As shown in fig 3.2 a solution of 1M $H^+(aq)$ is taken in a beaker at 298 K. In this solution, the platinum strip which is electroplated with platinum black is dipped. This strip is connected with platinum wire in a tube closed at one end. Mercury is added on this wire to keep electrical contact and the other end of the wire is connected outside. Dihydrogen gas at 298 K temperature and 1 bar pressure is passed over the platinum.

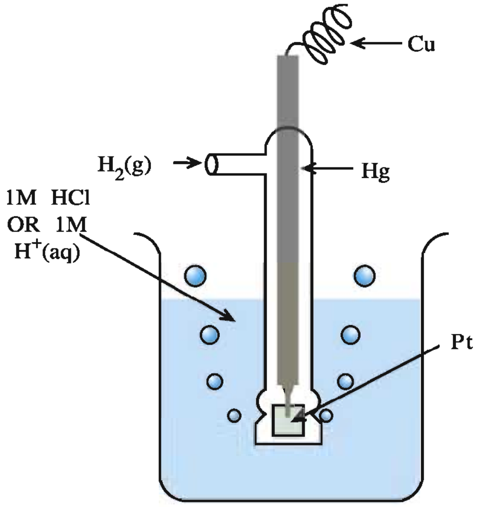

Fig. 3.2 Standard hydrogen gas electrode

When this half cell is connected with other half cell and a complete cell is formed, it acts as cathode or anode. If it acts as cathode, the following reduction reaction takes place on the platinum strip.

$$H^+(aq, 1M) + e^- \rightleftharpoons \frac{1}{2}H_2(g, 1\ bar)$$

But if the standard hydrogen gas electrode acts as an anode the oxidation reaction takes place on the anode as shown below :

$$\frac{1}{2}H_2(g, 1\ bar) \rightleftharpoons H^+(aq, 1M) + e^-$$

Thus, standard hydrogen gas electrode possesses the tendency to receive the electron or to release the electron. The intensity of this tendency is accepted as zero volt at all temperatures. Hence, it is easy to obtain the relative values of intensity of the tendency of receiving the electron or the tendency of releasing the electron. **The relative intensity of tendency of receiving the electron is called reduction potential E_{red} or E^0_{red} and the relative intensity of electrodes for releasing electron is called oxidation potential E_{oxi} or E^0_{oxi}.**

Standard hydrogen electrode works as a reference electrode for other half cells. If the tendency of the other half cell to receive electron is more then standard hydrogen gas electrode acts as an anode and if standard hydrogen gas electrode has more tendency to receive the electron, it acts as a cathode.

Hence, the dependence of another half cell as anode or cathode remains with reference to standard hydrogen electrode, so it is called reference electrode. With reference to standard hydrogen gas electrode, standard Zn-half cell act as anode while standard Cu-half cell act as cathode.

3.4 Cell potential

The electrochemical cell is a device which can transform chemical energy into electrical energy. When two electrodes are joined, then the flow of electrons due to chemical reaction will be from anode to cathode in the external circuit under produced electromotive force. This electromotive force is called cell potential E_{Cell}. If the cell is in standard state, the standard potential is expressed as E^0_{Cell}. The voltage measured with voltmeter is really not the correct potential. **Potentiometer should be used to measure the correct potential.**

The cell potential is in fact the difference between the intensities of receiving electron of each electrode and possess the tendency to release the electron. The proof of this is obtained. From the following experimental results.

(i) $^{\ominus}\ Zn(s) \mid Zn^{2+}(1\,M) \parallel Cu^{2+}(1M) \mid Cu(s)\ ^{\oplus}$

When the above cell is in operation, the following reaction takes place:

$$Zn(s) + Cu^{2+}(aq, 1M) \rightleftharpoons Zn^{2+}(aq, 1M) + Cu(s)$$

Hence n equal to 2

$$E_{Cell} = E^0_{Cell} - \frac{RT}{2F} ln \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 3.17 - \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 3.17 - \frac{0.059}{2} \log \frac{[0.130]}{(0.0001)^2}$$

$$= 3.17 - 0.21 = 2.96 \text{ volt}$$

3.6.1 Concentration Cell :

If the two electrodes of the electrochemical cell are same but the concentrations of the solutions of the electrolyte are different, then it is called concentration cell. viz

$Cu(s) \mid Cu^{2+}\ (C_1) \parallel Cu^{2+}\ (C_2) \mid Cu(s)$

The concentrations of ions change in cell reaction of concentration cell as shown below; which is the result of redox reaction. The ions of concentrated solution move towards dilute solution and so this type of cell is called concentration cell.

