

Q1. Why does the conductivity of a solution decrease with dilution?

A1. Conductivity of a solution is the conductance of ions present in a unit volume of the solution. On dilution the number of ions per unit volume decreases. Hence, the conductivity decreases.

Q2) What does the negative sign the expression $E^0_{\text{Zn}^{2+} / \text{Zn}} = -0.76 \text{ V}$ mean?

A2) Negative sign shows that zinc is more reactive than hydrogen. This means that when zinc electrode is connected to SHE, Zn will be oxidized to Zn^{2+} and H^+ will be reduced to H_2 .

Q3) State Kohlrausch laws of independent migration of ions?

A3) It states that “ At infinite dilution, when the dissociation of the electrolyte is complete, each ion makes a definite contribution to the total molar conductivity of the electrolyte irrespective of the nature of the other ion with which it is associated.

Q4) Write two advantages of H_2O_2 fuel cell over ordinary cell?

or

What advantage do the fuel cells have over primary and secondary batteries?

or

Name the type of cell which was used in Apollo space programme for providing electrical power?

A4) (a) Fuel cells can be run continuously so long as the reactants are supplied, primary batteries become dead and secondary batteries take a long time for recharging .

(b) Fuel cells do not cause any pollution

$\text{H}_2\text{-O}_2$ fuel cell was used in Apollo Space programme for providing electrical power.

Q5) Express the relation among the conductivity of a solution in the cell, the cell constant and the resistance of solution in the cell?

A5)
$$K = \frac{l}{R} \times \frac{1}{A}$$

Where K = Conductivity

l/A = Cell constant

R = Resistance.

Q6) What is electrode potential?

A6) It is defined as the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.

Q7) Is it safe to stir AgNO_3 solution with a copper spoon? Why or Why not ?

Given :- $E^0_{\text{Ag}^+/\text{Ag}} = 0.8 \text{ volt}$ and $E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ volt}$

A7) The given values of reduction potentials show that Cu is more reactive than Ag. i.e Cu reacts with AgNO₃ solution. Hence it is not safe to stir AgNO₃ solution with copper spoon.

Q8) What is the role of ZnCl₂ in a dry cell?

A8) ZnCl₂ combines with the NH₃ produced to form the complex salt [Zn (NH₃)₂ Cl₂] as otherwise the pressure developed due to NH₃ would crack the seal of the cell.

Q9) State faraday's first law of electrolysis ?

A9) The mass of any substance (w) deposited or liberated at any electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte or $W \propto Q$

$$W = ZQ$$

Z = electrochemical equivalent

Q10. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

A10. $H^+ + e^- \longrightarrow \frac{1}{2} H_2$

Applying Nernst eqⁿ

$$E_{H^+/1/2 H_2} = E_{H^+}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$

$$= 0 - \frac{0.0591}{1} \log \frac{1}{10^{-10}}$$

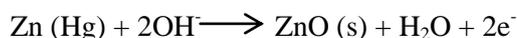
because pH = 10 means $[H^+] = 10^{-10}$ M.

$$= -0.0591 \times -10$$

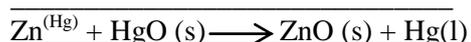
$$= +0.591V$$

Q11. Mention the reactions occurring at (i) Anode (ii) Cathode, during the working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation?

A11. At Anode :-



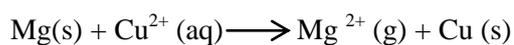
At Cathode



The voltage of a mercury cell remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life .

