Doon Public School, Bhuj

Holiday Homework

Dear Students,

“The hardest part of remote learning is that we aren’t together. We want our students to know that even though we aren’t together, you are still very much cared and everything we do is for you.” It is now the time to take this task on as a lesson in space management, time management, and self-management. It is also time to embrace technology, make judicious use of it to plan and prepare for your academics.

This is your Holiday Homework which must be written in fair chemistry notebook. Make this time absolutely useful for you.

Class-XII **Subject- Chemistry**

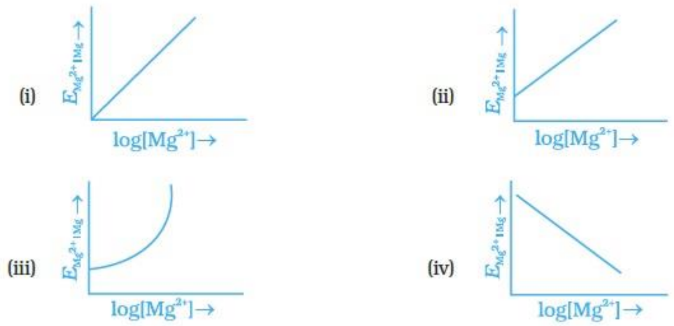
Chapter- Electrochemistry

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

(i) Pt (s) | H_2 (g,0.1 bar) | H^+ (aq.,1 M) || Cu^{2+}(aq.,1M) | Cu
(ii) Pt(s) | H_2 (g, 1 bar) | H^+ (aq.,1 M) || Cu^{2+} (aq.,2 M) | Cu
(iii) Pt(s)| H_2 (g, 1 bar) | H^+ (aq.,1 M) || Cu^{2+} (aq.,1 M) | Cu
(iv) Pt(s) | H_2 (g, 1 bar) | H^+ (aq.,0.1 M) || Cu^{2+} (aq.,1 M) | Cu

1. Electrode potential for Mg electrode varies according to the equation

$E_{Mg^{2+}|Mg} = E^{\ominus}_{Mg^{2+}|Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}$. The graph of $E_{Mg^{2+}|Mg}$ vs $\log[Mg^{2+}]$ is



2. Which of the following statement is correct?

(i) E_{Cell} and Δ_rG of cell reaction both are extensive properties.
(ii) E_{Cell} and Δ_rG of cell reaction both are intensive properties.
(iii) E_{Cell} is an intensive property while Δ_rG of cell reaction is an extensive property.
(iv) E_{Cell} is an extensive property while Δ_rG of cell reaction is an intensive property.

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

(i) Cell potential

(ii) Cell emf

(iii) Potential difference

(iv) Cell voltage

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

(i) It does not participate in the cell reaction.

(ii) It provides surface either for oxidation or for reduction reaction.

(iii) It provides surface for conduction of electrons.

(iv) It provides surface for redox reaction.

5. An electrochemical cell can behave like an electrolytic cell when ____________.

(i) $E_{cell} = 0$
(ii) E_{cell} > Eext
(iii) $E_{ext} > E_{cell}$
(iv) $E_{cell} = E_{ext}$

6. Which of the statements about solutions of electrolytes is not correct?

(i) Conductivity of solution depends upon size of ions.

(ii) Conductivity depends upon viscosiy of solution.

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

(iv) Conductivity of solution increases with temperature.

7. Using the data given below find out the strongest reducing agent.

$$E^{\ominus}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V \quad E^{\ominus}_{Cl_2/Cl^-} = 1.36V$$

$$E^{\ominus}_{MnO_4^-/Mn^{2+}} = 1.51V \quad E^{\ominus}_{Cr^{3+}/Cr} = -0.74V$$

(i) Cl^-
(ii) Cr
(iii) Cr^{3+}
(iv) Mn^{2+}

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

(i) Cl^-
(ii) Mn^{2+}
(iii) MnO^-_4
(iv) Cr^{3+}

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

(i) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$
(ii) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$
(iii) $Cr^{3+} < Cl^- < Cr_2O_7^{2-} < MnO^-_4$
(iv) Mn2+ < Cr3+ < Cl– < Cr

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

(i) Cl^-
(ii) Cr^{3+}
(iii) Cr
(iv) Mn^{2+}

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

(i) Cr^{3+}
(ii) MnO^-_4
(iii) $Cr_2O_7^{2-}$
(iv) Mn^{2+}

12. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is ___________.

