl} + \text{CH}_3\text{COOH} \mid \text{Pt} (\text{H}_2)</math><br/>0.1 M      0.2 M      1M</p> |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
- $[\text{K}_{\text{sp}} \text{ of } \text{Mg}(\text{OH})_2 = 4 \times 10^{-6} \text{ } K_{\text{a}} (\text{CH}_3\text{COOH}) = 10^{-5}, \text{ } K_{\text{b}} (\text{NH}_4\text{OH}) = 10^{-5}$   
 $K_{\text{a}} (\text{HCOOH}) = 10^{-4}$
- Q.13** If the electrode potential for the half cell,  $\text{HA} \mid \text{Pt}(\text{H}_2)$  is -0.236 V, then calculate the dissociation constant of HA.  
0.1M      2 atm
- Q.14** The standard oxidation potential of  $\text{Ni}/\text{Ni}^{2+}$  electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured e.m.f. be zero at  $25^\circ\text{C}$  ? Assume  $[\text{Ni}^{2+}] = 1 \text{ M}$  and  $p_{\text{H}_2} = 1 \text{ atm}$ .
- Q.15** If  $\text{NO}_3^- \longrightarrow \text{NO}_2$  (acidic medium) ;  $E^\circ = 0.790 \text{ V}$  &  $\text{NO}_3^- \longrightarrow \text{NH}_2\text{OH}$  (acidic medium);  $E^\circ = 0.731 \text{ V}$ . At what pH the above two half reaction will have same E values. Assume the concentrations of all the species to the unity.
- Q.16** What ratio of  $\text{Pb}^{+2}$  to  $\text{Sn}^{+2}$  concentration is needed to reverse the following cell reaction ?
- $$\text{Sn} (\text{s}) + \text{Pb}(\text{aq})^{+2} \rightleftharpoons \text{Sn}(\text{aq.})^{+2} + \text{pb}(\text{s})$$
- $E^\circ_{\text{Sn}^{+2}/\text{Sn}} = -0.136 \text{ V}$  and  $E^\circ_{\text{Pb}^{+2}/\text{Pb}} = -0.126 \text{ V}$
- Q.17** A cell is set up where the overall reaction is,  $\text{H}_2(\text{g}) + \text{Sn}^{4+} \longrightarrow 2\text{H}^+ + \text{Sn}^{2+}$   
The hydrogen electrode is under standard condition and  $E_{\text{cell}}$  is found to be +0.20 V . What is the ratio of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  around the other electrode ? Given  $E^\circ_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.15 \text{ V}$ .
- Q.18** A galvanic cell is constructed with  $\text{Ag}^+/\text{Ag}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  electrodes. Find the concentration of  $\text{Ag}^+$  at which the e.m.f. of cell is zero at equimolar concentration of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .  
Given :  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$  and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$ .
- Q.19** The e.m.f. of the cell  $\text{Pt}(\text{H}_2) \mid \text{HOCN} \mid \left| \text{Ag}^+ \right| \text{Ag}(\text{s})$  is 0.982 V . Calculate the  $K_{\text{a}}$  for HOCN .  $\text{Ag}^+ + \text{e} \longrightarrow \text{Ag}(\text{s})$  ;  $E^\circ = 0.80 \text{ V}$ .
- Q.20** The standard reduction potential of  $E^\circ_{\text{Bi}^{3+}/\text{Bi}}$  and  $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$  are 0.226 V and 0.344 V respectively. A mixture of salts of  $\text{Bi}^{3+}$  and  $\text{Cu}^{2+}$  at unit concentration each is electrolysed at  $25^\circ\text{C}$ . To what value can  $[\text{Cu}^{2+}]$  be brought down before bismuth starts to deposit during electrolysis.



## 4. Daily Practice Problem Sheet

**Q.1** Identify the type of the given half cells and write corresponding half cell reactions. Also write nernst equation for each half cell

- |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>(a) <math>\text{Pt}(\text{Cl}_2)   \text{HCl}</math></p> <p>(c) <math>\text{Zn}   \text{Zn}^{+2}</math></p> <p>(e) <math>\text{MnO}_4^- , \text{Mn}^{+2}, \text{H}^+   \text{Pt}</math></p> <p>(g) <math>\text{Cl}^-   \text{Hg}_2\text{Cl}_2   \text{Hg}</math></p> <p>(i) <math>\text{Cl}^-   \text{AgCl}   \text{Hg}</math></p> <p>(k) <math>\text{Pt}(\text{Cl}_2) \Big  \text{HCl} \Big  \text{Pt}(\text{Cl}_2)</math><br/> <math>\text{P}_1 \qquad \qquad \qquad \text{P}_2</math></p> <p>(m) <math>\text{Pb}   \text{saturated PbSO}_4</math></p> <p>(o) <math>\text{Pt}   \text{Au}^{+3}, \text{Au}^+</math></p> <p>(q) <math>\text{Pt}(\text{H}_2)   \text{H}_2\text{SO}_4    \text{HCl}   \text{Pt}(\text{H}_2)</math></p> <p>(s) <math>\text{CNS}^-   \text{CuCNS}   \text{Cu}</math></p> <p>(u) <math>\text{CaBr}_2   \text{AgBr}   \text{Ag}</math></p> | <p>(b) <math>\text{Pt}   \text{Fe}^{+2}, \text{Fe}^{+3}</math></p> <p>(d) <math>\text{Pt}(\text{H}_2)   \text{H}^+</math></p> <p>(f) <math>\text{Ag}   \text{Saturated. AgCl}</math></p> <p>(h) <math>\text{Bi}^{+5}, \text{Bi}^{+3}   \text{Pt}</math></p> <p>(j) <math>\text{Zn} \Big  \text{Zn}^{+2} \Big  \Big  \text{Zn}^{+2} \Big  \text{Zn}</math><br/> <math>\text{C}_1\text{M} \qquad \qquad \qquad \text{C}_2\text{M}</math></p> <p>(l) <math>\text{Pb}   \text{PbSO}_4   \text{SO}_4^{-2}</math></p> <p>(n) <math>\text{CaCl}_2   \text{Pt}(\text{Cl}_2)</math></p> <p>(p) <math>\text{Cr}_2\text{O}_7^{-2}, \text{Cr}^{+3}, \text{OH}^-   \text{Pt}</math></p> <p>(r) <math>\text{Ag}   \text{AgCl}, \text{KCl}    \text{KBr}, \text{AgBr}   \text{Ag}</math></p> <p>(t) <math>\text{SnCl}_2   \text{Sn}</math></p> <p>(v) <math>\text{Pb}   \text{PbSO}_4, \text{K}_2\text{SO}_4</math></p> |
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**Q.2** Write chemical reaction for anodic half cell, cathodic half cell and for complete cell. Also write nernst equation for each galvanic cell

- (a)  $\text{Pt} | \text{Fe}^{+2}, \text{Fe}^{+3} || \text{Cr}_2\text{O}_7^{-2}, \text{Cr}^{+3}, \text{H}^+ | \text{Pt}$
- (b)  $\text{Ag} | \text{AgI}, \text{KI} || \text{KBr}, \text{AgBr} | \text{Ag}$
- (c)  $\text{Cu} | \text{CuSO}_4 || \text{CuSO}_4 | \text{Cu}$
- (d)  $\text{Pt} | \text{C}_2\text{O}_4^{-2}, \text{CO}_2 || \text{MnO}_4^-, \text{Mn}^{+2}, \text{H}^+ | \text{Pt}$
- (e)  $\text{Zn} | \text{ZnSO}_4 || \text{HCl} | \text{Pt}(\text{H}_2)$
- (f)  $\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{KCl} || \text{NaCl} | \text{Pt}(\text{Cl}_2)$
- (g)  $\text{Pt} | \text{Fe}(\text{CN})_6^{-4}, \text{Fe}(\text{CN})_6^{-3} || \text{CrO}_4^{-2}, \text{Cr}^{+3}, \text{OH}^- | \text{Pt}$
- (h)  $\text{Ag} | \text{AgBr}, \text{CN}^- || \text{AgCl}, \text{NH}_3 | \text{Ag}$
- (i)  $\text{Pt}(\text{H}_2) | \text{HSO}_3^-, \text{SO}_3^{-2} || \text{ZnSO}_4 | \text{Zn}$
- (j)  $\text{Cu} | \text{CuSO}_4, \text{NH}_3 || \text{AgCl}, \text{NH}_3 | \text{Ag}$
- (k)  $\text{Pb} | \text{Pb}^{+2} || [\text{Co}(\text{en})_3]^{+3}, [\text{Co}(\text{en})_3]^{+2} | \text{Pt}$
- (l)  $\text{Pt}(\text{Cl}_2) | \text{HCl} || \text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4 | \text{Pt}(\text{H}_2)$
- (m)  $\text{Pt} | \text{Mn}^{+2}, \text{MnO}_2 || \text{MnO}_4^-, \text{Mn}^{+2}, \text{H}^+ | \text{Pt}$
- (n)  $\text{Ag} | \text{Ag}^+ || \text{KCl}, \text{AgCl} | \text{Ag}$
- (o)  $\text{Pt} | \text{Co}(\text{CN})_6^{-4}, \text{Co}(\text{CN})_6^{-3} || \text{Co}^{+3}, \text{Co}^{+2} | \text{Pt}$

**Q.3** The e.m.f. of the cell obtained by combining Zn and Cu electrodes of a Daniel cell with N calomel electrodes are 1.083 V and –0.018 V respectively at 25°C. If the potential of N calomel electrode is –0.28 V, find e.m.f. of Daniel cell.

**Q.4** Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contains 0.1 M  $\text{MnO}_4^-$  and 0.8 M  $\text{H}^+$  and which was treated with  $\text{Fe}^{2+}$  necessary to reduce 90 % of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ .  $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.51 \text{ V}$ .

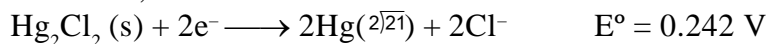
**Q.5** Determine potential for the cell,  $\text{Pt} | \text{Fe}^{+2}, \text{Fe}^{+3} || \text{Cr}_2\text{O}_7^{-2}, \text{Cr}^{+3}, \text{OH}^- | \text{Pt}$

$$E_{\text{Fe}^{+3}|\text{Fe}^{+2}}^0 = 0.7 \text{ V}, \quad E_{\text{Cr}_2\text{O}_7^{-2}|\text{Cr}^{+3}}^0 = 1.35 \text{ V}$$

in which  $[\text{Fe}^{+2}]$  and  $[\text{Fe}^{+3}]$  are 1 M and 2 M respectively and  $[\text{Cr}_2\text{O}_7^{-2}]$ ,  $[\text{Cr}^{+3}]$  and  $[\text{H}^+]$  are 2M, 4M and  $10^{-13} \text{ M}$  respectively.