**Q12. Calculate ΔG for the reaction, $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$
Given E° cell = + 2.71V $1F = 96500$ (Cmol⁻¹)**

A12. For the reaction



$$n = 2$$

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

$$= -2 \times 96500 \times 2.71$$

$$= -523030 \text{ J mol}^{-1}$$

Q13. Calculate the degree of dissociation of acetic acid at 298K given that

$$\lambda_m^\circ(\text{CH}_3\text{COOH}) = 11.7 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(\text{H}^+) = 349.1 \text{ Scm}^2 \text{ mol}^{-1}$$

A13. Degree of dissociation

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ}$$

$$\lambda_m^\circ = \lambda_m^\circ(\text{CH}_3\text{COO}^-) + \lambda_m^\circ(\text{H}^+)$$

$$= 40.9 + 349.1$$

$$= 390 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ} = \frac{11.7}{390}$$

$$\alpha = 3 \times 10^{-2}$$

Q14. A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolyzed between platinum electrodes using a current of 5 A for 20 min. What mass of nickel will be deposited at the cathode?

$$\text{Given : Atomic mass of Ni} = 58.7 \text{ gmol}^{-1} \quad 1F = 96,500 (\text{mol}^{-1})$$

A14. Given :- $I = 5\text{A}$ Time (t) = $20 \times 60 = 1200\text{s}$

$$Q = I \times t = 5 \times 1200 = 6000\text{C.}$$

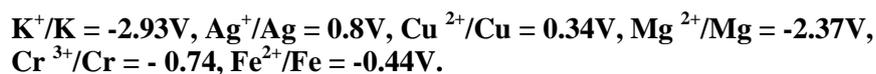
$$M = Z \times I \times t$$

$$M = \frac{\text{Eq. wt} \times I \times t}{96,500}$$

$$M = \frac{58.7}{2 \times 96500} \times 6000 = 1.82\text{g}$$

Q15. (a) Define electrochemical series .

(b) Given that the standard electrode potentials (E°) metals are :-



Arrange these metals in an increasing order of their reducing power.

A15. (a) The arrangement of the various electrodes in order of their increasing values of standard reduction potentials is called electrochemical series.

(b) Greater the negative value of the standard electrode potential (E°) greater is the reducing power of the electrode. Thus the increasing order of reducing power is $\text{Ag}^+/\text{Ag} < \text{Cu}^{2+}/\text{Cu} < \text{Fe}^{2+}/\text{Fe} < \text{Cr}^{3+}/\text{Cr} < \text{Mg}^{2+}/\text{Mg} < \text{K}^+/\text{K}$

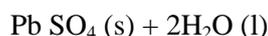
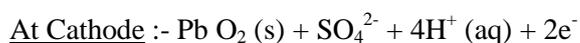
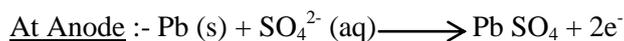
Q16. What type of battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery?

A16. Lead storage battery is a secondary cell i.e it can be recharged by passing direct current through it and can be reused.

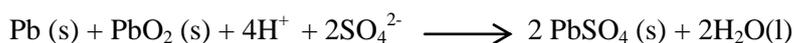
Anode :- Spongy lead.

Cathode :- Grid of lead packed with PbO_2

Electrolyte :- 38% H_2SO_4



Overall cell reaction \longrightarrow



Q17. The resistance of 0.01M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution.

A17. Given Resistance $\mathcal{R} = 200 \Omega$

Molarity of NaCl solution = 0.01M

Cell constant (l/A) = 1cm^{-1}

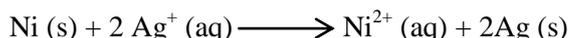
$$\text{Conductivity (K)} = \frac{1}{R} \times \frac{1}{A}$$

$$= \frac{1}{200}$$

$$= 5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

$$\begin{aligned}\text{Molar conductivity } \lambda_M &= \frac{1000K}{\text{Molarity}} \\ &= \frac{(5 \times 10^{-3}) \times 1000}{0.01} \\ &= 500 \text{ Scm}^2 \text{ mol}^{-1}\end{aligned}$$

Q18. Determine the values of equilibrium constant (Kc) and ΔG^0 for the following reaction.



