CHAPTER 03

Electrochemistry

1. **Cells** are the devices in which interconversion of electrical energy and chemical energy takes place. *It is of two basic types:*
   (i) Electrochemical cell
   (ii) Electrolytic cell
2. An **electrochemical cell** is a device in which chemical energy of the redox reaction is converted into electrical energy. e.g. Daniell cell
3. While **writing a cell**, the anode is written on the left and the cathode on the right. A vertical line separates the metal from the metal ion (electrolyte solution) and a double vertical line indicates a salt-bridge which is written between the two half-cells (two electrolytes).

   The Daniell cell is represented as :

   $$\text{Zn}\ (s)\ |\ \text{Zn}^{2+}(aq)\ ||\ \text{Cu}^{2+}(aq)\ |\ \text{Cu}\ (s)$$
4. The electrode potential under the conditions of unit concentration at 25°C of all the species in the half-cell is called the **standard electrode potential** and the electrodes of known potential is known as **reference electrode**, e.g. standard hydrogen electrode (potential of which is arbitraily taken as zero) and calomel electrode.
5. The potential difference between the electrode potentials of the cathode and anode is called the **cell potential.**

   Electromotive force (emf) is the potential given as $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
6. The arrangement of various standard half-cells in order of their decreasing values of standard reduction potentials is called **electrochemical series**. If the standard electrode potential of an electrode is greater than zero (positive value) then its reduced form is more stable as compared to hydrogen gas.
   Similarly, in case of standard electrode potential being less than zero (negative value), hydrogen gas is more stable than the reduced form of the species.
7. **Nernst equation** is the equation which gives the relation between electrode potential and concentration of metal ions at given temperature Nernst equation for the electrode reaction (half cell reaction) is as follows :

   $M^{n+}\ (aq) + ne^- \longrightarrow M(s)$ is:

   $$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

   For a general electrochemical reaction of the type

   $$aA + bB \xrightarrow{ne^-} cC + dD$$

   The Nernst equation can be written as

   $$\boxed{E_{(\text{cell})} = E^\ominus_{(\text{cell})} - \frac{RT}{nF} \ln Q}$$

   $$E_{(\text{cell})} = E^\ominus_{(\text{cell})} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

   In general, at equilibrium,

   $$E_{\text{cell}} = 0$$

   $$\boxed{E^\ominus_{(\text{cell})} = \frac{2.303\ RT}{nF} \log K_C}$$
8. **Gibb's energy of the reaction** The emf of a cell is related to the Gibb's free energy $\Delta_r G^\ominus$ as

   $$\Delta_r G = -nFE_{\text{cell}}$$

   If the concentration of all the reacting species is unity, then $E_{\text{cell}} = E^\circ_{\text{cell}}$ and we have

   $$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$$

   Relation between Gibb's energy and equilibrium constant (K)

   $$\Delta_r G^\circ = -RT \ln K$$
9. **Resistance** (R) of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A).

   Its unit is ohm (Ω). $R = \frac{\rho l}{A}$

   The constant of proportionality, ρ is called resistivity (specific resistance). Its units are Ωm **or** Ω cm.
10. **Conductance** (G) of electrolytic solutions is the inverse of resistance (R). Its unit is Ω^{-1}.

    $$G = \frac{1}{R} = \frac{A}{\rho l}$$

11. The inverse of resistivity is called the **conductivity** or **specific conductance** (κ).
Its units are $\Omega^{-1}\,m^{-1}$ or $S\,m^{-1}$.

$$\kappa = \frac{\text{Cell constant } (G^*)}{R} \qquad \left[\text{where}, G^* = \frac{l}{a}\right]$$

12. **Molar conductivity** (Λ_m) of a solution is the conductance of the volume of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and sufficient cross-sectional area to contain the electrolyte. The unit of Λ_m will be $\Omega^{-1} m^2 mol^{-1}$ or $Sm^2\ mol^{-1}$.

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

13. **Variation of conductivity and molar conductivity with concentration** The conductivity of an electrolyte increases with the decrease in concentration, i.e. increase in dilution. Although, at infinite dilution, the conductivity of weak as well as strong electrolyte are nearly same, i.e. equal to one (as weak electrolyte is assumed to be completely ionised at infinite dilution) but their variation is not same with the increase in dilution. Upon dilution, equivalent and molar conductivities increases, while specific conductivity decreases. It is because concentration of ions per cubic centimetre decreases upon dilution.