In this cell for the reaction $\ominus$ $Cu(s) \mid Cu^{2+}(C_1) \parallel Cu^{2+}(C_2) \mid Cu(s)$ $\oplus$, $E^0_{Cell} = 0.0$ volt

Cathode : $Cu^{2+}(C_2) + 2e^- \rightleftharpoons Cu(s)$

Anode : $Cu(s) \rightleftharpoons Cu^{2+}(C_1) + 2e^-$

Cell reaction : $Cu^{2+}(C_2) \rightleftharpoons Cu^{2+}(C_1)$

Generally reduction occurs in concentrated solution and so it will be written on right hand side and will act as cathode. The cell potential of concentration cell is calculated by the following formula.

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n} \log \frac{[C_1]}{[C_2]}$$

Here, $E^0_{Cell} = 0.0$ volt because both the electrodes are same and the values of their standard oxidation and reduction potentials are same but the sign is positive or negative and so its sum will be zero. In both the half cells, concentrations of Cu^{2+} are different, but positive ion is same in the solution. The values of electrode potentials of anode half cell and cathode half cell are same but of opposite signs. Hence, $E^0_{Cell} = 0.0$ volt.

$$E_{Cell} = 0.0 - \frac{0.059}{n} \log \frac{[C_1]}{[C_2]}$$

Example 7 : The standard reduction potential of $Ag^+ \mid Ag$ half cell is 0.80 volt. Calculate the potential of the following given cell at 298 K.

$\ominus$ $Ag(s) \mid Ag^+(0.25M) \parallel Ag^+(0.75M) \mid Ag(s)$ $\oplus$

Solution :

Cathode : $Ag^+\ (0.75M) + e^- \rightleftharpoons Ag(s)$ (Reduction)

Anode : $Ag(s) \rightleftharpoons Ag^+(0.25M) + e^-$ (Oxidation)

Cell reaction : $Ag^+(0.75M) \rightleftharpoons Ag^+\ (0.25M)$

$$\therefore \frac{-0.044}{0.0295} = 1.3010 + 2\log[H^+]$$

$$\therefore -1.491 = -1.3010 + 2\log[H^+]$$

$$\therefore 1.491 + 1.3010 = -2\log[H^+]$$

$$\therefore 1.491 + 1.3010 = 2 \times pH$$

$$\therefore \frac{2.792}{2} = pH$$

$$\therefore pH = 1.396$$

Example 12 : The potential of the given following cell is 0.53 volt. Calculate the ionic product (K_W) of water.

$$\ominus\ Pt \mid H_2(1\ bar) \mid KOH(0.002M) \parallel HCl(0.005M) \mid H_2(1\ bar) \mid Pt\ \oplus$$

Solution :

Cathode : $H^+(0.005M) + e^- \rightleftharpoons \frac{1}{2} H_2(1\ bar)$ (reduction)

Anode : $\frac{1}{2} H_2(1\ bar) \rightleftharpoons H^+(xM) + e^-$ (oxidation)

Cell reaction : $H^+(0.005\ M) \longrightarrow H^+(xM)$

The change is only in concentrations of H^+.

$\therefore E^0_{Cell} = 0.00$ volt in this cell.

The concentration of OH^- in 0.002 M KOH is 0.002 M. In any aqueous solution, existence of H^+ and OH^- is there and the product of their concentration is K_w. Hence, for KOH solution.