### ELECTROCHEMISTRY

- Q.6** How much is the oxidizing power of  $(0.1 \text{ M}, \text{MnO}_4^-/\text{Mn}^{+2}, 0.2\text{M})$  couple decreased if the  $\text{H}^+$  concentration is decreased from  $0.1\text{M}$  to  $10^{-6} \text{ M}$  at  $25^\circ\text{C}$  ?
- Q.7** The cell  $\text{Pt}(\text{H}_2) (1\text{atm}) \mid \text{H}^+ (\text{pH} = X) \parallel$  Normal calomel electrode has e.m.f. of  $0.67 \text{ V}$  at  $25^\circ\text{C}$ . Calculate pH of solution. The oxidation potential of calomel electrode on H scale is  $-0.28 \text{ V}$ .
- Q.8** A hydrogen electrode having pressure is equal to  $1.00 \text{ atm}$  is combined with a standard calomel electrode, whose half-reaction is



If the cell potential is  $0.800 \text{ V}$ , what is the pH of the solution around the hydrogen electrode ?  
What will the cell potential be if the hydrogen electrode is immersed in a neutral solution ?

- Q.9** What is the e.m.f. of a cell containing two H electrodes, the negative one in contact with  $10^{-8}$  molar  $\text{OH}^-$  and the positive one in contact with  $10^{-3}$  molar  $\text{H}^+$  ?
- Q.10** Neglecting the liquid junction potential, calculate the e.m.f. of the following cell at  $25^\circ\text{C}$ .

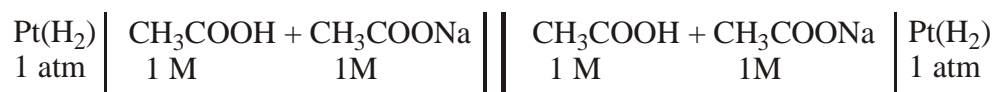


$K_a$  for  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  are  $1.77 \times 10^{-4}$  and  $1.8 \times 10^{-5}$  respectively.

- Q.11** Write the cell reaction and calculate the e.m.f. of the cell for  $\text{Pt}(\text{Cl}_2) \mid \text{NaCl} (\text{aq}) \mid \text{Pt}(\text{Cl}_2)$ .
- $10 \text{ atm} \quad 1 \text{ atm}$

Will the cell reaction be spontaneous

- Q.12** The e.m.f. of a galvanic cell composed of two H electrodes is  $272 \text{ millivolt}$ . What is the pH of the solution in which the anode is immersed if the cathode is in the solution of  $\text{pH} = 3$  ?
- Q.13** Calculate the potential of a cell in which H electrodes are immersed in a solution with a pH of  $3.5$  and in a solution with a pH of  $10.7$  at  $30^\circ\text{C}$ .
- Q.14** The reversible reduction potential of water is  $-0.414 \text{ V}$  under  $1 \text{ atm H}_2$  pressure. If the reduction is  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ , calculate  $[\text{H}^+]$  in pure water.
- Q.15** A cell designed below contains one litre of buffer mixture of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  each  $1 \text{ M}$  in two compartments using platinum electrodes.  $\text{pK}_a$  for  $\text{CH}_3\text{COOH} = 4.74$ .



**Calculate :**

- (i) the pH in the each compartment
  - (ii) the e.m.f. of cell
  - (iii) the pH and e.m.f. of the cell each compartment after passage of  $1.25 \text{ A}$  current for  $241.25 \text{ minute}$ .
- Q.16** Calculate the e.m.f. of the cell at  $18^\circ\text{C}$  for :



$\text{HCl}$  is  $90\%$  dissociated and  $\text{KOH}$  is  $75\%$  ionised.

## 5. Daily Practice Problem Sheet

- Q.1** The equilibrium constant for a reaction is  $1 \times 10^{20}$  at 300 K. The standard free energy change for this reaction is :  
 (A)  $-115 \text{ kJ}$  (B)  $+115 \text{ kJ}$  (C)  $+166 \text{ kJ}$  (D)  $-166 \text{ kJ}$
- Q.2** Standard electrode potentials of  $\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$  and  $\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$  are  $-0.440 \text{ V}$  and  $-0.036 \text{ V}$  respectively. The standard electrode potential ( $E^\circ$ ) for  $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$  is :  
 (A)  $-0.476 \text{ V}$  (B)  $-0.404 \text{ V}$  (C)  $+0.404 \text{ V}$  (D)  $+0.772 \text{ V}$
- Q.3** Consider the cell,  $\text{Mg(s)} \mid \text{Mg}^{2+} (0.2\text{M}) \parallel \text{Ag}^+ (10^{-3} \text{M}) \mid \text{Ag}$   
 Given  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.8 \text{ volt}$  ;  $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ volt}$   
 (i) What will the effect on emf if concentration of  $\text{Mg}^{2+}$  ion is decreased to  $0.1 \text{ M}$   
 (A) decreased to  $3.022 \text{ V}$  (B) increased by  $3.022 \text{ V}$   
 (C) remains same (D) none  
 (ii) In the above question maximum work that can be obtained by operating the cell is :  
 (A)  $611.8 \text{ kJ}$  (B)  $61.18 \text{ kJ}$  (C)  $107.2 \text{ kJ}$  (D)  $1072.5 \text{ kJ}$
- Q.4** Consider the following cell reaction :  
 $\text{Tl}^{+3} + 2\text{e}^- \longrightarrow \text{Tl}^+ ; E^\circ = 1.26 \text{ V}$   
 $\text{Tl}^+ + \text{e}^- \longrightarrow \text{Tl} ; E^\circ = -0.336 \text{ V}$   
 The standard potential of the  $\text{Tl}^{+3} \mid \text{Tl}$  electrode is :  
 (A)  $0.728 \text{ V}$  (B)  $0.824 \text{ V}$  (C)  $1.596 \text{ V}$  (D)  $2.52 \text{ V}$
- Q.5** Two electro chemical cells are assembled in which the following reactions occur,  
 $\text{V}^{2+} + \text{VO}^{2+} + 2\text{H}^+ \longrightarrow 2\text{V}^{3+} + \text{H}_2\text{O} ; E^\circ_{\text{cell}} = 0.616 \text{ V}$   
 $\text{V}^{3+} + \text{Ag}^+ + \text{H}_2\text{O} \longrightarrow \text{VO}^{2+} + 2\text{H}^+ + \text{Ag(s)} ; E^\circ_{\text{cell}} = 0.439 \text{ V}$   
 then  $E^\circ$  for the half reaction,  $\text{V}^{3+} + \text{e}^- \longrightarrow \text{V}^{2+}$ , is : [ Given :  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.799 \text{ V}$  ]  
 (A)  $-0.256 \text{ V}$  (B)  $+0.256 \text{ V}$  (C)  $-1.05 \text{ V}$  (D)  $+1.05 \text{ V}$
- Q.6** For the reaction,  $\text{H}_2(\text{g}) + 2\text{AgCl(s)} + 2\text{H}_2\text{O(l)} \longrightarrow 2\text{Ag(s)} + 2\text{H}_3\text{O}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$   
 at  $25^\circ \text{C}$ , the standard free energy of formation of  $\text{AgCl(s)}$ ,  $\text{H}_2\text{O(l)}$  and  $(\text{H}_3\text{O}^+ + \text{Cl}^-)$  are :  $109.7$ ,  $-237.2$  and  $-368.4 \text{ kJ mol}^{-1}$  respectively . Then  $\Delta G^\circ$  and  $E^\circ$  for the reaction is :  
 (A)  $-43 \text{ kJ}, 0.22 \text{ V}$  (B)  $+43 \text{ kJ}, 0.22 \text{ V}$   
 (C)  $-21.5 \text{ kJ}, 0.11 \text{ V}$  (D)  $+21.5 \text{ kJ}, 0.22 \text{ V}$
- Q.7** Given :  $\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+ ; E^\circ = 0.15 \text{ V}$   
 $\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu} ; E^\circ = 0.5 \text{ V}$   
 Potential for  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu} ;$  is :  
 (A)  $0.325 \text{ V}$  (B)  $0.650 \text{ V}$  (C)  $0.050 \text{ V}$  (D)  $1.30 \text{ V}$
- Q.8** Which of the following is always true regarding the spontaneity of reaction occurring in a galvanic cell ?  
 (A)  $E^\circ_{\text{cell}} > 0, \Delta G^\circ < 0$  and  $Q > K_c$  (B)  $E^\circ_{\text{cell}} < 0, \Delta G^\circ < 0$  and  $Q < K_c$   
 (C)  $E^\circ_{\text{cell}} > 0, \Delta G^\circ > 0$  and  $Q > K_c$  (D)  $E^\circ_{\text{cell}} > 0, \Delta G^\circ < 0$  and  $Q < K_c$
- Q.9** If  $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = x_1 \text{ volt}$  and  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = x_2 \text{ volt}$ , then  $E^\circ_{\text{Fe}^{3+}/\text{Fe}}$  will be :  
 (A)  $(2x_1 + x_2)\text{V}$  (B)  $(3x_2 - x_1)\text{V}$  (C)  $\frac{(2x_1 + x_2)}{3} \text{ V}$  (D)  $\frac{(x_1 + 2x_2)}{3} \text{ V}$
- Q.10** Given that  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$  ;  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$  ;  $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37$  and  $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$   
 in which of the following cells the standard free energy decrease is maximum :  
 (A)  $\text{Mg} \mid \text{Mg}^{2+} (1\text{M}) \parallel \text{Cu}^{2+} (1\text{M}) \mid \text{Cu}$  (B)  $\text{Mg} \mid \text{Mg}^{2+} (1\text{M}) \parallel \text{Ag}^+ (1\text{M}) \mid \text{Cu}$   
 (C)  $\text{Ag} \mid \text{Ag}^+ (1\text{M}) \parallel \text{Al}^{3+} (1\text{M}) \mid \text{Al}$  (D)  $\text{Cu} \mid \text{Cu}^{2+} (1\text{M}) \parallel \text{Ag}^+ (1\text{M}) \mid \text{Ag}$