(i) 1F

(ii) 6F

(iii) 3F

(iv) 2F

13. The cell constant of a conductivity cell _____________.

(i) changes with change of electrolyte.

(ii) changes with change of concentration of electrolyte.

(iii) changes with temperature of electrolyte.

(iv) remains constant for a cell.

14. While charging the lead storage battery _______________.

(i) $PbSO_4$ anode is reduced to Pb.
(ii) $PbSO_4$ cathode is reduced to Pb.
(iii) $PbSO_4$ cathode is oxidised to Pb.
(iv) $PbSO_4$ anode is oxidised to PbO2.

15. $\Lambda^0_{m\,(NH_4OH)}$ is equal to _______________.

(i) $\Lambda^0_{m\,(NH_4OH)} + \Lambda^0_{m\,(NH_4Cl)} - \Lambda^0_{(HCl)}$

(ii) $\Lambda^0_{m\,(NH_4Cl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{(NaCl)}$

(iii) $\Lambda^0_{m\,(NH_4Cl)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{(NaOH)}$

(iv) $\Lambda^0_{m\,(NaOH)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{(NH_4Cl)}$

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

(i) $Na^+ (aq) + e^- \longrightarrow Na (s)$; $E^\ominus_{Cell} = -2.71V$

(ii) $2H_2O (l) \longrightarrow O_2 (g) + 4H^+ (aq) + 4e^-$; $E^\ominus_{Cell} = 1.23V$

(iii) $H^+ (aq) + e^- \longrightarrow \frac{1}{2} H_2 (g)$; $E^\ominus_{Cell} = 0.00 V$

(iv) $Cl^- (aq) \longrightarrow \frac{1}{2} Cl_2 (g) + e^-$; $E^\ominus_{Cell} = 1.36 V$

Multiple Choice Questions (Type-II)

Note : In the following questions two or more than two options may be correct.

1. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that _____________.
(i) this redox couple is a stronger reducing agent than the H^+/H_2 couple.
(ii) this redox couple is a stronger oxidising agent than H^+/H_2.
(iii) Cu can displace H_2 from acid.
(iv) Cu cannot displace H2 from acid.

2. $E^\ominus_{Cell}$ for some half cell reactions are given below. On the basis of these mark the correct answer.

(a) $H^+ (aq) + e^- \longrightarrow \frac{1}{2} H_2 (g)$; $E^\ominus_{Cell} = 0.00V$

(b) $2H_2O (l) \longrightarrow O_2 (g) + 4H^+ (aq) + 4e^-$; $E^\ominus_{Cell} = 1.23V$

(c) $2SO_4^{2-} (aq) \longrightarrow S_2O_8^{2-} (aq) + 2e^-$; $E^\ominus_{Cell} = 1.96 V$

(i) In dilute sulphuric acid solution, hydrogen will be reduced at cathode.

(ii) In concentrated sulphuric acid solution, water will be oxidised at anode.

(iii) In dilute sulphuric acid solution, water will be oxidised at anode.

(iv) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate ion at anode.

3. $E^{\ominus}_{Cell} = 1.1V$ for Daniel cell. Which of the following expressions are correct description of state of equilibrium in this cell?

(i) $1.1 = K_c$

(ii) $\frac{2.303RT}{2F}\log K_c = 1.1$

(iii) $\log K_c = \frac{2.2}{0.059}$

(iv) $\log K_c = 1.1$

4. Conductivity of an electrolytic solution depends on ____________.

(i) nature of electrolyte.

(ii) concentration of electrolyte.

(iii) power of AC source.

(iv) distance between the electrodes.

5. $\Lambda^0_m H_2O$ is equal to ______________.

(i) $\Lambda^0_{m\,(HCl)} + \Lambda^0_{m\,(NaOH)} - \Lambda^0_{m\,(NaCl)}$

(ii) $\Lambda^0_{m\,(HNO_3)} + \Lambda^0_{m\,(NaNO_3)} - \Lambda^0_{m\,(NaOH)}$

(iii) $\Lambda^0_{(HNO_3)} + \Lambda^0_{m\,(NaOH)} - \Lambda^0_{m\,(NaNO_3)}$

(iv) $\Lambda^0_{m\,(NH_4OH)} + \Lambda^0_{m\,(HCl)} - \Lambda^0_{m\,(NH_4Cl)}$

6. What will happen during the electrolysis of aqueous solution of $CuSO_4$ by using platinum electrodes?
(i) Copper will deposit at cathode.

