ELECTROCHEMISTRY

ONE Mark Each

1. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _____.

2. Under what condition an electrochemical cell can behave like an electrolytic cell ?

3. What is the quantity of charge in faraday is required to obtain one mole of aluminum from Al_2O_3 ?

4. How the cell constant of a conductivity cell changes with change of electrolyte, concentration and temperature?

5. What will happen at anode during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?

6. Under what condition is $E_{Cell} = 0$ or $\Delta_r G = 0$?

OR Give the condition for Daniell Cell in which there is no flow of electrons or current.

7. Why is alternating current used for measuring resistance of an electrolytic solution?

8. How will the pH of brine (aq. NaCl solution) be affected when it is electrolyzed ?

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

10. Mention the purpose of salt-bridge placed between two half-cells of a galvanic cell?

11. Two metals A and B have electrode potential values of – 0.25V and 0.80V respectively. Which of these will liberate hydrogen gas from dilute H_2SO_4 ?

12. What is the effect of temperature on molar conductivity?

13. What is the role of $ZnCl_2$ in the dry cell ?

14. Why is the equilibrium constant K, related to only E°_{cell} and not E_{cell} ?

15.Rusting of iron is quicker in saline water than in ordinary water. Why is it so?

16. Why rusting of iron prevented in alkaline medium?

17.Which will have greater molar conductivity and why?

1 mole KCl dissolved in 200 cc of the solution OR 1 mole KCl dissolved in 500 cc of the solution. 18.Why Lead storage battery as a secondary cell can be recharged?

19.Write the name of a chemical substance which is used to prevent corrosion.

20.Write the unit of Faraday constant.

Answer of one mark

1. Cell emf

2. When $E_{ext} > E_{cell}$

3. 3F

4. Remain unchanged for a cell

5. Copper will dissolve at anode

6. When the cell reaction reaches equilibrium

7. Alternating current is used to prevent electrolysis so that concentration of ions in the solution remains constant. Otherwise if DC is used the ions will get discharged and electrolysis will occur

8. The pH of the solution will rise as NaOH is formed in the electrolytic cell.)

9. Ions are not involved in the overall cell reaction of mercury cells.

10. Neutralize the two half cell.

11. Metal - A

12. Molar conductivity of an electrolyte increases with increase in temperature.

13. $ZnCl_2$ absorbs ammonia produced in the reaction by forming a complex $[Zn(NH_3)_4]^{2+}$

14. This is because E_{cell} is zero at equilibrium.

15.Due to presence of ions in saline water conductivity is more than the ordinary water. Hence in miniature electrochemical cell flow of electrons will increase, consequently rusting of iron is increased.

16. In alkaline medium, atmospheric oxygen is unable to take electron which is given by the oxidation of Fe.

17. 1 mole KCl dissolved in 500 cc of the solution, Due to more mobility of ions and more degree of dissociation.

18. Recharging is possible in this case because $PbSO_4$ formed during discharging is a sticky solid which sticks to the electrode. Therefore it can either take up or give up electrons during recharge.

19. Bisphenol

20. Coulomb/ mol

ELECTROCHEMISTRY

TWO Marks Each

1.Solutions of two electrolytes 'A' and 'B' are diluted. The Λ_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.

2. When acidulated water (dil.H_2SO_4 solution) is electrolysed, will the p^H of the solution be affected? Justify your answer.

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

4. How does the density of the electrolyte change when the lead storage battery is discharged ?

5. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?

6. 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?

7.Define corrosion. Write chemical formula of rust.

8.Can you store copper sulphate solutions in a zinc pot?

9.Write the cell reaction which occur in the lead storage battery
(a) when the battery is in use (b) when the battery is on charging.

10.Write the product of electrolysis of aqueous copper sulphate by using platinum electrode.

Answer

1.Electrolyte 'B' is strong as on dilution the number of ions remains the same, only interionic attraction decreases therefore increase in Λ is small.

