UNIT 1

ELECTROCHEMISTRY AND BATTERY CHEMISTRY

PART-A

SHORT QUESTIONS WITH SOLUTIONS

Q1. What is electrochemistry?

Answer :

Electrochemistry is a branch of physical chemistry which deals with the inter-conversion of electrical and chemical energy. The chemical reactions which involve electricity are known as electrochemical reactions.

Basically, the electrochemical reactions are of two types. They are,

(i) Induced electrolytic reactions

(ii) Spontaneous oxidation-reduction reactions.

Q2. What is an electrochemical cell?

Answer :

A device that converts the change in free energy (ΔG) obtained from redox reactions of the electrodes into electrical energy is known as electrochemical cell. Mathematically, it is expressed as,

$$\Delta G = -nEF$$

Where,

F - Faraday constant = 96485° C

n - Number of moles of electrons in the equation of reaction

E - Potential of cell measured in volts.

Electrochemical cells are of four types. They are,

(i) Voltaic cell or Galvanic cell

(ii) Electrolytic cell

(iii) Concentration cell

(iv) Fuel cell.

Q3. What is e.m.f of an electrochemical cell?

Answer :

Electro Motive Force (EMF) of an electrochemical cell is the algebraic sum of the single electrode potential of the cell. It can be calculated as,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Where,

E_{cell} - E.M.F of an electrochemical cell

E_{right} - Reduction potential of right hand side electrode

E_{left} - Reduction potential of left hand side electrode.

Positive or negative sign depends on the occurrence of reaction on the electrode.

Q4. What do you understand by electrode potential?

Answer :

When a metal is dipped into a solution of its own ions, potential difference is developed at the interface of the metal and solution. This potential difference is known as 'electrode potential'.

It is also defined as the measure of tendency of an electrode to gain or lose electrons.

❖ The tendency of an electrode to lose electrons (or to get oxidized) is known as oxidation potential.

i.e., $M \rightarrow M^{n+} + ne^-$

(Metal (or) Electrode)

❖ The tendency of an electrode to gain electrons (or to get reduced) is known as reduction potential.

i.e., $M^{n+} + ne^- \rightarrow M$

The reduction potential measures the opposite tendency and is numerically equal but, opposite in sign to the oxidation potential. Metal with high oxidation potentials are more reactive and are better reducing agents than those with low oxidation potential.

Q5. Differentiate between a galvanic cell and an electrolytic cell. Give one example for each kind.

Answer :

The differences between galvanic cell and elctrolytic cell are,

	Galvanic Cell		Electrolytic Cell
1	The cells used for generation of electrical energy from chemical reactions are called galvanic cell.	1	The cells used for electrolysis are called electrolytic cells.
2	In galvanic cell, the electrical energy arises due to the decrease in free energy of the chemical reaction taking place in the cell.	2	In electrolytic cell, the electrical energy arises due to decrease in free energy of concentration of the electrolyte.
3	There is net chemical reaction in galvanic cell.	3	There is no net chemical reaction in electrolytic cell.
4	Example: Daniel cell	4	Example: Concentration cell

Q6. Define single electrode potential. How Zn/Zn^{2+} electrode potential is determined?

Answer :

Single Electrode Potential

The electrode potential of a metal measured with respect to a reference electrode in the absence of any additional metal-solution interface is called single electrode potential. It can also be referred as the electronic energy difference between a point present inside a metal of electrode and a point present outside the electrolyte (in which the metal is kept).

Determination of Electrode Potential of Zn/Zn^{2+}

The electrode potential (E°) of zinc can be determined by coupling Zn electrode (Zn is dipped in 1N $ZnSO_4$ solution) with the potential of any other electrode like, calomel electrode as shown in figure (1).

The cell is represented as,

$$Zn \mid ZnSO_4\ (1N) \parallel KCl\ (1N)\ Hg_2Cl_2 \mid Hg$$

The coupled Zn electrode has less reduction potential when compared to electrode potential of calomel electrode (i.e., + 0.2422 V). Here calomel electrode acts as a cathode and the reaction is,

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-$$

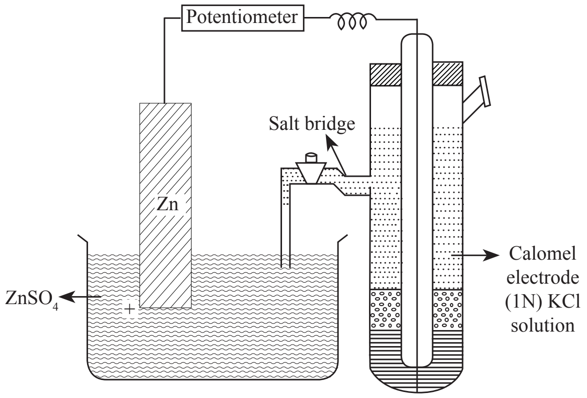


Figure (1): Determination of Electrode Potential of Zinc Electrode

$$E_{cell} = E^\circ_{right} - E^\circ_{left}$$

$$\Rightarrow \quad E_{cell} = E^\circ_{calomel} - E^\circ_{zinc}$$

$$\Rightarrow \quad E_{cell} = E^\circ_{calomel} - E^\circ_{Zn^{2+}/Zn}$$

$$\Rightarrow \quad E^\circ_{Zn^{2+}/Zn} = E_{calomel} - E_{cell}$$

As zinc electrode acts as anode, its oxidation potential is – 0.76 V.

Q7. Define standard electrode potential.

Answer :

The standard electrode potential (E^0) is the electrode potential developed, when the electrode is placed in a solution containing its own ions under standard conditions (i.e., concentration of ionic species = 1 M at a temperature of 298 K).

Q8. What is a reference electrode?

Answer :

Reference electrode is defined as an electrode of standard potential against which other electrode potentials are compared. Hydrogen electrode is the best reference electrode whose electrode potential is taken as zero at all temperatures.

Q9. Represent calomel electrode and write the electrodic reaction for reduction process and mention its S.R.P. value. Dec.-17,Q1

OR

Represent calomel electrode and write the electrodic reaction process and mention the S.R.P. value of the electrode. June/July-15, Q1

Answer :

Calomel electrode is the most commonly used secondary standard reference electrode for potential measurement. It consists of a glass tube containing mercury at its bottom, which is covered by a solid mercurous chloride Hg_2Cl_2 (calomel). The tube is then filled with saturated potassium chloride (KCl). A platinum wire which is used for making electrical contact, is dipped into the mercury layer. A side tube attached to the glass tube provides electrical contact with a salt bridge as shown in figure,

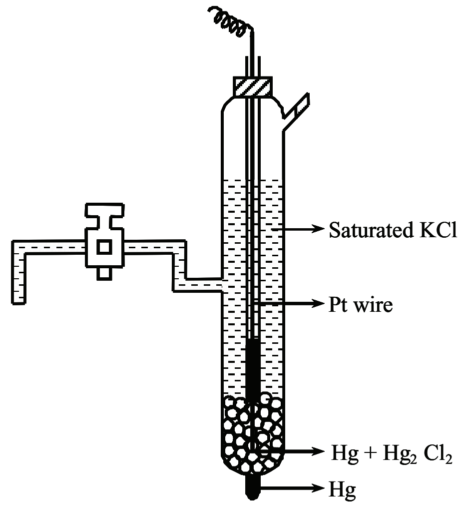


Figure: Saturated Calomel Electrode

The general cell notation of calomel electrode is,

$$Cl^-_{(saturated)},| Hg_2Cl_{2(s)} | Hg_{(l)} | Pt$$

The calomel electrode when combined with standard hydrogen electrode, acts as a cathode (or positive electrode). Thus, reduction reaction takes place in the half cell which is given by,

$$HgCl_2\ (s) + 2e^- \rightarrow Hg(l) + 2Cl^-(aq)$$

And its potential is given by,

$$E = E^0_{cal} - \frac{2.303RT}{2F}.\log[Cl^-]^2 \quad \text{... (1)}$$

Where,

R - Universal gas constant (8.314 J/mole-Kelvin)

T - Temperature (in Kelvin)

F - Faraday's constant (96500 coulombs).

From equation (1), it can be observed that the electrode potential of the calomel electrode depends on the potential (E) concentration of chloride ions (i.e., Cl^-). Increase in the concentration of Cl^- decreases the electrode potential (E).

The potential of any electrode can be obtained by combining it with the calomel electrode and measuring the emf of the resulting electrode.

The Standard Reduction Potential (S.R.P) value of a calomel electrode is + 0.26808 V.

Q10. Represent Quinhydrone electrode and write the electrodic reaction for reduction and mention its S.R.P value. June-17, Q2

OR

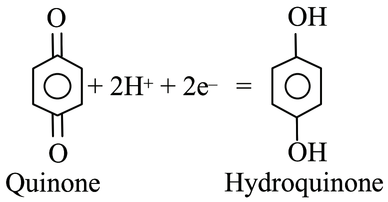
Represent Quinhydrone electrode and write the electrodic reaction for reduction process. April-16, Q1

OR

What is quinhydrone electrode? Write the reduction electrode reaction of it.

