

# 3

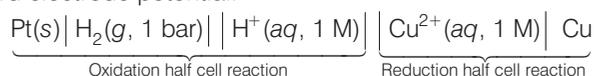
## Electrochemistry

### Multiple Choice Questions (MCQs)

**Q. 1** Which cell will measure standard electrode potential of copper electrode?

- (a)  $\text{Pt (s)} | \text{H}_2(\text{g}, 0.1 \text{ bar}) | \text{H}^+(\text{aq}, 1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) | \text{Cu}$   
 (b)  $\text{Pt (s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq}, 1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 2 \text{ M}) | \text{Cu}$   
 (c)  $\text{Pt (s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq}, 1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) | \text{Cu}$   
 (d)  $\text{Pt (s)} | \text{H}_2(\text{g}, 0.1 \text{ bar}) | \text{H}^+(\text{aq}, 0.1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) | \text{Cu}$

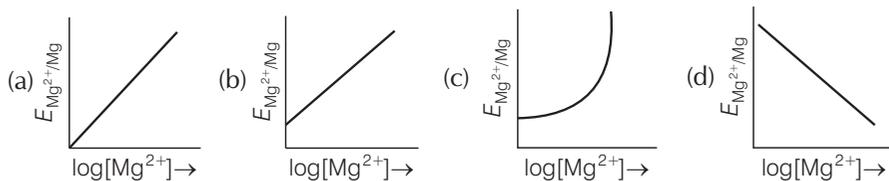
**Ans. (c)** Standard electrode potential of copper electrode can be calculated by constructing a concentration cell composed of two half cell reactions in which concentration of species on left hand and right hand side are unity. In such case cell potential is equal to standard electrode potential.



**Q. 2** Electrode potential for Mg electrode varies according to the equation

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^s - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

vs  $\log [\text{Mg}^{2+}]$  is



### Thinking Process

This problem includes concept of Nernst equation and its transformation to equation of straight line.

**Ans.** Electrode potential for Mg electrode varies according to the equation

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} + \frac{0.059}{2} \log [\text{Mg}^{2+}]$$

$$E_{\text{Mg}^{2+}/\text{Mg}} = \frac{0.059}{2} \log [\text{Mg}^{2+}] + E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$$

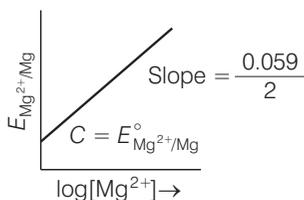
This equation represents equation of straight line. It can be correlated as

$$E_{\text{Mg}^{2+}/\text{Mg}} = \left( \frac{0.059}{2} \right) \log [\text{Mg}^{2+}] + E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$$

$\uparrow$                      $\uparrow$                      $\uparrow$                      $\uparrow$   
 Y                    M                    X                    + C

So, intercept (C) =  $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$

Thus, equation can be diagrammatically represented as



**Q. 3** Which of the following statement is correct?

- (a)  $E_{\text{cell}}$  and  $\Delta_r G$  of cell reaction both are extensive properties
- (b)  $E_{\text{cell}}$  and  $\Delta_r G$  of cell reaction both are intensive properties
- (c)  $E_{\text{cell}}$  is an intensive property while  $\Delta_r G$  of cell reaction is an extensive property
- (d)  $E_{\text{cell}}$  is an extensive property while  $\Delta_r G$  of cell reaction is an intensive property

**Thinking Process**

*This problem is based on thermodynamical concept of intensive and extensive property. During answering this question must keep in mind that intensive property is independent on number of particles and extensive property is dependent on number of particles.*

**Ans. (c)**  $E_{\text{cell}}$  is an intensive property as it does not depend upon mass of species (number of particles) but  $\Delta_r G$  of the cell reaction is an extensive property because this depends upon mass of species (number of particles).

**Q. 4** The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called.....

- (a) cell potential
- (b) cell emf
- (c) potential difference
- (d) cell voltage

**Ans. (b)** **Cell emf** The difference between the electrode potential of two electrodes when no current is drawn through the cell is called cell emf.

**Q. 5** Which of the following statement is not correct about an inert electrode in a cell?

- (a) It does not participate in the cell reaction
- (b) It provides surface either for oxidation or for reduction reaction
- (c) It provides surface for conduction of electrons
- (d) It provides surface for redox reaction

**Ans. (d)** An inert electrode in a cell provide surface for either oxidation or for reduction reaction by conduction of electrons through its surface but does not participate in the cell reaction.

It does not provide surface for redox reaction.

**Q. 6** An electrochemical cell can behave like an electrolytic cell when .....

(a)  $E_{\text{cell}} = 0$

(b)  $E_{\text{cell}} > E_{\text{ext}}$

(c)  $E_{\text{ext}} > E_{\text{cell}}$

(d)  $E_{\text{cell}} = E_{\text{ext}}$

**Ans. (c)** If an external opposite potential is applied on the galvanic cell and increased reaction continues to take place till the opposing voltage reaches the value 1.1 V.

At this stage no current flow through the cell and if there is any further increase in the external potential then reaction starts functioning in opposite direction.

Hence, this works as an electrolytic cell.

**Q. 7** Which of the statements about solutions of electrolytes is not correct?

(a) Conductivity of solution depends upon size of ions

(b) Conductivity depends upon viscosity of solution

(c) Conductivity does not depend upon solvation of ions present in solution

(d) Conductivity of solution increases with temperature

**Ans. (c)** Solution consists of electrolytes is known as electrolytic solution and conductivity of electrolytic solution depends upon the following factors

(i) **Size of ions** As ion size increases, ion mobility decreases and conductivity decreases.

(ii) **Viscosity of solution** Greater the viscosity of the solvent lesser will be the conductivity of the solution.

(iii) **Solvation of ions** Greater the solvation of ions of an electrolyte lesser will be the electrical conductivity of the solution.

(iv) **Temperature of medium** Conductivity of solution increases with increase in temperature.

**Q. 8** Using the data given below find out the strongest reducing agent.

$$E^{\circ}_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33\text{V}; E^{\circ}_{\text{Cl}_2/\text{Cl}^-} = 1.36\text{V}$$

$$E^{\circ}_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51\text{V}; E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$$

(a)  $\text{Cl}^-$

(b) Cr

(c)  $\text{Cr}^{3+}$

(d)  $\text{Mn}^{2+}$

### 🔦 Thinking Process

*This problem includes concept of electrochemical series and standard reduction potential of the metal.*

*Higher the negative value of standard reduction potential, strongest will be the reducing agent.*

*As value of SRP increases from negative to positive value nature of species changes from reducing to oxidising nature.*

**Ans. (b)** Here, out of given four options standard reduction potential of chromium has highest negative value hence most powerful reducing agent is chromium.