14. **Kohlrausch's law of independent migration of ions** states that limiting molar conductivity of strong electrolyte is the sum of the individual contributions of the cation and the anion of the strong electrolyte. In general, if an electrolyte produces ν_+ cations and ν_- anions, then its limiting molar conductivity is given by

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$$

15. **Electrolytic cells** are those cells in which electrical energy is used to carry out non-spontaneous chemical reactions and the reaction takes place in an electrolytic cell is called **electrolysis**.

16. **Faraday's Laws of Electrolysis**

- **Faraday's first law** states that, the amount of substance deposited at an electrode by passing current is proportional to the quantity of electricity passed through the electrolyte (in solution or in molten state).

$$W = Zit$$

where, Z = electrochemical equivalent

$$Z = \frac{\text{equivalent weight of substances}}{96500}$$

- **Faraday's second law** states that, when the same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at respective electrodes are proportional to their chemical equivalent weights.

$$\boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} = \ldots}$$

where, W is the mass of substance and E is its equivalent weight.

17. A **battery** contains one or more than one electrochemical cells connected in series. It may be a primary battery (non-chargeable battery, like dry cell or a Leclanche cell) or secondary battery (rechargeable), like lead storage battery.

- **Reactions involved in dry cell**

At anode

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

At cathode

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

- **Reactions involved in mercury cell**

At anode

$$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

At cathode

$$HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

- When the **lead storage battery is in use** (discharging), the cell reactions are:

At anode $Pb\,(s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode

$$\underset{\text{Lead dioxide}}{PbO_2(s)} + SO_4^{2-}\ (aq) + 4H^+\ (aq) + 2e^- \longrightarrow \underset{\text{Lead sulphate}}{PbSO_4\ (s)} + 2H_2O\ (l)$$

The overall reaction of the cell is written as :

$$Pb(s) + PbO_2(s) + \underset{\text{Sulphuric acid}}{2H_2SO_4\ (aq)} \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

On charging the battery, the reaction is reversed. Actually, it forces the electrons to flow in opposite direction resulting $PbSO_4(s)$ on the anode as Pb and PbO_2 on the cathode. In this case, batteries behave, like electrochemical batteries.

18. A **fuel cell** is a galvanic cell in which chemical energy is converted into electrical energy by combustion of fuels. One of the most successful fuel cell is H_2-O_2 fuel cell. It was used for providing electrical power in Apollo space programme.
The electrode reactions are :

At cathode $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

At anode $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

The overall reaction of the cell is written as

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (l)$$

Fuel cells are pollution free, produce electricity with an efficiency of about 70% and never become dead due to continuous supply of fuel.

19. **Corrosion** is an electrochemical process in which a metal oxide or other salt of the metal forms a coating over the metal surface. e.g. the rusting of iron, tarnishing of silver surface, turning of surface of copper and bronze into green colour.

- The anodic and cathodic reactions occurring in the process of rusting are :

At anode $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$;

(Oxidation) $E^{\ominus}_{(Fe^{2+}/Fe)} = -0.44$ V

At cathode $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$;

(Reduction) $E^{\ominus}_{H^+|O_2|H_2O} = 1.23$ V

- The overall reaction of the cell is written as:

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l); \quad E^{\ominus}_{(cell)} = 1.67 \text{ V}$$

- Ferrous ions produced are further oxidised by atmospheric oxygen.

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

$$\Big\downarrow xH_2O$$

$$\underset{\text{Rust}}{Fe_2O_3 \cdot xH_2O}$$

Hydrated ferric oxided ($Fe_2O_3 \cdot xH_2O$) is called rust.

- The methods used for prevention of corrosion are covering the surface with paint or by some chemical (bisphenol) to provide a sacrificial electrode of another metal (Mg, Zn, etc).

Practice Questions

1. $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

The above redox reaction is used in

(a) Galvanic cell *(b)* Daniell cell
(c) Voltaic cell *(d)* All of these

2. Electrolytic cell is a device

(a) in which a non-spontaneous chemical reaction is carried out at the expense of electrical energy
(b) in which a spontaneous chemical reaction is carried out to generate electrical energy
(c) in which applied opposite potential is less than the cell potential
(d) Both (a) and (c)

3. For the electrochemical cell, $Ag^-|AgCl|KCl \,||\, AgNO_3|Ag^+$, the overall cell reaction is

(a) $Ag^+ + KCl \longrightarrow AgCl(s) + K^+$
(b) $Ag + AgCl \longrightarrow 2Ag + \frac{1}{2}Cl_2$
(c) $AgCl(s) \longrightarrow Ag^+ + Cl^-$
(d) $Ag^+ + Cl^- \longrightarrow AgCl(s)$