2.pH of the solution will not be affected as[H^+] remains constant.

At anode: $2\,H_2O \longrightarrow O_2 + 4H^+ + 4\,e^-$

At cathode: $4\,H^+ + 4\,e^- \longrightarrow 2\,H_2$

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

4.Density of electrolyte decreases as water is formed and sulphuric acid is consumed as the product during discharge of the battery.

$$Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$$

5.In the case of CH_3 COOH, which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation. In the case of strong electrolyte the number of ions remains the same but the inter ionic attraction decreases.

6.$\Delta rG = -nFE_{(cell)}$If the concentration of all the reacting species is unit.

7.Corrosion is a process of formation sulphides, oxides, carbonates, hydroxides, etc. of metal on its surface as a result of its reaction with air and water, surrounding it. Formula of rust- $Fe_2O_3.XH_2O$

8.No, We cannot store $CuSO_4$ solution in zinc pot, because electrode potential of zinc is less than copper,so Cu^{2+} ions get replaced by Zn^{2+} ions in solution . Zn is more reactive metals than Cu . (Displacement reaction)

9.

(a) When battery is in use

Oxd^n React^n $\quad Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2\,e^-$

Red^n React^n $\quad PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O$

Cell React^n $\quad Pb + PbO_2 + 2SO_4^{2-} + 4\,H^+ \longrightarrow 2\,PbSO_4 + 2\,H_2O$

(b) When the battery is on charging

Red^n React^n $\quad PbSO_4 + 2\,e^- \longrightarrow Pb + SO_4^{2-}$

Oxd^n React^n $\quad PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^-$

Cell React^n $\quad 2\,PbSO_4 + 2\,H_2O \longrightarrow Pb + PbO_2 + 2\,SO_4^{2-} + 4\,H^+$

10.

Electrolysis of aqueous $CuSO_4$ using Pt electrode

$CuSO_4 \longrightarrow Cu^{2+} + SO_4\ 2-$ $\qquad$ $H_2O \rightleftharpoons H^+ + HO^-$

Anode [$SO_4\ 2-$ $\quad HO^-$] $\quad 4\ HO^- \longrightarrow 2\ H_2O + O_2 + 4\ e-$

Cathode [Cu^{2+} $\quad H^+$] $\quad Cu^{2+} + 2\ e- \longrightarrow Cu$

ELECTROCHEMISTRY

THREE Marks Each

1.Calculate the EMF of the cell in which the following reaction take place:

2.If a current of 0·5 ampere flows through a metallic wire for 2 hours, then how many electrons flow through the wire

3.Calculate the potential of hydrogen electrode in contact with a solution whose P^H is 10.

4.The molar conductivity of 0·025 mol L^{-1} methanoic acid is 46·1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0_{H^+}$ = 346·6 S cm^2 mol^{-1} and $\lambda^0_{HCOO^-}$ = 54·6 S cm^2 mol^{-1}

5.If a current of 0·5 ampere flows through a metallic wire for 2 hours, then how many electrons flow through the wire ?

6. Calculate $\wedge^o_m$ for $CaCl_2$ and $MgSO_4$ from the data given in the table of Book.

7.The Conductivity of 0·001028 mol L^{-1} acetic acid is 4·95 × 10^{-5} S cm^{-1}. Calculate its dissociation constant if $\wedge^0$ for acetic acid is 390·5 S cm^2 mol^{-1}.

8. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1·5 amperes. What is the mass of copper deposited at the cathode ?

9.The conductivity of 0·20 M solution of KCl at 298 K is 0·0248 S cm^{-1}. Calculate its molar conductivity.