**Q. 9** Use the data given in Q. 8 and find out which of the following is the strongest oxidising agent?

- (a)  $\text{Cl}^-$  (b)  $\text{Mn}^{2+}$   
 (c)  $\text{MnO}_4^-$  (d)  $\text{Cr}^{3+}$

**Ans. (c)** Higher the positive value of standard reduction potential of metal ion higher will be its oxidising capacity.

Since,  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}$  has value equal to 1.51 V hence it is the strongest oxidising agent.

**Q. 10** Using the data given in Q.8 find out in which option the order of reducing power is correct.

- (a)  $\text{Cr}^{3+} < \text{Cl}^- < \text{Mn}^{2+} < \text{Cr}$  (b)  $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$   
 (c)  $\text{Cr}^{3+} < \text{Cl}^- < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$  (d)  $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$

**Ans. (b)**

Species (ions)	SRP values
$\text{Mn}^{2+}$	1.51 V
$\text{Cl}^-$	1.36 V
$\text{Cr}^{3+}$	1.33 V
Cr	-0.74 V

On moving top to bottom SRP value decreases from positive to negative value which will increase the reducing capacity. So, the correct option is (b).

**Q. 11** Use the data given in Q. 8 and find out the most stable ion in its reduced form.

- (a)  $\text{Cl}^-$  (b)  $\text{Cr}^{3+}$  (c) Cr (d)  $\text{Mn}^{2+}$

**Ans. (d)**  $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}$  has +ve value equal to 1.51 V which is highest among given four choices. So,  $\text{Mn}^{2+}$  is most stable ion in its reduced form.

**Q. 12** Use the data of Q. 8 and find out the most stable oxidised species.

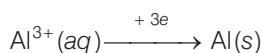
- (a)  $\text{Cr}^{3+}$  (b)  $\text{MnO}_4^-$  (c)  $\text{Cr}_2\text{O}_7^{2-}$  (d)  $\text{Mn}^{2+}$

**Ans. (a)**  $E^\circ_{\text{Cr}^{3+}/\text{Cr}}$  has most -ve value equal to -0.74 among given four choices. So,  $\text{Cr}^{3+}$  is the most stable oxidised species.

**Q. 13** The quantity of charge required to obtain one mole of aluminium from  $\text{Al}_2\text{O}_3$  is .....

- (a) 1 F (b) 6 F (c) 3 F (d) 2 F

**Ans. (c)** The quantity of charge required to obtain one mole of aluminium from  $\text{Al}_2\text{O}_3$  is equal to number of electron required to convert  $\text{Al}_2\text{O}_3$  to Al.



Hence, total 3F is required.

**Q. 14** The cell constant of a conductivity cell .....

- (a) changes with change of electrolyte
- (b) changes with change of concentration of electrolyte
- (c) changes with temperature of electrolyte
- (d) remains constant for a cell

**Ans. (d)** Cell constant is defined as the ratio of length of object and area of cross section.

$$G = \frac{l}{A}$$

Since,  $l$  and  $A$  remain constant for any particular object hence value of cell constant always remains constant.

**Q. 15** While charging the lead storage battery .....

- (a)  $\text{PbSO}_4$  anode is reduced to  $\text{Pb}$
- (b)  $\text{PbSO}_4$  cathode is reduced to  $\text{Pb}$
- (c)  $\text{PbSO}_4$  cathode is oxidised to  $\text{Pb}$
- (d)  $\text{PbSO}_4$  anode is oxidised to  $\text{PbO}_2$

**Ans. (a)** While charging the lead storage battery the reaction occurring on cell is reversed and  $\text{PbSO}_4$  (s) on anode and cathode is converted into  $\text{Pb}$  and  $\text{PbO}_2$  respectively

Hence, option (a) is the correct choice

The electrode reactions are as follows

**At cathode**  $\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$  (Reduction)

**At anode**  $\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2(\text{s}) + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$  (Oxidation)

**Overall reaction**  $2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq.}) + 2\text{SO}_4^{2-}(\text{aq.})$

**Q. 16**  $\Lambda_m^\circ(\text{NH}_4\text{OH})$  is equal to .....

- (a)  $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{HCl})$
- (b)  $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$
- (c)  $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NaOH})$
- (d)  $\Lambda_m^\circ(\text{NaOH}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$

### Thinking Process

This question is based on the concept of Kohlrausch law and can be solved by using the concept involved in calculation of limiting molar conductivity of any salt. According to Kohlrausch law limiting molar conductivity of any salt is equal to sum of limiting molar conductivity of individual molar conductivity of cations and anions of electrolyte.

**Ans. (b)**

$$\Lambda_m^\circ(\text{NH}_4\text{Cl}) = \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{Cl}^-)$$

$$\Lambda_m^\circ(\text{NaOH}) = \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-)$$

$$\Lambda_m^\circ(\text{NaCl}) = \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{Cl}^-)$$

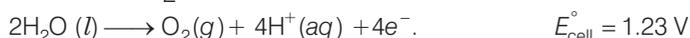
$$\frac{\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})}{\phantom{\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})}} = \Lambda_m^\circ(\text{NH}_4\text{OH})$$

Hence, option (b) is correct choice.

**Q. 17** In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?

- (a)  $\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s}); E_{\text{cell}}^{\text{s}} = -2.71 \text{ V}$
- (b)  $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-; E_{\text{cell}}^{\text{s}} = -1.23 \text{ V}$
- (c)  $\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2(\text{g}); E_{\text{cell}}^- = 0.00 \text{ V}$
- (d)  $\text{Cl}^-(\text{aq}) \longrightarrow \frac{1}{2} \text{Cl}_2(\text{g}) + \text{e}^-; E_{\text{cell}}^{\text{s}} = 1.36 \text{ V}$

**Ans. (d)** In case of electrolysis of aqueous NaCl oxidation reaction occurs at anode as follows



But due to lower  $E_{\text{cell}}^\circ$  value water should get oxidised in preference of  $\text{Cl}^- (\text{aq})$ .

However, the actual reaction taking place in the concentrated solution of NaCl is (d) and not (b) *i.e.*,  $\text{Cl}_2$  is produced and not  $\text{O}_2$ .