Answer : June-11, Q1

Quinhydrone electrode is a secondary standard electrode involving the following reaction between quinone and hydroquinone.



$$Q + 2H^+ + 2e^- = QH_2$$

The electrode has a glass tube containing quinhydrone at its bottom. A platinum strip is immersed in the tube containing quinhydrone at a definite H^+ concentration. This establishes a potential E_Q which is given as,

$$E_Q = E^0_Q - \frac{2.303RT}{2F}\log\left(\frac{[QH_2]}{[Q][H^+]^2}\right)$$

Where,

E^0_Q - Standard potential of the electrode

R - Universal gas constant (8.3141 J/mole-Kelvin)

T - Absolute temperature (in Kelvin)

F - Faraday's constant (96,500 C).

The SRP value of quinhydrone electrode is assumed to be 0.06944 V.

Q11. Derive nernst equation using equation relating ΔG and ΔG°.

Answer : June-14, Q4

Nernst equation is used in calculating the unknown potentials of an electrode.

A general redox-reaction occurring in any electrode is represented as,

$$M^{n+} + ne^- \rightleftharpoons M$$

According to Van't Hoff's reaction isotherm, change in free energy (ΔG) in an electrode potential is given by,

$$\Delta G = \Delta G^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \qquad \text{... (1)}$$

Where,

R - Universal gas constant (8.314 J/mole-Kelvin)

T - Absolute temperature (in Kelvin)

For any reversible reaction,

Change in free energy is,

$$\Delta G = -\,nEF \qquad \text{... (2)}$$

And standard change in free energy is,

$$\Delta G^0 = -\,nE^0F \qquad \text{... (3)}$$

Where,

n - Number of electrons

E - Electrode potential

E^0 - Standard electrode potential

F - Faraday's constant (96500 Coulombs)

Substituting equations (2) and (3) in equation (1), we get,

$$-\,nFE = -\,nFE^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

Dividing both sides by '$-nF$',

$$\therefore \quad E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]} \qquad \text{... (4)}$$

Equation (4) represents the Nernst equaiton.

Q12. Calculate the single electrode potential for zinc metal in contact with 0.01 M zinc sulphate solution at 25^0C. E^0 for Zn is – 0.76 V.

Answer :

Given that,

In an electrolytic cell,

Concentration of zinc sulphate solution, $[Zn^{2+}] = 0.01M$

Temperature of the electrode, $T = 25^\circ C$

Standard electrode potential, $E^0 = -\,0.76$ V

The expression for single electrode potential for a metal in contact with a solution at 25ºC is given by,

$$E = E^0 + \frac{0.0592}{n} \log [M^{n+}]$$

$$\Rightarrow \quad E = -\,0.76 + \frac{0.0592}{2} \log [Zn^{2+}]$$

$$= -\,0.76 + \frac{0.0592}{2} \log [0.01]$$

$$= -\,0.76 + \frac{0.0592}{2} \times -\,2$$

$$= -\,0.76 - 0.0592$$

$$= -\,0.8192$$

$$\therefore \quad E = -0.8192 \text{ V}$$

Q13. What are batteries? Mention their types.

Answer :

Batteries are the electrochemical power sources which convert chemical energy into electrical energy. These are also considered as store houses for electrical energy.

Types

Batteries are generally classified into two types. They are,

(i) Primary battery

(ii) Secondary battery.

Q14. Differentiate primary and secondary battery.

June-17, Q3

OR

Differentiate between primary and secondary battery.

June-14, Q3

OR

Distinguish between primary and secondary batteries.

Answer : Jan.-12, Q2

Primary Battery

In primary battery, the cell reaction cannot be reversed. If the battery has discharged full of its energy, then it cannot be recharged once again (i.e., it becomes dead).

Secondary Battery

In secondary battery, the cell reaction can be reversed. If the battery has discharged full of its energy, then it can be recharged and used through a large number of cycles.

Q15. Write the applications of Lead-acid batteries.

Answer :

The following are the applications of Lead-acid batteries,

(i) Lead-acid battery is used in Uninterrupted Power Supply (UPS), because of its recharging capability.

(ii) These batteries are also used in:

  (a) Automobiles and trains

  (b) Hospitals

  (c) Telephone exchanges

  (d) Gas engine ignition.

Q16. Define fuel cell.

Answer :

A fuel cell is an electrochemical cell, which directly converts the given chemical energy into electrical energy (i.e., without any combustion).

Q17. Write the characteristics of fuel cells.

Answer : June-17, Q4

The important characteristics of fuel cells are,

(i) They should work at high efficiency.

(ii) They should have low emission level and low noise level.

(iii) They should be free from vibration and heat transfer.

(iv) They must not cause thermal pollution.

Q18. Write the advantages of fuel cells?

Dec.-17, Q4

OR

What are the advantages of fuel cells?

Answer : (June-13, Q10 | June-12, Q11(c))

The various advantages of fuel cells are,

1. Fuel cells are highly efficient in converting chemical energy into electrical energy.
2. They offer low levels of emission of gases, noise pollution, vibrations, thermal pollution and heat transfer.
3. Fuel cells work about 72 – 82.5 % better than the other conventional power plants that generate electricity.
4. Low cost fuels can be used with high temperature systems.
5. They offer the best method for the efficient utilization of fossil fuels, thereby saving large quantities of fossil fuels.
6. Parts of fuel cells are exchangeable and maintenance cost is low.
7. The start-up time of low temperature systems is fast.
8. Automatic batteries working through fuel cells render electric vehicles efficient and refillable.

PART-B

ESSAY QUESTIONS WITH SOLUTIONS

1.1 ELECTROCHEMISTRY

1.1.1 Electrochemical Cells – Electrolytic and Galvanic Cells – Notation, Cell Reaction and Cell Potentials

Q19. Explain the concept of electrochemistry.

Answer :

Electrochemistry

For answer refer Unit-1, Q1.

(i) Induced Electrolytic Reactions

Induced electrolytic reactions are the non-spontaneous reactions which convert electrical energy to chemical energy. The equipment used in the conversion phenomenon are known as electrolytic cells.

Example

Passage of electricity through an acidified water yields H_2 and O_2 at different electrodes of the cell.

i.e., $2H_2O \xrightarrow{\text{decomposes}} 2H_2 + O_2$

(ii) Spontaneous Oxidation-Reduction Reactions

Spontaneous redox reactions convert chemical energy to electrical energy. In this process, electricity is produced by the motion of electrons. Hence, it is known as electromotive process and the device used is termed as electrochemical cell.

Example

Galvanic cells, Fuel cells and Batteries.

Applications

The important applications of electrochemistry are,

(i) It is used in the study of many industrial materials.

(ii) Electrochemistry helps in the physiological studies of nerve actions in living systems.

(iii) It is also used in the electrolytic production of metals and their compounds.

Q20. What are concentration cells? Discuss their types.

Answer :

Concentration cell is an electrochemical cell which is a combination of two equivalent half cells of same material, but with different concentrations. The electrical energy produced in the cell is due to the transfer of ions from a solution of higher concentration to a solution of lower concentration. In other words, the voltage developed is due to its attempt to reach equilibrium, which stops when both the half-cells reach the same concentration.

The potential developed at the electrodes is determined using the Nernst equation,

i.e., $$E = E^0 + \frac{2.303RT}{nF}.\log[M^{n+}]$$

Where,

E^0 - Standard electrode potential

R - Universal gas constant

T - Temperature

n - Number of electrons

F - Faraday's constant

$[M^{n+}]$ - Concentration of metal ion.

Types of Concentration Cells

Concentration cells are of two types,

(a) Electrode concentration cells

(b) Electrolyte concentration cells.

(a) Electrode Concentration Cells

In an electrode concentration cell, potential difference is developed between two identical electrodes of different concentrations. These two electrodes are dipped into the same solution of electrolyte.

Example

Two hydrogen electrodes dipped into the same solution of hydrogen ions and maintained at 25ºC with different gas pressures is shown in figure (1). This concentration cell is represented as,

Pt | H_2 (pressure P_1) | HCl | H_2 (pressure P_2) | Pt

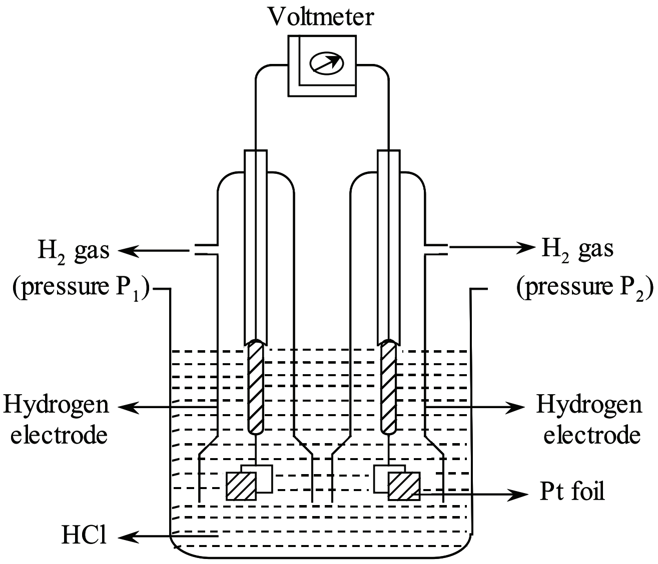


Figure (1): Electrode Concentration Cell

If pressure, p_1 is greater than pressure, p_2. Oxidation takes place at the left electrode and reduction on the right electrode.

