ELECTROCHEMISTRY

1. Two half cell reactions of an electrochemical cell are given below :
   $MnO^-4(aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H2O (I)$, E° = + 1.51 V
   $Sn^{2+} (aq) \rightarrow 4 Sn^{4+} (aq) + 2e^-$, E° = + 0.15 V
   Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation
2. Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity?
3. Given that the standard electrode potentials (E°) of metals are :
   K^+/K = -2.93 V, Ag^+/Ag = 0.80 V, Cu^{2+}/Cu = 0.34 V,
   Mg^{2+}/Mg = -2.37 V, Cr^{3+}/Cr = -0.74 V, Fe^{2+}/Fe = -0.44 V.
   Arrange these metals in increasing order of their reducing power
4. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere
5. Determine the values of equilibrium constant (Kc) and ΔG° for the following reaction :
   $Ni(s) + 2Ag^+ (aq) \rightarrow Ni^{2+} (aq) + 2Ag(s)$,
   E° = 1.05 V
   ($1F = 96500\ C\ mol^{-1}$)
6. A zinc rod is dipped in 0.1 M solution of ZnSO4. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential.
   [$E°Zn^{2+}/Zn$ = – 0.76 V]

7. Write the cell reactions which occurs in lead storage battery when the battery is on charging mode.
8. Give reasons for the following:
   (i) Rusting of iron is quicker in saline water than in ordinary water.
   (ii) Aluminium metal cannot be produced by the electrolysis of aqueous solution of aluminium salt.

9 .(i) Which electrolyte is used in dry cell?
(iii) What type of metals can be used for cathodic protection of iron against rusting?

9. What is limiting molar conductivity?
10. Express the relation between conductivity and molar conductivity of a solution held in a cell.
11. What is the effect of catalyst on:
    (i) Gibbs energy (ΔG) and
    (ii) activation energy of a reaction?
12. Two half cell reactions of an electrochemical cell are given below :
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    K^+/K = -2.93 V, Ag^+/Ag = 0.80 V, Cu^{2+}/Cu = 0.34 V,
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    Arrange these metals in increasing order of their reducing power.
15. The chemistry of corrosion of iron is essentially an electrochemical phenomenon.

Explain the reactions occurring during the corrosion of iron in the atmosphere.

16. Determine the values of equilibrium constant (K_c) and $\Delta G°$ for the following reaction :
$Ni(s) + 2Ag^+ (aq) \rightarrow Ni^{2+} (aq) + 2Ag(s)$,
$E° = 1.05$ V
(1F = 96500 C mol^{-1})

17. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity.

18. The standard electrode potential (E°) for Daniel cell is +1.1 V. Calculate the $\Delta G°$ for the reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(1 F = 96500 C mol^{-1}).

19. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol.

20. Define the following terms :
(i) Fuel cell
(ii) Limiting molar conductivity (Λ°_m)

21. Define the following terms :
(i) Rate constant (k)
(ii) Activation energy (E_a)

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

23. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2A was passed through the solution of $CuSO_4$.
(Molar mass of Cu = 63.5 g mol^{-1},1 F = 96500 C mol^{-1})

24. From the given cells: Lead storage cell, Mercury cell, Fuel cell and Dry cell Answer the following:
(i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo Space Programme?
(iii) Which cell is used in automobiles and inverters?
(iv) Which cell does not have long life?

25. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell.

26. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell

27. A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential is measured 0,422 V. Determine the concentration of silver ion in the cell.
Given : $E°_{Ag^+/Ag} = + 0.80$ V, $E°_{Cu^{2+}/Cu} = + 0.34$ V.

28. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

29. What is corrosion? Explain the electrochemical theory of rusting of iron and write the reactions involved in the rusting of iron

30. When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

Answer key:

1. At anode : [Sn2+(aq) → Sn4+(aq)+2e−]×5

At cathode : $[MnO_4^-(aq)+8H^+(aq)+5e^- \rightarrow Mn^{2+}(aq)+4H_2O(l)]\times 2$

Cell reaction : $2MnO_4^-(aq)+5Sn^{2+}(aq)+16H^+(aq)\rightarrow 2Mn^{2+}(aq)+5Sn^{4+}(aq)+8H_2O(l)$

$E^\circ_{cathode}-E^\circ_{anode}=1.51V-0.15V = 1.36V$

2. $G=1/R$

$K=G\times G^*$

Substitue the value of conductance in the above equation

$K=1/R\times G^*$

$R=1/G$

Molar conductivity is defined as the conductivity of an electrolyte solution divided by the molar concentration of the electrolyte, and so measures the efficiency with which a given electrolyte conducts electricity in solution.

$\wedge=K\times V$

G is conductance.

K is conductivity.

G^* is cell constant.

$\wedge$ is molar conductivity.

$GG^*=K$

Where, G=conductance, G^*=cell constant, K = conductivity

$G^*\times 1/2=K\Rightarrow G^*=RK$

$\Lambda m=Ck\times 1000\ Scm^2mol^{-1}$

3. The lower the electrode potential, the stronger is the reducing agent. Therefore, the increasing order of the reducing power of the given metals is Ag < Hg < Cr < Mg < K.
4. According to electrochemical theory of rusting the impure iron surface behaves like small electrochemical cell in presence of water containing dissolves oxygen or carbon dioxide . In this cell pure iron acts as anode and impure iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte . The reactions are given below.

   At anode : $Fe\rightarrow Fe^{2+};RFe^{2+}/Fe^\circ=-0.44V$

   At cathode : $2H^++21O_2+2e^-\rightarrow H_2O;EH^+/O_2/H_2O^\circ=1.23V$

   Overall reaction: $Fe+2H^++21O_2\rightarrow Fe^{2+}+H_2O;Ecell^\circ=1.67V$

The Fe^{2+} ions are further oxidized by atmospheric oxygen to Fe^{3+} ions , which comes out in the form of hydrated oxide (rust).

$2Fe2++21O2+2H2O \rightarrow Fe2O3+4H+$

$Fe2O3+xH2O \rightarrow Fe2O3.xH2O$ (rust)

5.

ΔG∘=−nFE∘cellΔG∘=-nFEcell∘

=(−2)×(96500 C mol−1)×(1.05V)=−202650CV mol−1

=-202650 J mol−1mol-1=-202.65 kJ mol−1mol-1

(ii) Calculate of equilibrium constant (Kc)(Kc) for the reaction

E∘=2.303RTnFlog Kc=0.0591nlogKcE∘=2.303RTnFlog Kc=0.0591nlogKc

logKc=n×E∘0.0591V=2×(1.05V)(0.0591V)=35.53logKc=n×E∘0.0591V=2×(1.05V)(0.0591V)=35.53

Kc=Antilog 35.53=3.41×1035

6. -0.9V
7. 2PbSO4(s)+2H2O(l)→Pb(s)+PbO2(s)+4H+(aq)+2SO42−(aq)
8. 0.015
9. A metal which is more electropositive than iron such as Al , Zn , Mg can be used in cathodic protection of iron against rusting.
10. **The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ_m.**
11. **Λ_m = KC= Conductivity * Concentration**
12. **(i) There will be no effect of catalyst on Gibbs .energy.**

    (ii) The catalyst provides an alternative pathway by decreasing the activation energy of a reaction
13. **The reactions can be represented at anode and at cathode in the following ways :**

    At anode (oxidation) :

    $Sn^{2+} \rightarrow = Sn^{4+}$ (aq) + $2e^-$] × 5 E° = + 0.15 V

    At cathode (reduction) :

    MnO^-_4(aq) + $8H^+$ (aq) + $5e^- \rightarrow Mn^{2+}$ (aq) + $4H_2O$ (I)] × 2 E° = + 1.51 V

    The Net R × M = $2MnO^-_4$(aq) + $16H^+$ + $5Sn^{2+} \rightarrow 2Mn^{2+}$ + $5Sn^{4+}$ + $8H_2O$

    Now $E°_{cell} = E°_{cathode} - E°_{anode}$

= 1.51 − 0.15 = + 1.36 V

∴ Positive value of $E°_{cell}$ favours formation of product

14. **1R×1a = Conductance (C) × Cell constant**

    Molar conductance : (Λ_m) = K×1000c

15. **$Ag^+/Ag < Cu^{2+}/Cu < Fe^{2+}/Fe < Cr^{3+}/Cr < Mg^{2+}/ Mg < K^+/K$**

    More negative the value of standard electrode potentials of metals is, more will be the reducing power.