This unexpected result is explained on the basis of the concept of 'overvoltage', *i.e.*, water needs greater voltage for oxidation to  $\text{O}_2$  (as it is kinetically slow process) than that needed for oxidation of  $\text{Cl}^-$  ions to  $\text{Cl}_2$ . Thus, the correct option is (d) not (b).

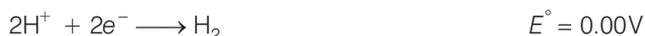
## Multiple Choice Questions (More Than One Options)

**Q. 18** The positive value of the standard electrode potential of  $\text{Cu}^{2+} / \text{Cu}$  indicates that.....

- (a) this redox couple is a stronger reducing agent than the  $\text{H}^+ / \text{H}_2$  couple
- (b) this redox couple is a stronger oxidising agent than  $\text{H}^+ / \text{H}_2$
- (c) Cu can displace  $\text{H}_2$  from acid
- (d) Cu cannot displace  $\text{H}_2$  from acid

**Ans. (b, d)**

'Lesser the  $E^\circ$  value of redox couple higher the reducing power'

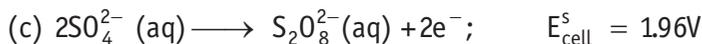
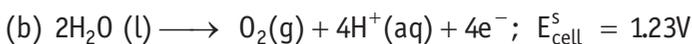
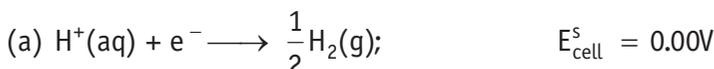


Since,  $2\text{H}^+ / \text{H}_2$  has lesser SRP than  $\text{Cu}^{2+} / \text{Cu}$  redox couple. Therefore,

- (i) This redox couple is a stronger oxidising agent than  $\text{H}^+ / \text{H}_2$ .
- (ii) Cu can't displace  $\text{H}_2$  from acid.

Hence, (b) and (d) are correct.

**Q. 19**  $E_{\text{cell}}^{\text{s}}$  for some half cell reactions are given below. On the basis of these mark the correct answer.

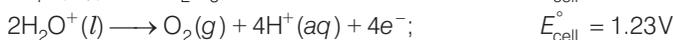


- (a) In dilute sulphuric acid solution, hydrogen will be reduced at cathode
- (b) In concentrated sulphuric acid solution, water will be oxidised at anode
- (c) In dilute sulphuric acid solution, water will be oxidised at anode
- (d) In dilute sulphuric acid solution,  $\text{SO}_4^{2-}$  ion will be oxidised to tetrathionate ion at anode

**Ans. (a, c)**

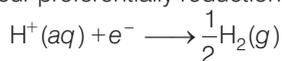
During the electrolysis of dilute sulphuric acid above given three reaction occurs each of which represents particular reaction either oxidation half cell reaction or reduction half cell reaction.

Oxidation half cell reactions occur at anode are as follows



Reaction having lower value of  $E_{\text{cell}}^\circ$  will undergo faster oxidation.

Hence, oxidation of water occur preferentially reduction half cell reaction occurs at cathode



At cathode

Hence, options (a) and (b) are correct.

**Q. 20**  $E_{\text{cell}}^\circ = 1.1\text{ V}$  or Daniel cell. Which of the following expressions are correct description of state of equilibrium in this cell?

- (a)  $1.1 = K_C$  (b)  $\frac{2.303 RT}{2F} \log K_C = 1.1$   
 (c)  $\log K_C = \frac{2.2}{0.059}$  (d)  $\log K_C = 1.1$

**Ans. (b, c)**

At state of equilibrium

$$\Delta G = - RT \log K$$

$$- nFE^\circ = - RT 2.303 \log K_C$$

$$E^\circ = \frac{+RT 2.303 \log K_C}{+ 2F} \quad (n = 2 \text{ for Daniel cell})$$

$\therefore$  At equilibrium  $E^\circ = 1.1$

$$\therefore \frac{2.303 RT}{2 F} \log K_C = 1.1$$

$$\log K_C = \frac{2.2}{0.059} \quad [\text{on solving}]$$

Hence, options (b) and (c) are the correct choices.

**Q. 21** Conductivity of an electrolytic solution depends on

- (a) nature of electrolyte  
 (b) concentration of electrolyte  
 (c) power of AC source  
 (d) distance between the electrodes

**Ans. (a, b)**

Conductivity of electrolytic solution is due to presence of mobile ions in the solution. This type of conductance is known as ionic conductance. Conductivity of these type of solutions depend upon

- (i) the nature of electrolyte added  
 (ii) size of the ion produced and their solvation  
 (iii) concentration of electrolyte  
 (iv) nature of solvent and its viscosity  
 (v) temperature

While power of source or distance between electrodes has no effect on conductivity of electrolyte solution.

Hence, options (a) and (b) are the correct choices.

**Q. 22**  $\Lambda_m^\circ \text{H}_2\text{O}$  is equal to.....

- (a)  $\Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$       (b)  $\Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaNO}_3) - \Lambda_m^\circ(\text{NaOH})$   
 (c)  $\Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaNO}_3)$       (d)  $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$

**Thinking Process**

This problem includes concept of Kohlrausch law and its application in determination of molar conductivity of species. This problem can be solved by following three steps.

- (i) Write the molar conductance of each species in terms of sum of their constituent ions.  
 (ii) Now operate the equation of each option given above by using information provided in the question.  
 (iii) At last if the sum of molar conductivity remaining constituent ions is equal to the molar conductivity of species asked (here  $\Lambda_m^\circ(\text{H}_2\text{O})$ ) then that will be the correct choice.

**Ans. (a, c)**

(a)

$$\begin{aligned} \Lambda_m^\circ(\text{HCl}) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{Cl}^-) \\ \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-) \\ \Lambda_m^\circ(\text{NaCl}) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{Cl}^-) \\ \hline \Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl}) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{OH}^-) \\ &= \Lambda_m^\circ(\text{H}_2\text{O}) \end{aligned}$$

(d)

$$\begin{aligned} \Lambda_m^\circ(\text{NH}_4\text{OH}) &= \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{OH}^-) \\ \Lambda_m^\circ(\text{HCl}) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{Cl}^-) \\ \Lambda_m^\circ(\text{NH}_4\text{Cl}) &= \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{Cl}^-) \\ \hline \Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl}) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{OH}^-) = \Lambda_m^\circ(\text{H}_2\text{O}) \end{aligned}$$

This type of decomposition is not possible due to weak basic strength of  $\text{NH}_4\text{OH}$ . This line will be placed above.