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

$Mg(s) | Mg^{2+}$ (0·001 M) $|| Cu^{2+}$ (0·0001 M) $| Cu(s)$

Answer

1.Ni + 2 Ag^+ (0·002M) $\longrightarrow$ Ni^{2+} (0·160 M) + 2 Ag

Given that $E^0_{Cell} = 1\cdot05\,V$

(According to Nernst equation : $E_{Cell} = E^0_{Cell} - \frac{0\cdot059}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$

$= 1\cdot05 - \frac{0\cdot059}{2}\log\frac{0\cdot160}{(0\cdot002)^2} = 0\cdot9143V$

2.Quantity of electricity (Q) = Current (ampere) × time (second) = 0·5 × 2 × 60 × 60 = 3600 C (Coulombs) A flow of 69487 C of electricity ≅ 6·022 × 10^{23} electrons

∴ 3600 C of electricity = $\frac{6\cdot022\times10^{23}}{96487}\times3600 = 2\cdot246\times10^{22}$ electrons

3.P^H = 10 means $[H^+] = 10^{-10}$ M

Now for the electrode; H^+ + e^- --------> $\frac{1}{2}H_2$ (Here n = 1)

$E_{H^+|H_2} = E^0_{H^+|H_2} - \frac{0\cdot059}{n}\log\frac{1}{[H^+]}$ = 0 – 0·059 $\log\frac{1}{10^{-10}}$ = – 0·059 log 10^{10} = – 0·059 × 10 = – 0·59 v

4.λ^C = 46·1 S cm^2 mol^{-1} C = 0·025 mol L^{-1}

$\lambda^0_{HCOO^-} = \lambda^0_{H^+}$ + $\lambda^0_{HCOO^-}$ = 349.6 + 54·6 = 404·2 S cm^2 mol^{-1}

Degree of dissociation $(\alpha) = \frac{\lambda^C}{\lambda^0} = \frac{46\cdot1}{404\cdot2} = 0\cdot114$

Dissociation constant $(K_a) = \frac{c\alpha^2}{1-\alpha} = \frac{0\cdot025\times(0\cdot114)^2}{1-0\cdot114} = 0\cdot0003667 = 3\cdot67\times10^{-4}$

5.Quantity of electricity (Q) = Current (ampere) × time (second) = 0·5 × 2 × 60 × 60 = 3600 C (Coulombs) A flow of 69487 C of electricity ≅ 6·022 × 10^{23} electrons

∴ 3600 C of electricity = $\frac{6\cdot022\times10^{23}}{96487}\times3600 = 2\cdot246\times10^{22}$ electrons

6. $\wedge^o_{m(CaCl_2)} = \wedge^o_{Ca^{2+}} + 2\wedge^o_{Cl^-} = 119\cdot0 + 2\times76\cdot3 = 119\cdot0 + 152\cdot6 = 271\cdot6\,S\,cm^2\,mol^{-1}$

$\wedge^o_{m(MgSO_4)} = \wedge^o_{Mg^{2+}} + \wedge^o_{SO_4^{2-}} = 106\cdot0 + 160\cdot0 = 266\,S\,cm^2\,mol^{-1}$

7. $\wedge_m = \frac{k\times1000}{C} = \frac{4\cdot95\times10^{-5}\,1000}{0\cdot001028}$ = 48·15 cm2 mol^{-1}

$$\alpha = \frac{\wedge_m}{\wedge_m^o} = \frac{48 \cdot 15}{390 \cdot 0} = 0 \cdot 1233$$

Dissociation constant (K_a) = $\frac{C\alpha^2}{1-\alpha} = \frac{0 \cdot 001028 \times (0 \cdot 1233)^2}{1 - 0 \cdot 1233} = 1 \cdot 78 \times 10^{-5}$

8.Quantity of electricity (Q) = Current × time = 1·5 × 10 × 60 = 900 C

According to the reaction : Cu^{2+} + $2e^-$ ------> Cu

We required 2 F or 2 × 96487 C of electricity to deposit 1 mol or 63 g of Cu

∴ 900 C electricity will deposit = $\frac{63}{2 \times 96487} \times 900$ = 0·2938 g of Cu at the cathode