### ELECTROCHEMISTRY

- Q.11** The electrical work done during the reaction at 298 K :  $2\text{Hg}(l) + \text{Cl}_2(g) \longrightarrow \text{Hg}_2\text{Cl}_2(s)$  is :  
 given that :  $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$  ;  $E^\circ_{\text{Hg}_2\text{Cl}_2/\text{Hg}, \text{Cl}^-} = 0.27 \text{ V}$  ;  $p_{\text{Cl}_2} = 1 \text{ atm}$ ,  
 (A)  $210.37 \text{ kJ mol}^{-1}$  (B)  $105.185 \text{ kJ mol}^{-1}$   
 (C)  $420.74 \text{ kJ mol}^{-1}$  (D)  $110.37 \text{ kJ mol}^{-1}$
- Q.12** Which of the following changes will cause the free energy of the cell reaction to decrease :  
 $\text{Zn} | \text{ZnSO}_4(\text{aq}) (x_1 \text{ M}) || \text{HCl}(\text{aq}) (x_2 \text{ M}) | \text{H}_2(g) , \text{Pt}$   
 (A) increase in the volume of HCl solution from 100 ml to 200 ml  
 (B) increase in pressure of hydrogen from 1 atm to 2 atm  
 (C) increase in molarity  $x_2$  from 0.1 to 1 M  
 (D) decrease in molarity  $x_1$  from 1M to 0.1 M
- Q.13** If  $\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$   $E^\circ = -0.14 \text{ V}$   
 $\text{Sn}^{4+} + 2e^- \longrightarrow \text{Sn}^{2+}$   $E^\circ = 0.13 \text{ V}$  then :  
 (A)  $\text{Sn}^{2+}$  is unstable and disproportionates to  $\text{Sn}^{4+}$  and Sn  
 (B)  $\text{Sn}^{2+}$  is stable and disproportionation reaction is not spontaneous  
 (C)  $\text{Sn}^{4+}$  is easily reduced to Sn (D) none of these
- Q.14** For the reactions ,  $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ ,  $E^\circ = 1.51 \text{ V}$   
 $\text{MnO}_2 + 4\text{H}^+ + 2e^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$ ,  $E^\circ = 1.23 \text{ V}$   
 then for the reaction ,  $\text{MnO}_4^- + 4\text{H}^+ + 3e^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ ,  $E^\circ$  is :  
 (A) 1.70 V (B) 5.09 V (C) 0.28 V (D) 0.84 V
- Q.15** For the fuel-cell reaction :  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ ,  $\Delta G = -475 \text{ kJ}$ . Hence  $E_{\text{cell}}$  is :  
 (A) 1.23 V (B) 2.46 V (C) 0.615 V (D) 0.31 V
- Q.16** (i) For the following cell-reaction ,  $\text{Cu}(s) + 2\text{Ag}^+(\text{aq}) \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(\text{aq})$ .  
 $E_{\text{cell}}$  is 0.46 V at 300 K and 0.48 V at 310 K. Hence, entropy change is :  
 (A)  $193 \text{ JK}^{-1}$  (B)  $386 \text{ JK}^{-1}$  (C)  $579 \text{ JK}^{-1}$  (D)  $-193 \text{ JK}^{-1}$   
 (ii) The temperature coefficient of the e.m.f. of the cell in above question is :  
 (A)  $0.02 \text{ VK}^{-1}$  (B)  $0.2 \text{ VK}^{-1}$  (C)  $0.002 \text{ VK}^{-1}$  (D)  $2 \text{ VK}^{-1}$
- Q.17** For this cell  $\text{Zn} | \text{Zn}^{2+} (C_1 \text{ M}) || \text{Zn}^{2+} (C_2 \text{ M}) | \text{Zn}$ .  $\Delta G$  is negative if :  
 (A)  $C_1 = C_2$  (B)  $C_1 > C_2$  (C)  $C_2 > C_1$  (D) none of these
- Q.18** For a Ag-Zn button cell, net reaction is ,  $\text{Zn}(s) + \text{Ag}_2\text{O}(s) \longrightarrow \text{ZnO}(s) + 2\text{Ag}(s)$   
 $\Delta G_f(\text{Ag}_2\text{O}) = -11.21 \text{ kJ mol}^{-1}$   $\Delta G_f(\text{ZnO}) = -318.3 \text{ kJ mol}^{-1}$   
 Hence,  $E^\circ_{\text{cell}}$  of the button cell is :  
 (A) 3.182 V (B) 1.71 V (C) -1.591 V (D) 1.591 V
- Q.19**  $\text{Zn} + \text{Cu}^{+2} \rightleftharpoons \text{Zn}^{+2} + \text{Cu}$  ;  $E^\circ_{\text{cell}} = 1.1 \text{ V}$   
 value of equilibrium constant for the above reaction :  
 (A)  $1.95 \times 10^{37}$  (B)  $4.4 \times 10^{18}$  (C)  $2 \times 10^{35}$  (D)  $4.4 \times 10^{20}$
- Q.20** Consider the following equations for a cell reaction ,  
 $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$   $E^\circ = x$  ;  $K_{\text{eq}} = K_1$   
 $2\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + 2\text{D}$   $E^\circ = y$  ;  $K_{\text{eq}} = K_2$   
 (A)  $x = y$ ,  $K_1 = K_2$  (B)  $x = 2y$ ,  $K_1 = 2K_2$   
 (C)  $x = y$ ,  $K_1^2 = K_2$  (D)  $x_2 = y$ ,  $K_1^2 = K_2$
- Q.21** For a reaction ,  $\text{A} + \text{B}^{+2} \longrightarrow \text{B} + \text{A}^{+2}$  ;  $E^\circ = 0.2955$   
 Hence equilibrium constant of the reaction is :  
 (A) 10 (B)  $10^{10}$  (C) -10 (D)  $10^{-10}$

- Q.22** If for a half cell reactions .  $E^\circ$  values are known ,  
 $\text{Cu}^{+2} + e^- \longrightarrow \text{Cu}^+ \quad ; \quad E^\circ = 0.15 \text{ V}$   
 $\text{Cu}^{+2} + 2e^- \longrightarrow \text{Cu} \quad ; \quad E^\circ = 0.34 \text{ V}$   
 Predict which exist in aqueous solution :  
 (A) copper (I) sulphate (B) copper (II) sulphate  
 (C) both (D) none of these
- Q.23** For the half-cell reaction ,  $2 \text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2 + 2\text{OH}^-$ ,  $E^\circ = -0.8277 \text{ V}$  at 298 K .  
 Hence, autoprotolysis constant for water is :  
 (A)  $1 \times 10^{-10}$  (B)  $1 \times 10^{-12}$  (C)  $1 \times 10^{-13}$  (D)  $1 \times 10^{-14}$
- Q.24** If a chemical reaction is carried out in a fuel cell, the maximum amount of useful work that can be obtained from the cell is :  
 (A)  $\Delta G$  (B)  $\Delta H$  (C)  $\frac{\Delta G}{\Delta H}$  (D)  $T\Delta S$
- Q.25** For electrosynthesis of a substance :  
 (A)  $\Delta G = +ve$  and  $E_{\text{cell}} = -ve$  (B)  $\Delta G = -ve$  and  $E_{\text{cell}} = +ve$   
 (C)  $\Delta G = -ve$  and  $E_{\text{cell}} = -ve$  (D)  $\Delta G = +ve$  and  $E_{\text{cell}} = +ve$
- Q.26** For hydrogen-oxygen fuel cell with reaction ,  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$   
 $\Delta G_f^\circ(\text{H}_2\text{O}) = -237.2 \text{ kJ mol}^{-1}$ . Hence e.m.f. of the fuel cell is :  
 (A) +2.46 V (B) -2.46 V (C) +1.23 V (D) -1.23 V
- Q.27** For the reaction ,  $4\text{Al}(\text{s}) + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O} + 4\text{OH}^- \longrightarrow 4\text{Al}(\text{OH})_4^-$  ;  $E_{\text{cell}}^\circ = 2.73 \text{ V}$   
 (i) If free energy of formation of  $\text{OH}^-$  ( $\Delta G_f^\circ[\text{OH}^-] = -157 \text{ kJ mol}^{-1}$ , & free energy of formation of  $\text{H}_2\text{O} = -237.2 \text{ kJ mol}^{-1}$  then  $\Delta G^\circ$  for this reaction is :  
 (A)  $-3.16 \times 10^3 \text{ kJ mol}^{-1}$  (B)  $-0.79 \times 10^3 \text{ kJ mol}^{-1}$   
 (C)  $-0.263 \times 10^3 \text{ kJ mol}^{-1}$  (D)  $0.263 \times 10^3 \text{ kJ mol}^{-1}$   
 (ii)  $\Delta G_f^\circ[\text{Al}(\text{OH})_4^-]$  for the above case is :  
 (A)  $-1.3 \times 10^3 \text{ kJ mol}^{-1}$  (B)  $-3.16 \times 10^3 \text{ kJ mol}^{-1}$   
 (C)  $-5.21 \times 10^3 \text{ kJ mol}^{-1}$  (D) 0
- Q.28** Given that  $E^\circ = 0.036 \text{ V}$ , the free energy change  $\Delta G^\circ$  for the reaction  
 $\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe}(\text{s})$  is :  
 (A) 20.84 kJ (B) 3.47 kJ (C) 5.21 kJ (D) 10.42 kJ
- Q.29** (i) The standard emf of the cell,  
 $\text{Cd}(\text{s}) | \text{CdCl}_2(\text{aq}) || \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$   
 (0.1 M)  
 in which the cell reaction is ,  $\text{Cd}(\text{s}) + 2\text{AgCl}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \text{Cd}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$   
 is 0.6915 V at  $0^\circ\text{C}$  and 0.6753 V at  $25^\circ\text{C}$ .  $\Delta G$  for the reaction at  $25^\circ\text{C}$  is :  
 (A) -176 kJ (B) -130.3 kJ (C) -167.26 kJ (D) -125.06 kJ  
 (ii) In the above questions,  $\Delta H$  of the reaction at  $25^\circ\text{C}$  is :  
 (A) +123.5 kJ (B) -167.26 kJ (C) +64.8 kJ (D) -125.06 kJ
- Q.30** For the cell reaction ,  $\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$   
 $(\text{C}_1) \quad (\text{C}_2)$   
 of an electrochemical cell , the change in free energy  $\Delta G$  at a given temperature is a function of :  
 (A)  $2\sqrt{21}n(\text{C}_1)$  (B)  $2\sqrt{21}n(\text{C}_2/\text{C}_1)$  (C)  $2\sqrt{21}n(\text{C}_1 + \text{C}_2)$  (D)  $2\sqrt{21}n(\text{C}_2)$
- Q.31** The standard emf of the cell reaction ,  $\frac{1}{2} \text{Cu}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \frac{1}{2} \text{Cu}^{2+} + \text{Cl}^-$   
 is 1.02 V . The value of  $\Delta G^\circ$  will be :  
 (A) unpredictable (B) -98.43 kJ (C) -196.86 kJ (D) -188.43 kJ

## SECTION -III (CONDUCTION)

### 10. Electrolytic Conductance :

#### Specific Conductance

The resistance (R) of a metallic conductor is directly proportional to its length ( $l$ ) and inversely proportional to its cross-sectional area (a), i.e.,

$$R \propto \frac{l}{a} \quad \Rightarrow \quad R = \rho \cdot \frac{l}{a}$$

$$\Rightarrow \quad \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a} \quad \dots\dots(1)$$

Where  $\rho$  is a constant depending upon the nature of the material and is called specific resistance of the material.