$[H^+][OH^-] = K_w$, but $[OH^-] = 0.002$ M

$$\therefore [H^+] \text{ in KOH solution} = \frac{K_W}{(0.002)}$$

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{1} \log \frac{(\text{Concentration } H^+ \text{ in KOH solution})}{(\text{Concentration } H^+ \text{ in HCl solution})}$$

$$0.53 = 0.00 - \frac{0.059}{1} \log \frac{K_W/0.002}{0.005}$$

$$\frac{0.53}{0.059} = -\log\left(\frac{K_W}{0.002 \times 0.005}\right) = -\log K_w + \log(10^{-5})$$

$$8.983 = -\log K_w - 5.0$$

$$\log K_w = -8.983 - 5.0 = -13.983$$

$$\therefore K_w = \text{antilog } \bar{14}.017 = 1.04 \times 10^{-14}$$

This reduction half cells indicate that if 1 mole electrons electric current is passed, 1 mole sodium, $\frac{1}{2}$ mole magnesium and $\frac{1}{3}$ mole aluminium masses will be respectively obtained.

The quantity of electricity passed by 1 mole electrons is called one Faraday. It is expressed as F.

The electric quantity on one electron is 1.602×10^{-19} coulomb

Hence, the electric quantity of one mole of electron is

$$1 \text{ Faraday (F)} = 1.602 \times 10^{-19} \times 6.022 \times 10^{23} \text{ electron mole}^{-1}$$

$$= 96487 \ (\cong 96500) \text{ Coulomb mole}^{-1} \text{ (electron)}$$

In Coulomb unit, 1 Faraday = 96487 coulombs

But generally **96500** coulombs is accepted for calculations.

If I ampere current is passed through electrolytic cell for t seconds, the quantity of electricity Q in coulomb units can be calculated by the following equation.

$$Q = I \times t \ (\ I = \text{electric current in amperes, } t = \text{time in seconds})$$

The amounts of substances liberated at the electrodes depend upon the quantity of electricity passed. If quantity of electricity equal to 1 Faraday is passed then $\frac{1}{n}$ mole substance will be liberated at the electrode; where n is the number of moles of electrons associated with the reaction at the cathode.

Table 3.2 Electricity Quantity and Electrolysis

Sr	Reaction occurring at the electrode	Number of moles of electron	Quantity of electricity (F)	Moles / F
1.	$Ag^+(aq) + e^- \rightarrow Ag(s)$	1	1	1
2.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	2	2	$\frac{1}{2}$
3.	$Al^{3+}(l) + 3e^- \rightarrow Al(s)$	3	3	$\frac{1}{3}$
4.	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	2	2	$\frac{1}{2}$
5.	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	4	4	$\frac{1}{4}$

The efficiency of the electrolytic cell is not always 100 percent. Hence, the efficiency of the cell can be calculated by the following formula.

$$\text{Efficiency of cell (\%)} = \frac{\text{Experimental value of product}}{\text{Theoretical value of product}} \times 100$$

Reaction at cathode : $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

Reaction at anode : $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

The complete equation of these reactions is as follows :

$Zn(Hg) + HgO \rightarrow ZnO(s) + Hg(l)$

The cell potential of this cell is about 1.35 volt and during the whole life of this cell, no ions are produced in the complete reaction.

3.19.2 Secondary cells : The cells which can be regenerated or reproduced are called secondary cells. Lead storage cell and Ni-Cd storage cells are secondary cells.

Lead storage cell : When two or more cells are joined in series to obtain more voltage which can be recharged are called storage cells.

In the construction of this cell, sponge like lead plate and thin plate of lead on which layer of PbO_2 is applied are dipped in 38 % (W/W) concentration sulphuric acid containg vessel. When these two plates are connected by conducting wire the following discharging reactions take place and electric current is produced.