Electrode Reactions

At L.H.S : $\frac{1}{2}H_2(P_1) \rightarrow H^+ + e^-$

At R.H.S : $H^+ + e^- \rightarrow \frac{1}{2}H_2(P_2)$

Overall reaction : $H_2(P_1) \rightarrow H_2(P_2)$

i.e., the cell reaction is a spontaneous expansion of H_2 gas from P_1 to P_2.

Emf of the cell, $E_{cell} = E_{oxi} + E_{Red}$

From Nernst's equation,

$$E_{cell} = \left[E^0 - 0.059.\log\frac{[H^+]}{P_1^{1/2}}\right] + \left[E^0 - 0.059.\log\frac{[H^+]}{P_2^{1/2}}\right]$$

As $E^0 = 0$ for concentration cells,

$$E_{cell} = -0.059 \log\frac{[H^+]}{P_1^{1/2}} - 0.059 \log\frac{[H^+]}{P_2^{1/2}}$$

$$= -0.059.\log\frac{[H^+]}{P_1^{1/2}} \times \frac{P_2^{1/2}}{[H^+]}$$

$$= -0.059.\log\left(\frac{P_2}{P_1}\right)^{1/2}$$

$$= \frac{-0.059}{2}\left(\frac{P_2}{P_1}\right)$$

$$\therefore E_{\text{cell}} = -\frac{0.059}{2}\log\frac{P_2}{P_1}$$

(b) Electrolyte Concentration Cells

In electrolyte concentration cells, the electrodes are identical and are immersed into two solutions of same electrolyte with different concentrations. The electrical energy in this cell is due to the tendency of electrons to diffuse from a solution of higher concentration to a solution of lower concentration. The concentration of the cell tends to become equal as the expiry time approaches. Initially, the emf of the cell is maximum which gradually becomes zero.

These cells are represented as,

$M \mid M^{n+}(C_1) \parallel M^{n+}(C_2) \mid M$

Where,

M - Metal

M^{n+} - Metal ion and

Concentration, C_2 > Concentration, C_1

Electrolyte concentration cells are further divided into,

(i) Concentration cell with transference

(ii) Concentration cell without transference.

(i) Electrolyte Concentration Cell with Transference

A cell with a salt bridge or a liquid junction is called as a concentration cell with transference. Salt bridge acts as a medium for transferring ions between two solutions of different concentration as shown in figure (2).

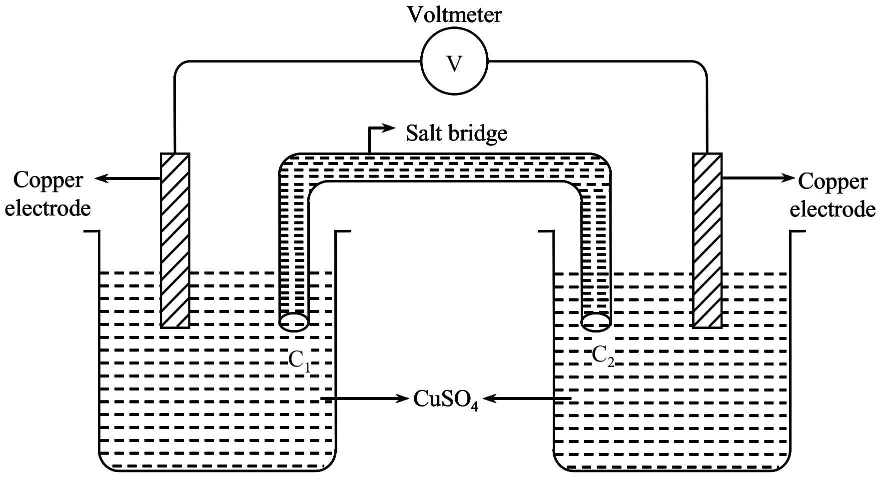


Figure (2): Electrolyte Concentration Cell

Example

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

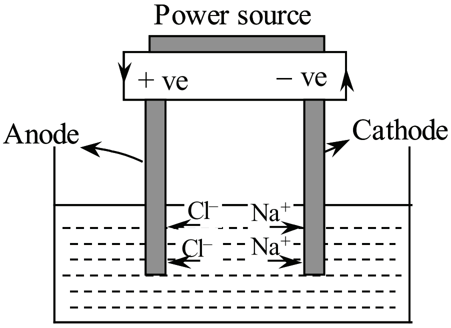
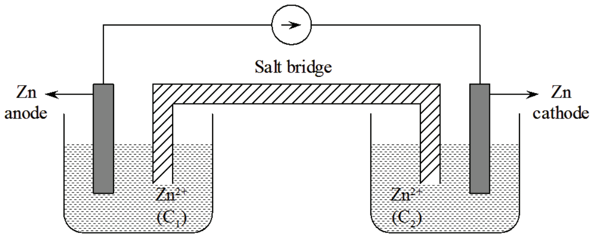
Anode Salt bridge Cathode

(ii) Electrolyte Concentration Cell without Transference

A cell with no salt bridge or liquid junction and no material transfer is called as a concentration cell without transference.

Q21. Differentiate between electrolytic cells and concentration cells with suitable examples.

Answer :

	Electrolytic Cell		Concentration Cell
1.	It is a device used for the decomposition of chemical compounds by using electrical energy.	1.	It is a device which produces an electrical energy.
2.	The diagrammatic representation of an electrolytic cell is shown in figure (1).  **Figure (1): Electrolytic Cell**	2.	The diagrammatic representation of a concentration cell is shown in figure (2).  **Figure (2): Concentration Cell**
3.	In electrolytic cell, both the electrodes are dipped in the same solution of equal concentration.	3.	In concentration cell, both the electrodes are dipped in the same solution of different concentration.
4.	Emf of an electrolytic cell is due to a chemical reaction taking place within the cell.	4.	Emf of as concentration cell is due to the transfer of material from one electrode to the other.
5.	The cell potential (E_{cell}) is calculated using, $E_{cell} = E^0 - \frac{0.0591}{n}.\log\frac{M_2}{M_1}$ Where, E^0 - Standard electrode potential M_2, M_1 - Concentration	5.	The cell potential (E_{cell}) is given by, $E_{cell} = \frac{0.0591}{n}.\log\frac{M_2}{M_1}$ Where, M_2, M_1 - Concentration
6.	No salt bridge is required.	6.	Requires salt bridge for connecting two electrolytes.
7.	In electrolytic cell, negative charge is carried by the cathode and positive charge is carried by anode.	7.	Electrode with lower electrolyte connection acts as the anode and the one with higher electrolyte acts as the cathode.

Table

Q22. Describe the typical galvanic cell and show how the chemical energy is converted into electrical energy.

Answer :

Galvanic Cell

A Galvanic cell is a device which converts the free energy of a chemical process into electrical energy.

Principle

An electrochemical cell consisting of two electrodes, when dipped into an electrolyte solution and connected by a metallic conductor generates an electric current in the external circuit.

Example

Daniel cell is a practical example of galvanic cell.

Daniel Cell Construction

Daniel cell consists of a zinc electrode which is immersed in zinc sulphate solution ($ZnSO_4$) and a copper electrode dipped in copper sulphate solution ($CuSO_4$). The two solutions are kept in two separate containers and are connected by a salt bridge. The salt bridge is a U-tube, filled with either jelly (containing KCl or NH_4NO) or a saturated solution of KCl or NH_4NO. Both the ends of the U-tube are plugged with porous plugs as shown in figure.

