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:

Anode : $2\,Cl^- \longrightarrow Cl_{2(g)} + 2e^-$

Cathode : $Na^+ + e^- \longrightarrow Na_{(s)}$

Overall Reaction : $2\,Na^+ + 2Cl^- \longrightarrow 2Na_{(s)} + Cl_{2(g)}$

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:

Cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ or $2H^+ + 2e^- \longrightarrow H_2$

Anode $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ or $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

Overall Reaction $2H_2O \longrightarrow O_2 + 2H_2$

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 Na^+, Cl^- and H_2O. The possible cathode half-reactions are

$$Na^+_{(aq)} + e^- \longrightarrow Na_{(s)} \qquad E^o = -2.71V$$

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad E^o = -0.83V$$

Under standard conditions, you expect H_2O to be reduced in preference to Na^+, which agrees with what you observe. Hydrogen is evolved at the cathode.

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \qquad -E^o = -1.36V$$

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e \qquad -E^o = -1.23V$$

Under standard-state conditions, you might expect H_2O to be oxidized in preference to 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 Cl^-, Cl_2 is the product; but in dilute solution, O_2 is the product. To see this, you would simply apply the Nernst equation of the $Cl^-|Cl_2$ half reaction.

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$$

Starting with very dilute NaCl solutions, you would find that the oxidation potential of Cl^- is very negative, so H_2O is reduced in preference to Cl^-. But as you increase the NaCl concentration, you would find that the oxidation potential of Cl^- increases until eventually Cl^- is oxidized in preference to H_2O. The product changes from O_2 to Cl_2.

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

$$2\,H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad \text{(cathode)}$$

$$2\,Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \qquad \text{(anode)}$$

$$2H_2O_{(l)} + 2Cl^-_{(aq)} \longrightarrow H_{2(g)} + Cl_{2(g)} + 2OH^-_{(aq)}$$

Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is 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 NO_3^-, PO_4^{3-} and 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 = Current in amperes (i) × 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 kg C^{-1}.

1 F of charge = Charge on one mole of electron

$= N_A \times e$

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

$= 96514.8C \approx 96500C$

= 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

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

Now substituting the value of Z in the reaction.

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

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 :

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \text{ of } \frac{Z_1 it}{Z_2 it} = \frac{E_1}{E_2} \quad (\therefore W = Zit)$$

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

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 Faraday = 96500 coulombs

Example 1.

How much electric charge is required to oxidise :

(a) 1 mole of H_2O to O_2 (b) 1 mole of FeO to Fe_2O_3?

Solution :

(a) The oxidation reaction is :

$$\underset{\text{1 mole}}{H_2O} \longrightarrow \tfrac{1}{2}O_2 + \underset{\text{2 mole}}{2H^+ + 2e^-}$$

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

(b) The oxidation reaction is

$$FeO + \tfrac{1}{2}H_2O \longrightarrow \tfrac{1}{2}Fe_2O_3 + H^+ + e^-$$

Q = F = 96500 coulomb

Example 2.

Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing $AgNO_3$, second $CuSO_4$ and third $FeCl_3$ 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,

$$Ag^+ + e^- \longrightarrow Ag$$

1 mole 1 mole

108 g 1 F

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

1 mole 1 mole

63.5 g 2 F

and

$$Fe^{3+} + 3e^- \longrightarrow Fe$$

1 mole 1 mole

56 g 3 F

Hence, Ag deposited = 108 × 0.4 = 43.2 g

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

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

Example 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

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

71.0 g 71.0 g 2 × 96500 coulomb

1 mole

$Q = i \times t = 100 \times 5 \times 60 \times 60$ coulomb

The amount of chlorine liberted by passing 100 × 5 × 60 × 60 coulomb of electric charge.

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

Volume of Cl_2 liberated at NTP = 9.3264 × 22.4 = 208.91 L

Example4.

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 × 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 = 10g, $Z = \frac{35.5}{96500}$, t = 60×60 = 3600 second

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

Example 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 :

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

1 mole 2 × 96500 C

$$Cu \longrightarrow Cu^{2+} + 2e^- \text{ (Anode)}$$

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 × 60 × 60 coulomb

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

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

Example 6.

