Q 3.1:
Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn

Solution:
According to their reactivity, the given metals replace the others from their salt solutions in the said order: Mg, Al, Zn, Fe, Cu.
Mg: Al: Zn: Fe: Cu

Q 3.2:
Given the standard electrode potentials,
\( K^+/K = -2.93 \text{V} \),
\( Ag^+/Ag = 0.80 \text{V} \),
\( Hg^{2+}/Hg = 0.79 \text{V} \),
\( Mg^{2+}/Mg = -2.37 \text{V} \),
\( Cr^{3+}/Cr = -0.74 \text{V} \)
Arrange these metals in their increasing order of reducing power.

Solution:
The reducing power increases with the lowering of reduction potential. In order of given standard electrode potential (increasing order) : \( K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag \)
Thus, in the order of reducing power, we can arrange the given metals as Ag < Hg < Cr < Mg < K

Q 3.3:

Depict the galvanic cell in which the reaction \( Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s) \) takes place. Further show:
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.

Solution:
The galvanic cell in which the given reaction takes place is depicted as:

\[
Zn(s) \mid Zn^{2+}_{(aq)} \parallel Ag^+_{(aq)} \parallel Ag(s)
\]

(i) The negatively charged electrode is the Zn electrode (anode)
(ii) The current carriers in the cell are ions. Current flows to zinc from silver in the external circuit.
(iii) Reaction at the anode is given by :

\[
Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-
\]

Reaction at the anode is given by :
Q 3.4:
Calculate the standard cell potentials of galvanic cell in which the following reactions take place:
(i) \(2\text{Cr}(s) + 3\text{Cd}^{2+}(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 3\text{Cd}\)
(ii) \(\text{Fe}^{2+}(aq) + \text{Ag}^{+}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Ag}(s)\)
Calculate the \(\Delta_r G\) and equilibrium constant of the reactions.

Solution:

(i) \(E^\Theta_{\text{Cr}^{3+}/\text{Cr}} = 0.74 \text{ V}\)

\(E^\Theta_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}\)

The galvanic cell of the given reaction is depicted as:

\[
\text{Cr}(s) | \text{Cr}^{3+}(aq) || \text{Cd}^{2+}(aq) | \text{Cd}(s)
\]

Now, the standard cell potential is

\[E^\Theta_{\text{cell}} = E^\Theta_g - E^\Theta_L\]

\[= -0.40 - (-0.74)\]

\[= +0.34 \text{ V}\]

In the given equation, \(n = 6\)

\(F = 96487 \text{ C mol}^{-1}\)

\[E^\Theta_{\text{cell}} = +0.34 \text{ V}\]

Then, \(\Delta_r G^\Theta = -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V}\)

\[= -196833.48 \text{ CV mol}^{-1}\]

\[= -196833.48 \text{ J mol}^{-1}\]

\[= -196.83 \text{ kJ mol}^{-1}\]

Again,
Q 3.5: Write the Nernst equation and emf of the following cells at 298 K:

(i) Mg(s)|Mg$^{2+}$ (0.001 M)||Cu$^{2+}$ (0.0001 M)|Cu(s)
(ii) Fe(s)|Fe$^{2+}$ (0.001 M)||H$^+$ (1 M)|H$\textsubscript{2}$ (g) (1 bar)| Pt(s)
(iii) Sn(s)|Sn$^{2+}$ (0.050 M)||H$^+$ (0.020 M)|H$\textsubscript{2}$ (g) (1 bar)|Pt(s)
(iv) Pt(s)|Br$^-$ (0.010 M)|Br$\textsubscript{2}$ (l) ||H$^+$ (0.030 M)| H$\textsubscript{2}$ (g) (1 bar)|Pt(s).