4. Calculate the standard cell potential for the following Galvanic cell, $Cr|Cr^{3+}||Cd^{2+}|Cd$

[Given, $E^{\circ}_{Cr^{3+}/Cr} = -0.74$V and $E^{\circ}_{Cd^{2+}/Cd} = -0.40$V]

(a) 0.74 V *(b)* −0.34 V *(c)* + 0.34 V *(d)* 1.14 V

5. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15V and that for the Cr^{3+}/Cr couple is −0.74V. These two couples in their standard state are connected to make a cell. The cell potential will be

(a) + 1.83 V *(b)* +1.19 V
(c) + 0.89 V *(d)* + 0.18 V

6. If $E^{\circ}(Zn^{2+}/Zn) = -0.763$ V and $E^{\circ}(Fe^{2+}/Fe) = -0.44$ V, then the emf of the cell $Zn|Zn^{2+}(a = 0.001)||Fe^{2+}(a = 0.005)|Fe$ is

(a) equal to 0.323 V *(b)* less than 0.323 V
(c) greater than 0.323 V *(d)* equal to 1.103 V

7. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl at pH = 10 and by passing hydrogen gas around the platinum wire at 1 atm pressure. The oxidation potential of electrode would be

(a) 0.059 V *(b)* 0.59 V
(c) 0.118 V *(d)* 0.18 V

8. In the electrochemical cell,

$Zn|ZnSO_4\ (0.01\text{ M})||CuSO_4(1.0\text{M})|Cu$, the emf of this Daniell cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to E_2. From the following, which one is the correct relationship between E_1 and E_2? (Given, $\frac{RT}{F} = 0.059$)

(a) $E_1 = E_2$ *(b)* $E_1 < E_2$
(c) $E_1 > E_2$ *(d)* $E_2 = 0 \neq E_1$

9. In the given reaction,

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

$E^{\circ}_{Cu^+/Cu} = 0.6$ V and $E^{\circ}_{Cu^{2+}/Cu} = 0.41$ V

The equilibrium constant for this reaction will be

(a) 2.76×10^2 *(b)* 2.76×10^4
(c) 2.76×10^6 *(d)* 2.76×10^8

10. The standard Gibbs free energy of

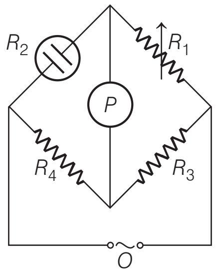
$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \text{ is}$$

(a) $-91\, FE_{\text{cell}}$ *(b)* $-2FE_{\text{cell}}$
(c) $-3\, FE_{\text{cell}}$ *(d)* $-4\, FE_{\text{cell}}$

11. KCl solution is generally used to determine the cell constant because

(a) it is highly ionic in nature
(b) its conductivity is known accurately at various concentration and different temperatures
(c) size of cations and anions are comparable
(d) All of the above

12. Which of the following information is false for the below given figure?



(a) This assembly is used for measuring conductivity of solution
(b) *O* is an oscillator, i.e. a source of AC power
(c) *P* is the conductivity cell
(d) Unknown resistance is measured by using the formula, $R_2 = \dfrac{R_1 R_4}{R_3}$

13. The conductance of electrolytic solution kept between the electrodes of conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution is called

(a) limiting molar conductivity
(b) molar conductivity
(c) conductivity
(d) All of the above

14. The resistance of the cell containing KCl solution at 23°C was found to be 55 Ω. Its cell constant is 0.616 cm^{-1}. The conductivity of KCl solution $(\Omega^{-1}\text{ cm}^{-1})$ is

(a) 1.21×10^{-3} *(b)* 1.12×10^{-2}
(c) 1.12×10^{-3} *(d)* 1.21×10^{-2}

15. If resistance of a conductivity cell filled with 2 mol L^{-1} KCl solution is $100\ \Omega$. The resistance of the same cell when filled with 0.2 mol L^{-1} KCl solution is $520\ \Omega$. Then the conductivity of 0.2 mol L^{-1} KCl solution will be (Given the conductivity of 1 mol L^{-1} KCl solution is 1.29 S/m.)

(a) 0.248 S cm^{-1} *(b)* 0.248 S m^{-1}
(c) 2.48 S cm^{-1} *(d)* 2.48 S m^{-1}

16. "Limiting molar conductivity of an electrolyte can be represented as sum of the individual contributions of anion and cation of the electrolyte".
Which law states the above statement?