9.0·2 M ⇒ 0·2 moles KCl present in 1 litre i.e. 1000 cm^3 of solution

∴ 1 mole KCl present in $\frac{1000}{0 \cdot 2}$ $cm^3$of solution

K = 0·0248 S cm^{-1}⇒ Conductance of 1 cm^3 solution = 0·0248 S

∴ Conductance of $\frac{1000}{0 \cdot 2}$ cm^3 solution = 0·0248 × $\frac{1000}{0 \cdot 2}$ = 124 S cm^2 mol^{-1}

So Molar conductivity (λ) = 124 S cm^2 mol^{-1}

10. Oxidation Half Mg ------> Mg^{2+} + $2e^-$

Reduction Half Cu^{2+} + $2e^-$ ------> Cu

Cell Reaction Mg + Cu^{2+} ------> Mg^{2+} + Cu

Here number of moles of electrons (n) = 2

$E^o_{cell} = E^o_{Cu^{2+}|Cu} - E^o_{Mg^{2+}|Mg}$ = 0·34 – (– 2·37) = 2·71 V

The Nernst equation for the cell : $E_{cell} = E^o_{cell} - \frac{0 \cdot 059}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$

$E_{cell} = 2 \cdot 71 - \frac{0 \cdot 59}{2} \log \frac{0 \cdot 001}{0 \cdot 0001}$ = 2·71 – 0·0295 log 10 = 2·71 – 0·0295 = 2·6805 V

FIVE Marks Each

1. (a) A Leclanche cell is also called dry cell. Why?

(b)Why is the voltage of a mercury cell constant during its working?

(c)Name two metals that can be used for cathodic protection of iron?

(d)What do you mean by primary and secondary battery? [1+1+1+2]

2. (a)What do you understand by strong and weak electrolytes? [1+2+2]

(b)State Faraday's Laws of electrolysis?

(c)Silver is deposited on a metallic vessel by passing a current of 0.2 amps. for 3 hrs. Calculate the weight of silver deposited. (At mass of silver = 108 amu, F = 96500 C?

3. (a)Define the term resistivity and give its SI unit . [1+2+2]

(b) What are the factors on which conductivity of an electrolyte depend?

(c) The molar conductivity of 0.1M CH_3COOH solution is 4.6 cm^2 mol^{-1}. What is the conductivity and resistivity of the solution?

4.(a) State the factors that affect the value of electrode potential? [1+2+2]

(b) Write Nernst equation for a Al-$ZnSO_4$ cell?

(c) write the chemistry of rusting of iron

5.(a) Can an electrochemical cell act as electrolytic cell? How? [1+2+2]

(b) Explain construction and working of standard Hydrogen electrode?

(c) What is an electrochemical series? How does it predict the feasibility of a certain redox reaction?

Answer

1. (a) Leclanche cell consists of zinc anode (container) and carbon cathode. The electrolyte isa moist paste of MnO_2, $ZnCl_2$, NH_4Cl and carbon black. Because there is no free liquid inthe cell, it is called dry cell.

(b)As all the products and reactants are either in solid or liquid state, their concentration does not change with the use of the cell.

(c)Names of the metals are –Zinc and Magnesium.

(d)In the primary batteries, the reaction occurs only once and after the use over a period of time battery becomes dead and cannot be reused again. A secondary battery , after used,can be recharged by passing current through it in the opposite direction so that it can beused again.

2. (a)An electrolyte that ionizes completely in solution is a strong electrolyte eg. NaCl , $CaCl_2$ etc and an electrolyte that ionizes partially in solution is weak electrolyte eg CH_3COOH , NH_4OH etc.

(b) Faraday's Laws of electrolysis

First Law: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.

Second Law: The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

(c) 2.417 g of silver.