Solution:

(i) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

= 2.7 - 0.02955
= 2.67 V (approximately)
(ii) For the given reaction, the Nernst equation can be given as:

\[ E_{\text{cell}} = E_0^{0} - \frac{0.591}{n} \log \left( \frac{[Fe^{2+}]}{[H^+]} \right) \]

\[ = 0 - (-0.14) - \frac{0.591}{n} \log \left( \frac{0.050}{(0.020)^2} \right) \]

\[ = 0.52865 \text{ V} \]

\[ = 0.53 \text{ V (approximately)} \]

(iii) For the given reaction, the Nernst equation can be given as:

\[ E_{\text{cell}} = E_0^{0} - \frac{0.591}{n} \log \left( \frac{[Sn^{2+}]}{[H^+]} \right) \]

\[ = 0 - (-0.14) - \frac{0.591}{2} \log \left( \frac{0.050}{(0.020)^2} \right) \]

\[ = 0.14 - 0.0295 \times \log 125 \]

\[ = 0.14 - 0.052 \]

\[ = 0.078 \text{ V} \]

\[ = 0.08 \text{ V (approximately)} \]

(iv) For the given reaction, the Nernst equation can be given as:

\[ E_{\text{cell}} = E_0^{0} - \frac{0.591}{n} \log \left( \frac{[Br^-]}{[H^+]} \right)^2 \]

\[ = 0 - 1.09 - \frac{0.591}{2} \log \left( \frac{0.010}{(0.030)^2} \right) \]

\[ = -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \]

\[ = -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \]

\[ = -1.09 - 0.02955 \times \log (1.11 \times 10^7) \]

\[ = -1.09 - 0.02955 \times (0.0453 + 7) \]

\[ = -1.09 - 0.203 \]

\[ = -1.298 \text{ V} \]
Q 3.6:
In the button cells widely used in watches and other devices the following reaction takes place:

\[
\begin{align*}
\text{Zn}_{(s)} & \rightarrow \text{Zn}^{2+}_{(aq)} + 2\text{e}^- & E^\circ = 0.76\text{V} \\
\text{Ag}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} + 2\text{e}^- & \rightarrow 2\text{Ag}^{(g)} + 2\text{OH}^-_{(aq)} & E^\circ = 0.344\text{V} \\
\text{Zn}_{(s)} + \text{Ag}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} & \rightarrow \text{Zn}^{2+} + 2\text{Ag}^{(s)} + 2\text{OH}^-_{(aq)} & E^\circ = 1.104\text{V}
\end{align*}
\]

Determine $\Delta_r G^\circ$ and $E_J$ for the reaction.

Solution:

\[E^0 = 1.104 \text{V}\]

We know that,

\[\Delta_r G^\circ = -nF E^0\]

\[= -2 \times 96487 \times 1.04\]

\[= -213043.296 \text{J}\]

\[= -213.04 \text{kJ}\]

Q 3.7:
Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Solution:

The conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq cm. Specific conductance is the inverse of resistivity and it is represented by the symbol $\kappa$. If $\rho$ is resistivity, then we can write:

\[\kappa = \frac{1}{\rho}\]

At any given concentration, the conductivity of a solution is defined as the unit volume of solution kept between two platinum electrodes with the unit area of the cross-section at a distance of unit length.
NCERT Solutions for Class 12 Chemistry Chapter 3
Electrochemistry

Q 3.8:
The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm\(^{-1}\). Calculate its molar conductivity

Solution:
Given, \( \kappa = 0.0248 \text{ S cm}^{-1} \)
\( c = 0.20 \text{ M} \)
Q 3.9:
The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$

Solution:

Given,

Conductivity, $k = 0.146 \times 10^{-3} \text{ S cm}^{-1}$

Resistance, $R = 1500 \Omega$

Cell constant $= k \times R$

$= 0.146 \times 10^{-2} \times 1500$

$= 0.219 \text{ cm}^{-1}$

Q 3.10:
The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

<table>
<thead>
<tr>
<th>Concentration/M</th>
<th>0.001</th>
<th>0.010</th>
<th>0.020</th>
<th>0.050</th>
<th>0.100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2 \times \kappa/\text{S m}^{-1}$</td>
<td>1.237</td>
<td>11.85</td>
<td>23.15</td>
<td>55.53</td>
<td>106.74</td>
</tr>
</tbody>
</table>

Calculate $\Lambda_m$ for all concentrations and draw a plot between $\Lambda_m$ and $c^{1/2}$. Find the value of $\Lambda_m^C$.