(b)

$$\begin{aligned} \Lambda_m^\circ(\text{HNO}_3) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \Lambda_m^\circ(\text{NaNO}_3) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-) \\ \hline \Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaNO}_3) - \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{H}^+) + 2\Lambda_m^\circ(\text{NO}_3^-) - \Lambda_m^\circ(\text{OH}^-) \end{aligned}$$

(b) is incorrect

(c)

$$\begin{aligned} \Lambda_m^\circ(\text{HNO}_3) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \Lambda_m^\circ(\text{NaOH}) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{OH}^-) \\ \Lambda_m^\circ(\text{NaNO}_3) &= \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{NO}_3^-) \\ \hline \Lambda_m^\circ(\text{HNO}_3) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaNO}_3) &= \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{OH}^-) = \Lambda_m^\circ(\text{H}_2\text{O}) \end{aligned}$$

Hence, Options (a) and (c) are the correct choices.

**Q. 23** What will happen during the electrolysis of aqueous solution of  $\text{CuSO}_4$  by using platinum electrodes?

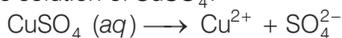
- (a) Copper will deposit at cathode      (b) Copper will deposit at anode  
 (c) Oxygen will be released at anode    (d) Copper will dissolve at anode

**💡 Thinking Process**

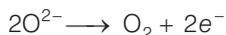
*This problem is based on electrolysis of electrolytes.*

**Ans. (a, c)**

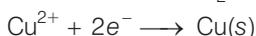
For electrolysis of aqueous solution of  $\text{CuSO}_4$ .



At anode



At cathode



**Q. 24** What will happen during the electrolysis of aqueous solution of  $\text{CuSO}_4$  in the presence of Cu electrodes?

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

**Ans. (a, b)**

Electrolysis of  $\text{CuSO}_4$  can be represented by two half cell reactions these occurring at cathode and anode respectively as



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

Hence, options (a) and (b) are the correct choices.

**Q. 25** Conductivity  $\kappa$ , is equal to.....

(a)  $\frac{1}{R} \frac{l}{A}$

(b)  $\frac{G^*}{R}$

(c)  $\Lambda_m$

(d)  $\frac{l}{A}$

**Ans. (a, b)**

As we know that, conductance is reciprocal of resistance and conductivity is the conductance of  $1 \text{ cm}^3$  of substance. Also, conductivity is reciprocal of resistivity.

$$\kappa = \frac{1}{\rho}$$

$\therefore$

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

$$\rho = \frac{R \cdot A}{l} \Rightarrow \kappa = \frac{1}{\left(\frac{R \cdot A}{l}\right)}$$

$$\kappa = \frac{1}{R} \cdot \frac{l}{A} = \frac{1}{R} \times G^* = \frac{G^*}{R}$$

Hence, options (a) and (b) are the correct choices.

**Q. 26** Molar conductivity of ionic solution depends on .....

- (a) temperature  
 (b) distance between electrodes  
 (c) concentration of electrolytes in solution  
 (d) surface area of electrodes

**Ans. (a, c)**

Molar conductivity is the conductivity due to ions furnished by one mole of electrolyte in solution. Molar conductivity of ionic solution depends on

- (i) **Temperature** Molar conductivity of electrolyte solution increases with increase in temperature.
- (iii) **Concentration of electrolytes in solution** As concentration of electrolyte increases, molar conductivity decreases.

$$\therefore \lambda = \frac{\kappa}{C}$$

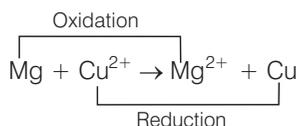
**Q. 27** For the given cell,  $\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$ 

- (a) Mg is cathode
- (b) Cu is cathode
- (c) The cell reaction is  $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$
- (d) Cu is the oxidising agent

**Ans. (b, c)**

Left side of cell reaction represents oxidation half cell *i.e.*, oxidation of Mg and right side of cell represents reduction half cell reactions *i.e.*, reduction of copper.

- (ii) Cu is reduced and reduction occurs at cathode.
- (iii) Mg is oxidised and oxidation occurs at anode.
- (iv) whole cell reaction can be written as



Hence, options (b) and (c) both are correct choices.

## Short Answer Type Questions

**Q. 28** Can absolute electrode potential of an electrode be measured ?

**Ans.** No, only the difference in potential between two electrodes can be measured. This is due to the reason that oxidation or reduction cannot occur alone. So, when we measure electrode potential of any electrode we have to take a reference electrode.

**Q. 29** Can  $E_{\text{cell}}^{\circ}$  or  $\Delta_r G^{\circ}$  for cell reaction ever be equal to zero ?

**Ans.** No, otherwise the reaction become non-feasible.

The reaction is feasible only at  $E_{\text{cell}}^{\circ} = \text{positive}$  or  $\Delta_r G^{\circ} = \text{negative}$ .  
when  $E^{\circ} = \Delta_r G^{\circ} = 0$  the reaction reaches at equilibrium.

**Q. 30** Under what condition is  $E_{\text{cell}} = 0$  or  $\Delta_r G = 0$  ?

**Ans.** At the stage of chemical equilibrium in the cell.

$$\begin{aligned} E_{\text{cell}} &= 0 \\ \Delta_r G^{\circ} &= -n F E_{\text{cell}}^{\circ} \\ &= -n \times F \times 0 = 0 \end{aligned}$$

**Q. 31** What does the negative sign in the expression  $E^{\text{S}}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$  mean?

**Ans.** Greater the negative reactivity of standard reduction potential of metal greater is its reactivity. It means that Zn is more reactive than hydrogen. When zinc electrode will be connected to standard hydrogen electrode, Zn will get oxidised and  $\text{H}^+$  will get reduced.

Thus, zinc electrode will be the anode of the cell and hydrogen electrode will be the cathode of the cell.

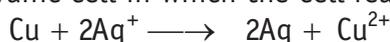
**Q. 32** Aqueous copper sulphate solution and aqueous silver nitrate solution are electrolysed by 1 ampere current for 10 minutes in separate electrolytic cells. Will the mass of copper and silver deposited on the cathode be same or different? Explain your answer.

**Ans.** Different masses of Cu and Ag will be deposited at cathode. According to Faraday's second law of electrolysis amount of different substances liberated by same quantity of electricity passes through electrolyte solution is directly proportional to their chemical equivalent weight.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

where,  $E_1$  and  $E_2$  have different values depending upon number of electrons required to reduce the metal ion. Thus, masses of Cu and Ag deposited will be different.