The reciprocal of the resistance is called conductance and similarly, the reciprocal of specific resistance is called specific conductance,

Thus, from equation (1)

$$\text{Specific conductance} = \text{observed conductance} \times \frac{l}{a} \quad \dots\dots(2)$$

When  $l = 1 \text{ cm}$  and  $a = 1 \text{ cm}^2$

Specific conductance = observed conductance

Thus, specific conductance is the conductance of a conductor which is observed when it is 1 cm in length and 1 sq. cm in cross-sectional area. In other words, it is the conductance of 1 cc of the conductor.

The unit of resistance is ohm ( $\Omega$ ) so unit of conductance will be  $\text{ohm}^{-1}$ , mho or  $\Omega^{-1}$  and expressing  $l$  in cm and  $a$  in  $\text{cm}^2$ , the unit of specific conductance will be  $\text{ohm}^{-1} \text{cm}^{-1}$ ,  $\Omega^{-1} \text{cm}^{-1}$  or mho  $\text{cm}^{-1}$ . In SI system, the units of specific conductance are  $\text{Sm}^{-1}$  where S stands for Siemen.

The equation (2) mentioned above is also applicable for solution of an electrolyte i.e. electrolytic conductor. The specific conductance of an electrolytic solution is defined as the conductance that is observed when two electrodes each of 1 sq. cm in cross-sectional area are dipped into solution at a distance of 1 cm apart. In other words, specific conductance is the conductance per c.c. solution of the electrolyte. It is denoted by the symbol  $\kappa$  (kappa). Sometimes  $\kappa_v$  or  $\kappa_c$  is also used, the subscript v or c standing for dilution or concentration, respectively, signifying that  $\kappa$  is dilution or concentration dependent.

#### Equivalent Conductance

Equivalent conductance is the conducting power of all the ions produced by one g-equivalent i.e. one equivalent of an electrolyte in a given solution. The equivalent conductance may, therefore, be defined as the conductance which is observed when two sufficiently large electrodes are dipped into solution at such a distance so as to enclose in between them the entire volume of solution containing one equivalent of the electrolyte. It is denoted by the symbol  $\wedge$ .

Let one equivalent of an electrolyte is dissolved in  $V$  mL solution. Then all the ions produced by 1 equivalent of the electrolyte will be present in this  $V$  mL solution. So, the conductance of this  $V$  c.c. solution will be the equivalent conductance of the electrolyte i.e.

$$\wedge_{\text{eq}} = \text{Conductance of } V \text{ c.c. solution containing one equivalent of the dissolved}$$

$$\begin{aligned}
 & \text{electrolyte.} \\
 & = \text{Conductance of 1 c.c solution} \times V \\
 & = \kappa \times V \quad \dots\dots(3a)
 \end{aligned}$$

Where  $v$  = volume of solution in c.c containing 1 equivalent of the electrolyte

If  $C$  be the normality of solution i.e. concentration of electrolytic solution in equivalent/L, then

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

$$\therefore \quad \wedge = \frac{1000\kappa}{C} \quad \dots\dots(3b)$$

Unit of  $\wedge$ :  $\text{Ohm}^{-1} \text{cm}^{-1} \times \text{cm}^3$  i.e.  $\text{Ohm}^{-1} \text{cm}^2$  or  $\Omega^{-1} \text{cm}^2$

## Molar Conductance

The recent trend is to describe electrolytic conductance in terms of molar conductance which is defined as the conductance of solution due to all the ions produced by one mole of the dissolved electrolyte in a given solution.

It is denoted by the symbol  $\wedge_m$

$\wedge_m$  and  $\kappa$  are inter-related as

$$\wedge_m = \kappa \times v$$

$$\Rightarrow \quad \wedge_m = \frac{1000\kappa}{C} \quad \dots\dots(4)$$

Where  $v$  = Volume of solution in c.c. containing one mole of the electrolyte and

$C$  = Concentration of solution in mole  $\text{L}^{-1}$  i.e. molarity

The above inter-relationship may also be expressed as

Unit of  $\wedge_m$ :  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

In SI system it is  $\text{S m}^2 \text{mol}^{-1}$

### Relation between $\phi$ and $\phi_m$ ;

$$\wedge_m = n \text{ factor} \times \wedge_{eq}$$

Where  $n$  = n-factor of the electrolyte = total charge carried by either ion =  $\frac{M}{E}$

## 11. Variation of Conductance with Dilution :

Upon dilution i.e. lowering concentration, specific conductance decreases while equivalent and molar conductances increase. At infinite or almost zero concentration equivalent conductance and molar conductance attain their respective limiting values called equivalent conductance at infinite dilution ( $\wedge^\infty$ ) or zero concentration ( $\wedge^0$ ) and molar conductance at infinite dilution ( $\wedge_m^\infty$ ) or zero concentration ( $\wedge_m^0$ ), respectively. The increase of  $\wedge_{eq}$  or  $\wedge_m$  with dilution of a weak electrolyte is attributable to increase of degree of dissociation with dilution resulting into more number of ions in solution. Note that ions are carriers of electricity. The increase of  $\wedge_{eq}$  and  $\wedge_m$  of a strong electrolyte which remains completely ionised at all dilutions, is attributed to increase in the ionic mobilities of ions due to decrease in inter-ionic attraction. As dilution approaches infinity, the degree of dissociation of weak electrolyte approaches unity, the number of ions becomes maximum and hence  $\wedge_{eq}$  as well as  $\wedge_m$  approach their respective maximum value. In the case of strong electrolyte, however, the maximum value of  $\wedge_{eq}$  or  $\wedge_m$  is attained due to the maximum ionic mobilities of the ions since at infinite dilution the dissociation of strong electrolyte is complete and inter-ionic attraction ceases to exist completely.



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The decrease in  $\kappa$  may also be explained in the following way: Upon dilution the number of ions, in the case of weak electrolyte, increases but volume of solution also increases. The increase of volume is in greater proportion than the increase of number of ions resulting into decrease in number of ions per c.c. solution. The specific conductivity being the conductivity of 1 c.c. solution, should obviously decrease.

The variation of molar conductance of a strong electrolyte with concentration is theoretically given by Debye-Hückel-Onsager equation:

$$\Lambda_m = \Lambda_m^0 - (A + B \Lambda_m^0) \sqrt{C}$$

Where A and B are the Debye-Hückel constants depending upon nature of the solvent and temperature and C is the molar concentration of solution.

For aqueous medium at 25°C:

$$\Lambda_m = \Lambda_m^0 - (60.2 + 0.229 \Lambda_m^0) \sqrt{C}$$

According to this equation a plot of  $\Lambda_m$  vs  $\sqrt{C}$  should be a straight line having the slope equal to  $60.2 + 0.229 \Lambda_m^0$  and intercept equal to  $\Lambda_m^0$ . This has been checked in the case of a number of uni-univalent electrolytes and found to be positive for  $C \leq 0.02$  M. At higher concentration, the observed deviation from linearity is attributable to large inter-ionic attraction.

### Determination of Conductance ( $\kappa$ ), $\Lambda_{eq}$ and $\Lambda_m$ )

As already mentioned above

$$\kappa = \text{Observed conductivity} \times \frac{l}{a}$$

For a given conductivity cell in a given experiment,  $\frac{l}{a} = \text{constant called cell constant (x)}$ .

$$\text{Thus, } \kappa = \text{Observed conductance} \times x = \frac{1}{\text{Observed resistance}} \times x$$

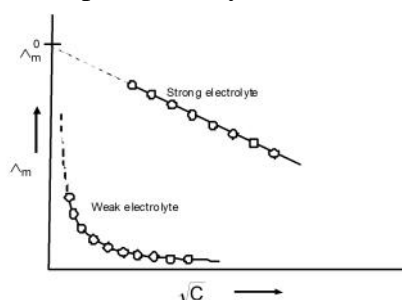
The resistance of a solution is determined by Wheatstone bridge method using a meter bridge the conductivity cell remains dipped in the test solution. The current used is AC.

The specific conductance of 0.1M KCl solution is known. The resistance of 0.1M KCl solution is first determined experimentally and thereby cell constant is calculated. The KCl solution is removed from the cell, it is washed with conductivity water and then filled with test solution. The resistance of the test solution is measured and since cell constant is already known so specific conductance of the test solution can be calculated.

From specific conductance, we determine  $\Lambda_{eq}$  and  $\Lambda_m$  using the equation (3) and equation (4) respectively.

### Determination of $\Lambda_m^0$ or $\Lambda^0$

A plot of  $\Lambda_m$  vs  $\sqrt{C}$  as found experimentally is as shown below graphically.



The  $\Lambda_m$  vs  $\sqrt{C}$  plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus,  $\Lambda_m$  values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\Lambda_m$  values are then plotted against  $\sqrt{C}$  when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects  $\Lambda_m$  axis is  $\Lambda_m^0$  of the strong electrolyte.

However, the plot in the case of weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to  $\Lambda_m$  axis. Hence extrapolation in this case is not possible. Thus,  $\Lambda_0$  of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

**Illustration 25.**

**1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.**

**Solution :**

Given  $l = 2.1$  cm,  $a = 4.2$  sq. cm,  $R = 50$  ohm

Specific conductance,  $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

$$\text{or } \kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductivity =  $\kappa \times V$

$V =$  the volume containing 1 g equivalent = 1000 ml

$$\begin{aligned} \text{So } \text{Equivalent conductivity} &= 0.01 \times 1000 \\ &= 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1} \end{aligned}$$

**Illustration 26.**

**Specific conductance of a decinormal solution of KCl is  $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of a cell containing the solution was found to be 56. What is the cell constant?**

**Solution :**

We know that

Sp. conductance = Cell constant  $\times$  conductance

$$\begin{aligned} \text{or } \text{Cell constant} &= \frac{\text{Sp. conductance}}{\text{Conductance}} \\ &= \text{Sp. conductance} \times \text{Resistance} \\ &= 0.0112 \times 56 \\ &= 0.6272 \text{ cm}^{-1} \end{aligned}$$

**Illustration 27.**

**The specific conductivity of 0.02 M KCl solution at 25 °C is  $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of this solution at 25 °C when measured with a particular cell was 250.2 ohms. The resistance of 0.01 M  $\text{CuSO}_4$  solution at 25 °C measured with the same cell was 8331 ohms. Calculate the molar conductivity of the copper sulphate solution.**

**Solution :**

$$\text{Cell constant} = \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}}$$

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$$\begin{aligned}
 &= \frac{2.768 \times 10^{-3}}{1/250.2} \\
 &= 2.768 \times 10^{-3} \times 250.2
 \end{aligned}$$

For 0.01 M  $\text{CuSO}_4$  solution

Sp. conductivity = Cell constant  $\times$  conductance

$$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

Molar conductance = Sp. cond.  $\times \frac{1000}{C}$

$$\begin{aligned}
 &= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} \\
 &= 8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}
 \end{aligned}$$

### Illustration 28.

*A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of  $4.5 \text{ cm}^2$  has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.*

**Solution :**

Specific conductance = conductance  $\times$  cell constt.

$$\begin{aligned}
 K &= C \times \frac{l}{A} &= \frac{1}{R} \times \frac{l}{A} &= \frac{1}{250} \times \frac{1.72}{4.5} \\
 & &= 1.5288 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}
 \end{aligned}$$

$$\Lambda_e = K \times \frac{1000}{N} = 1.5288 \times 10^{-3} \times \frac{1000}{0.05} = 30.56 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

## 12. Kohlrausch's Law of Independent Migration of Ions :

Kohlrausch determined  $\Lambda_0$  values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in  $\Lambda_0$  values in each case remains the same .