Solution:

Given,

$k = 1.237 \times 10^{-2} \text{ S m}^{-1}, \ c = 0.001 \text{ M}$

Then, $k = 1.237 \times 10^{-4} \text{ S cm}^{-1}, \ c^{1/2} = 0.0316 \text{ M}^{1/2}$

$\Lambda_m = \frac{k}{c} = \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol} \cdot \text{L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{L}$

$= 123.7 \text{ S cm}^2 \text{ mol}^{-1}$

Given,

$k = 11.85 \times 10^{-2} \text{ S m}^{-1}, \ c = 0.010 \text{ M}$

Then, $k = 11.85 \times 10^{-4} \text{ S cm}^{-1}, \ c^{1/2} = 0.1 \text{ M}^{1/2}$
\[ \Lambda_m = \frac{k}{c} = \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{L} \]

= 118.5 S cm² mol⁻¹

Given,
\[ \kappa = 23.15 \times 10^{-2} \text{ S m}^{-1}, \ c = 0.020 \text{ M} \]

Then, \[ \kappa = 23.15 \times 10^{-4} \text{ S cm}^{-1}, \ c^{1/2} = 0.1414 \text{ M}^{1/2} \]

\[ \Lambda_m = \frac{k}{c} = \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{L} \]

= 115.8 S cm² mol⁻¹

Given,
\[ \kappa = 55.53 \times 10^{-2} \text{ S m}^{-1}, \ c = 0.050 \text{ M} \]

Then, \[ \kappa = 55.53 \times 10^{-4} \text{ S cm}^{-1}, \ c^{1/2} = 0.2236 \text{ M}^{1/2} \]

\[ \Lambda_m = \frac{k}{c} = \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{L} \]

= 111.1 S cm² mol⁻¹

Given,
\[ \kappa = 106.74 \times 10^{-2} \text{ S m}^{-1}, \ c = 0.100 \text{ M} \]

Then, \[ \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, \ c^{1/2} = 0.3162 \text{ M}^{1/2} \]

\[ \Lambda_m = \frac{k}{c} = \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{L} \]

= 106.74 S cm² mol⁻¹

Now, we have the following data:

<table>
<thead>
<tr>
<th>( C^{1/2} \text{ M}^{1/2} )</th>
<th>0.0316</th>
<th>0.1</th>
<th>0.1414</th>
<th>0.2236</th>
<th>0.3162</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Lambda_m ) (S cm² mol⁻¹)</td>
<td>123.7</td>
<td>118.5</td>
<td>115.8</td>
<td>111.1</td>
<td>106.74</td>
</tr>
</tbody>
</table>
Since the line interrupts $\Lambda_m$ at 124.0 S cm$^2$ mol$^{-1}$, $\Lambda_m^0 = 124.0$ S cm$^2$ mol$^{-1}$

### Q 3.11:

**Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5}$ S cm$^{-1}$. Calculate its molar conductivity. If $\Lambda_m^0$ for acetic acid is 390.5 S cm$^2$ mol$^{-1}$, what is its dissociation constant?**

**Solution:**

Given, $\kappa = 7.896 \times 10^{-5}$ S m$^{-1}$ cm$^{-1}$

= 0.00241 mol L$^{-1}$

Then, molar conductivity, $\Lambda_m = \frac{\kappa}{\epsilon}$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L}$$

= 32.76 S cm$^2$ mol$^{-1}$

$\Lambda_m^0 = 390.5$ S cm$^2$ mol$^{-1}$

Again,

$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$

= $\frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$

Now,

= 0.084

Dissociation constant, $K_a = \frac{\alpha^2}{(1-\alpha)}$

$$= \frac{(0.00241 \text{ mol L}^{-1})(0.084)^2}{(1-0.084)}$$

= $1.86 \times 10^{-5}$ mol L$^{-1}$

### Q 3.12:

How much charge is required for the following reductions:
Q 3.13:
How much electricity in terms of Faraday is required to produce
(i) 20.0 g of Ca from molten CaCl$_2$?
(ii) 40.0 g of Al from molten Al$_2$O$_3$?