**Q. 33** Depict the galvanic cell in which the cell reaction is

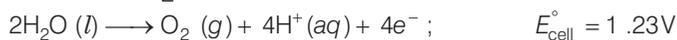
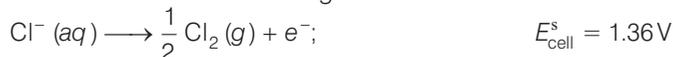


**Ans.** In a galvanic cell, oxidation half reaction is written on left hand side and reduction half reaction is on right hand side. Salt bridge is represented by parallel lines  
 $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^+ | \text{Ag}$ .

**Q. 34** Value of standard electrode potential for the oxidation of  $\text{Cl}^-$  ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is  $\text{Cl}^-$  oxidised at anode instead of water?

**Ans.** Under the condition of electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential. So,  $\text{Cl}^-$  is oxidized at anode instead of water.

Possible oxidation half cell reactions occurring at anode are

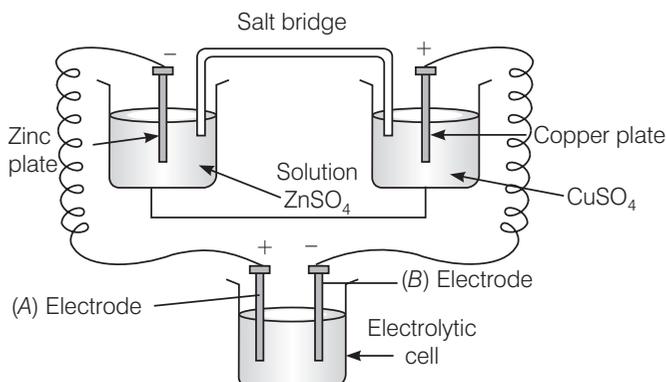


Species having lower  $E_{\text{cell}}^{\circ}$  cell undergo oxidation first than the higher value but oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$  is kinetically so slow that it needs some overvoltage.

**Q. 35** What is electrode potential?

**Ans.** The potential difference between the electrode and the electrolyte in an electrochemical cell is called electrode potential.

**Q. 36** Consider the following diagram in which an electrochemical cell is coupled to an electrolytic cell. What will be the polarity of electrodes 'A' and 'B' in the electrolytic cell?



**Ans.** The cell drawn above represents electrochemical cell in which two different electrodes are fitted in their respective electrolytic solution and cell drawn at bottom represents electrolytic cell.

Cell representation can be represented as  $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$ .

Zn is losing electrons which are going towards electrode (A) and copper is accepting electron from electrode B. Hence,

Charge on electrode A = +

Charge on electrode B = -

**Q. 37** Why is alternating current used for measuring resistance of an electrolytic solution?

**Ans.** Alternating current is used in electrolysis so that concentration of ions in the solution remains constant and exact value of resistance is measured.

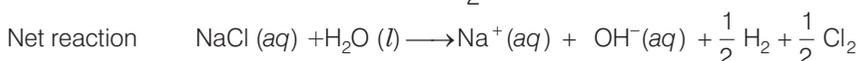
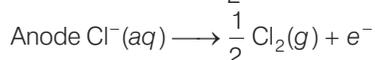
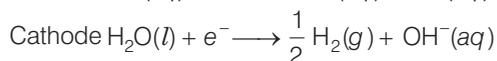
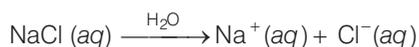
**Q. 38** A galvanic cell has electrical potential of 1.1V. If an opposing potential of 1.1V is applied to this cell, what will happen to the cell reaction and current flowing through the cell ?

**Ans.** When an opposing potential of 1.1V is applied to a galvanic cell having electrical potential of 1.1V then cell reaction stops completely and no current will flow through the cell.

**Q. 39** How will the pH of brine (aq NaCl solution) be affected when it is electrolysed?

**Ans.** The pH of the solution will rise as NaOH is formed in the electrolytic cell.

Chemical reaction occurring at cell when aqueous brine solution is electrolysed are as follows



**Q. 40** Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why ?

**Ans.** Life time of any cell depends upon ions present in cell. Ions are not involved in the overall cell reaction of mercury cell. Hence, mercury cell has a constant cell potential throughout its useful life.

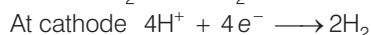
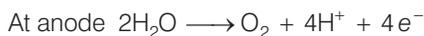
**Q. 41** Solutions of two electrolytes A and B are diluted. The  $\Lambda_m$  of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte ? Justify your answer.

**Ans.** Strong electrolytes dissociate almost completely even on high concentration. Therefore, concentration of such solutions remain almost same on dilution. Electrolyte 'B' is stronger than 'A' because in 'B' the number of ions remains the same on dilution, but only interionic attraction decreases.

Therefore,  $\Lambda_m$  increases only 1.5 times. While in case of weak electrolyte on dilution, number of constituent ions increases.

**Q. 42** When acidulated water (dil.  $H_2SO_4$  solution) is electrolysed, with pH of the solution be affected ? Justify your answer.

**Ans.** Since pH of solution depends upon concentration of  $H^+$  presence in solutions. pH of the solution will not be affected as  $[H^+]$  remains constant.



**Q. 43** In an aqueous solution how does specific conductivity of electrolytes change with addition of water?

**Ans.** Conductivity of solution due to total ions present in per unit volume of solution is known as specific conductivity. Specific conductivity decreases due to decrease in the number of ions per unit volume. We add water to aqueous solution, number of ions present in per unit volume decreases.

**Q. 44** Which reference electrode is used to measure the electrode potential of other electrodes?

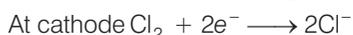
**Ans.** Standard hydrogen electrode (SHE) is the reference electrode whose electrode potential is taken to be zero. The electrode potential of other electrodes are measured with respect to it .

**Q. 45** Consider a cell given below



Write the reactions that occur at anode and cathode.

**Ans.** Cell reaction represented in the question is composed of two half cell reactions. These reactions are as follows



Copper is getting oxidised at anode.  $Cl_2$  is getting reduced at cathode.

**Q. 46** Write the Nernst equation for the cell reaction in the Daniel cell. How will the  $E_{\text{cell}}$  be affected when concentration of  $\text{Zn}^{2+}$  ions is increased?