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

He also determined  $\Lambda_0$  values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in  $\Lambda_0$  values in each case remains the same .

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions . Thus

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0 \quad \dots\dots(5)$$

Where  $\lambda_+^0$  is the contribution of the cation and  $\lambda_-^0$  is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus,  $\lambda_+^0$  is the molar ionic conductance of cation and  $\lambda_-^0$  is the molar ionic conductance of anion, at infinite dilution. The above equation (5) is, however, correct only for binary electrolyte like NaCl,  $\text{MgSO}_4$  etc.

For an electrolyte of the type of  $\text{A}_x\text{B}_y$ , we have :

$$\Lambda_m^0 = x\lambda_+^0 + y\lambda_-^0$$

## Application of Kohlrausch's Law

### (i) Determination of $\Lambda_m^0$ of a weak electrolyte :

In order to calculate  $\Lambda_m^0$  of a weak electrolyte say  $\text{CH}_3\text{COOH}$ , we determine experimentally  $\Lambda_m^0$  values of the following three strong electrolytes :

- (a) A strong electrolyte containing same cation as in the test electrolyte, say HCl
- (b) A strong electrolyte containing same anion as in the test electrolyte, say  $\text{CH}_3\text{COONa}$
- (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\Lambda_m^0$  of  $\text{CH}_3\text{COOH}$  is then given as :

$$\Lambda_m^0 (\text{CH}_3\text{COOH}) = \Lambda_m^0 (\text{HCl}) + \Lambda_m^0 (\text{CH}_3\text{COONa}) - \Lambda_m^0 (\text{NaCl})$$

Proof :

$$\Lambda_m^0 (\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \text{I}$$

$$\Lambda_m^0 (\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots \text{II}$$

$$\Lambda_m^0 (\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \text{III}$$

Adding equation (I) and equation (II) and subtracting (III) from them :

$$\Lambda_{(\text{HCl})}^0 + \Lambda_{(\text{CH}_3\text{COONa})}^0 - \Lambda_{(\text{NaCl})}^0 = \lambda_{(\text{H}^+)}^0 + \lambda_{(\text{CH}_3\text{COO}^-)}^0 = \Lambda_{0(\text{CH}_3\text{COOH})}$$

### (ii) Determination of degree of dissociation ( $\alpha$ ) :

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

### (iii) Determination of solubility of sparingly soluble salt :

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

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

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

### (iv) Determination of ionic product of water :

From Kohlrausch's law, we determine  $\Lambda_m^0$  of  $\text{H}_2\text{O}$  where  $\Lambda_m^0$  is the molar conductance of water at infinite dilution when one mole of water is completely ionised to give one mole of  $\text{H}^+$  and one mole of  $\text{OH}^-$  ions i.e.

$$\Lambda_m^0 (\text{H}_2\text{O}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{OH}^-}^0$$

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Again using the following

$$\Lambda_m = \frac{\kappa \times 1000}{C}, \text{ where } C = \text{molar concentration i.e. mol L}^{-1} \text{ or mol dm}^{-3}$$

$$\Rightarrow \Lambda_m = \frac{\kappa}{C}, \text{ where } C = \text{concentration in mol m}^{-3}$$

Assuming that  $\Lambda_m$  differs very little from  $\Lambda_m^0$

$$\Lambda_m^0 = \frac{\kappa}{C} \Rightarrow C = \frac{\kappa}{\Lambda_m^0}$$

Specific conductance ( $\kappa$ ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation.  $K_w$  is then calculated as:  $K_w = C^2$

### Illustration 29.

*The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm<sup>-1</sup> cm<sup>2</sup> equiv<sup>-1</sup>, respectively at 25 °C. Calculate the equivalent conductance of acetic acid at infinite dilution.*

**Solution :**

According to Kohlrausch's law,

$$\Lambda_{\infty \text{CH}_3\text{COONa}} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} = 91.0 \quad \text{.....(i)}$$

$$\Lambda_{\infty \text{HCl}} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.16 \quad \text{.....(ii)}$$

$$\Lambda_{\infty \text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.45 \quad \text{.....(iii)}$$

Adding equations (i) and (ii) and subtracting (iii),

$$\begin{aligned} \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} \\ = 91.0 + 426.16 - 126.45 \end{aligned}$$

$$\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} = \Lambda_{\infty \text{CH}_3\text{COOH}} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

### Illustration 30.

*A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductance of Na<sup>+</sup> and Cl<sup>-</sup> ions at the same temperature are 43.0 and 65.0 ohm<sup>-1</sup> respectively, calculate the degree of dissociation of NaCl solution.*

**Solution :**

Equivalent conductance of N/10 NaCl solution

$$\begin{aligned} \Lambda_v &= \text{Sp. conductivity} \times \text{dilution} \\ &= 0.0092 \times 10000 \\ &= 92 \text{ ohm}^{-1} \end{aligned}$$

$$\begin{aligned} \Lambda_{\infty} &= \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} \\ &= 43.0 + 65.0 = 108 \text{ ohm}^{-1} \end{aligned}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_{\infty}} = \frac{92}{108} = 0.85$$

**Illustration 31.**

*The specific conductivity of a saturated solution of silver chloride is  $2.30 \times 10^{-6} \text{ mho cm}^{-1}$  at  $25^\circ\text{C}$ . Calculate the solubility of silver chloride at  $25^\circ\text{C}$  ;*

*if  $\lambda_{\text{Ag}^+} = 61.9 \text{ mho cm}^2 \text{ mol}^{-1}$  and  $\lambda_{\text{Cl}^-} = 76.3 \text{ mho cm}^2 \text{ mol}^{-1}$ .*

**Solution :**

Let the solubility of AgCl be  $s$  gram mole per litre

$$\text{Dilution} = \frac{1000}{s}$$

$$\begin{aligned}\Lambda_{\infty \text{AgCl}} &= \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-} \\ &= 61.9 + 76.3 \\ &= 138.2 \text{ mho cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\text{Sp. conductivity} \times \text{dilution} = \Lambda_{\infty \text{AgCl}} = 138.2$$

$$2.30 \times 10^{-6} \times \frac{1000}{s} = 138.2$$

$$\begin{aligned}s &= \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mole per litre} \\ &= 1.66 \times 10^{-5} \times 143.5 \text{ gL}^{-1} \\ &= 2.382 \times 10^{-3} \text{ gL}^{-1}\end{aligned}$$

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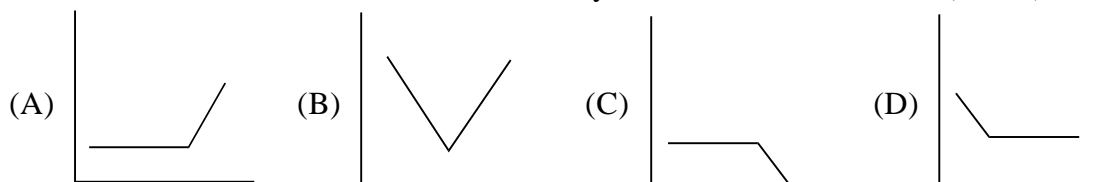
## 6. Daily Practice Problem Sheet

### Conductance (Objective Questions)

- Q.1** The specific conductance of 0.01 M solution of KCl is  $0.0014 \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ . Its equivalent conductance is :  
(A) 14 (B) 140 (C) 1.4 (D) 0.14
- Q.2** The equivalent conductivity of 0.1 N  $\text{CH}_3\text{COOH}$  at  $25^\circ\text{C}$  is 80 and at infinite dilution  $400 \text{ ohm}^{-1}$ . The degree of dissociation of  $\text{CH}_3\text{COOH}$  is :  
(A) 1 (B) 0.2 (C) 0.1 (D) 0.5
- Q.3** The equivalent conductance at infinite dilution of NaCl, HCl and  $\text{CH}_3\text{COONa}$  at 298 K are 126.0, 426.0 and  $91.0 \text{ ohm}^{-1} \text{ cm}^2$  respectively. The value of equivalent conductance of acetic acid at infinite dilution at the same temperature is :  
(A) 644.0 (B) 300.0 (C) 517.0 (D) 391.0
- Q.4** The specific conductance of a salt of 0.01M concentration is  $1.061 \times 10^{-4}$ . Molar conductance of the same solution will be :  
(A)  $1.061 \times 10^{-4}$  (B) 1.061 (C) 10.61 (D) 106.1
- Q.5** At infinite dilution of an electrolyte, the equivalent conductances of cations and anions are :  
(A) independent of each other (B) interdependent of each other  
(C) dependent on solvent molecules (D) dependent on charge carried by ions
- Q.6** The specific conductances of a 0.1 N KCl solution at  $23^\circ\text{C}$  is  $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of the cell containing solution at the same temperature was found to be 55 ohm. The cell constant will be :  
(A)  $0.142 \text{ cm}^{-1}$  (B)  $0.918 \text{ cm}^{-1}$  (C)  $1.12 \text{ cm}^{-1}$  (D)  $0.616 \text{ cm}^{-1}$
- Q.7** The conductivity of  $0.01 \text{ mol/dm}^3$  aqueous acetic acid at 300 K is  $19.5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  and the limiting molar conductivity of acetic acid at the same temperature is  $390 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . The degree of dissociation of acetic acid is :  
(A) 0.5 (B) 0.05 (C)  $5 \times 10^{-3}$  (D)  $5 \times 10^{-7}$
- Q.8** The ionization constant of a weak electrolyte is  $25 \times 10^{-6}$  while the equivalent conductance of its 0.01 M solution is  $19.6 \text{ S cm}^2 \text{ eq}^{-1}$ . The equivalent conductance of the electrolyte at infinite dilution (in  $\text{S cm}^2 \text{ eq}^{-1}$ ) will be :  
(A) 250 (B) 196 (C) 392 (D) 384
- Q.9** The resistance of 1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant  $1.15 \text{ cm}^{-1}$ . The equivalent conductance (in  $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) of 1 N acetic acid is :  
(A) 4.6 (B) 9.2 (C) 18.4 (D) 0.023
- Q.10** The cell constant of a given cell is  $0.47 \text{ cm}^{-1}$ . The resistance of a solution placed in this cell is measured to be 31.6 ohm. The conductivity of the solution (in  $\text{S cm}^{-1}$  where S has usual meaning) is :  
(A) 0.15 (B) 1.5 (C) 0.015 (D) 150
- Q.11** If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of  $0.4 \text{ cm}^{-1}$  then its molar conductance in  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  will be :  
(A)  $10^4$  (B)  $10^3$  (C)  $10^2$  (D) 10
- Q.12** Which of the following solutions of KCl has the lowest value of specific conductance ?  
(A) 1M (B) 0.1 M (C) 0.01 M (D) 0.001 M
- Q.13** Which of the following solutions of KCl has lowest value of equivalent conductance ?  
(A) 1M (B) 0.1M (C) 0.01 M (D) 0.001 M