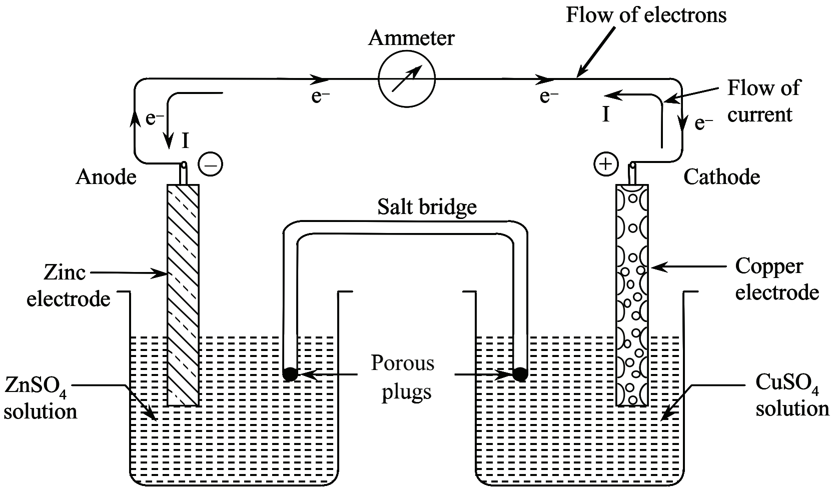


Figure: Daniel Cell

Working

When the zinc and copper electrodes are connected using a metallic conductor, electrons start flowing from zinc to copper. This flow of electrons generates an electric current in the cell. Thus, an oxidation reaction takes place at zinc (anode) whereas the copper electrode (cathode) undergoes a reduction reaction.

Oxidation (At Zinc Electrode)

Zinc goes into the solution as Zn^{++} ions, liberating two electrons.

i.e., $Zn \rightarrow Zn^{++} + 2e^-$

Reduction (At Copper Electrode)

Copper ions from the solution deposit metallic copper on the copper rod by accepting two electrons.

i.e., $Cu^{++} + 2e^- \rightarrow Cu$

Thus, electrons are liberated at the zinc electrode and consumed at the copper electrode. Therefore,when the circuit is closed, electrons flow from zinc to copper electrode through an external wire, thus, producing electrical energy (or) current.

Cell Reaction

At anode, $Zn \longrightarrow Zn^{++} + 2e^-$ (Oxidation)

At cathode, $Cu^{++} + 2e^- \longrightarrow Cu$ (Reduction)

Net reaction: $Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$

Electricity is the flow of electrons and the direction of current is opposite to that of flow of electrons. Therefore, the current direction is from the copper to the zinc electrode.

Q23. What is a single electrode potential? Describe a method for its determination.

Answer :

Single Electrode Potential

For answer refer Unit-1,Q6, Topic: Single electrode potential.

Determination of Single Electrode Potential

There is no direct method to determine single electrode potential i.e., potential of a single electrode. It is measured by combining the single electrode with a universal reference electrode to form a complete cell. After forming a complete cell, potential difference between the reference electrode and single electrode is calculated. The potential of the single electrode can be easily calculated, as the potential of the reference electrode is already known. Standard Hydrogen Electrode (SHE) is the most commonly used reference electrode due to its characteristic of arbitrary zero potential at all the temperatures. Therefore, the potential difference between the electrodes (SHE and single electrode potential) of complete cell equals potential of single electrode because, the potential of reference electrode SHE is already fixed to zero.

Single electrode potential is negative when the electrode reaction involves oxidation. Similarly, it is positive, when the electrode reaction involves reduction.

Q24. Write a note on standard electrode potential. What is its significance?

Answer :

Standard Electrode Potential

For answer refer Unit-1,Q7.

The standard electrode potential E^0 is the electrode potential developed when the electrode (say zinc rod) is placed in a solution containing its own ions (say Zn^{2+}) under standard conditions (i.e., concentration of ionic species = 1 M at a temperature of 298 K).

❖ The $E°$ is referred as oxidation potential, when the oxidation tendency of the metal is high ($M \rightarrow M^{n+} + ne$). It is referred as reduction potential, when the reduction tendency is high ($M^{n+} + ne \rightarrow M$).

The standard oxidation potential of Zn / Zn^{+} is 0.76 V, whereas the reduction potential of Zn^{++} / Zn is – 0.76 V.

❖ Metals with high oxidation potentials are more reactive and are better reducing agents, than those with low oxidation potential. The reduction potential measures the opposite tendency and is numerically equal, but opposite in sign to oxidation potential.

❖ The E^0 values of different electrodes are arranged on hydrogen scale.

Significance of Standard Electrode Potential

While calculating potential difference between an electrode and a solution, it requires an additional electrode and a solution whose potential difference is already known. The additional electrode is used as primary reference electrode i.e., standard electrode potential. It is then combined with other half cell (electrode) to form a voltaic cell. The potential of other electrode is calculated by determining emf of the voltaic cell and then using the relation,

e.m.f of voltaic cell = Potential of SEP ± Potential of unknown electrode

Thus, standard electrode potential plays a very significant role in calculating potential difference between an electrode and a solution.

1.1.2 Types of Electrodes, Calomel, Quinhydrone and Glass Electrodes. Determination of pH of a Solution by Using Quinhydrone Electrode

Q25. What is calomel electrode? Give its reduction half-cell reaction.

Answer : Jan.13, Q4

Calomel Electrode

For answer refer Unit-1, Q9.

Advantages of Calomel Electrode

1. The cell potential of calomel electrode is reproducable.
2. Construction and operation of calomel electrode is very simple.
3. The potential developed in the electrode remains constant for a long duration of time.
4. It is less prone to contamination.
5. Calomel electrode provides better thermal hysteresis than silver/silver chloride electrode.

Disadvantages of Calomel Electrode

1. Calomel electrodes cannot be used above 50ºC, because of the breakdown in mercurous chloride.
2. The use of calomel electrode is limited due to its toxic nature.

Q26. Write a note on Ion selective electrodes.

Answer :

Ion selective electrodes (ISE) are also referred as ion sensitive electrodes. They are membrane electrodes which act as sensors for specific ions dissolved in a solution and converts the activity of these specific ions into electrical potential. This potential is ultimately measured by a pH meter or potentiometer. The potential produced by an ISE is directly proportional to the concentration of the ions. These electrodes though sensitive towards a particular ion(s), can respond to other ions (particularly towards those ions which have similar characteristics like charge, type and chemical nature as that of the selective ion).

ISE consists of an electro conductive thin semi-permeable membrane (ion sensitive membrane) of low soluble solids and semi solids (or polyenes). This membrane separates the internal reference electrode contained in an internal solution from the external solution (test solution). This results in the generation of a potential gradient across the semi-permeable membranes which is determined using Nernst equation (E).

General Principle of Ion Selective Electrode (ISE) Analysis

Ion selective electrode operates on the basis of Nernst principle. This principle gives a logarithmic relationship between the electrical potential developed between an ISE, a reference electrode (immersed in the same solution) and the effective concentration of the ions in the solution.

i.e., $$E = E^0 + \frac{2.303\,RT}{nF} \,.\, \log\,[M]$$

Where,

E - Total electrical potential generated between sensing and reference electrode

E^0 - Standard electrode potential

R - Universal gas constant

T - Absolute temperature

n - Charge on the ion (or number of electrons)

F - Faraday’s constant

$\log\,[M]$ - Concentration of metal ion.

Working of ISE

An ion selective electrode operates on the principle of galvanic cell. It measures the electric potential of a specific ion in the solution and compares this potential with the constant potential of a stable reference electrode. The potential difference between the two electrodes is directly related to the concentration of that specific ion in the solution.

$$E_{ISE} - E_{ref} = E_{cell}$$

Q27. Explain the measurement of pH of a solution using quinhydrone electrode. Mention the advantages and disadvantages of this electrode.

Answer :

Measurement of pH using Quinhydrone Electrode

For answer refer Unit-1, Q10.

If Q and QH_2 are taken in equimolar concentration,

i.e., For $[Q] = [QH_2]$,

$$E_Q = E_Q^0 - \frac{2.303\,RT}{2F} \log\left(\frac{1}{[H^+]^2}\right)$$

Substituting the corresponding values of R and F at 25°C (i.e., for $T = 25 + 273 = 298$ K),

$$\Rightarrow \quad E_Q = E_Q^0 - 0.05915 \log[H]$$

The standard electrode potential (E_Q^0) is assumed to be equal to 0.06944.

$$\therefore \quad E_Q = 0.6944\text{ V} - 0.0592\text{ VpH} \quad (\because \log[H] = \text{pH})$$

The potential thus developed is measured against a calomel or hydrogen electrode.

Figure illustrates the setup used in determining pH of a solution using quinhydrone and a reference electrode (Calomel electrode).