**Ans.**  $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \left[ \frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right]$$

$$E_{\text{cell}}^{\circ} = E_{\text{cell}} + \frac{0.0591}{2} \log \left[ \frac{\text{Cu}^{2+}}{\text{Zn}^{2+}} \right]$$

According to this equation

$E_{\text{cell}}^{\circ}$  is directly dependent on concentration of  $\text{Cu}^{2+}$  and inversely dependent upon concentration of  $\text{Zn}^{2+}$  ions.

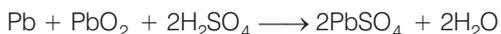
$E_{\text{cell}}$  decreases when concentration of  $\text{Zn}^{2+}$  ions is increased.

**Q. 47** What advantage do the fuel cells have over primary and secondary batteries ?

**Ans.** Primary batteries contain a limited amount of reactants and are discharged when the reactants have been consumed. Secondary batteries can be recharged but it take a long time. Fuel cell run continuously as long as the reactants are supplied to it and products are removed continuously.

**Q. 48** Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?

**Ans.** When a lead storage battery is discharged then the following cell reaction takes place



Density of electrolyte depends upon number.of constituent ions present in per unit volume of electrolyte solution.In this case density of electrolyte decreases as water is formed and sulphuric acid is consumed as the product during discharge of the battery.

**Q. 49** Why on dilution the  $\Lambda_m$  of  $\text{CH}_3\text{COOH}$  increases drastically, while that of  $\text{CH}_3\text{COONa}$  increases gradually?

**Ans.** In the case of  $\text{CH}_3\text{COOH}$ , which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.



In case of strong electrolyte, the number of ions remains the same but the interionic attraction decreases.

## Matching The Columns

**Q. 50** Match the terms given in Column I with the units given in Column II.

Column I	Column II
A. $\wedge_m$	1. $\text{S cm}^{-1}$
B. $E_{\text{cell}}$	2. $\text{m}^{-1}$
C. $\kappa$	3. $\text{S cm}^2 \text{ mol}^{-1}$
D. $G^*$	4. V

**Ans.** A.  $\rightarrow$  (3)    B.  $\rightarrow$  (4)    C.  $\rightarrow$  (1)    D.  $\rightarrow$  (2)

Column I	Column II (Unit of parameter)
A. $\wedge_m$	$\text{S cm}^2 \text{ mol}^{-1}$
B. $E_{\text{cell}}$	V
C. $\kappa$ (conductivity)	$\text{S cm}^{-1}$
D. $G^* = \frac{l}{a}$	$\text{m}^{-1}$

**Q. 51** Match the terms given in Column I with the items given in Column II.

Column I	Column II
A. $\wedge_m$	1. Intensive property
B. $E_{\text{cell}}^{\circ}$	2. Depends on number of ions/volume
C. $\kappa$	3. Extensive property
D. $\Delta_r G_{\text{cell}}$	4. Increases with dilution

**Ans.** A.  $\rightarrow$  (4)    B.  $\rightarrow$  (1)    C.  $\rightarrow$  (2)    D.  $\rightarrow$  (3)

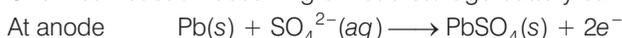
- A.  $\wedge_m$  (molar conductivity) is the conductivity due to number of ions furnished by one mole of electrolyte. As dilution increases number of ions present in the solution increases hence molar conductivity increases.
- B.  $E_{\text{cell}}^{\circ}$  of any atom/ion does not depend upon number of atom/ion, hence  $E_{\text{cell}}^{\circ}$  of any atom/ion is an intensive properties.
- C.  $\kappa$  represents specific conductivity which depends upon number of ions present in per unit volume.
- D.  $\Delta_r G_{\text{cell}}$  is an extensive property as it depends upon number of particles(species).

**Q. 52** Match the items of Column I and Column II.

Column I	Column II
A. Lead storage battery	1. Maximum efficiency
B. Mercury cell	2. Prevented by galvanisation
C. Fuel cell	3. Gives steady potential
D. Rusting	4. Pb is anode, PbO <sub>2</sub> is cathode

**Ans.** A. → (4)    B. → (3)    C. → (1)    D. → (2)

A. Chemical reaction occurring on lead storage battery can be represented as



Thus, Pb is anode and PbO<sub>2</sub> is cathode.

B. Mercury cell does not include ions during their function hence produce steady current.

C. Fuel cell has maximum efficiency as they produce energy due to combustion reaction of fuel.

D. Rusting is prevented by corrosion.

**Q. 53** Match the items of Column I and Column II.

Column I	Column II
A. $\kappa$	1. $I \times t$
B. $\wedge_m$	2. $\wedge_m / \wedge_m^0$
C. $\alpha$	3. $\frac{\kappa}{C}$
D. $Q$	4. $\frac{G^*}{R}$

**Ans.** A. → (4)    B. → (3)    C. → (2)    D. → (1)

A. Conductivity ( $\kappa$ ) =  $\frac{G^*}{R}$

B. Molar conductivity ( $\wedge_m$ ) =  $\frac{\kappa}{C}$

C. Degree of dissociation ( $\alpha$ ) =  $\frac{\wedge_m^0}{\wedge_m}$

D. Charge  $Q = I \times t$

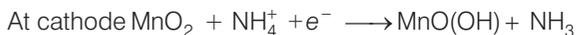
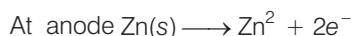
where,  $Q$  is the quantity of charge in coulomb when  $I$  ampere of current is passed through an electrolyte for  $t$  second.

**Q. 54** Match the items of Column I and Column II.

Column I	Column II
A. Leclanche cell	1. Cell reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
B. Ni-Cd cell	2. Does not involve any ion in solution and is used in hearing aids.
C. Fuel cell	3. Rechargeable
D. Mercury cell	4. Reaction at anode, $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$
	5. Converts energy of combustion into electrical energy

**Ans. A.** → (4)   **B.** → (3)   **C.** → (1, 5)   **D.** → (2)

A. Leclanche cell The electrode reaction occurs at Leclanche cell are



- B. Ni-Cd cell is rechargeable. So, it has more life time.  
 C. Fuel cell produces energy due to combustion. So, fuel cell converts energy of combustion into electrical energy e.g.,  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$   
 D. Mercury cell does not involve any ion in solution and is used in hearing aids.