$$E^0 = 1.05\text{V} \quad (1F = 96500 \text{ cmol}^{-1})$$

A18. Given $E^0 = 1.05\text{V}$

$$n = 2$$

$$\text{Therefore } \Delta G^0 = -nf E^0$$

$$\Delta G^0 = -2 \times 96500 \times 1.05 = -202.65 \text{ KJ mol}^{-1}$$

$$-nfE^0 = -2.303RT \log Kc \quad (\text{because } \Delta G^0 = -2.303 RT \log Kc)$$

$$\text{Log Kc} = \frac{nE^0}{0.0591}$$

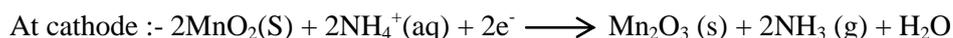
$$= \frac{2 \times 1.05}{0.0591} = 35.5329$$

$$Kc = \text{antilog } 35.5329$$

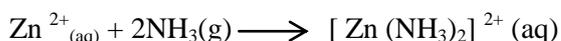
$$Kc = 3.411 \times 10^{35}$$

Q19. Set up Nernst equation for the standard dry cell. Using this equation show that the voltage of a dry cell has to decrease with use?

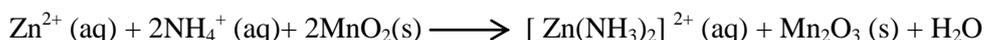
A19. Dry cell (Leclanche cell) consists of a zinc container which acts as anode and cathode is a graphite rod surrounded by powdered MnO_2 and 'C'. The space between the electrodes is filled by a moist paste of NH_4Cl and ZnCl_2 .



NH_3 formed combines immediately with Zn^{2+} ions to form complex ion $[\text{Zn}(\text{NH}_3)_2]^{2+}$



Overall reaction :-



Nernst equation for dry cell

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[\text{Zn}(\text{NH}_3)_2]^{2+}}{[\text{NH}_4^+]^2}$$

Due to the presence of ions in the overall reaction, its voltage decreases with time.

Q 20. What is the relationship between Gibbs free energy of the cell reaction in a galvanic cell and emf of the cell. When will the maximum work be obtained from a galvanic cell?

A20. In a galvanic cell –

Electrical work done = Electrical energy produced =

= Quantity of electricity flowing x EMF
for n moles of electrons transferred in any cell reaction. The quantity of electricity flowing = nf faradays.

Therefore Electrical work done = $nF E_{\text{cell}}$.

Also electrical work done = Decrease in free energy

Therefore - $\Delta G = nF E_{\text{cell}}$. Or - $\Delta G^{\circ} = nF E_{\text{cell}}^{\circ}$

$$\Delta_r G^{\circ} = -2.303 RT \log K_c$$

Hence, knowing E_{cell}° , ΔG° can be calculated which in turn can be used for the calculation of the equilibrium constant K_c .

$-\Delta G = W_{\text{max}}$. Hence, the decrease in free energy is equal to the maximum work that can be obtained from the cell.

Q21. (i) Predict the product of electrolysis in each of the following :-

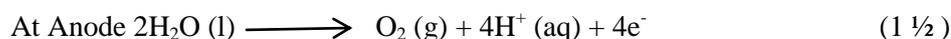
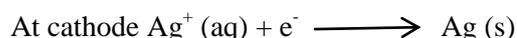
(a) An aqueous solution of AgNO_3 with platinum electrodes.

(b) An aqueous solution of H_2SO_4 with platinum electrodes.

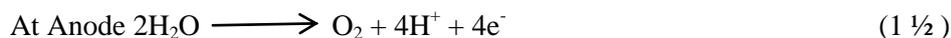
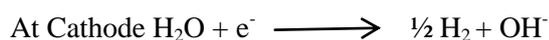
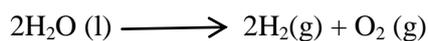
(ii) Estimate the maximum potential difference needed to reduce Al_2O_3 at 500°C . The Gibbs energy change for the decomposition reaction



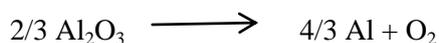
A21. (i) (a) Electrolysis of AgNO_3 (aq) using Pt electrodes



(b) Electrolysis of H_2SO_4 (aq) using Pt electrodes.