(a) Henry's law
(b) Debye Onsager's law
(c) Kohlrausch's law of independent migration of ions
(d) All of the above

17. Molar conductivities (Λ°_m) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4,425.9 and $91.0\text{ S cm}^2\text{mol}^{-1}$ respectively. Λ°_m for CH_3COOH will be

(a) $425.5\text{ S cm}^2\text{ mol}^{-1}$ *(b)* $180.5\text{ S cm}^2\text{ mol}^{-1}$
(c) $290.85\text{ S cm}^2\text{ mol}^{-1}$ *(d)* $390.5\text{ S cm}^2\text{ mol}^{-1}$

18. 1.5 A current is flowing through a metallic wire. If it flows for 3 hrs, how many electrons would flow through the wire?

(a) 2.05×10^{22} electrons *(b)* 1.0×10^{23} electrons
(c) 10^{24} electrons *(d)* 4.5×10^{23} electrons

19. A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to evolution of chlorine gas at one of the electrodes. The total charge required for the complete electrolysis will be

(a) 96500 C *(b)* 24125 C
(c) 48250 C *(d)* 193000 C

20. The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolysed in g during the process is (Molar mass of $PbSO_4 = 303\text{g mol}^{-1}$)

(a) 11.4 *(b)* 7.6 *(c)* 15.2 *(d)* 22.8

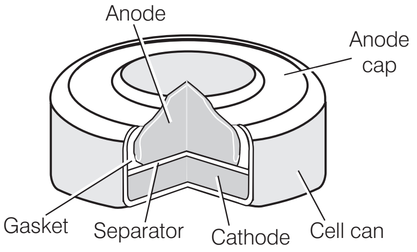
21. When aqueous sodium chloride solution is electrolysed

(a) at cathode H^+ is reduced into H_2 instead of Na^+
(b) at cathode Na^+ is reduced to Na
(c) Cl^- is oxidised into Cl_2 at cathode
(d) Both (b) and (c)

22. What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of copper electrodes?

(a) Copper will deposit at cathode
(b) Copper will dissolve at anode
(c) Oxygen will be released at anode
(d) Both (a) and (b)

23. In the given mercury cell,



The reaction occuring at cathode will be

(a) $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

(b) $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

(c) $Zn + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

(d) $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

24. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as

(a) fuel cell *(b)* electrolytic cell
(c) dynamo *(d)* Ni-Cd cell

25. Galvanisation is

(a) zinc plating on aluminium sheet
(b) zinc plating on iron sheet
(c) iron plating on zinc sheet
(d) aluminium plating on zinc sheet

ANSWERS

1. (d)	**2.** (a)	**3.** (c)	**4.** (c)	**5.** (c)	**6.** (c)	**7.** (b)	**8.** (c)	**9.** (c)	**10.** (b)
11. (b)	**12.** (c)	**13.** (b)	**14.** (b)	**15.** (b)	**16.** (c)	**17.** (d)	**18.** (b)	**19.** (d)	**20.** (b)
21. (a)	**22.** (d)	**23.** (b)	**24.** (a)	**25.** (b)					

Hints & Solutions

2. (*a*) When $E_{ext} > E$ generated, the cell behaves like an electrolytic cell. In this cell, a non-spontaneous reaction is carried out at the expense of electrical energy.

3. (*c*) For the electrochemical cell,

$$Ag \mid AgCl \mid KCl \parallel AgNO_3 \mid Ag^+$$

The cell reaction is

$$AgCl\,(s) + e^- \longrightarrow Ag + Cl^-(aq)$$

$$\underline{Ag \longrightarrow Ag^+(aq) + e^-}$$

Overall cell reaction,

$$AgCl(s) \longrightarrow Ag^+ + Cl^-$$

4. (*c*) Standard cell potential for the given cell,

$$E^\circ_{cell} = E^\circ_{Cd^{2+}/Cd} - E^\circ_{Cr^{3+}/Cr}$$

$$= -0.40 - (-0.74) = +0.34\text{ V}$$

5. (*c*) The cell potential is given as,

$$E^\circ_{cell} = E^\circ_{cathode(RP)} - E^\circ_{anode(RP)}$$

$$\therefore \quad E^\circ_{cell} = 0.15 - (-0.74) = +0.89\text{ V}$$

6. (*c*) The cell reaction is,

$$Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$$

From Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{a_{Zn^{2+}}}{a_{Fe^{2+}}}$$

$$= (E^\circ_{cathode} - E^\circ_{anode}) - \frac{0.0591}{n}\log\frac{a_{Zn^{2+}}}{a_{Fe^{2+}}}$$

$$= (-0.44 + 0.763) - \frac{0.0591}{n}\log\frac{a_{Zn^{2+}}}{a_{Fe^{2+}}}$$

$$= (0.763 - 0.44) - \frac{0.0591}{1}\log\frac{0.001}{0.005} = 0.364\text{ V}$$

7. (*b*) For hydrogen electrode, oxidation half-reaction is

$$\underset{(1\text{ atm})}{H_2} \longrightarrow \underset{(\text{at pH }10)}{2H^+} + 2e^-$$