(ii) Copper will deposit at anode.

(iii) Oxygen will be released at anode.

(iv) Copper will dissolve at anode.

7. What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?
(i) Copper will deposit at cathode.

(ii) Copper will dissolve at anode.

(iii) Oxygen will be released at anode.

(iv) Copper will deposit at anode.

8. Conductivity κ , is equal to ____________.

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

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

(iii) Λ_m

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

9. Molar conductivity of ionic solution depends on ___________.

(i) temperature.

(ii) distance between electrodes.

(iii) concentration of electrolytes in solution.

(iv) surface area of electrodes.

10. For the given cell, $Mg|Mg^{2+}||\ Cu^{2+}|Cu$

(i) Mg is cathode

(ii) Cu is cathode

(iii) The cell reaction is $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

(iv) Cu is the oxidising agent

Answers to Multiple Choice Questions

MCQ (Type I)

1. (iii)	2. (ii)	3. (iii)	4. (ii)	5. (iv)	6. (iii)
7. (iii)	8. (ii)	9. (iii)	10. (ii)	11. (iv)	12. (i)
13. (iii)	14. (iv)	15. (i)	16. (ii)	17. (ii)	

MCQ (Type II)

1. (ii), (iv)	2. (i), (iii)	3. (ii), (iii)	4. (i), (ii)
5. (i), (iv)	6. (i), (iii)	7. (i), (ii)	8. (i), (ii)
9. (i), (iii)	10. (ii), (iii)		

Very Short Answer Type Questions (1 mark)

1. Can you store AgCl solution in Zinc pot?

Ans. No. We can't store AgCl solution in Zinc pot because standard electrode potential of Zinc is less than silver.

2. Define the term – standard electrode potential?

Ans. When the concentration of all the species involved in a half-cell is unity, then the

electrode potential is called standard electrode potential.

3. What is electromotive force of a cell?

Ans. Electromotive force of a cell is also called the cell potential. It is the difference between

the electrode potentials of the cathode and anode.

4. Can an electrochemical cell act as electrolytic cell? How?

Ans. Yes, An electrochemical cell can be converted into electrolytic cell by applying an

external opposite potential greater than its own electrical potential.

5. Single electrode potential cannot be determined. Why?

Ans. A single half cell does not exist independently as reduction and oxidation occur

simultaneously therefore single electrode potential cannot be measured.

6. What is SHE? What is its electrode potential?

Ans. SHE stands for standard Hydrogen electrode. By convention, its electrode potential is

taken as 0 (zero).

7. What does the positive value of standard electrode potential indicate?

Ans. The positive value of standard electrode potential indicates that the element gets

reduced more easily than ions and its reduced form is more stable than Hydrogen gas.

8. What is an electrochemical series? How does it predict the feasibility of a certain

redox reaction?

Ans. 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 will not occur.

9. Give some uses of electrochemical cells?

Ans. Electrochemical cells are used for determining the

a) pH of solutions

b) solubility product and equilibrium constant

c) in potentiometric titrations

10. A cell is represented by notation – $Cu(s)/cu^{2+}(aq)//Ag^{+}(aq)/Ag(s)$

Calculate e.m.f of the cell if $E^0Cu^{2+}/Cu = +0.34V$ **and** $E^0Ag^{+}/Ag = 0.08V$ **?**

Ans. $E^0_{cell} = E^0_{cathode} - E^0_{Anode}$

$= E^0_{Ag+/Ag} - E^0_{Cu^{2+}/Cu}$

=0.80V – (+0.34V)

=+0.46V

11. What would happen if Nickel spatula is used to stir a solution of $CuSO_4$ **?**

$E^0Cu^{2+}/Cu = 0.34\ V$, $E^0_{Ni}\ 2^+/Ni = -0.25V$ **?**

Ans. From the reduction potential values, it is indicated that Nickel (more negative value) is more reactive than copper and will, then displace copper from $CuSO_4$

$$Ni(s) + Cu^{2+}(aq) \rightarrow \grave{a}Ni^{2} + (aq) + Cu(s).$$

12. State the factors that affect the value of electrode potential?

Ans. Factors affecting electrode potential values are –

a) Concentration of electrolyte

b) Temperature.