(i) Reaction involved



Here $n = 4$

$$\text{Given, } \Delta G = 960 \text{ kJ} \implies \Delta G = -nFE^0$$

$$-960 \text{ kJ} = -4 \times 96500 \times E^0$$

$$E^0 = \frac{960000 \text{ J}}{4 \times 96500} = 2.48 \text{ V} \approx 2.5 \text{ V} \quad (2)$$

Q22. (i) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

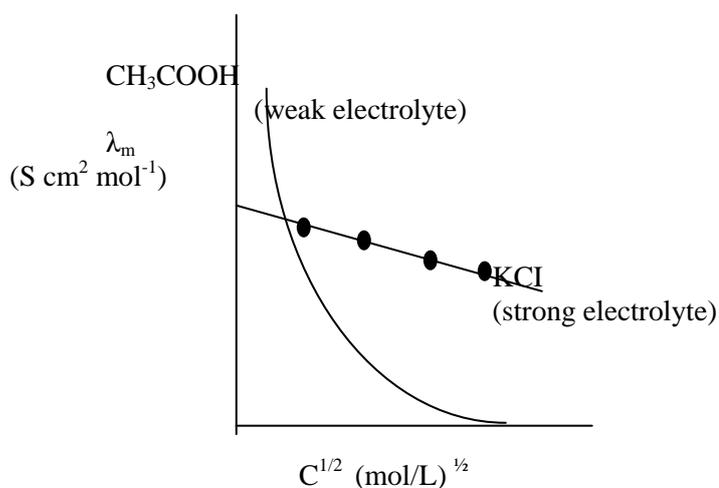
(ii) The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$?

A22. Molar conductivity. It is defined as the conductivity of the solution which contains one mole of the electrolyte such that entire solution is in between the two electrodes kept one centimeter apart.

Molar conductivity,

$$\lambda_m = \frac{K}{C} \quad \text{where } k = \text{conductivity.} \\ \text{c is concentration of solution}$$

Variation of conductivity and molar conductivity with concentration.



Conductivity and molar conductivity change with change in concentration of electrolyte. Conductivity always decreases with decrease in concentration for both weak as well as strong electrolytes.

But molar conductivity increases with decreases in concentration. For strong electrolytes λ_m increases slowly with dilution but for weak electrolytes λ_m increases steeply on dilution, especially near lower concentrations.

Molar conductivity increases with decrease in concentration because both the number of ions as well as the mobility of increase with dilution.

(ii) Given, conductivity $k = 0.146 \times 10^{-3} \text{ S cm}^{-1}$

Resistance, $R = 1500\Omega$

Therefore Cell constant, $G^* = K \times R$

$$= 0.146 \times 10^{-3} \times 1500$$

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

Q23 (a) What is standard hydrogen electrode? Give reactions that occur at this electrode when it acts as a positive electrode in an electro chemical cell.

(b) What is the function of salt bridge in an electrochemical cell.

(c) $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}, \quad E^{\circ} = + 0.34 \text{ V}$

$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}, \quad E^{\circ} = + 0.80 \text{ V}$

(i) Construct a galvanic cell using the above data.

(ii) For what concentration of Ag^+ ions will the emf of the cell be zero at 25°C , if the concentration of Cu^{2+} is 0.01 M ?

A23 (a) It is a reference electrode used to measure the electrode potential of other electrode. The electrode potential of SHE is taken as zero.

(b) Salt bridge performs the following functions :-

(i) It completes the inner circuit by flow of ions.

(ii) It maintains the electrical neutrality in the solution of half cells.