- Q.14** Under which of the following conditions, conductance, sp conductance and eq. conductance are all equal ?  
 (A) 1000 cc of solution contains 1 eq. of electrolyte  
 (B) 100 cc of solution contains 1 eq. of electrolyte  
 (C) 10 cc of solution contains 1 eq. of electrolyte  
 (D) 1 cc of solution contains 1 eq. of electrolyte
- Q.15** If  $V$ , in the equation  $\Lambda = \text{sp. cond} \times V$ , is the volume in cc containing 1 eq. of the electrolyte ;  $V$  for a  $N/10$  solution will be :  
 (A) 10 cc (B) 100 cc (C) 1000 cc (D) 10,000 cc
- Q.16** At infinite dilution, the eq. conductances of  $\text{CH}_3\text{COONa}$ ,  $\text{HCl}$  and  $\text{CH}_3\text{COOH}$  are 91, 426 and 391  $\text{mho cm}^2$  respectively at  $25^\circ\text{C}$ . The eq. conductance of  $\text{NaCl}$  at infinite dilution will be :  
 (A) 126 (B) 209 (C) 391 (D) 908
- Q.17**  $\lambda_{\text{CH}_3\text{COOH}} = 20 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$  and  $\lambda_{\text{CH}_3\text{COOH}}^\infty = 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ , then pH of 1 M  $\text{CH}_3\text{COOH}$  solution is :  
 (A) 1.3 (B) 0 (C) 1.7 (D) 4
- Q.18** The equivalent conductivity of 0.1 M weak acid is 100 times less than that at infinite dilution. The degree of dissociation is :  
 (A) 100 (B) 10 (C) 0.01 (D) 0.001
- Q.19** Molar ionic conductivities of a bivalent electrolyte are 57 and 73. The molar conductivity of the solution will be :  
 (A)  $130 \text{ S cm}^2 \text{ mol}^{-1}$  (B)  $65 \text{ S cm}^2 \text{ mol}^{-1}$  (C)  $260 \text{ S cm}^2 \text{ mol}^{-1}$  (D)  $187 \text{ S cm}^2 \text{ mol}^{-1}$
- Q.20** The conductivity of the saturated solution of some bivalent salt XY is  $3.06 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  and its equivalent conductivity is  $1.53 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ . The value of  $K_{\text{sp}}$  of XY is :  
 (A)  $4 \times 10^{-6}$  (B)  $2.5 \times 10^{-9}$  (C)  $2.5 \times 10^{-13}$  (D)  $1 \times 10^{-6}$
- Q.21** The conductivity of 0.25 M solution of univalent weak electrolyte XY is  $0.0125 \Omega^{-1} \text{ cm}^{-1}$ . The value of  $\Lambda_m^\infty$  of XY is  $500 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . the value of Ostwald dilution constant of AB is :  
 (A)  $2.5 \times 10^{-3}$  (B)  $2.5 \times 10^{-4}$  (C)  $2.8 \times 10^{-3}$  (D)  $2.8 \times 10^{-4}$
- Q.22** Equivalent conductance at infinite dilution of  $\text{BaCl}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  aq. solutions are  $x_1$ ,  $x_2$  and  $x_3$  respectively. Equivalent conductance of  $\text{BaSO}_4$  solution is :  
 (A)  $x_1 + x_2 - x_3$  (B)  $x_1 - x_2 - x_3$  (C)  $x_1 + x_2 - 2x_3$  (D)  $x_1 - 2x_2 + x_3$
- Q.23**  $\text{CH}_3\text{COOH}$  is titrated with  $\text{NaOH}$  solution. Which is true statement ?  
 (A) conductance decreases upto equivalence point, after which it increases  
 (B) conductance increases upto equivalence point, after which it decreases  
 (C) conductance first increases (but not rapidly) upto equivalence point and then increases rapidly after equivalence point  
 (D) none of these
- Q.24** If molar conductance at infinite dilution of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$  solutions are  $x_1$ ,  $x_2$  and  $x_3$  respectively, then molar conductance of  $\text{NH}_4\text{OH}$  solution is -  
 (A)  $\frac{x_1 + 2x_2 - x_3}{2}$  (B)  $x_1 + 2x_2 - x_3$  (C)  $\frac{x_1 + x_2 - x_3}{2}$  (D)  $x_1 + x_2 - x_3$
- Q.25** If  $\text{NaOH}$  with  $\text{HCl}$ , variation of conductance y-axis with addition of  $\text{HCl}$  (x-axis) will be :



## SOLVED PROBLEMS

### SUBJECTIVE

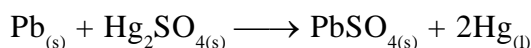
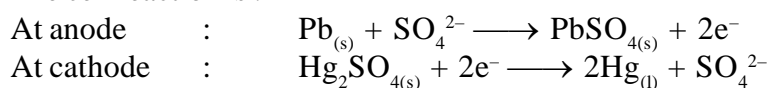
**Problem 1.**

Consider the cell :  $Pb / PbSO_4 / Na_2SO_4 \cdot 10H_2O \parallel Hg_2SO_4 | Hg$

The temperature coefficient of the emf of above cell is  $0.000174V\ deg^{-1}$  and heat of reaction is  $-176.146\ kJ$ . Calculate emf of the cell .

**Solution :**

The cell reaction is :

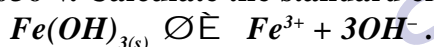


i.e. the number of electrons involved are two, substituting the values of known terms in equation (3)

$$\begin{aligned} -176146\ J &= -(2) (96500\ J\ V^{-1}) E^0 + (298\ K) (96500\ J\ V^{-1}) (2) (0.00174\ VK^{-1}) \\ E^0 &= 0.9645V \end{aligned}$$

**Problem 2.**

The solubility product of  $Fe(OH)_2$  at  $25^\circ C$  is  $10^{-36.4}$  and  $E^0 (Fe^{3+}/Fe) = -0.036\ V$ . Calculate the standard emf of the reaction ,



**Solution :**

The cell can be formed as :  $Fe | Fe^{3+} || OH^- | Fe(OH)_{3(s)} | Fe$

The electrode reactions can be written as :  $Fe_{(s)} \longrightarrow Fe^{3+} + 3e^-$



Overall reaction is i.e., by adding

$$\text{i.e. } E^0 = E^0_{OH^- / Fe(OH)_3 / Fe} - E^0_{Fe^{2+} / Fe}$$

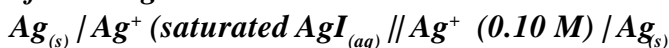
$E^0_{OH^- / Fe(OH)_3 / Fe}$  can be calculated if we know  $E^0$  and  $E^0$  can be calculated as follows

$$E^0 = \frac{0.0591}{0.3} \log 10^{-36.4} = \frac{0.0591 \times (-36.4)}{3} = -0.75V$$

$$E^0_{OH^- / Fe(OH)_3 / Fe} = -0.75 - 0.036 = -0.786V$$

**Problem 3.**

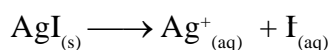
For the following cell :



$E_{cell} = 0.417$ . Calculate  $K_{sp}$  of  $AgI$

$$E^0_{Ag^+ / Ag} = 0.80V$$

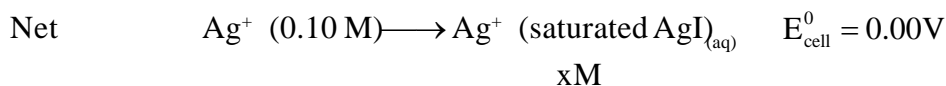
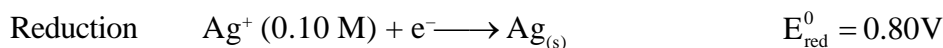
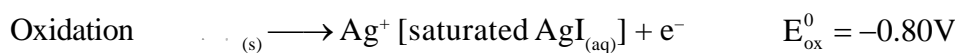
**Solution :**



$$K_{sp} = [Ag^+] [I^-]$$

$$\text{Since } [Ag^+] = [I^-] \quad \therefore K_{sp} = [Ag^+]^2$$

If we manage to calculate  $[Ag^+]$  in saturated in L.H.S. oxidation half cell (anode), then  $K_{sp}$  can be calculated.



$$K = \left( \frac{x}{0.1} \right)$$

$$E_{cell} = 0.417V \text{ (given)}$$

Using Nernst equation  $E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log K$

$$0.417 = 0.00 - \frac{0.0591}{1} \log \left( \frac{x}{0.1} \right)$$

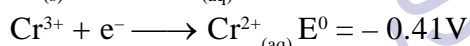
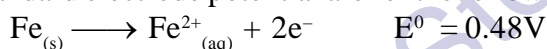
$$\log \left( \frac{x}{0.1} \right) = \frac{0.417}{0.0591} = -7.0558$$

$$x = [Ag^+] \text{ in saturated } AgI = 8.79 \times 10^{-9}$$

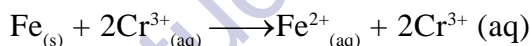
$$K_{sp} = [Ag^+]^2 = (8.79 \times 10^{-9})^2 = 7.73 \times 10^{-17}$$

#### Problem 4.

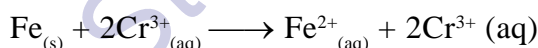
The standard electrode potential are for the following reactions :



If the excess of  $Fe_{(s)}$  is added to a solution in which  $[Cr^{3+}] = 1 M$ , what will be  $[Fe^{2+}]$  when equilibrium is established at 298K ?