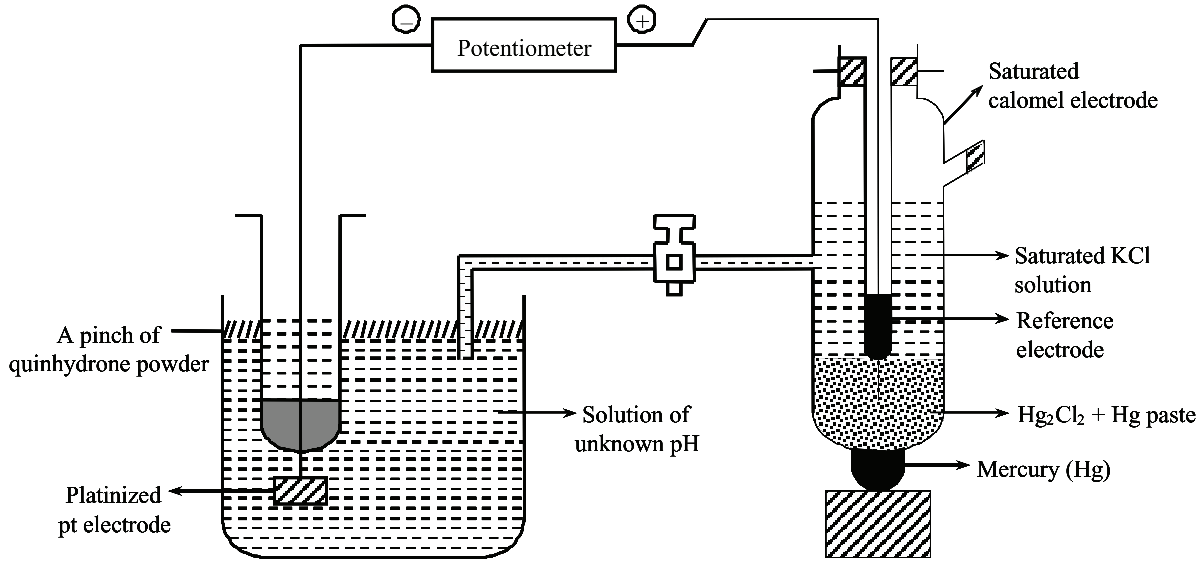


Figure: Determination of pH using Quinhydrone and Calomel Electrode

This complete cell is represented by,

$$^{-}\text{Pt} \mid H_2Q, Q, H^+ \text{ (unknown)} \parallel \text{KCl (satd)}, Hg_2Cl_2\text{ (s)} \mid Hg^+$$

$$\therefore \quad E_{\text{cell}} = E_{\text{calomel}} - E_{\text{quinhydrone}}$$

$$= 0.2422\text{ V} - (0.6994\text{ V} - 0.0592\text{ VpH}) \qquad (\because E_{\text{calomel}} = 0.2422\text{ V})$$

$$\therefore \quad \text{pH} = \frac{0.6994\text{ V} - 0.2422\text{ V} + E_{\text{cell}}}{0.0592\text{ V}}$$

Advantages of Quinhydrone Electrode

(i) Quinhydrone electrode is very easy to setup.

(ii) It is used even if the quantity of solution is less.

(iii) It is also used in the presence of heavier ions or in unsaturated organic substances.

(iv) Reversible equilibrium is achieved rapidly.

(v) The overall resistance of the electrode is less.

(vi) Quinhydrone electrode gives very accurate values of pH.

Disadvantages of Quinhydrone Electrode

(i) Potential value of the electrode is altered due to the changes in the ionic strength.

(ii) It cannot be used in alkaline medium i.e., (pH > 8.5).

(iii) It cannot be used in the presence of oxidizing and reducing agents.

(iv) When the concentration of solution is greater 0.1 M, quinhydrone suffers from salt error defects.

(v) The solution under test gets contaminated.

1.1.3 Thermodynamics of EMF of Cells, Nernst Equation and its Derivation. Applications of Nernst Equation to Electrode Potential and EMF of Cells

Q28. Define the term single electrode potential and derive the Nernst equation.

April-16, Q16(a)

OR

Derive Nernst equation.

June/July-15, Q16(a)

OR

What is nernst equation? Derive it for metal-metal ion electrode.

Jan-12, Q11(a)

OR

Derive the Nernst equation thermodynamically and explain its significance.

Answer : **May/June-12, Q11(b)**

Single Electrode Potential

For answer refer Unit - 1, Q6, Topic: Single electrode potential.

Nernst Equation

For answer refer Unit - 1, Q11.

Nernst Equation for Oxidation Potential

An oxidation reaction is generally expressed as,

$$\mathrm{M} \xrightarrow{\qquad} \mathrm{M}^{n+} + ne^-$$

(Reactant) (Product)

From equation (4),

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

As concentration of metal, $[M] = 1$,

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

(or)

$$\Rightarrow \quad E = E^0_{oxi} - 2.303.\frac{RT}{nF}\log[M^{n+}]_{oxi}$$

Substituting the values of R, F and T (at 25ºC),

$$\Rightarrow \quad E = E^0_{oxi} - \frac{0.0591}{n}.\log[M^{n+}]_{oxi}$$

∴ Nernst equation for oxidation potential is,

$$E = E^0_{oxi} - \frac{0.0591}{n}.\log[M^{n+}]_{oxi} \quad \text{... (5)}$$

Nernst Equation for Reduction Potential

A reduction reaction is generally represented as,

$$\mathrm{M}^{n+} + ne^- \xrightarrow{\qquad} \mathrm{M}$$

[Reactant] [Product]

From equation (4),

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

(or)

$$\Rightarrow \quad E = E^0_{\text{Red}} - 2.303.\frac{RT}{nF}\log\frac{[M]}{[M^{n+}]_{\text{Red}}}$$

As $[M] = 1$,

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

$$= E^0_{\text{Red}} + 2.303.\frac{RT}{nF}.\log[M^{n+}]_{\text{Red}}$$

On substituting the values of R, F and T (at 25ºC), we get,

$$E = E^0_{\text{Red}} + \frac{0.0591}{n}\log[M^{n+}]_{\text{Red}} \quad \text{... (6)}$$

It can be observed from equations (5) and (6) that, the electrode potential increases with increasing concentration of solution $[M^{n+}]$ and temperature (T).

Nernst Equation for emf of the Cell

Emf of a cell is given by,

$$E^0 = E_{\text{oxi}} + E_{\text{red}} \quad \text{... (7)}$$

Substituting equations (5) and (6) in equation (7),

$$E = E^0_{\text{oxi}} - \frac{0.0591}{n}.\log[M^{n+}]_{\text{Red}} + E^0_{\text{Red}} + \frac{0.0591}{n}.\log[M^{n+}]_{\text{Red}}$$

$$E = E^0_{oxi} + E^0_{\text{Red}} + \frac{0.0591}{n}.[\log[M^{n+}]_{\text{Red}} - \log[M^{n+}]_{\text{oxi}}]$$

$$E = E^0 + \frac{0.0591}{n}.\log\frac{[M^{n+}]_{\text{Red}}}{[M^{n+}]_{\text{Oxi}}} \quad (\because E_{\text{Oxi}} + E_{\text{red}} = E^0)$$

$$\text{Emf of a cell, } E = E^0 + \frac{0.0591}{n}.\log\frac{[M^{n+}]_{\text{Red}}}{[M^{n+}]_{\text{oxi}}}$$

Applications

(i) Nernst equation can be used in calculating emf of a cell.

(ii) Electrode potential of unknown metal can be measured using Nernst equation.

(iii) It is also used in predicting the corrosion tendency of metals.

(iv) Nernst equation is used in determining ion concentration and cell potentials at non-standard conditions.

Significance

Nernst equation gives a relation between the electrode potential (E) and the standard potential (E^0).

1.1.4 Numerical Problems

Q29. Calculate the single electrode potential of copper metal in contact with 0.1 molar copper sulphate solution at 25°C. The standard electrode potential for Cu^{+2}/Cu is 0.34 V at 25°C.

Answer :

Given that,

$T = 25°C + 273 = 298$ K

$C_{Cu^{+2}} = 0.1$ M

$n = 2$ (for Cu^{+2} solution)

Standard electrode potential, $E^o = 0.34$ V

$R = 8.314\ JK^{-1}\ mol^{-1}$

$F = 96500$ coulomb mol^{-1}

The expression for single electrode potential is,

$$E = E^o + \frac{2.303RT}{nF}\log C_{Cu^{+2}}$$

$$\Rightarrow \quad E = 0.34\text{V} + \frac{2.303\times8.314\times298}{2\times96500}\log(0.1)$$

$$= 0.31043 \text{ V}$$

∴ Single electrode potential of copper metal in contact with 0.1 M $CuSO_4$ solution is 0.31043 V.

Q30. Calculate single electrode potential of zinc of 0.05 M zinc solution at 25°C.

$\{E^0_{Zn/Zn^{+2}} = 0.763$ volts$\}$.

Answer :

Given that,

In an electrolytic cell,

Concentration of zinc sulphate solution $[Zn^{2+}] = 0.05$ M

Temperature, $T = 25$ºC

Standard electrode potential, $E^0_{Zn/Zn^{+2}} = 0.763$ volts

The expression for single electrode potential at 25ºC is,

$$E = E^0 + \frac{0.0592}{\text{n}}.\log[M^{n+}]$$

$$\Rightarrow \quad E = E^0 + \frac{0.0592\text{ V}}{2}\log[Zn^{2+}]$$

$$= 0.763\text{ V} + \frac{0.0592\text{ V}}{2}\log(0.05)$$

$$= 0.763\text{ V} - 0.0385\text{ V} = 0.7245\text{ V}$$

$$\therefore E = 0.7245\text{ V}$$

Q31. The e.m.f. of a cell consisting of a quinhydrone electrode and a saturated calomel electrode is 0.2640 Volts at 300k, what will be the pH of a solution?