If $\text{pH} = 10,\ H^+ = 1\times10^{-\text{pH}} = 1\times10^{-10}$

From Nernst equation, $E = E^\circ - \dfrac{0.0591}{2}\log\dfrac{[H^+]^2}{p_{H_2}}$

For hydrogen electrode, $E^\circ = 0$

$$E = -\frac{0.0591}{2}\log\frac{(10^{-10})^2}{1} = -\frac{0.0591\times2}{2}\log(10)^{-10}$$

$$= 0.0591\times10\times\log10 = 0.59\text{V}$$

8. (*c*) For the electrochemical cell,

$$Zn|ZnSO_4\ (0.01M)||CuSO_4(1M)|Cu$$

Cell reaction is

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu;\ n = 2$$

$$E_1 = E^\circ - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = E^\circ - \frac{0.059}{2}\log\frac{0.01}{1}$$

$$E_1 = E^\circ - \frac{0.059}{2}\log\frac{1}{100} = (E^\circ + 0.059)$$

For the electrochemical cell,

$$Zn|ZnSO_4(1M)||CuSO_4(0.01M)|Cu$$

$$E_2 = E^\circ - \frac{0.059}{2}\log\frac{1}{0.01}$$

$$E_2 = E^\circ - \frac{0.059}{2}\log 100 = (E^\circ - 0.059)$$

$$\therefore \quad E_1 > E_2$$

9. (*c*) Right hand cell reaction,

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

Left hand cell reaction,

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

Overall cell reaction,

$$2\mathrm{Cu^+}(aq) \longrightarrow \mathrm{Cu^+}(s) + \mathrm{Cu^{2+}}(aq)$$

$$\therefore \text{ Cell potential } (E^\circ_{\text{cell}}) = E^\circ_{\mathrm{Cu^+/Cu}} - E^\circ_{\mathrm{Cu^{2+}/Cu^+}}$$

$$= 0.60 - 0.41 = 0.19\ \mathrm{V}$$

As we know that,

$$-nFE^\circ = -RT \ln K_{\text{eq}}$$

$$\Rightarrow \quad \log K_{\text{eq}} = \frac{nE^\circ}{(2.303RT/F)} = \frac{2 \times 0.19\ \mathrm{V}}{0.059\ \mathrm{V}} = 6.44$$

$$K_{\text{eq}} = 10^{6.44} = 2.76 \times 10^6$$

10. (*b*) As we know that,

$$\Delta_r G = -nFE_{\text{cell}}$$

$\because\ n = 2$, for the given reaction.

So, $\quad \Delta_r G = -2FE_{\text{cell}}$

11. (*b*) Conductivity of KCl solution is known accurately at various concentrations and different temperatures, so it is generally used in conductivity cell to measure cell constant.

12. (*c*) Wheatstone bridge consists of two resistance, R_3 and R_4 and a variable resistance R_1 and conductivity cell having unknown resistance R_2. O is the source of AC power called oscillator. Under no current condition, minimum or no sound can be heard from the earphone, P (a detector).

The unknown resistance, R_2 is calculated as

$$R_2 = \frac{R_1 R_4}{R_3}.$$

Hence, the option (c) is false.

13. (*b*) Molar conductivity (Λ_{m}) is defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accomodate sufficient volume of solution that contains one mole of the electrolyte.

14. (*b*) Conductivity, $(\kappa) = \dfrac{\text{Cell constant}}{\text{Resistance}} = \dfrac{0.616\ \mathrm{cm^{-1}}}{55\ \Omega}$

$$= 1.12 \times 10^{-2}\,\Omega^{-1}\ \mathrm{cm^{-1}}$$

15. (*b*) The cell constant is given by the equation:

Cell constant, $G^* = \text{conductivity} \times \text{resistance}$

$$= 1.29\ \mathrm{S/m} \times 100\ \Omega = 129\ \mathrm{m^{-1}} = 1.29\ \mathrm{cm^{-1}}$$

Conductivity of 0.2 mol $\mathrm{L^{-1}}$ KCl solution

$$= \text{cell constant/ resistance}$$

$$= \frac{G^*}{R} = \frac{129\ \mathrm{m^{-1}}}{520\ \Omega} = 0.248\ \mathrm{S\ m^{-1}}$$

16. (*c*) According to Kohlrausch's law of independent migration, "the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte".