Reaction at cathode : $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Reaction of anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

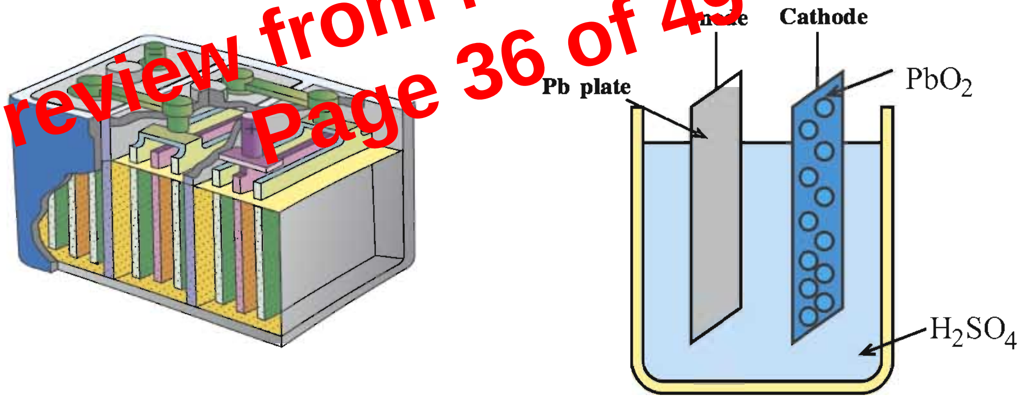

Fig. 3.6 Lead storage battery

$PbSO_4$ produced here remains stuck to the surface of the electrodes. The cell potential of this cell is about 2 volt. When the cell is in operation the density of sulphuric acid solution in reaction decreases. In the beginning the density of the solution is 1.25-1.30 gm ml^{-1} but when cell stops producing electric current, the density of the solution decreases and becomes 1.10-1.15 gm ml^{-1}. If the cell is joined to a high electrical voltage containing any cell and passing the electric curent in opposite direction, the reverse reactions take place on the electrodes and the cell becomes capable to produce electric current again. Even then, the efficiency of the method to regenerate is not 100 %. Hence, at intervals, solution of H_2SO_4 containing 38% (W/W) concentration is to be added. After a long time use, this cell becomes useless. The charging reactions taking place in lead storage cell are as follows :

(5) The electrochemical cell stops working after sometime. Why ?

(A) Increase of temperature

(B) The difference of cell potentials of both electrodes become zero.

(C) By reversing the direction of reaction taking place in the cell.

(D) Due to change in concentration

(6) What is used for the measurement of accurate potential of electrochemical cell ?

(A) Galvanometer (B) Ammeter (C) Voltmeter (D) Potentiometer

(7) If M, N, O, P and Q are in the increasing order of their standard potentials in standard conditions of their standard half cells, then by combination of which two half cells maximum cell potential will be obtained ?

(A) M and N (B) M and Q (C) M and P (D) M and O

(8) E^0_{red} =

(A) E^0_{oxi} (B) $-E^0_{red}$ (C) $-E^0_{oxi}$ (D) E^0_{redox}

(9) What will be the symbolic representation of the cell for the given following reaction :

$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

(A) $^{\ominus}$ Fe(s) | Fe^{2+}(1M) || Cd(s) | Cd^{2+}(1M) $^{\oplus}$

(B) $^{\ominus}$ Cd(s) | Cd^{2+}(1M) | Fe^{2+}(1M) | Fe(s) $^{\oplus}$

(C) $^{\ominus}$ Cd(s) | Cd^{2+}(1M) || Fe(s) | Fe^{2+}(1M) $^{\oplus}$

(D) $^{\ominus}$ Fe(s) | Fe^{2+}(1M) || Cd^{2+}(1M) | Cd(s) $^{\oplus}$

(10) The solution of silver nitrate becomes coloured when pieces of nickel are added to solution of silver nitrate because

(A) Nickel is oxidised (B) Silver is oxidised

(C) Nickel is reduced (D) Silver is precipitated

(11) The values of standard reduction potential of X, Y and Z metals are 0.34 V, 0.80 V and –0.45 V. Mention their order of strength as reducing agent

(A) Z > Y > X (B) Z > X > Y (C) X > Y > Z (D) Y > Z > X

(12) If one mole electrons are passed through solutions of $MgSO_4$, $AgNO_3$ and $AlCl_3$, in what mole ration the metals Mg, Ag and Al will be deposited at the electrodes ?

(A) 1 : 1 : 1 (B) 1 : 2 : 3 (C) 2 : 1 : 3 (D) 3 : 6 : 2

(13) What will be obtained at cathode and anode obtained respectively when electrolysis of aqueous solution of concentrated NaCl, out between graphite electrodes ?