Given $E^0_{SCE} = +0.242$ V and $E^0_{(CH+Q.QH_2)} = +0.6996$ V

Answer :

Given that,

For an electrochemical cell,

E.M.F of the cell, $E = 0.2640$ V

Standard potential of calomel electrode, $E^0_{SCE} = 0.242$ V

Standard potential of quinhydrone electrode,

$$\overset{\circ}{E}_{(CH^+,\, Q,\, QH_2)} = +0.6996 \text{ V}$$

The complete cell reaction is represented as,

Hg, Hg_2Cl_2(s), KCl (satd) || H^+ (unknown), Q, QH_2, Pt.

EMF of a cell is given by,

$$E = E_{\text{right}} - E_{\text{left}} \quad \text{... (1)}$$

Where,

E_{right} - refers to quinhydrone electrode

E_{left} - refer to calomel electrode

Substituting corresponding values in equation (1),

$$0.2640 = 0.6996\text{ V} - 0.0591\text{pH} - 0.242\text{ V}$$

$$\text{pH} = \frac{0.6996 - 0.242 - 0.2640}{0.0591}$$

$$= 3.276$$

$$\therefore \quad \text{pH} = 3.276.$$

Q32. The electrolytic conductivity of a 0.1N acetic acid solution at 291K is 0.000471 S.cm^{-1} and that of a 0.001N Sodium acetate solution is 0.000781S.cm^{-1}. What are the equivalent conductivities of acetic acid and sodium acetate?

Answer :

Given that,

For an electrolytic solution,

Electrolytic conductivity (or) specific conductivity of acetic acid solution, $k_1 = 0.000471$ S.cm^{-1}

Concentration of the solution, $C_1 = 0.1$ N

Electrolytic conductivity of sodium acetate solution, $k_2 = 0.000781$ S.cm^{-1}

Concentration of the solution, $C_2 = 0.001$N

Then, the expression for equivalent conductivity of acetic acid solution is given by,

$$\lambda_{eq} = \frac{k_1 \times 1000}{C_1}$$

$$= \frac{0.000471 \times 1000}{0.1}$$

$$= 4.71$$

$\therefore$ λ_{eq} of acetic acid solution = 4.71 S.cm^2 eq^{-1}

The expression for equivalent conductivity of 0.001N sodium acetate solution is given by,

$$\lambda_{eq} = \frac{k_2 \times 1000}{C_2}$$

$$= \frac{0.000781 \times 1000}{0.001}$$

$$= 781$$

$\therefore$ λ_{eq} of sodium acetate solution = 781 S.cm^2 eq^{-1}.

Q33. Calculate the e.m.f of the following cell at 25ºC.

$$\mathbf{\begin{matrix}Zn\\(m)\end{matrix}\left|\begin{matrix}Zn^{2+}\\(e = 0.1m)\end{matrix}\right|\left|\begin{matrix}Cu^{2+}\\(e = 0.001m)\end{matrix}\right|Cu\,(m)}$$

$$\mathbf{(E^o{}_{Zn^{2+}/Zn} = -\,0.76\ V,\ E^o{}_{Cu^{2+}/Cu} = +\,034\ V)}$$

Answer : **April-16, Q11(a)**

Given representation of an electrolytic cell is,

$$Zn_{(s)} / Zn^{2+}(0.1M) // Cu^{2+}(0.001M) / Cu_{(s)}$$

Temperature, T = 25ºC

Standard electode potential of Zinc,

$$E^o{}_{Zn^{2+}/Zn_{(s)}} = -0.76V$$

Standard electrode potential of Copper,

$$E^o{}_{Cu^{2+}/Cu_{(s)}} = +0.34V$$

The reduction concentration, [Zn^{2+}] = 0.1 M

The oxidation concentration, [Cu^{2+}] = 0.001 M

According to Nernst equation, the e.m.f of a cell is given by,

$$E = E^0 + \frac{0.059}{n}\log\frac{[Mn^+]_{red}}{[Mn^+]_{oxi}}$$

Where,

E^o - Standard electrode potential

n - Number of valence electrons

[Mn$^+$] - Concentration of metal ion

$$\Rightarrow E = \left(E^o{}_{Zn^{2+}/Zn_{(s)}} - E^o{}_{Cu^{2+}+Cu_{(s)}}\right) + \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= (-\,0.76 - 0.34) + \frac{0.059}{2}\log\frac{0.1}{0.001}$$

$$= -\,1.1 + 0.0295 \log 100$$

$$= -\,1.1 + 0.0295\ (2)$$

$$= -\,1.1 + 0.059$$

$$= -\,1.041\ V$$

$\therefore$ E = –1.041 V.

Q34. For the cell reaction Zn(s) + Fe^{2+} = Zn^{2+} + Fe(s). Calculate the reactive concentration of Zn^{2+} and Fe^{2+} at which the overall cell E.M.F. becomes zero.

$$\mathbf{E^o{}_{Fe^{2+}/Fe} = -\,0.440\ V\ and\ E_{Zn^{2+}/Zn} = 0.760\ V}$$

Answer : **June/July-15, Q11(a)**

Given that,

For a cell reaction,

$$Zn(s) + Fe^{2+} \Longrightarrow Zn^{2+} + Fe(s)$$

Single electrode potential of Fe, $E^0(Fe^{2+}/Fe) = -\,0.440$ V

Single electrode potential of Zn, $E^0(Zn^{2+}/Zn) = -\,0.760$ V

Overall emf of the cell, $E_{\text{cell}} = 0$

As $E^0{}_{(Zn^{2+}/Zn)} < E^0{}_{(Fe^{2+}/Fe)}$, the zinc electrode is the left half cell. Thus, the cell can be represented as,

$$Zn/Zn^{2+}(a_1M)\ ||\ Fe^{2+}(a_2M)/Fe$$

The expressions for reduction reactions at the two electrodes are given as,

Cathode : $Fe^{2+} + 2e^- = Fe(s)$

Anode : $Zn^{2+} + 2e^- = Zn(s)$

Overall reaction : $Fe^{2+} + Zn(s) \rightarrow Fe(s) + Zn^{2+}$

The expression for cell potential is given as,

$$E_{\text{cell}} = E^0{}_{\text{cell}} + \frac{2.303RT}{nF}\log\frac{[Zn^{2+}]}{[Fe^{2+}]} \qquad \text{... (1)}$$

Where,

E^0_{cell} - Standard potential of cell,

$= E^0_R - E^0_L$

$= -0.440 - (-0.760)$

∴ $E^0_{cell} = 0.32$

Substituting the corresponding values in equation (1),

$$0 = 0.32 + \frac{2.303RT}{nF}\log\frac{[Zn^{2+}]}{[Fe^{2+}]}$$

Where,

$R = 8.314\ Jk^{-1}\ mol^{-1}$

$F = 96{,}500$ coulomb mol^{-1}

$n = 2$

Therefore at 298° K temperature, equations (2) becomes,

$$0.32 + \frac{2.303(8.314)(298)}{2\times 96.500}\log\frac{[Zn^{2+}]}{[Fe^{2+}]} = 0$$

$$0.32 + \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Fe^{2+}]} = 0$$

$$\Rightarrow \quad \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Fe^{2+}]} = -0.32$$

$$\Rightarrow \quad \log\frac{[Zn^{2+}]}{[Fe^{2+}]} = \frac{-0.32\times 2}{0.0591}$$

$$\Rightarrow \quad \log\frac{[Zn^{2+}]}{[Fe^{2+}]} = -10.829$$

$$\Rightarrow \quad \frac{[Zn^{2+}]}{[Fe^{2+}]} = 10^{-10.829}$$

$$\Rightarrow \quad \frac{[Zn^{2+}]}{[Fe^{2+}]} = 1.482\times 10^{-11}$$

Therefore, relative concentration of Zn^{2+} and Fe^{2+} is equal to 1.482×10^{-11}.

Q35. Write the cell reaction and calculate the emf of the following cell at 25°C.

Zn(s)|Zn^{+2} (0.2 M)||Ag^{+} (0.02 M) | Ag(s).