13. Write Nernst equation for a Daniel cell?

Ans. Daniel cell:

$Zn(s)/Zn^{2}+(aq)//Cu^{2}+(aq)/Cu(s)$

Nernst equation – at 298 K

$$E_{cell} = \left(E^0_{Cu^{2}+/Cu} - E^0_{Zn^{2}+/Zn}\right) - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[cu^{2+}]}$$

14. Define the term specific resistance and give its SI unit

Ans. The specific resistance of a substance is its resistance when it is one meter long and its area of cross Section is one m2 . Its SI unit is Ωm (ohm meter)

15. Give the unit of conductance?

Ans. The SI unit of conductance is Siemens, denoted by the symbol, S & is equal to Ω^{-1}.

<u>Short Type Questions (2 Mark)</u>

1. How is standard electrode potential of a cell related to :-

1) Equilibrium constant?

2) Gibbs free energy change.

Ans. (i) Standard electrode potential and equilibrium constant

Where E^0_{cell}= standard electrode potential of cell

$$E^0_{cell} = \frac{2.303RT}{nF} \log k_c$$

R = Gas constant T = temperature in Kelvin

n = no. of electrons. F = Faraday's constant and

Kc = Equilibrium constant

(ii) Standard electrode potential and Gibbs free energy change

$\Delta G°$=- nF E^0_{cell} Where $\Delta G°$= Change in Gibbs' free energy

n = No. of electrons F = Faraday's Constant

E^0_{cell} = Standard electrode Potential of cell.

2. What is the half cell potential for Fe^{3+}/Fe **electrode in which** $\left[Fe^{3+}\right] = 0.1\,m$.

$$E^0 Fe^{3+}/Fe = +0.771V$$

Ans. $Fe^{3+} + 3e^- \rightarrow Fe$

According to Nernst Equation –

$$E_{Fe^{3+}/Fe} = E^0_{Fe^{3+}/Fe} - \frac{0.059}{n} \log \frac{1}{[Fe^{3+}]}$$

$$= 0.771\text{ V} - \frac{0.059}{3} \log \frac{1}{0.1}$$

= 0.771 V - 0.0197 V

= +0.7513V

3. Calculate pH of following half cell. Pt , H_2 / H_2SO_4**, if its electrode potential is 0.03V.**

Ans. $P^H = -Log\left[H^+\right]$

The cell reaction is –

$$H^+ + e \longrightarrow H_2(g)$$

According to Nearest Equation

$$E = E^0 - \frac{0.059}{n} \log \frac{1}{[H^+]}$$

$$0.03\text{V} = 0 + \frac{0.059}{1} \left(-\log \frac{1}{[H^+]}\right)$$

$$= 0 + 0.059\,{}_{P}{}^{H}$$

pH= 0.03V/0.059= 5,07

4. What are the factors on which conductivity of an electrolyte depend?

Ans. 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

5. How is molar conductance related to conductivity of an electrolyte ?

Ans. Molar conductance, Ωm is related to conductively by the relation.

$$\Omega m = \frac{k}{c}$$

Where κ = conductivity in s/m.

C = concentration in mol / m^3

6. Write an expression relating cell constant and conductivity?

Ans. Cell constant and conductivity are related by the expression-

$\kappa = \frac{G}{R}$ where G = Cell constant

κ = conductivity

R = Resistance.

7. The conductivity of an aqueous solution of NaCl in a cell is 92 Ω^{-1}cm-^{1} the resistance offered by this cell is 247.8 Ω . Calculate the cell constant?

Ans. Specific conductivity = $\frac{\text{cell constant}}{\text{Resistance}}$

Or cell constant = $conductivity \times Resistance$

= 92 Ω^{-1} cm^{-1} $\times$ 247.8 Ω

= 22797.6 Ω^{-1}

8. 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?

Ans. $\lambda m = \frac{\kappa}{C} \times 1000\ \text{S cm}^2\ \text{mol}_{-1}$

= $\frac{1000\ \kappa}{M}$

κ = $\frac{\lambda m \times M}{1000}$

= 0.00046 s/cm

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

= $\frac{1}{0.00046\ \text{S cm}^{-1}}$ $= 2174\ \Omega\ \text{cm}$.

9. The conductivity of metals decreases while that of electrolytes increases with

increases in temperature. Why?