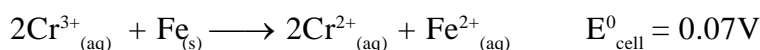
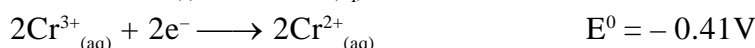
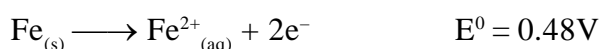


**Solution :**



$$K = \frac{[Fe^{2+}][Cr^{2+}]^2}{[Cr^{3+}]^2}$$

$$K = \frac{x(2x)^2}{[Cr^{3+}]^2} = \frac{4x^3}{(1-2x)^2} \quad x < 0.5$$



When equilibrium is attained  $E_{cell} = 0$

By Nernst equation  $E_{cell} = E_{cell}^0 - \frac{0.0691}{2} \log K$



$$K_{sp} = [Ag^+][Cl^-]$$

$$[Ag^+]_C = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-8}}{x}$$

$$[Cl^-]$$

$$E_{cell} = E_{cell}^0 = \frac{0.0591}{1} \log \frac{[Ag^+]_A}{[Ag^+]_C}$$

$$0.0860 = -0.0591 \log \frac{0.9220x \times 10^{-8}}{1.8 \times 10^{-10}} - \frac{0.0860}{0.0591} = \log 51.22x$$

$$-1.4562 = \log 51.22 + \log x = 1.7095 + \log x$$

$$\log x = -3.1647$$

$$x = 7 \times 10^{-4} M$$

$$[Cl^-] = 7 \times 10^{-4} M$$

**Problem 7.**

*The emf of the cell is 0.788V*

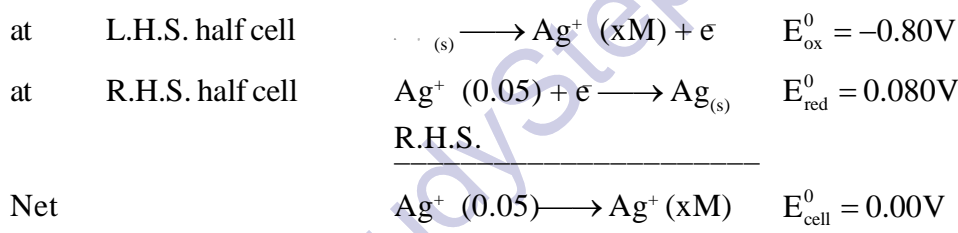
*Ag / AgI, 0.05 M KI // 0.05 M AgNO<sub>3</sub> / Ag*

*Calculate the solubility product of AgI.  $E_{Ag^+/Ag}^0 = 0.80V$*

**Solution :**

KI is strong electrolyte, hence,  $[I^-]_{L.H.S.} = 0.05 M$

AgI<sub>(s)</sub> is sparingly soluble. If we manage to calculate Ag<sup>+</sup> (Ag) in L.H.S., half cell, K<sub>sp</sub> can be calculated.



$$K = \frac{[Ag^+]_{L.H.S.}}{[Ag^+]_{R.H.S.}} = \frac{x}{0.05}$$

$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log K \Rightarrow 0.788 = 0 - \frac{0.0591}{1} \log \left( \frac{x}{0.05} \right)$$

$$\log \left( \frac{x}{0.05} \right) = -13.3333 = 14.66671$$

$$\frac{x}{0.05} = 4.6416 \times 10^{-14}; x = 2.231 \times 10^{-15}$$

$$[Ag^+]_{L.H.S.} = 2.31 \times 10^{-15} M$$

$$[I^-]_{L.H.S.} = 0.05 M$$

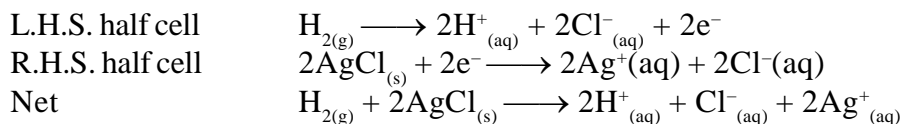
$$K_{sp} = [Ag^+][I^-] = 2.31 \times 10^{-15} \times 0.05 = 1.16 \times 10^{-16}$$

**Problem 8.**

*The emf of the following cell 0.265V at 25°C and 0.2595V at 35°C. Calculate heat of reaction taking place at 25°C. Pt (H<sub>2</sub>) / HCl(aq) // AgCl / Ag*

## ELECTROCHEMISTRY

**Solution :**



$$\Delta H \text{ (heat of reaction)} = nF \left[ T \left( \frac{dE}{dT} \right) - E \right]$$

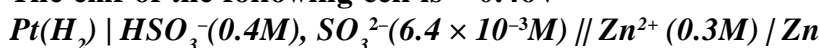
$$\frac{dE}{dT} = \frac{0.2595 - 0.265}{308 - 298} = 5.5 \times 10^{-4}$$

$$n = 2, F = 96500 \text{ C}, E = 0.265 \text{ V at } 298 \text{ K}$$

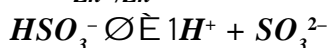
$$= -82777.7 \text{ J} = -82.8 \text{ kJ}$$

**Problem 9.**

**The emf of the following cell is  $-0.46 \text{ V}$**



**If  $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$ , calculate  $\text{pK}_a$  of  $\text{HSO}_3^-$  i.e. for the equilibrium**



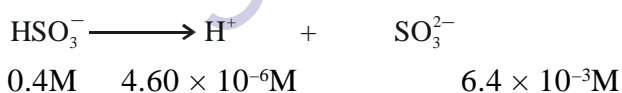
**Solution:**

Half cell	Reaction	$E^0$
L.H.S.	$\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$	$E_{\text{ox}}^0 = 0.00 \text{ V}$
R.H.S.	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	$E_{\text{cell}}^0 = 0.76 \text{ V}$
Net	$\text{Zn}^{2+} + \text{H}_2 \longrightarrow \text{Zn} + 2\text{H}^+$	$E_{\text{cell}}^0 = 0.76 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K$$

$$-0.46 = -0.76 - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{(0.3)}$$

$$[\text{H}^+] = 4.60 \times 10^{-6} \text{ M}$$



$$K = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = \frac{4.6 \times 10^{-6} \times 6.4 \times 10^{-3}}{0.4} = 7.36 \times 10^{-8}$$

$$\text{pK}_a = 7.13$$

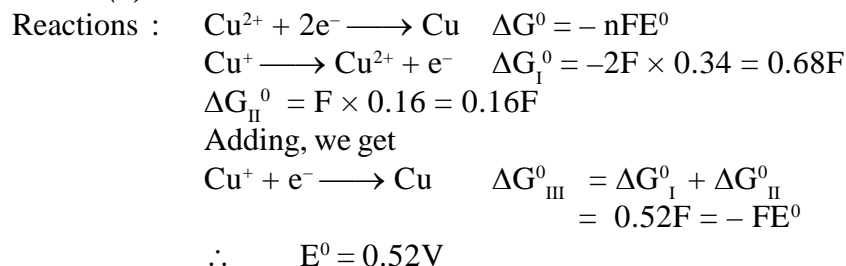
## OBJECTIVE

### Problem 1.

*The standard oxidation potentials of  $\text{Cu}/\text{Cu}^{2+}$  and  $\text{Cu}^+/\text{Cu}^{2+}$  are  $-0.4\text{V}$  and  $-0.16\text{V}$  respectively. The standard electrode potential of  $\text{Cu}^+/\text{Cu}$  would be :*

- (a)  $0.18\text{V}$                       (b)  $0.52\text{V}$                       (c)  $0.82\text{V}$                       (d)  $0.49\text{V}$

**Solution :** (b)

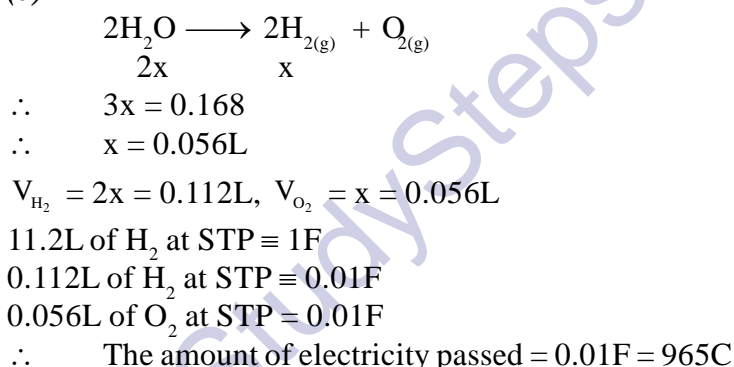


### Problem 2.

*Acidified water is electrolysed using an inert electrode. The volume of gases liberated at STP is  $0.168\text{L}$ . The quantity of charge passed through the acidified water would be :*

- (a)  $96,500\text{C}$                       (b)  $9,650\text{C}$                       (c)  $965\text{C}$                       (d)  $168\text{C}$

**Solution :** (c)



### Problem 3.

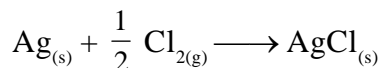
*The useful work done during the reaction  $\text{Ag}_{(\text{s})} + \frac{1}{2}\text{Cl}_{2(\text{g})} \rightleftharpoons \text{AgCl}_{(\text{s})}$  would be*

- (a)  $110\text{kJ mol}^{-1}$                       (b)  $220\text{kJ mol}^{-1}$                       (c)  $55\text{kJ mol}^{-1}$                       (d)  $100\text{kJ mol}^{-1}$

*Given  $E_{\text{Cl}_2/\text{Cl}^-}^0 = 1.36\text{V}, E_{\text{AgCl}/\text{Ag}/\text{Cl}^-}^0 = 0.220\text{V}$  ,  $P_{\text{Cl}_2} = 1\text{atm}$  and  $T = 298\text{K}$*

**Solution :** (a)

For the cell reaction



$$E^0 = -1.14\text{V} \qquad \text{or} \qquad E = E^0 - \frac{0.0592}{1} \log P_{\text{Cl}_2}^{1/2}$$

Under standard conditions,  $P_{\text{Cl}_2} = 1$

$$\therefore \log P_{\text{Cl}_2}^{1/2} = 0$$

$$\therefore \text{Useful work} = -W_{\text{max}} = -nFE = (-1) \times (-1.14) \times 96500 \times 10^{-3} \text{ kJ} = 110 \text{ kJ mol}^{-1}$$



## ELECTROCHEMISTRY

### Problem 4.

A current of 0.250 A is passed through 400 ml of a 2.0 M solution of NaCl for 35 minutes. What will be the pH of the solution after the current is turned off?