Given that,

$$E°_{Zn/Zn^{+2}} = +0.76\text{ V and } E°_{Ag/Ag^{+}} = -0.80\text{ V.}$$

Answer : **Jan.-12, Q11(b)**

Given that,

Concentration of Zn = 0.2 M

Concentration of Ag = 0.02 M

Single electrode potential of Zn, $E°_{Zn/Zn^{+2}} = 0.76$ V

Single electrode potential of Ag, $E°_{Ag/Ag^{+}} = -0.8$ V

Cell Reaction

As zinc has weaker reduction potential, so it gets oxidized.

$$Ag^{+1}_{(aq)} + e^- \longrightarrow Ag_{(s)}$$

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + e^-$$

$$\therefore \quad 2\,Ag^{+1}_{(aq)} + Zn_{(s)} \longrightarrow 2\,Ag_{(s)} + Zn^{+2}_{(aq)}$$

Emf of the cell is given by,

$$E = E°_{cell} - \frac{0.059}{2}\log\left[\frac{E°_{Zn/Zn^{+2}}}{E°_{Ag/Ag^{+}}}\right] \quad \text{... (1)}$$

Where,

$E°_{cell}$ - Standard potential of cell

$E°_{cell} = E^o_{Z_n/Z_n^{+2}} - E°_{Ag/Ag+}$

$= 0.76 - (-0.8)$

$\Rightarrow \quad E°_{cell} = 1.56$ V

Substituting the above value in equation (1),

$$E = 1.56 - \frac{0.059}{2}\log\left[\frac{0.2}{0.02}\right]$$

$= 1.56 - 0.0295 \log 10$

$= 1.56 - 0.0295$

$\Rightarrow \quad E = 1.5305$ V

∴ Emf of the cell = 1.5305 V

Q36. Calculate the EMF of a daniel cell at 25°C, when the concentration of ZnSO$_4$ and CuSO$_4$ are 0.001 M and 0.1 M respectively. The standard electrode potential of copper and zinc electrodes are 0.34 V and – 0.76 V respectively.

Answer : **May/June-12, Q16(b)**

Given that,

For a Daniel cell operating at 25°C,

Concentration of $ZnSO_4$, $[Zn^{+2}] = 0.001$ M

Concentration of $CuSO_4$, $[Cu^{+2}] = 0.1$ M

Standard electrode potential of copper, $E^o_{cu} = 0.34$ V

Standard electrode potential of zinc, $E^0_{zn} = -0.76$ V

The complete reaction occuring in Daniel cell is,

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

And the expression for EMF induced in the Daniel cell is given by,

$$E = E° - \frac{0.059}{2}\log\frac{[Zn^{2+}(aq)]}{[Cu^{2}(aq)]} \quad \text{... (1)}$$

Where,

E^0 - Standard potential of cell E^0 is given as,

$$E^0 = E^o_{cu} - E^0_{zn}$$

$$= 0.34 - (-0.76) = 0.34 + 0.76 \text{ V}$$

$$E^0 = 1.1 \text{ V}$$

Substituting the values of E^0, $[zn^{+2}]$, and $[cu^{+2}]$ in equation (1),

$$\Rightarrow \quad E = 1.1 - \frac{0.059}{2} \log \left[\frac{0.001}{0.1}\right]$$

$$= 1.1 - \frac{0.059}{2} \log (10^{-2})$$

$$= 1.1 - \frac{0.059}{2} (-2)$$

$$\Rightarrow \quad E = 1.1 + 0.059$$

$$= 1.159 \text{ eV}$$

$$\therefore \quad E = 1.159 \text{ eV}$$

1.2 BATTERIES

1.2.1 Primary Batteries : Zn-Carbon Battery. Secondary Batteries : Pb-Acid Battery and Li–Ion Battery, Applications

Q37. What are batteries? How are they classified? Write their applications.

Answer :

Batteries

For answer refer Unit-1, Q13.

(i) Primary Battery

A primary battery converts the free energy change (ΔG) of the active material (produced during the electrode process) into the electrical energy. These batteries cannot be recharged and are discarded after their use. In other words, the net cell reaction occurring in the primary battery is irreversible.

Example

Zn – MnO_2 dry cell

Features

- Primary batteries have high energy densities.
- These cells can generate current instantaneously.

(ii) Secondary Battery

A secondary battery is a storage device for electrical energy and is also known as 'Storage battery', 'Galvanic battery' or 'Rechargeable battery'. These batteries can be fully recharged by passing an electrical current through the cell. In other words, the net cell reaction occurring in the secondary battery is reversible.

Examples

Lead-acid battery, Nickel-Cadmium battery.

Features

- Secondary batteries can be recharged fully.
- A significant amount of current can be withdrawn during the discharge process of a secondary battery.
- These batteries have better life cycle and storage capacity than the primary batteries.
- Secondary batteries can be used repeatedly (i.e., over and over again).

Applications

Batteries are used as a source of D.C power where convenience is of major importance and where electrical power is not readily available.

The various applications of batteries are,

1. Batteries are used in industrial and military applications where high reliability and long life are required.
2. These are used for starting aircraft and motor cars.
3. These are also used for train lighting and emergency power supplies.
4. These are used in equipments where standby power is of major concern (such as emergency light, telephone exchange, laptops, cellular phones, electric vehicles and pacemakers).

Q38. What are primary batteries? Explain the construction and working of Zinc-Carbon battery.

Answer :

Primary Batteries

For answer refer Unit-1, Q14, Topic: Primary Battery.

Zinc-Carbon Cell

Zinc-carbon cell (or) Leclanche cell is a primary battery. It consists of zinc anode and manganese dioxide as cathode. Powdered carbon is mixed with manganese dioxide to improve cell conductivity and to retain moisture in the cell. Ammonium chloride dissolved in water is used as electrolyte.

In a modified Leclanche cell, which is a dry cell, a cup shaped zinc container acts as anode and a graphite rod inserted in the centre acts as cathode for the electrolyte. The cathode is surrounded by MnO_2 and a paste of NH_4Cl and $ZnCl_2$. The leakage of the paste is prevented by mixing the paste with starch.

Cell Reaction

When the cell is discharged zinc oxidised and manganese dioxide is reduced.

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

At cathode: $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Overall: $Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \longrightarrow Zn^{2+}(aq) + 2NH_3(aq) + H_2O(l) + Mn_2O_3(s)$

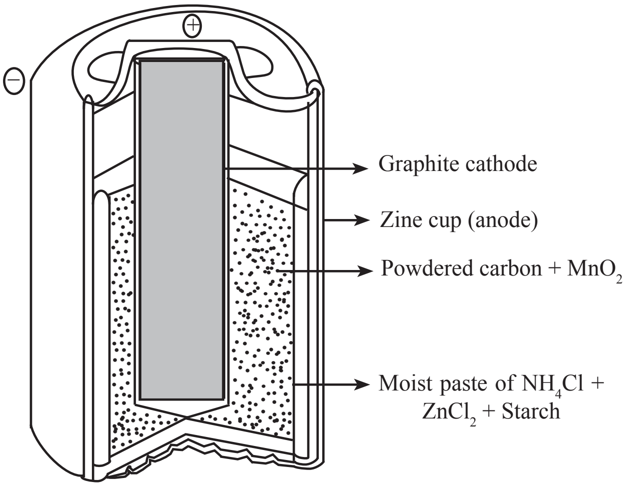


Figure: Interior View of Zinc-Carbon Cell

The cell produces a voltage of about 1.5 V. Zinc carbon battery is non rechargeable.

Merits

(i) Zinc-carbon battery is small, light and portable.

(ii) It has low cost of production.

(iii) These cells have reasonable power density and good shelf life.

Demerits

(i) Continuous use of these cells tends to reduce the output voltage.

(ii) Unused cells lose the capacity with time, as zinc gets dissolved in the electrolyte.

Applications

Zinc-carbon batteries are mostly used in,

1. Flash lights
2. Radios and calculators
3. Portable electronic gadgets etc.

Q39. Write the charging and discharging reactions in lead-acid battery. **Dec.-17, Q3**

OR

Explain lead-acid battery with suitable reactions. **June-17, Q12(a)**

Answer :

Secondary Batteries

For answer refer Unit-1, Q14, Topic : Secondary Battery.

Lead-acid Accumulator (or) Lead-acid Cell

Lead-acid cell is a storage cell which can act as both voltaic cell and electrolytic cell. It gives electrical energy when used as a voltaic cell whereas it acts as an electrolytic cell on its recharge.

Figure below illustrates a diagrammatic representation of a lead-acid cell.

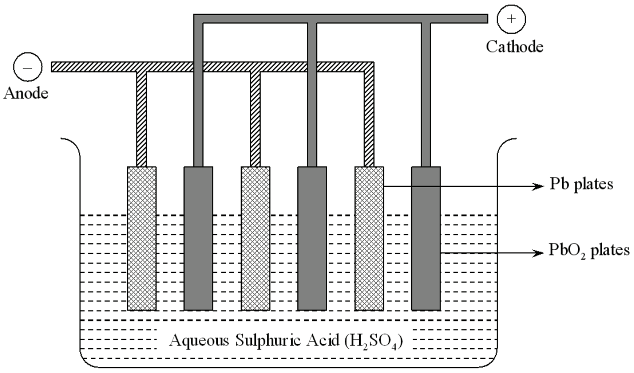


Figure: Lead-acid Cell

The negative pole (anode) of the cell consists of spongy lead and the positive pole (cathode) consists of lead-antimony alloy coated with lead dioxide. A number of pairs (electrode pairs) containing partition between them are dipped in to the electrolyte containing 20% of sulphuric acid (H_2SO_4) with a specific gravity of 1.15 at 25ºC.