16. **The mechanism of corrosion is explained on the basis of electrochemical theory. By taking example of rusting of iron, we Refer tothe formation of small electrochemical cells on the surface of iron. The redox reaction involves**

    At anode : $Fe(S) \rightarrow Fe^{2+} (aq) + 2e^-$

    At cathode : $H_2O + CO_2 \rightleftharpoons H_2CO_3$ (Carbonic acid)

    $H_2CO_3 \rightleftharpoons 2H^+ + CO_2^{2-}$

    $H_2O \rightleftharpoons H^+ + OH^-$

    $H^+ + e^- \rightarrow H$

    $4H + O_2 \rightarrow 2H_2O$

    Then net resultant Redox reaction is

    $2Fe(s) + O_2 (g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

17. 035*10^7
18. **Λ_m = 125 S cm^2 mol^{-1}**
19. **-212.3 KJ mol^{-1}**
20. **1**.46*10^-6
21. Kohlrausch law of independent migration of ions: **The limiting molar conductivity of an electrolyte (i.e. molar conductivity at infinite dilution) is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte**

    $\Lambda°m$ for $A_xB_y = x\lambda°_+ + y\lambda°_-$

    For acetic acid $\Lambda°$ (CH_3COOH) = $\lambda°_{CH3}COO^- + \lambda°_H{}^+$

    $\Lambda°(CH_3COOH) = \Lambda° (CH_3COOK) + \Lambda° (HCl) − \Lambda° (KCl)$

22. (i) Fuel cells : **These cells are the devices which convert the energy produced during combustion of fuels like H_2, CH_4, etc. directly into electrical energy.**

(ii) The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ°_{m}.

23. i) Rate constant (k): **It is a proportionality constant and is equal to the rate of reaction when the molar concentration of each of the reactants is unity.**

    (ii) Activation energy (E_a): **The minimum extra amount of energy absorbed by the reactant molecules to form the activated complex is called activation energy.**

24. **Cell reaction of a dry cell can be represented as**

    $Zn + Hg^{2+} \rightarrow Zn^{2+} + Hg$ (n = 2)

    Nemst equation

    $E_{cell} = E°_{cell}$ – 0.05912log[Zn2+]Hg2+

    The voltage of dry cell has to decrease because the concentration of electrolyte decreases in the reactions.

25. 1930 seconds

26. i) Mercury cell is used in hearing aids.

    (ii) Fuel cell was used in the Apollo Space Programme.

    (iii) Lead storage cell is used in automobiles and inverters.

    (iv) Dry cell does not have a long life.

27. Leclanche cells (Dry cell) is used in transistors.

    Reaction at Anode:

    $Zn(s) \rightarrow Zn^{2+} + 2e^-$

    At Cathode:

    MnO_2 + NH+4 + $e^- \rightarrow MnO(OH) + NH_3$

28. Lead storage battery is used in inverters.

    At Anode:

    Pb(s) + SO2−4(aq) → $PbSO_4$ (s) + $2e^-$

    At Cathode:

    PbO_2(s) + SO2−4(aq) + $4H^+$ (aq) + $2e^-$

    $PbSO_4$ (s) + $2H_2O$

29. 13.93M

30. $229.6 cm^2 mol^{-1}$

31. **Corrosion:** Corrosion is defined as the deterioration of a substance because of its reaction with its environment. Corrosion is an electrochemical

phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and the reaction is

At Anode : $2Fe \rightarrow 2Fe^{+2} + 4e^{-}$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^{+}. This spot behaves as cathode

At Cathode : $O_2 + 4H^{+} + 4e-$

Overall reaction : $2Fe + O_2 + 4H^{+} \rightarrow 2Fe^{+2} + 2H_2O$

32. **219.**23ohm-^{1}cm^{2}mol^{-1}