Solution:

(i) $Ca^{2+} + 2e^- \rightarrow Ca$

Electricity required to produce 40 g of calcium = 2 F
Therefore, electricity required to produce 20 g of calcium = $2 \times 20 / 40$ F
Q 3.14:
How much electricity is required in coulomb for the oxidation of
(i) 1 mol of $\text{H}_2\text{O}$ to $\text{O}_2$?
(ii) 1 mol of $\text{FeO}$ to $\text{Fe}_2\text{O}_3$?

Solution:
(i) From given data,

$$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$$

Electricity required to produce 27 g of Al = 3 F
Therefore, electricity required to produce 40 g of Al = \( \frac{3 \times 40}{27} \) F
= 4.44 F

Q 3.15:
A solution of $\text{Ni(NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Solution:
Given,
Q 3.16:
Three electrolytic cells A, B, C containing solutions of ZnSO₄, AgNO₃ and CuSO₄, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Solution:

According to the reaction:

\[ Ag^{+} (aq) + e^- \rightarrow Ag(s) \]

i.e., \( \frac{108\text{ g of Ag}}{96487\text{ C}} \).

Therefore, 1.45 g of Ag is deposited by \( \frac{96487 \times 1.45}{108} \text{ C} \)

= 1295.43 C

Given,

Current = 1.5 A
Time = 1295.43/ 1.5 s
= 863.6 s
= 864 s
Q 3.17:

Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:
(i) Fe\(^{3+}\) (aq) and I\(^{-}\) (aq)
(ii) Ag\(^{+}\) (aq) and Cu(s)
(iii) Fe\(^{3+}\) (aq) and Br\(^{-}\) (aq)
(iv) Ag(s) and Fe\(^{3+}\) (aq)
(v) Br\(_2\) (aq) and Fe\(^{2+}\) (aq).

Solution:

(i) 
\[
\begin{align*}
\text{Fe}^{3+}(aq) + e^- & \rightarrow \text{Fe}^{2+}(aq) \quad [\times 2] \quad E^o = 0.76 V \\
2I^-(aq) & \rightarrow I_2(aq) + e^- \quad E^o = 0.54 V \\
\text{Fe}^{3+}(aq) + 2I^-(aq) & \rightarrow 2\text{Fe}^{2+}(aq) + I_2(s) \quad E^o = 0.23 V
\end{align*}
\]

E\(^o\) is positive, hence reaction is feasible
(ii)

\[
\begin{align*}
\text{Ag}^{+}{}_{(aq)} + \text{e}^- & \rightarrow \text{Ag}{}_{(s)} \times 2 \quad E^\circ = +0.80\text{V} \\
\text{Cu}{}_{(s)} & \rightarrow \text{Cu}^{2+}{}_{(aq)} + 2\text{e}^- \quad E^\circ = -0.34\text{V} \\
2\text{Ag}^{+}{}_{(aq)} + \text{Cu}{}_{(s)} & \rightarrow 2\text{Ag}{}_{(s)} + \text{Cu}^{2+}{}_{(aq)} \quad E^\circ = +0.46\text{V}
\end{align*}
\]

\(E^\circ\) is positive, hence reaction is feasible.

(iii)

\[
\begin{align*}
\text{Fe}^{3+}{}_{(aq)} + \text{e}^- & \rightarrow \text{Fe}^{2+}{}_{(aq)} \times 2 \quad E^\circ = +0.77\text{V} \\
2\text{Br}{}_{(aq)} & \rightarrow \text{Br}_2{}_{(l)} + 2\text{e}^- \quad E^\circ = -1.09\text{V} \\
2\text{Fe}^{3+}{}_{(aq)} + 2\text{Br}{}_{(aq)} & \rightarrow 2\text{Fe}^{2+}{}_{(aq)} \text{ and } \text{Br}_2{}_{(l)} \quad E^\circ = -0.32\text{V}
\end{align*}
\]

\(E^\circ\) is negative, hence reaction is not feasible.