- (a) 12.98                      (b) 12.13                      (c) 10.48                      (d) 9.24

**Solution :** (b)

After electrolysis aqueous NaCl is converted into aqueous NaOH.

$$\begin{aligned}\text{The quantity of electricity passed} &= \frac{0.250 \times 35 \times 60}{96500} F \\ &= 5.44 \times 10^{-3} F\end{aligned}$$

The number of equivalents of OH<sup>-</sup> ion formed =  $5.44 \times 10^{-3}$

$$\therefore \text{Molarity of NaOH} = \frac{5.44 \times 10^{-3}}{0.4L} = 1.36 \times 10^{-2}$$

$$\therefore \text{pOH} = -\log (1.36 \times 10^{-2}) = 1.87$$

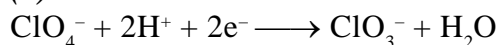
$$\therefore \text{pH} = 12.13$$

### Problem 5.

How much charge should be supplied to a cell for the electrolytic production of 245 gm NaClO<sub>4</sub> from NaClO<sub>3</sub> if the anode efficiency for the required reaction is 60%?

- (a)  $6.43 \times 10^5 C$                       (b) 6.67F                      (c)  $6.43 \times 10^6$                       (d) 66.67F

**Solution :** (a)



$$\text{Number of equivalents of NaClO}_4 = \frac{245}{61.25} = 4 \equiv 4F$$

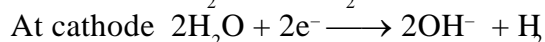
$$\text{No. of Faradays} = \frac{4 \times 100}{60} = 6.67F = 6.43 \times 10^5 C$$

### Problem 6.

The volume of gases liberated at STP when a charge of 2F is passed through aqueous solution of sodium phosphate, is :

- (a) 11.2L                      (b) 44.8L                      (c) 33.6L                      (d) 22.4L

**Solution :** (c)



After passage of 2F, one mole of H<sub>2</sub> and 1/2 mole of O<sub>2</sub> would be produced. The total volume is 33.6L.

### Problem 7.

Specific conductance of 0.01 M KCl solution is  $x \text{ ohm}^{-1} \text{ cm}^{-1}$ . When conductivity cell is filled with 0.01 M KCl the conductance observed is  $y \text{ ohm}^{-1}$ . When the same cell is filled with 0.01 M H<sub>2</sub>SO<sub>4</sub>, the observed conductance was  $Z \text{ ohm}^{-1} \text{ cm}^{-1}$ . Hence specific conductance of 0.01 M H<sub>2</sub>SO<sub>4</sub> is :

- (a)  $xz$                       (b)  $\frac{z}{xy}$                       (c)  $\frac{xz}{y}$                       (d)  $\frac{xy}{z}$

**Solution :** (c)

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}} = \frac{x}{y} \text{ cm}^{-1}$$

Specific conductance of 0.01 M H<sub>2</sub>SO<sub>4</sub>

$$= \text{Observed conductance} \times \text{Cell constant} = z \times \frac{x}{y} \text{ ohm}^{-1} \text{ cm}^{-1}$$

**Problem 8.**

*Among the cation  $H^+$ ,  $Li^+$ ,  $Na^+$  and  $K^+$ , the one with highest ionic mobility and another with lowest ionic mobility respectively are :*

- (a)  $[H^+, K^+]$                       (b)  $[K^+, H^+]$                       (c)  $[Li^+, Na^+]$                       (d)  $[H^+, Li^+]$

**Solution :** (d)

$H^+$  ion has the maximum ionic mobility which is explainable by Grothus mechanics,  $Li^+$  having the maximum charge density, is the most hydrated ion among the lot and hence the lowest ionic mobility.

**Problem 9.**

*The specific conductance has the unit :*

- (a)  $ohm^{-1} cm^{-1}$                       (b)  $ohm.cm$                       (c)  $ohm cm^{-1}$                       (d)  $ohm^{-1}.cm$

**Solution :** (a)

$$\text{Specific conductance} = \text{Observed conductance} \times \frac{\lambda}{a}$$

$$= ohm^{-1} \times \frac{cm}{cm^2} = ohm^{-1}.cm^{-1}.$$

**Problem 10 :**

*The specific conductivity of solution depends upon :*

- (a) Number of ions as well as mobility of ions  
(b) Number of ions per c.c solution  
(c) Number of ions per cc as well as mobilities of ions  
(d) Mobilities of ions only

**Solution :** (c)

Specific conductance is the conductance per c.c. solution

## ANSWERS

### 1. Daily Practice Problem Sheet

1. At cathode = Na, at anode =  $Cl_{2(g)}$
2.  $5.61 \times 10^{19}$  molecules                      3. 6.06 litre
4. (i)  $H_2$  at cathode,  $Cl_2$  at anode                      (ii)  $H_2$  at cathode,  $O_2$  at anode  
(iii) Na at cathode,  $Cl_2$  at anode                      (iv) Ag at cathode,  $Ag^+$  at anode
5.  $1.93 \times 10^6$  coulomb, 800 g NaOH, 246 l
6. (i) increase (ii) No, (iii) No, (iv) No
7. 60%                      8. 16495.7 C
9. R-R and  $CO_2$  at anode  $H_2$  at cathode                      10. 1.762 lire
11. (i)  $H_2$  at cathode,  $O_2$  at anode                      (ii) Cu at cathode,  $Cu^{+2}$  at anode
12.  $V_{H_2} = 188.2$  ml,  $V_{O_2} = 94.1$  ml

**ELECTROCHEMISTRY**

**2. Daily Practice Problem Sheet**

1. (i)  $H_2$  at cathode,  $O_2$  at anode (ii)  $H_2$  at cathode,  $H_2S_2O_8$  at anode
2. (a) (i) Cu at cathode,  $O_2$  at anode (ii)  $Ag^+$  at anode, Ag at cathode  
(b) (i) Ag at cathode,  $O_2$  at anode (ii)  $Cu^{+2}$  at anode, Ag at cathode
3.  $[Cu^{+2}] = 0.988 M$ ,  $[SO_4^{-2}] = 1 M$ , No change in concentration
4. (i) 8.61 amp (ii)  $2.87 \times 10^{-4}$  amp, (iii) 2.4 A
5. 93.75 seconds. 6. 3.36g, 3,  $M_2O_3$  7. 0.05 M
8. 315.4 A 9.  $1.17 \times 10^5$  coulomb, 3.41 l 10. 27172 coulomb
11.  $602 cm^2$

**3. Daily Practice Problem Sheet**

1. (a) Q (b) P (c)  $Q \longrightarrow Q^{+n} + ne^-$  (d)  $P^{+m} + me^- \longrightarrow P$   
(e)  $mQ + nP^{+m} \longrightarrow mQ^{+n} + nP$  (f)  $E_{cell} = E_{cell}^0 - \frac{0.059}{mn} \log \frac{[Q^{+n}]^m}{[P^{+m}]^n}$
2. (a) 0.47 V (b) 0.78 V (c) -0.33 V (d) 0.78 V  
(e) 0.34 V (f) .44 V (g) .268 V (h) -0.737 V  
(i) 0.198 V (j) -0.07V
3.  $3 \times 10^{-2} M$  4. 0.81V 5. 0.55 V
6. (i) 0.32 V (ii) 0.46 V (iii) 0.12 V (iv) 0.656 V  
(v) 0.114V (vi) 1.1 V (vii) 0.926 V (viii) 0.008 V
7. (i) 0.699 V (ii) .463 V
8. (i) Anode-Cu, Cathode-Ag (ii) 0.46 V (iii) 0.342 V
9. (i)  $Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$  (ii) 1.1 V  
(iii)  $[Cu^{+2}] > 5.15 \times 10^{-38} M$
10. (a) 1.2 V (b) More (+) ve 11. 1.07 V
12. (i) standrad (ii) -0.1475 V (iii) standard (iv) 0.0855 V  
(v) standrad (v) -0.59V (vii) -0.755 V (viii) -0.234 V
13.  $2 \times 10^{-7}$  14. pH = 4 15. pH = 1.12 16.  $\frac{[Pb^{+2}]}{[Sn^{+2}]} < 0.458 V$
17. 0.02 18. 0.31 M 19.  $3.33 \times 10^{-4}$  20.  $10^{-4} M$

**4. Daily Practice Problem Sheet**

3. 1.1 V 4. 1.411 V 5. 0.95 V 6. 1.327 V
7. 6.6 8. 9.46, 0.655 V 9. -0.295 V 10.  $5.6 \times 10^{-3} V$
11. 0.0295 V 12. 7.6 13. 0.425 V 14.  $0.96 \times 10^{-7} m$
15. (i) 4.74 (ii) 0.0V (iii) (Anode)<sub>pH</sub> = 4.5752, (cathode)<sub>pH</sub> = 4.9048
16. - 0.076 V

**5. Daily Practice Problem Sheet**

1. A 2. D 3. (i)A, (ii)-A 4. A 5. A 6. A
7. A 8. D 9. C 10. B 11. A 12. C,D

ELECTROCHEMISTRY

- |                             |              |              |                           |              |
|-----------------------------|--------------|--------------|---------------------------|--------------|
| <b>13. B</b>                | <b>14. A</b> | <b>15. A</b> | <b>16. (i) -B (ii)–C,</b> | <b>17. C</b> |
| <b>18. D</b>                | <b>19. A</b> | <b>20. C</b> | <b>21. B</b>              | <b>22. B</b> |
| <b>24. A</b>                | <b>25. A</b> | <b>26. C</b> | <b>27. (i)-A, (ii)-A</b>  | <b>28. D</b> |
| <b>29. (i)–(B) (ii)–(B)</b> | <b>30. B</b> | <b>31. B</b> |                           |              |

**6. Daily Practice Problem Sheet**

- |              |              |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| <b>1. B</b>  | <b>2. B</b>  | <b>3. D</b>  | <b>4. C</b>  | <b>5. A</b>  | <b>6. D</b>  | <b>7. B</b>  |
| <b>8. C</b>  | <b>9. A</b>  | <b>10. C</b> | <b>11. B</b> | <b>12. D</b> | <b>13. A</b> | <b>14. D</b> |
| <b>15. D</b> | <b>16. A</b> | <b>17. A</b> | <b>18. C</b> | <b>19. A</b> | <b>20. D</b> | <b>21. A</b> |
| <b>22. C</b> | <b>23. C</b> | <b>24. A</b> | <b>25. B</b> |              |              |              |

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