Ans. With increase in temperature, the K.E. of metal cation increases and obstructs the free flow of electrons decreasing the conducts of metal while in case of electrolytes, increased temperature increases the mobility of ions this increases the conductance of ions.

10. The measured resistance of a cell containing $7.5 \times 10^{-3} M$ solution of KCl at $25^0 C$

was 1005 Ω calculate

(a) Specific conductance and

(b) Molar conductance of the solution. Cell Constant = $1.25\ cm^{-1}$

Ans. $k = 1.2\ 2/3 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$

$\lambda m = 165.7\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

Short Type Questions (3 Mark)

1.What is the cell potential for the cell at 25^0C $Cr / Cr^{3+} 10.1\ m] // Fe^{2+} (0.01m) / Fe$

$E^0_{cr+/cr} = -0.74V; E^0 Fe^{2+} / Fe = -0.44V$.

Ans. The cell reaction is

$2Cr + 3Fe^{2+} 6e^- \rightarrow 2Cr^{3+} + 3Fe$

Nernst Equation –

$$E_{cell} = \left(E^0_{Fe}{}^{2+}/_{Fe} - E^0_{cr}{}^{3+}/_{cr} \right) - \frac{0.059}{6} \log \frac{\left[Cr^{3+}\right]^2}{\left[Fe^{2+}\right]^3}$$

=(-0.44v – (-0.74v) - $\frac{0.059}{6} \log \frac{(0.10)^2}{(0.01)^3}$

= $0.3V - \frac{0.059}{6} \log 10^4$

= 0.3V – 0.0394V

= +0.2606 V

2.Calculate ΔG^0 **for the reaction at** 25^0C

$Zn(s) 1 Zn^2 + [0.0004m] 11 cd^2 + (0.2m) 1 cd (s)$ $E^0_{Zn}{}^{2+}/_{Zn} = -0.763V$,

$E^0_{cd}{}^{2+} / cd = -0.403v$, $F = 96500\ CMol^{-1}$, **R = 8.314 J/K.**

Ans. The half cell reactions are

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

Cathode: $Cd^{2} + (aq) + 2e^{-} \rightarrow Cd(s)$

Nernst Equation

$$E_{cell} = \left(E^{0}_{Cathode} - E^{0}_{anode}\right) - \frac{0.059}{n} \log \frac{\left[Zn^{2+}\right]}{\left[Cd^{2+}\right]}$$

= (- 0.403 – (-0.763) - $\frac{0.059}{2} \log \frac{0.0004}{0.2}$

= 0.36V - 0.0798V = 0.4398V

$$\Delta G^{0} = -\mathrm{n\,F\,E^{0}_{cell}}$$

$$= \frac{-2mol \times 96500\ C}{mol \times 0.4398V}$$

= -8488 J mol^{-1}

3.Calculate Equilibrium constant K for the reaction at

$298K\ Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+} / aq) + Cu\ E^{0}{}_{Zn}{}^{2+} 1Zn = -0.076v; E^{0}Cu^{2} + /Cu =$ **+0.34v.**

Ans. From the reaction, n =2

$$E^{0}_{cell} = E^{0}cu^{2} + /cu - E^{0}Zn^{2} + /Zn$$

= + 0.34v - (-0.76v) = 1.10V

$$E^{0}_{cell} = \frac{2.303RT}{nF} \log \mathrm{k_c}$$

At 298k , $E^{0}_{cell} \times \frac{n}{0.059} \log \mathrm{k_c}$

Log $k_c = E^0_{cell} \times \frac{n}{0.059}$

$= 1.10 \times \frac{2}{0.059} = 37.29$

$K_c = Antilog\ 37.29$

$= 1.95 \times 10^{37}$

4. For what concentration of $Ag+(aq)$ will the emf of the given cell be zero at 25^0C

if the concentration of $CU^{2+}(aq)$ is 0.1 M ?

$Cu(s) / Cu^{2+}(0.1M) // Ag^{+}(aq) / Ag(s)\ E^0 Ag^{+} / Ag = +0.80V;$
$E^0{}_{Cu}{}^{2+/Cu} = 0.34\ V$

Ans. $\left[Ag^{+} \right] = 5.3 \times 10^{-9} M$

5.Calculate the standard free energy change for the cell- reaction.