In a zinc maganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of MnO_2, carbon, NH_4Cl and $ZnCl_2$ in aqueous base.

The cathodic reaction may be represented as

$$2MnO_2(s) + Zn^{2+} + 2e^- \longrightarrow ZnMn_2O_4(s)$$

Let there be 8 g MnO_2 in the cathodic compartment. How many days will the dry cell continue to give a current or 4×10^{-3} ampere.

Solution :

When MnO_2 will be used up in cathodic process, the dry cell will stop to produce current .

Cathodic process :

$$2\overset{+4}{MnO_2}\,(s) + Zn^{2+} + 2e^- \longrightarrow Zn\overset{+3}{Mn_2}O_4$$

$$\text{Equivalent mass of } MnO_2 = \frac{\text{Molecular mass}}{\text{Change in oxidation state}} = \frac{87}{1} = 87$$

From first law of electrolysis,

$$W = \frac{ItE}{96500} \quad \Rightarrow \quad 8 = \frac{4\times10^{-3}\times t\times 87}{96500}$$

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

Example 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_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electro-deposition of copper from copper (II) solution, how many grams of copper will be deposited ?

Anode reaction : $H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

Cathode reaction : $O_2 + 2H_2O + 2e \longrightarrow 4OH^-$

Solution :

From the given reactions, it is obvious that

22.4 litres of H_2 gas require 2 Faraday electricity

$\therefore$ 67.2 litres of H_2 will require = 6 Faraday electricity

$Q = i \times t$

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

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

$w_{cu} = 31.75 \times 6 = 190.5$ 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 Cl_2 would be deposited from molten NaCl in one minute by a current of 300 milliampere ?

Q.3 Calculate the volume of Cl_2 at NTP produced during electrolysis of $MgCl_2$ 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 Cl_2 gas by electrolysing a conc. solution of NaCl. What weight of NaOH and what volume of H_2 at 27ºC 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 RCOONa is electrolised 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 CH_3COONa at 25ºC and 1 atm.

Q.11 Write cell representation & products formed at cathode & anode, when aqueous Na_2SO_4 is electrolysed using :

(i) Pt electrode **(ii)** Cu electrode

Q.12 The same charge is passed through acidulated water and $SnCl_2$ (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 H_2SO_4 is electrolised 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 $CuSO_4$ is carried out using :
(i) Pt electrode **(ii)** Ag as anode and Cu as cathode
(b) When electrolysis of aqueous $AgNO_3$ is done using
(i) Pt electrode **(ii)** Cu as anode & Ag as cathode

Q.3 500 mL of 1 M $CuSO_4$ 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 $[Cu^{2+}]$, and $[SO_4^{2-}]$ 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) H_2 gas at STP at the rate of 1 cc per second
(ii) O_2 gas at STP at the rate of 1 mm^3 per minute
(iii) Cl_2 gas at STP at the rate of 1 dm^3 per hour

Q.5 Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ 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 :

$$5e + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

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 H_2O_2 can be prepared by successive reactions,

$$2NH_4HSO_4 \longrightarrow H_2 + (NH_4)_2S_2O_8$$

$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$$

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 H_2O_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 27ºC. 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^{-1}. Find out the number of coulomb needed to plate an area of 10×10 cm^2 to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte.

Q.11 A current of 40 microampere is passed through a solution of $AgNO_3$ for 32 minutes using Pt electrodes. An 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^{-16} cm^2 ?

ANSWERS

1. Daily Practice Problem Sheet

1. At cathode = Na, at anode = $Cl_{2(g)}$

2. 5.61×10^{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. 1.93×10^6 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

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) 2.87×10^{-4} amp, (iii) 2.4 A

5. 93.75seconds. **6.** 3.36g, 3, M_2O_3 **7.** 0.05 M

8. 315.4 A **9.** 1.17×10^5 coulomb, 3.41 *l* **10.** 27172 coulomb

11. 602 cm^2