17. (*d*) $\mathrm{CH_3CO\overset{-}{O}\overset{+}{Na} + HCl \longrightarrow NaCl + CH_3COOH}$

$$\Lambda^\circ_{\mathrm{m\,(CH_3COOH)}} = \Lambda^\circ_{\mathrm{m\,(CH_3CO\overset{-}{O}\overset{+}{Na})}} + \Lambda^\circ_{\mathrm{m\,(HCl)}} - \Lambda^\circ_{\mathrm{m\,(NaCl)}}$$

$$\Lambda^\circ_{\mathrm{m\,(CH_3COOH)}} = (91.0 + 425.9 - 126.4)\ \mathrm{S\ cm^2\ mol^{-1}}$$

$$\Lambda^\circ_{\mathrm{m\,(CH_3COOH)}} = 390.5\ \mathrm{S\ cm^2\ mol^{-1}}$$

18. (*b*) We know that

Charge, $q = It = 1.5 \times 3 \times 60 \times 60 = 16200\,\mathrm{C}$

$\because$ Charge on one electron $= 1.6 \times 10^{-19}\,\mathrm{C}$

$\therefore$ 16200 C charge is on $\dfrac{1 \times 16200}{1.6 \times 10^{-19}} = 1.0 \times 10^{23}$ electrons

19. (*d*) $\mathrm{Na^+} + e^- \xrightarrow{\mathrm{Hg}} \mathrm{Na(Hg)}$

$$2\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2e^-$$

Moles of NaCl electrolysed $= 4 \times \dfrac{500}{1000} = 2.0$

Two Faraday of electric charge is required for electrolysis of 2 moles of NaCl.

Total coulombs $= 2 \times 96500 = 193000$ C.

20. (*b*) During charging:

$$\mathrm{Pb + SO_4^{2-} \longrightarrow PbSO_4} + 2e^-$$

$$\Rightarrow \quad 1\ \mathrm{F} \equiv 1\ \text{g-equiv. of } \mathrm{PbSO_4}$$

$$= \frac{1}{2} \text{ mol of } \mathrm{PbSO_4} \Rightarrow \frac{303}{2} \text{ g } \mathrm{PbSO_4}$$

$$\therefore \quad 0.05\ \mathrm{F} \equiv \frac{303}{2} \times 0.05 \text{ g of } \mathrm{PbSO_4} = 7.575 \text{ g of } \mathrm{PbSO_4}$$

21. (*a*) When aqueous solution of NaCl is electrolysed, there is a competition between the following reduction reactions at cathode.

$$\mathrm{Na^+} + e^- \longrightarrow \mathrm{Na}\,; \quad E^\circ_{\text{cell}} = -2.71\ \mathrm{V}$$

$$\mathrm{H^+} + e^- \longrightarrow \frac{1}{2}\mathrm{H_2}; \quad E^\circ_{\text{cell}} = 0.00\ \mathrm{V}$$

The reaction with higher value of E° is preferred and therefore, the second reaction occurs at cathode, i.e. $\mathrm{H^+}$ is reduced instead of $\mathrm{Na^+}$.

22. (*d*) Electrolysis of $\mathrm{CuSO_4}$ can be represented by following two half-cell reactions :

At cathode $\quad \mathrm{Cu^{2+}} + 2e^- \longrightarrow \mathrm{Cu}(s)$

At anode $\quad \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}} + 2e^-$

Here, Cu will deposit at cathode while copper will dissolved at anode.

23. (*b*) The reaction takes place in the given cell are as follows :

Anode $\quad \mathrm{Zn(Hg)} + 2\mathrm{OH^-}(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O} + 2e^-$

Cathode $\quad \mathrm{HgO}(s) + \mathrm{H_2O} + 2e^- \longrightarrow \mathrm{Hg}(l) + 2\mathrm{OH^-}$

The overall reaction is

$$\mathrm{Zn(Hg)} + \mathrm{HgO}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Hg}(l)$$

24. (*a*) Galvanic cell that are used to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc., directly into electrical energy is called fuel cells.