**Q. 55** Match the items of Column I and Column II on the basis of data given below

$$E_{\text{F}_2/\text{F}^{-}}^{\text{S}} = 2.87\text{V}, E_{\text{Li}^{+}/\text{Li}}^{\text{S}} = -3.5\text{V},$$

$$E_{\text{Au}^{3+}/\text{Au}}^{\text{S}} = 1.4\text{V}, E_{\text{Br}_2/\text{Br}^{-}}^{\text{S}} = 1.09\text{V}$$

Column I	Column II
A. $\text{F}_2$	1. Metal is the strongest reducing agent
B. Li	2. Metal ion which is the weakest oxidising agent
C. $\text{Au}^{3+}$	3. Non-metal which is the best oxidising agent
D. $\text{Br}^{-}$	4. Unreactive metal
E. Au	5. Anion that can be oxidised by $\text{Au}^{3+}$
F. $\text{Li}^{+}$	6. Anion which is the weakest reducing agent
G. $\text{F}^{-}$	7. Metal ion which is an oxidising agent

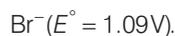
**Ans. A.** → (3)   **B.** → (1)   **C.** → (7)   **D.** → (5)   **E.** → (4)   **F.** → (2)   **G.** → (6)

A.  $\text{F}_2$  is a non-metal and best oxidising agent because SRP of  $\text{F}_2$  is + 2.87 V.

B. Li is a metal and strongest reducing agent because SRP of Li is – 3.05 V.

C.  $\text{Au}^{3+}$  is a metal ion which is an oxidising agent as SRP of  $\text{Au}^{3+}$  is +1.40 V.

D.  $\text{Br}^{-}$  is an anion that can be oxidised by  $\text{Au}^{3+}$  as  $\text{Au}^{3+}$  ( $E^{\circ} = 1.40$ ) is greater than



E. Au is an unreactive metal.

F.  $\text{Li}^{+}$  is a metal ion having least value of SRP (– 3.05 V), hence it is the weakest oxidising agent.

G.  $\text{F}^{-}$  is an anion which is the weakest reducing agent as  $\text{F}^{-} / \text{F}_2$  has low oxidation potential (–2.87 V).

## Assertion and Reason

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are true and the reason is the correct explanation of assertion.
- (b) Both assertion and reason are true and reason is not the correct explanation of assertion.
- (c) Assertion is true but the reason is false.
- (d) Both assertion and reason are false.
- (e) Assertion is false but reason is true.

**Q. 56** Assertion (A) Cu is less reactive than hydrogen.

Reason (R)  $E_{\text{Cu}^{2+}/\text{Cu}}^{\text{s}}$  is negative.

**Ans. (c)** Assertion is true but the reason is false. Electrode potential of  $\text{Cu}^{2+}/\text{Cu}$  is + 0.34V and Electrode potential of  $2\text{H}^+/\text{H}_2$  is 0.00 V.  
Hence, correct reason is due to positive value of  $\text{Cu}^{2+}/\text{Cu}$  it loses electron to  $\text{H}^+$  and get reduces, while  $\text{H}_2$  gas evolves out.

**Q. 57** Assertion (A)  $E_{\text{cell}}$  should have a positive value for the cell to function.

Reason (R)  $E_{\text{cathode}} < E_{\text{anode}}$

**Ans. (c)** Assertion is true but the reason is false. Feasibility of chemical reaction depends on Gibbs free energy which is related to  $E_{\text{cell}}^{\circ}$  as

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

When value of  $E_{\text{cell}}^{\circ}$  is positive then  $\Delta G^{\circ}$  becomes negative. Hence, reaction becomes feasible.

Correct reason is  $E_{\text{cathode}} > E_{\text{anode}}$ .

**Q. 58** Assertion (A) Conductivity of all electrolytes decreases on dilution.

Reason (R) On dilution number of ions per unit volume decreases.

**Ans. (a)** Both assertion and reason are correct and reason is the correct explanation of assertion.  
Since, conductivity depends upon number of ions per unit volume. Therefore, the conductivity of all electrolytes decreases on dilution due to decrease in number of ions per unit volume.

**Q. 59** Assertion (A)  $\Lambda_m$  for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

Reason (R) For weak electrolytes degree of dissociation increases with dilution of solution.

**Ans. (a)** Assertion and reason are true and the reason is the correct explanation of the assertion.  
Molar conductivity of weak electrolytic solution increases on dilution, because as we add excess water to increase the dilution degree of dissociation increases which lead to increase in number of ions in the solution. Thus,  $\Lambda_m$  show a very sharp increase.

**Q. 60** Assertion (A) Mercury cell does not give steady potential.  
Reason (R) In the cell reaction, ions are not involved in solution.

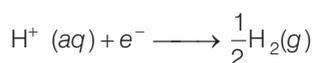
**Ans. (e)** Assertion is false but reason is true. Correct assertion is mercury cell gives steady potential.  
Reason is correct as ions are not involved in cell reaction.

**Q. 61** Assertion (A) Electrolysis of NaCl solution gives chlorine at anode instead of  $O_2$ .  
Reason (R) Formation of oxygen at anode requires over voltage.

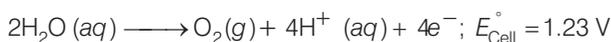
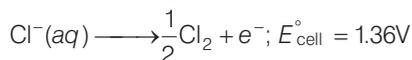
**Ans. (a)** Both assertion and reason are correct and reason is the correct explanation of assertion.

**Explanation** Electrolysis of NaCl is represented by following chemical reactions

At cathode



At anode



$E_{\text{cell}}^\circ$  for this reaction has lower value but formation of oxygen at anode requires over potential.

**Q. 62** Assertion (A) For measuring resistance of an ionic solution an AC source is used.

Reason (R) Concentration of ionic solution will change if DC source is used.

**Ans. (a)** Both assertion and reason are correct and reason is the correct explanation of assertion.

Concentration of ionic solution changes on using DC current as a source of energy while on passing AC current concentration does not change. Hence, AC source is used for measuring resistance.

**Q. 63** Assertion (A) Current stops flowing when  $E_{\text{cell}} = 0$ .

Reason (R) Equilibrium of the cell reaction is attained.

**Ans.(a)** Both assertion and reason are correct and reason is the correct explanation of assertion.

Current stop flowing when  $E_{\text{cell}} = 0$

As at  $E_{\text{cell}} = 0$  reaction reaches the equilibrium.

**Q. 64** Assertion (A)  $E_{\text{Ag}^+/\text{Ag}}$  increase with increase in concentration of  $\text{Ag}^+$  ions.

Reason (R)  $E_{\text{Ag}^+/\text{Ag}}$  has a positive value.