$Fe^{2+}(aq) + Ag^{+}(s)\ \grave{a} \rightarrow Fe^{3} + (aq) + Ag(s)$ **How is it related to the equilibrium constant of the reaction?** $E^0{}_{Fe}{}^{3+} / Fe^{2+} = +0.77V$, $E^0{}_{Ag}{}^{+1/Ag} = +0.08V\ F$
$= 96500\ C / mol.$

Ans. $E^0{}_{cell} = 0.03V$

$\Delta G^0 = -2895J$

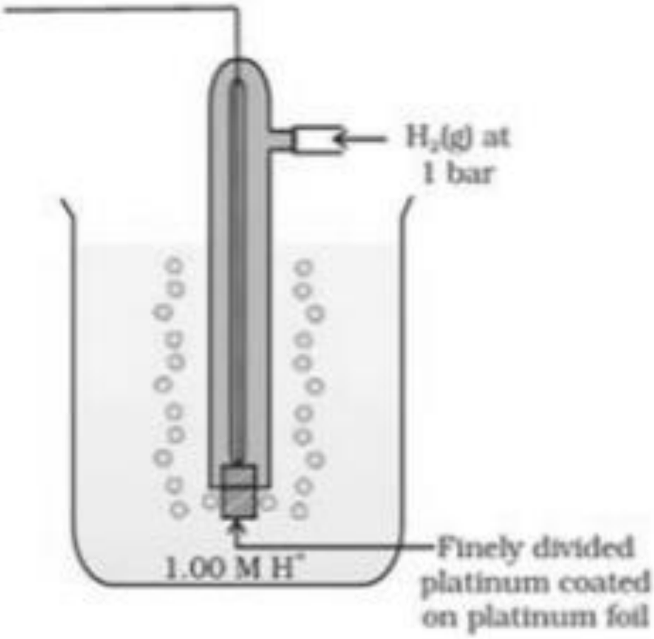
Long Type Questions (5 Marks)

1. Explain construction and working of standard Hydrogen electrode?

Ans. Construction :

SHE 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 oxidized. Forms of Hydrogen is maintained at unity i.e) pressure of H_2 gas is 1 bar and concentration of Hydrogen ions in the solution is 1 molar.

Working – The reaction taking place in SHE is $H^{+}(aq)+e^{-} \rightarrow \grave{a}H_2(g)$ At 298 K , the emf of the cell constructed by taking SHE as anode and other half cell as cathode, gives the reduction potential of the other half cell where as for a cell constructed by taking SHE as anode gives the oxidation potential of other half cell as conventionally the electrode potential of SHE is zero.



2. 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 $\lambda^{\circ}H^{+}$ = 349.6 S $cm^2\ mol^{-1}$ **and** $\lambda^{\circ}(HCOO-) = 54.6\, S\, cm^2\, mol$

Ans. *C* = 0.025 $mol\, L^{-1}$

$$\Lambda_m = 46.1\, S\, cm^2\, mol^{-1}$$
$$\lambda^{\circ}(H^{+}) = 349.6\, S\, cm^2\, mol^{-1}$$
$$\lambda^{\circ}(HCOO^{-}) = 54.6\, S\, cm^2\, mol^{-1}$$

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

= 349.6 + 54.6 = $404.2\, S\, cm^2\, mol^{-1}$

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m(HCOOH)}{\Lambda_m^{0}(HCOOH)}$$

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

= 0.114 (approximately)

Thus, dissociation constant:

$$K = \frac{c \propto^2}{(1 - \propto)}$$

$$= \frac{(0.025\, mol\, L^{-1})(0.114)^2}{(1 - 0.114)}$$

$$= 3.67 \times 10^{-4}\, mol\, L^{-1}$$

3. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Ans. In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by, $Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^{-}$

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of H^{+} ions, the electrons reduce oxygen. This spot behaves as the cathode. These H+ ions come either from H_2CO_3, which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given by, $O_{2(g)} + 4H^{+}{}_{(aq)} + 4e^{-} \rightarrow 2H_2O_{(l)}$

The overall reaction is: $2Fe_{(s)} + O_{2(g)} + 4H^{+}{}_{(aq)} \rightarrow 2Fe^{2+}{}_{(aq)} + 2H_2O_{(l)}$

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide $\left(Fe_2O_3, xH_2O\right)$ i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

4. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:

(i) $2Cr_{(s)} + 3Cd^{2+}{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3Cd$ **(ii)** $Fe^{2+}{}_{(aq)} + Ag^{+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + Ag_{(s)}$

Calculate the $\Delta_r G^{\ominus}$**, and equilibrium constant of the reactions**

Ans. (i)$E^{\ominus}{}_{Cr^{3+}/Cr} = 0.74V$

$E^{\ominus}{}_{Cd^{2+}/Cd} = 0.40V$

The galvanic cell of the given reaction is depicted as: $Cr_{(s)} \mid Cr^{3+}{}_{(aq)} \parallel Cd^{2+}{}_{(aq)} \mid Cd_{(s)}$

Now, the standard cell potential is $E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$

= 0.40 – (–0.74)

= +0.34 V

$\Delta_r G^\ominus = -nFE^\ominus_{cell}$

In the given equation,

$n = 6$

F = 96487 C mol - 1

$E^\ominus_{cell}$ = +0.34 V

Then, $\Delta_r G^\ominus = -\ 6 \times 96487\ \text{C mol}^{-1} \times 0.34\ \text{V}$

= –196833.48 CV mol^{-1}

= –196833.48 J mol^{-1}

= –196.83 kJ v

Again, $\Delta_r G^\ominus = -RT\ \text{In}\ K$

$\Delta_r G^\ominus = -2.303\,RT\ \text{In}\ K$

$$\log K = -\frac{\Delta_r G}{2.303\,RT}$$

$$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

= 34.496

Therefore, K = antilog (34.496)

$= 3.13 \times 1034$

(ii) $E^\ominus_{Fe^{3+}/Fe^{2+}} = 0.77\,V$

$E^{\ominus}_{Ag^+/Ag} = 0.80\,V$

The galvanic cell of the given reaction is depicted as: $Fe^{2+}_{(aq)} \mid Fe^{3+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$

Now, the standard cell potential is $E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$

= 0.80 – 0.77

= 0.03 V

Here, n = 1.

Then, $\Delta_r G^{\ominus} = -nFE^{\ominus}_{cell}$

= $-1 \times 96487\ C\ mol^{-1} \times 0.03\ V$

= –2894.61 J mol^{-1}

= –2.89 kJ mol^{-1}

Again, $\Delta_r G^{\ominus} = 2.303\,RT\ \ln K$

$$\log K = -\frac{\Delta_r G}{2.303\,RT}$$

$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

= 0.5073

Therefore, K = antilog (0.5073)

= 3.2 (approximately)

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

(i) $Mg_{(s)} \mid Mg^{2+} + (0.001M) \parallel Cu^{2+} (0.0001M)$

(ii) $Fe_{(s)} \mid Fe^{2+} (0.001M) \parallel H^{+} (1M) \mid H_{2(g)} (1bar) \mid Pt_{(s)}$

(iii) $Sn_{(s)} | Sn^{2+}(0.050M) || H^{+}(0.020M) H^{2}_{(g)}(1bar) | Pt_{(s)}$

(iv) $Pt_{(s)} | Br^{2}(l) | Br^{-}(0.010M) || H^{+}(0.030M) | H^{2}_{(g)}(1bar) | Pt_{(s)}$

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

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Mg^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$= \{0.34 - (-236)\} - \frac{0.0591}{2}\log\frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2}\log 10$$

= 2.7 – 0.02955

= 2.67 V (approximately)

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

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Fe^{2+}\right]}{\left[H^{+}\right]^{2}}$$

$$= \{0 - (-0.44)\} - \frac{0.0591}{2}\log\frac{0.001}{1^{2}}$$

= 0.44–0.02955(–3)

= 0.52865 V

= 0.53 V (approximately)

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

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Sn^{2+}\right]}{\left[H^{+}\right]^{2}}$$

$$= \{0-(-0.14)\} - \frac{0.0591}{2}\log\frac{0.050}{(0.020)^2}$$

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

= 0.14–0.062

= 0.078 V

= 0.08 V (approximately)

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

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{1}{[Br^-]^2[H^+]^2}$$

$$= (0-1.09) - \frac{0.0591}{2}\log\frac{1}{(0.010)^2(0.030)^2}$$

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

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

$$= -1.09 - 0.02955 \times \log(1.11\times 10^{7})$$

= –1.09–0.02955(0.0453+7)

= –1.09–0.208

= –1.298 V