(A) Cl_2 and Na metal (B) H_2 and O_2

(C) Cl_2 and H_2 (D) H_2 and Cl_2

(3) What is electrode ? Write its types and give one example of each.

(4) What is emf series ? Write the information available from it.

(5) Write the reaction of the electrochemical cell formed with the help of $E^0_{Ni^{2+}|Ni} = -0.23$ V, $E^0_{Ag^{+}|Ag} = 0.80$ and give symbolic representation.

(6) H_2 gas is liberated by reaction of Fe with HCl, but H_2 gas is not liberated when Cu reacts with HCl. Explain.

(7) Write usefulness of cell potential.

(8) Write Nernst equation and explain the terms involved in it.

(9) Write laws of Faraday for electrolysis.

(10) Explain the electrolysis of dilute aqueous solution of NaCl between graphite electrodes.

(11) If 1.08 gram Ag is deposited on the cathode when 7.5 ampere current passed through aqueous solution of $AgNO_3$ for 200 seconds, then calculate efficiency. (Ag = 108 u, N = 14 u 0 = 16 u)

(12) The electrolysis of aqueous solution of sodium sulphate is in fact the electrolysis of water. Explain.

(13) Explain Gibbs' free energy and cell potential.

(14) Find the change in free energy and equilibrium constant of an electrochemical cell having standard potentials, cell having

$E^0_{Cu^{2+}|Cu} = 0.34$ V and $E^0_{Fe^{2+}|Fe} = -0.45$ V.

(15) Explain resistivity and specific conductance.

(16) Write the classification of cells which are industrially useful and give example.

(17) Explain Lec Lanche cell.

(18) Write methods of preventing corrosion.

(19) Write reactions of corrosion of iron.

(20) Find the value of E_{Cell} of electrochemical cell.

$Zn(s) \mid Zn^{2+}(0.6M) \parallel Cd^{2+}(0.85M) \mid Cd(s)$.

($E^0_{Zn^{2+}|Zn} = -0.76$ V, $E^0_{Cd^{2+}|Cd} = -0.40$ V)

(3) The values of standard potentials of the half cells, $Sn^{2+} | Sn$ and $Ni^{2+} | Ni$ are –0.14 V and –0.23 V respectively. Calculate the equilibrium constant at 298 K temperature.

(4) The cell potential of the given following cell is 0.52 V at 298 K temperature, calculate the pH of HCl solution ($E^0_{Cu^{2+} | Cu}$ = 0.34 V)

$\ominus$ Pt | H_2(1bar) | HCl (xM) || Cu^{2+}(0.02M) | Cu(s) $\oplus$.

(5) The potential of the given following cell is 0.586 V at 298K temperature, calculate the ionic product (K_w) of water.

$\ominus$ Pt | H_2(1 bar) | NaOH (0.01M) || HCl (0.01M) | H_2 (1 bar) | Pt $\oplus$

(6) How many grams of Cu and what volume of O_2 gas will be obtained if 18.4 ampere electric current is passed through the electrolytic cell of $CuSO_4$ for 1 hour and 42 minutes between graphite electrodes at 298 K temperature and 1 bar pressure ? (Cu = 63.5u O = 16u)

(7) How many amperes of current should be passed when aqueous solutoin of Na_2SO_4 is electrolysed between graphite electrodes at 300 K temperature so, that 250 ml min^{-1} O_2 gas is obtained under 1.0 bar pressure.

(8) How many spoons can be electroplated by silver when 5 ampere current is passed through electrolytic cell of $AgNO_3$ for 2.7 hours ? 0.01 gram Ag layer is deposited on each spoon (Ag = 108 u).

(9) For how much time 48 ampere current should be passed through 400 ml 0.04M $AgNO_3$ solution during electrolysis so that Ag is completely deposited?

(10) How many grams of Cu will be obtained by passing 4.5 ampere current through 1 litre 0.6M $CuCl_2$ aqueous solution by dipping inert electrodes ? What will be the change in concentration ?