(iv)

\[
\begin{align*}
\text{Ag}{}_{(s)} + \text{e}^- & \rightarrow \text{Ag}^{+}{}_{(aq)} + \text{e}^- \quad E^\circ = -0.80\text{V} \\
\text{Fe}^{3+}{}_{(aq)} + \text{e}^- & \rightarrow \text{Fe}^{2+}{}_{(aq)} \quad E^\circ = +0.77\text{V} \\
\text{Ag}{}_{(s)} + \text{Fe}^{3+}{}_{(aq)} & \rightarrow \text{Ag}^{+}{}_{(aq)} + \text{Fe}^{2+}{}_{(aq)} \quad E^\circ = -0.03\text{V}
\end{align*}
\]

\(E^\circ\) is negative, hence reaction is not feasible.
E° is positive, hence reaction is feasible.

**Q 3.18:**

Predict the products of electrolysis in each of the following:
(i) An aqueous solution of AgNO₃ with silver electrodes.
(ii) An aqueous solution of AgNO₃ with platinum electrodes.
(iii) A dilute solution of H₂SO₄ with platinum electrodes.
(iv) An aqueous solution of CuCl₂ with platinum electrodes.

**Solution:**

(i) At cathode:
The following reduction reactions compete to take place at the cathode.

\[ Ag^{+}_{(aq)} + e^- \rightarrow Ag_{(s)} \quad ; \quad E^o = 0.80 \text{ V} \]

\[ H^{+}_{(aq)} + e^- \rightarrow \frac{1}{2}H_2(g) \quad ; \quad E^o = 0.00 \text{ V} \]

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:
The Ag anode is attacked by \( NO_3^+ \) ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag⁺.

(ii) At cathode:
The following reduction reactions compete to take place at the cathode.

\[ Ag^{+}_{(aq)} + e^- \rightarrow Ag_{(s)} \quad ; \quad E^o = 0.80 \text{ V} \]

\[ H^{+}_{(aq)} + e^- \rightarrow \frac{1}{2}H_2(g) \quad ; \quad E^o = 0.00 \text{ V} \]
The reaction with a higher value of $E^0$ takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

Since Pt electrodes are inert, the anode is not attacked by $NO_3^-$ ions. Therefore, OH$^-$ or $NO_3^-$ ions can be oxidized at the anode. But OH$^-$ ions having a lower discharge potential and get preference and decompose to liberate O$_2$.

\[ OH^- \rightarrow O + E^- + 4OH^- \rightarrow 2H_2O + O_2 \]

(iii) At the cathode, the following reduction reaction occurs to produce H$_2$ gas.

\[ H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_2(g) \]

At the anode, the following processes are possible.

\[ 2H_2O(l) \rightarrow O_2(g) + 4H^+_{(aq)} + 4e^-; E^0 = +1.23 \text{ V} \] —(i)

\[ 2SO_4^{2-}_{(aq)} \rightarrow S_2O_3^{2-}_{6(aq)} + 2e^-; E^0 = +1.96 \text{ V} \] —(ii)

For dilute sulphuric acid, reaction (i) is preferred to produce O$_2$ gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

The following reduction reactions compete to take place at the cathode.

\[ Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s); E^0 = 0.34 \text{ V} \]

\[ H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_2(g); E^0 = 0.00 \text{ V} \]

The reaction with a higher value of takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

At anode:

The following oxidation reactions are possible at the anode.

\[ Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_2(g) + e^-; E^0 = 1.36 \text{ V} \]

\[ 2H_2O(l) \rightarrow O_2(g) + 4H^+_{(aq)} + e^-; E^0 = +1.23 \text{ V} \]

At the anode, the reaction with a lower value of $E^0$ is preferred. But due to the over potential of oxygen, Cl$^-$ gets oxidized at the anode to produce Cl$_2$ gas.