Chapter_03

Electrochemistry

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

(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, $Zn|ZnSO_4\ (0.01\ M)||CuSO_4(1.0M)|Cu$, 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

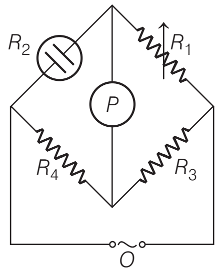
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ is

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

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

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 $(\Omega^{-1}\ cm^{-1})$ 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

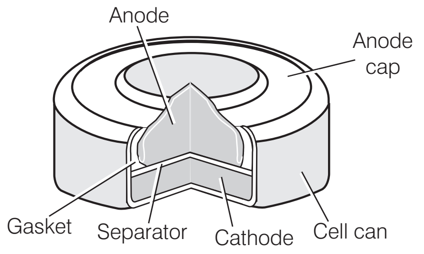
21. When aqueous sodium chloride solution is electrolysed

(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,

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

The cell reaction is

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

Overall cell reaction,

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

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

$$E^\circ_{cell} = E^\circ_{Cd^{2+}/Cd} - E^\circ_{Cr^{3+}/Cr}$$
$$= -0.40 - (-0.74) = +0.34\ V$$

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

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

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

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

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

From Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{a_{Zn^{2+}}}{a_{Fe^{2+}}}$$
$$= (E^\circ_{cathode} - E^\circ_{anode}) - \frac{0.0591}{n}\log\frac{a_{Zn^{2+}}}{a_{Fe^{2+}}}$$
$$= (-0.44 + 0.763) - \frac{0.0591}{n}\log\frac{a_{Zn^{2+}}}{a_{Fe^{2+}}}$$
$$= (0.763 - 0.44) - \frac{0.0591}{1}\log\frac{0.001}{0.005} = 0.364\ V$$

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

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

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

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

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

$$E = -\frac{0.0591}{2}\log\frac{(10^{-10})^2}{1} = -\frac{0.0591\times2}{2}\log(10)^{-10}$$
$$= 0.0591\times10\times\log10 = 0.59\,V$$

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,

$$Zn|ZnSO_4(1M)||CuSO_4(0.01M)|Cu$$
$$E_2 = E^\circ - \frac{0.059}{2}\log\frac{1}{0.01}$$

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

$\therefore \quad E_1 > E_2$

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

$$Cu^+ + e^- \longrightarrow Cu$$

Left hand cell reaction,

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

Overall cell reaction,

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

$\therefore$ Cell potential $(E°_{cell}) = E°_{Cu^+/Cu} - E°_{Cu^{2+}/Cu^+}$

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

As we know that,

$$-nFE° = -RT \ln K_{eq}$$

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

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

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

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

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

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

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

$$R_2 = \frac{R_1R_4}{R_3}.$$

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, $(\kappa) = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{0.616 \text{ cm}^{-1}}{55\ \Omega}$

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

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

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

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

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

= cell constant/ resistance

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

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*) $CH_3CO\overset{-}{O}\overset{+}{Na} + HCl \longrightarrow NaCl + CH_3COOH$

$$\Lambda°_{m(CH_3COOH)} = \Lambda°_{m(CH_3CO\overset{-}{O}\overset{+}{Na})} + \Lambda°_{m(HCl)} - \Lambda°_{m(NaCl)}$$

$$\Lambda°_{m(CH_3COOH)} = (91.0 + 425.9 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda°_{m(CH_3COOH)} = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

18. (*b*) We know that

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

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

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

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

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

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

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:

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

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

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

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

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

$$Na^+ + e^- \longrightarrow Na;\quad E°_{cell} = -2.71 \text{ V}$$

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

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

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

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

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

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

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

The overall reaction is

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

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.