Discharging

The various reactions that takes place during discharging of cell are,

At anode: $Pb \rightarrow Pb^{2+} + 2e^-$

$$\frac{Pb^2 + SO_4^{2-} \rightarrow PbSO_4 \downarrow}{Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-}$$

At cathode: $PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$

$$\frac{Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow}{PbO_2 + 4H^+ + 2e^- + SO_4^{2-} \rightarrow PbSO_4 + 2H_2O}$$

∴ The net reaction during discharge is,

$$PbO_2 + Pb + 2H_2SO_4 \xrightarrow{\text{discharging}} 2PbSO_4 + 2H_2O + \text{Energy}$$

During discharging process, the electricity (i.e., electric current) is produced and the concentration of sulphuric acid is decreased. This reduction in concentration of sulphuric acid is replaced by an equivalent quantity of water.

Charging

During charging process, the reaction is reversed. The quantity of water is decreased and the concentration of sulphuric acid increases, thus restoring the original strength of the acid. The various reactions taking place during charging are,

At anode: $PbSO_4 + 2H_2O - 2e^- \rightarrow PbO_2 + 4H^+ + SO_4^{2-}$

At cathode: $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$

∴ The net reaction during charging is,

$2PbSO_4 + 2H_2O + \text{Energy} \rightarrow Pb + PbO_2 + 2H_2SO_4$

Advantages

(i) Lead-acid cell is rechargeable, portable and has low maintenance requirements.

(ii) It is simple to manufacture.

(iii) It is relatively less expensive than other cells.

Disadvantages

(i) The electrolyte (H_2SO_4) used in the cell can cause environmental damage.

(ii) Improper charging of lead-acid cell may lead to thermal runway.

(iii) It cannot be stored in a discharged condition.

Applications

(i) Lead-acid cell is used in Uninterrupted Power Supply (UPS), because of its recharging capability.

(ii) These cells are also used in:

  (a) Automobiles and railway trains

  (b) Hospitals

  (c) Telephone exchanges

  (d) Gas engine ignition.

Q40. What are lithium ion batteries? Explain their advantages and applications. June-17, Q12(b)

OR

Write a note on Lithium-ion batteries. Dec.-17, Q16(b)

(Refer only Lithium-ion Battery)

Answer :

Lithium-ion Battery

A Lithium-ion battery includes the following participants in the electrochemical reactions,

1. Anode
2. Cathode
3. Electrolyte.

Lithium can migrate into or from anode and cathode, as they are being of materials. During insertion, lithium moves into the electrode. During the reverse process i.e., extraction, lithium moves back out. When a lithium-based battery is charging, the lithium is extracted from the cathode and inserted into the anode. When the battery is discharging, the reverse process occurs.

During the charging action,

Cathode Half-Reaction

$$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^-$$

Anode Half-reaction

$$xLi^+ + xe^- + 6C \rightleftharpoons Li_xC_6$$

In the net chemical reaction, over-discharge supersaturation lithium cobalt oxide leading to the production of lithium oxide as,

$$Li^+ + LiCoO_2 \rightarrow Li_2O + CoO$$

In the above case, if the overcharge is upto 5.2 V leads to the synthesis of cobalt oxide as,

$$LiCoO_2 \rightarrow Li^+ + CoO_2$$

In a Lithiumion battery, the Lithium ions are transported to and from the cathode or anode, with the transition metal, Cobalt (Co), in Li_xCoO_2 being oxidized from Co^{3+} to Co^{4-} during charging and reduced from Co^{4+} to Co^{3+} during discharge.

Advantages

1. Lithium-ion batteries have wide variety of shapes and sizes efficiently fitting the devices.
2. These are lighter than other energy-equivalent secondary batteries.
3. These have high open circuit voltage, which is useful in increasing the amount of power that can be transferred at a lower current.
4. There is no memory effect on these batteries.
5. Self-discharge rate of these batteries is less compared to other batteries i.e., approximately 5-10% per month.
6. In these batteries, components are environmentally safe as there is no free Lithium metal.

Disadvantages

1. In these batteries, poor ventilation may increase temperature and further shortening battery life.
2. Due to the high internal resistance, the voltage at the terminals to drop under load, which reduces the maximum current draw.
3. Lithium-ion batteries are not stable unlike Nickel-Cadmium batteries.

Applications

(i) Lithiumion batteries are selectively used in electronic gadgets, such as cell phones, laptops.

(ii) Due to its high energy to weight ratio and slow discharge when not in use qualities, they are used as portable consumer electronics.

1.3 FLOW BATERRIES (FUEL CELLS)

1.3.1 Methanol-Oxygen Fuel Cells, Construction, Applications

Q41. What are fuel cells? Explain with an example and give their advantages.

Answer : **June-14, Q12(a)**

A fuel cell is an electrochemical cell that converts chemical energy of the fuel directly into electricity in a readily available fuel-oxidant system where in the fuel gets oxidized at the anode.

Although, the basic principle of fuel cells is similar to that of the conventional electrochemical batteries, it is continuously supplied with a fuel and oxidant (stored outside the cell). The cell continuously produces electrical energy as long as it is provided with fuel and oxidant.

$$\text{Fuel} + \text{Oxygen} \rightarrow \text{Electricity} + \text{Oxidation product}$$

Every fuel cell consists of two electrodes, the anode (+ve) and the cathode (–ve) along with an electrolyte. The function of electrolyte is to carry the electrically charged particles from one electrode to the other. The fuel cell is continuously supplied with fuel, catalyst as well as the oxidizing agent for the continuous production of electricity at these electrodes.

Advantages

For answer refer Unit-1, Q18.

Disadvantages

1. Efficient auto-catalysts for electrodes are not freely available.
2. Reactants are to be continuously supplied.
3. Highly expensive.
4. Weight and volume of gas storage system is very large.

Application

❖ Fuel cells have been used as the main source of electrical energy for the spacecraft, namely the Apollo, the Gemini and for the space shuttle program of NASA.

Q42. Describe the working of a methanol oxygen fuel cell.

Answer :

Methanol-oxygen fuel cell uses methanol (CH_3OH) as the fuel and oxygen (or air) as an oxidant. The cell employs two platinum electrodes as cathode and anode. A mixture of methanol and sulphuric acid ($CH_3OH + H_2SO_4$) is used as electrolyte in the cell. This fuel cell can generate a voltage of about 1.2 V. Figure illustrates a schematic of methanol-oxygen fuel cell.

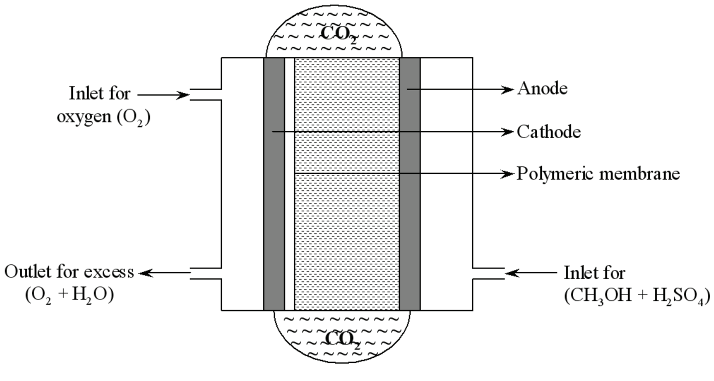


Figure: Methanol-Oxygen Fuel Cell

It can be observed from figure that polymeric membrane is placed near the cathode, in order to protect the oxidation of methanol. The electrolyte ($CH_3OH + H_2SO_4$) is sent through the inlet provided at the anodic chamber whereas water and oxygen are pumped through the cathodic chamber. The reactions taking place in the cell are,

Anode : $CH_3OH\,(l) + H_2O\,(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

Cathode : $\frac{3}{2}O_2(g) + 6H^+ + 6e^- \rightarrow 3H_2O$

Net cell reaction : $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2(g) + 2H_2O$

The cell releases Carbon dioxide (CO_2), which is non-toxic in nature.

Advantages

Methanol is an attractive fuel cell due to its cheap availability, easy handling and storage, solubility in aqueous electrolyte and high calorific value. It is derived from oil, natural gas, coal or biomass, therefore there is enough scope for the availability of methanol fuel.

This fuel cell requires platinum based catalysts for the fuel electrode. As the cost of platinum is high, the amount of metal that is used is minimized. A successful development in these fuel cells would lead to a progress in the transportation sector. These are of great advantage for city driving as there is an increase in their efficiency with a decrease in load. Therefore, methanol fuel cells are of great use.

Applications of Methanol-oxygen Fuel Cell

(i) Methanol-oxygen fuel cells are used as a source of continuous power supply in spacecrafts.

(ii) In military, methanol-oxygen fuel cells are used for large scale power production purposes.