(c) (i) $\text{Cu (s)} \mid \text{Cu}^{2+} (\text{aq}) \parallel \text{Ag}^+ (\text{aq}) \mid \text{Ag (s)}$

At Anode : $\text{Cu (s)} \longrightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{e}^-$

At Cathode $2 \text{Ag}^+ (\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Ag (s)}$

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

Thus, $n = 2$

$$E_{\text{cell}} = E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = + 0.80 \text{ V} - 0.34\text{V} = 0.46\text{V}$$

Using Nernst equation to calculate concentration of Ag^+

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{or } 0 = .46 \text{ V} - \frac{0.0591}{2} \log \frac{0.01}{[\text{Ag}^+]^2}$$

$$\text{or } \log \frac{0.01}{[\text{Ag}^+]^2} = \frac{+0.46 \text{ V} \times 2}{0.0591} = \frac{0.92}{0.0591} = 15.567$$

$$\text{or } \log \frac{0.01}{[\text{Ag}^+]^2} = \text{Antilog } 15.567 = 3.690 \times 10^{15}$$

$$\text{or } [\text{Ag}^+]^2 = \frac{0.01}{3.688 \times 10^{15}} = \frac{1}{3.688} \times 10^{-17} = 0.271 \times 10^{-17} = 2.71 \times 10^{-18}$$

$$\text{or } [\text{Ag}^+] = 1.65 \times 10^{-9} \text{ mol L}^{-1}$$

Q24. The molar conductivity of 0.025 mol L⁻¹ methanoic acid is

46.1 S cm² mol⁻¹. Calculate its degree of dissociation and dissociation constant. Given $\lambda^{\circ}(\text{H}^+)$

= 349.6 S cm² mol⁻¹ and $\lambda^{\circ}(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$, $C = 0.025 \text{ mol L}^{-1}$

$$\Lambda_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^{\circ}(\text{HCOOH}) = \lambda^{\circ}(\text{H}^+) + \lambda^{\circ}(\text{HCOO}^-)$$

$$= 349.6 + 54.6$$

$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m(\text{HCOOH})}{\Lambda_m^{\circ}(\text{HCOOH})}$$

$$= \frac{46.1}{404.2}$$

$$= 0.114 \text{ (approximately)}$$

Thus, dissociation constant:

$$\begin{aligned}
 K &= \frac{c \alpha^2}{(1-\alpha)} \\
 &= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1-0.114)} \\
 &= 3.67 \times 10^{-4} \text{ mol L}^{-1}
 \end{aligned}$$

25. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

$$I = 0.5 \text{ A}$$

$$t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$$

$$\text{Thus, } Q = It$$

$$= 0.5 \text{ A} \times 7200 \text{ s}$$

$$= 3600 \text{ C}$$

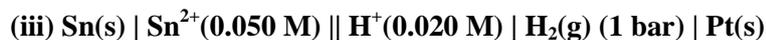
We know that $96487 \text{ C} = 6.023 \times 10^{23}$ number of electrons.

Then,

$$\begin{aligned}
 3600 \text{ C} &= \frac{6.023 \times 10^{23} \times 3600}{96487} \text{ number of electrons} \\
 &= 2.25 \times 10^{22} \text{ number of electrons}
 \end{aligned}$$

Hence, 2.25×10^{22} number of electrons will flow through the wire.

26. Write the Nernst equation and emf of the following cells at 298 K:



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

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \\
 &= \{0.34 - (-2.36)\} - \frac{0.0591}{2} \log \frac{.001}{.0001} \\
 &= 2.7 - \frac{0.0591}{2} \log 10
 \end{aligned}$$

$$= 2.7 - 0.02955$$

$$= 2.67 \text{ V (approximately)}$$

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

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \\
 &= \{0 - (-0.44)\} - \frac{0.0591}{2} \log \frac{0.001}{1^2} \\
 &= 0.44 - 0.02955(-3)
 \end{aligned}$$

$$= 0.52865 \text{ V}$$

$$= 0.53 \text{ V (approximately)}$$

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

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \\
 &= \{0 - (-0.14)\} - \frac{0.0591}{2} \log \frac{0.050}{(0.020)^2}
 \end{aligned}$$

$$= 0.14 - 0.0295 \times \log 125$$

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

$$= 0.08 \text{ V (approximately)}$$

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

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\ &= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2} \\ &= -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \\ &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\ &= -1.09 - 0.02955 \times \log(1.11 \times 10^7) \\ &= -1.09 - 0.02955(0.0453 + 7) \\ &= -1.09 - 0.208 \\ &= -1.298 \text{ V} \end{aligned}$$