**Ans. (b)** Both assertion and reason are correct but reason is not the correct explanation of assertion.

$$E = E^\circ - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$E = E^\circ + 0.059 \log [\text{Ag}^+]$$

Thus,  $E_{\text{Ag}^+/\text{Ag}}$  increases with increase in concentration of  $\text{Ag}^+$ .

**Q. 65** Assertion (A) Copper sulphate can be stored in zinc vessel.

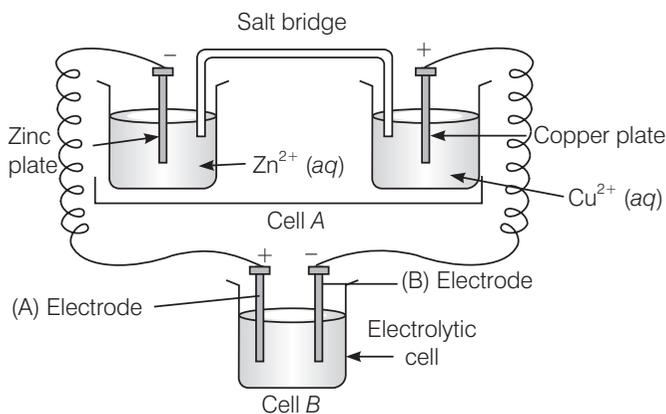
Reason (R) Zinc is less reactive than copper.

**Ans. (d)** Both assertion and reason are false.

Copper sulphate can't be stored in zinc vessel as zinc is more reactive than copper due to negative value of standard reduction potential of Zn.

## Long Answer Type Questions

**Q. 66** Consider the figure and answer the following questions.



(i) Cell 'A' has  $E_{\text{cell}} = 2\text{V}$  and Cell 'B' has  $E_{\text{cell}} = 1.1\text{V}$  which of the two cells 'A' or 'B' will act as an electrolytic cell. Which electrode reactions will occur in this cell?

(ii) If cell 'A' has  $E_{\text{cell}} = 0.5\text{V}$  and cell 'B' has  $E_{\text{cell}} = 1.1\text{V}$  then what will be the reactions at anode and cathode?

### 💡 Thinking Process

This problem includes concept of electrochemical cell, electrolytic cell and charge on electrode. To solve this problem identify the charge on each electrode first.

**Ans. (i)** Cell 'B' will act as electrolytic cell due to its lesser value of emf.

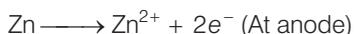
The electrode reactions will be



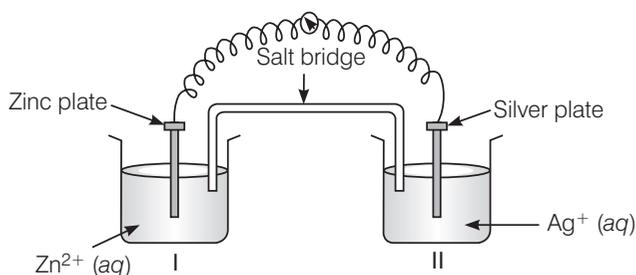
**(ii)** If cell 'B' has higher emf, it acts as galvanic cell.

Now it will push electrons into cell 'A'

In this case, the reactions will be

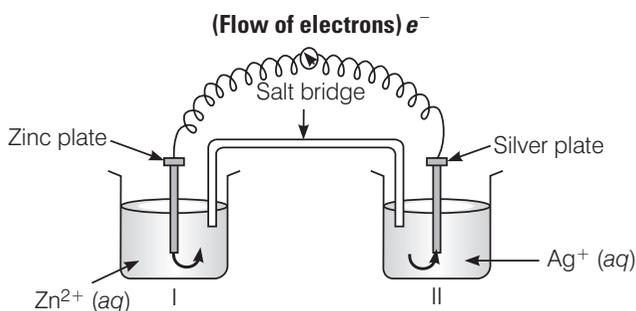


**Q. 67** Consider figure from the above question and answer the questions (i) to (vi) given below.



- (i) Redraw the diagram to show the direction of electron flow.
- (ii) Is silver plate the anode or cathode?
- (iii) What will happen if salt bridge is removed?
- (iv) When will the cell stop functioning?
- (v) How will concentration of  $\text{Zn}^{2+}$  ions and  $\text{Ag}^+$  ions be affected when the cell functions?
- (vi) How will the concentration of  $\text{Zn}^{2+}$  ions and  $\text{Ag}^+$  ions be affected after the cell becomes 'dead'?

**Ans. (i)** Electrons move from Zn to Ag as  $E^\circ$  is more negative for Zn, so Zn undergoes oxidation and  $\text{Ag}^+$  undergoes reduction.



- (ii)** Ag is the cathode as it is the site of reduction where  $\text{Ag}^+$  takes electrons from medium and deposit at cathode.
- (iii)** Cell will stop functioning because cell potential drops to zero. At  $E = 0$  reaction reaches equilibrium.

- (iv) When  $E_{\text{cell}} = 0$  because at this condition reaction reaches to equilibrium.
- (v) Concentration of  $\text{Zn}^{2+}$  ions will increase and concentration of  $\text{Ag}^+$  ions will decrease because Zn is converted into  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  is converted into Ag.
- (vi) When  $E_{\text{cell}} = 0$  equilibrium is reached and concentration of  $\text{Zn}^{2+}$  ions and  $\text{Ag}^+$  will not change.

**Q. 68** What is the relationship between Gibbs free energy of the cell reaction in a galvanic cell and the emf of the cell? When will the maximum work be obtained from a galvanic cell?

**Ans.** If concentration of all reacting species is unity, then  $E_{\text{cell}} = E_{\text{cell}}^{\circ}$  and  $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$  where,  $\Delta_r G^{\circ}$  is standard Gibbs energy of the reaction

$$E_{\text{cell}}^{\circ} = \text{emf of the cell}$$

$$nF = \text{charge passed}$$

If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly.

The reversibly work done by a galvanic cell is equal to decrease in its Gibbs energy.

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

As  $E_{\text{cell}}$  is an intensive parameter but  $\Delta_r G$  is an extensive thermodynamic property and the value depends on  $n$ .

For reaction,  $\text{Zn (s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu (s)}$  in a galvanic cell.

$$\Delta_r G = -2FE_{\text{cell}} \quad [\text{Here, } n = 2]$$