3. (a) The resistivity of a substance is its resistance when it is one meter long and its area of cross Section is one m^2. Unit: ohm .meter

(b) The conductivity of an electrolyte depends upon

i) The nature of electrolyte ii) Size of the ions produced

iii) Nature of solvent and its viscosity. iv) Concentration of electrolyte. v) Temperature

(c)

$$\lambda_m = \frac{\kappa \times 1000}{c} \quad => \kappa = \frac{\lambda_m \times c}{1000} => \frac{4.6 \times 0.1}{1000} = 0.00046 \frac{s}{cm}$$

$$\text{Resistivity } (\rho) = \frac{1}{\kappa} = \frac{1}{0.00046} \; 2174 \cdot \Omega cm$$

4.(a) Factors affecting electrode potential values are –

a) Concentration of electrolyte b) Temperature.

(b) TheNernst equation for a Al-$ZnSO_4$ cell:

The Cell is : $Al \mid Al^{3+} \parallel Zn^{2+} \mid Zn$

Anode reaction : $Al \longrightarrow Al^{3+} + 3e^{-}$] x 2

Cathode reaction : $Zn^{2+} + 2e^{-} \longrightarrow Zn$] x 3

Cell reaction : $2\,Al + 3\,Zn^{2+} \longrightarrow 2\,Al^{3+} + 3\,Zn$

$$E = E^0 - \frac{0.059}{6} \log \frac{[Al^{3+}]^2}{[Zn^{2+}]^3}$$

(c) The chemistry of rusting of iron

[1]Creation of Acidic medium: Atmospheric carbon dioxide and water vapour combine to form carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

[2] Iron will oxidise [Anode- Oxidation half] $Fe \longrightarrow Fe^{2+} + 2e^{-}$ X 2

[3] In another spot, oxygen of air will take the two electrons with help of H^+ ion and will be reduced to H_2O [Cathode - Reduction half]

$$O_2 + 4H^+ + 4e^- \longrightarrow 2\,H_2O$$

Cell React^{n} $2\,Fe + O_2 + 4\,H^+ \longrightarrow 2\,Fe^{2+} + 2\,H_2O$

In alkaline medium, atmospheric oxygen is unable to take electron which is given by the oxidation of Fe .

[4] Atmospheric oxygen further oxidises ferrous ion into ferric oxide.

$$2\,Fe^{2+} + 2\,H_2O + \tfrac{1}{2}\,O_2 \longrightarrow Fe_2O_3 + 4\,H^+$$

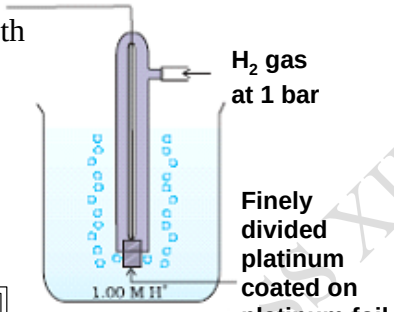
[5] Ferric oxide will hydrolyse with water to form rust.

$$Fe_2O_3 + x\,H_2O \longrightarrow Fe_2O_3 . x\,H_2O \text{ [Rust]}$$

5.(a) Yes, An electrochemical cell can be converted into electrolytic cell by applying anexternal opposite potential greater than its own electrical potential.}

(b) Standard Hydrogen electrode:

The Standard Hydrogen Electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity. This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.



Anode - $H_2 \longrightarrow 2\,H^+ + 2\,e^-$

Cathode - $2\,H^+ + 2\,e^- \longrightarrow H_2$

$\mathcal{E}^\circ_{2\,H^+ \mid H_2} = 0$

If it act as cathode ⟶ The maximum bubbling of hydrogen gas from the solution will evolve .

If it act as anode ⟶ The minimum bubbling of hydrogen gas from the solution will evolve

(c) The arrangement of metals and ions in increasing order of their electrode potential values is known as electrochemical series.

The reduction half reaction for which the reduction potential is lower than the other will act as anode and one with greater value will act as cathode .Reverse reaction willnot occur.