Electrochemistry

EXERCISE [PAGES 117 - 119]

Exercises | Q 1.01 | Page 117

Choose the most correct option.

Two solutions have the ratio of their concentrations 0.4 and ratio of their conductivities 0.216. The ratio of their molar conductivities will be ______.

1. **0.54**
2. 574
3. 0.0864
4. 1.852

Solution: Two solutions have the ratio of their concentrations 0.4 and ratio of their conductivities 0.216. The ratio of their molar conductivities will be **0.54**.

Exercises | Q 1.02 | Page 117

Choose the most correct option.

On diluting the solution of an electrolyte _______.

1. both ∧ and k increase
2. both ∧ and k decrease
3. **∧ increases and k decreases**
4. ∧ decreases and k increases

Solution: On diluting the solution of an electrolyte **∧ increases and k decreases**.

Exercises | Q 1.03 | Page 117

Choose the most correct option.

1 S m^2 mol^{-1} is equal to _______.

1. 10^{-4} S m^2 mol^{-1}
2. **10^4 Ω^{-1} cm^2 mol^{-1}**
3. 10^{-2} S cm^2 mol^{-1}
4. 10^2 Ω^{-1} cm^2 mol^{-1}

Solution: 1 S m^2 mol^{-1} is equal to **10^4 Ω^{-1} cm^2 mol^{-1}**.

Exercises | Q 1.04 | Page 117

Choose the most correct option.

The standard potential of the cell in which the following reaction occurs:

H_2 (g,1 atm) + Cu^{2+} (1M) → $2H^+$ (1M) + $Cu_{(s)}$,

$(E^{\circ}_{Cu} = 0.34V)$ is

1. - 0.34 V
2. **0.34 V**
3. 0.17 V
4. - 0.17 V

Solution: 0.34 V

Exercises | Q 1.05 | Page 117

Choose the most correct option.
For the cell,
$Pb_{(s)}$ $|Pb^{2+}$ (1 M)| $|Ag^{+}$ (1 M)| $Ag_{(s)}$,
if concentration of an ion in the anode compartment is increased by a factor of 10, the emf of the cell will

1. increase by 10 V
2. **increase by 0.0296 V**
3. decrease by 10 V
4. decrease by 0.0296 V

Solution: increase by 0.0296 V

Exercises | Q 1.06 | Page 117
Choose the most correct option.
Consider the half reactions with standard potentials _______.

i. $Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$ $E° = 0.8$ V

ii. $I_{2(s)} + 2e^{-} \rightarrow 2I^{-}_{(aq)}$ $E° = 0.53$ V

iii. $Pb^{2+}_{(aq)} + 2e^{-} \rightarrow Pb_{(s)}$ $E° = -0.13$ V

iv. $Fe^{2+} + 2e^{-} \rightarrow Fe_{(s)}$ $E° = -0.44$ V

The strongest oxidising and reducing agents respectively are

1. Ag and Fe^{2+}
2. **Ag^{+} and Fe**
3. Pb^{2+} and I
4. I^{2} and Fe^{2+}

Solution: Ag^{+} and Fe

Exercises | Q 1.07 | Page 117
Choose the most correct option.
For the reaction:
$Ni_{(s)} + Cu^{2+}$ (1 M) $\rightarrow Ni^{2+}$ (1 M) + $Cu_{(s)}$,
$E^{o}_{cell} = 0.57$ V, $\Delta G°$ of the reaction is

1. 110 kJ
2. **- 110 kJ**
3. 55 kJ
4. - 55 kJ

Solution: - 110 kJ

Exercises | Q 1.08 | Page 117
Choose the most correct option.
Which of the following is not correct?

1. Gibbs energy is an extensive property
2. Electrode potential or cell potential is an intensive property

3. Electrical work = – ΔG
4. **If half-reaction is multiplied by a numerical factor, the corresponding E° value is also multiplied by the same factor.**

Solution:

If half-reaction is multiplied by a numerical factor, the corresponding E° value is also multiplied by the same factor.

Exercises | Q 1.09 | Page 117

Choose the most correct option.

The oxidation reaction that takes place in lead storage battery during discharge is

$$Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)}$$

$$PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{2-}_{4(aq)} + 2e^{-}$$

$$Pb_s + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^{-}$$

$$PbSO_{4(s)} + 2e^{-} \rightarrow Pb_s + SO^{2-}_{4(aq)}$$

Solution:

$$Pb_s + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^{-}$$

Exercises | Q 1.1 | Page 118

Choose the most correct option.

Which of the following expressions represent molar conductivity of $Al_2(SO_4)_3$?

$$3\lambda^0_{Al^{3+}} + 2\lambda^0_{SO_4^{2-}}$$

$$2\lambda^0_{Al^{3+}} + 3\lambda^0_{SO_4^{2-}}$$

$$1/3\lambda^0_{Al^{3+}} + 1/2\lambda^0_{SO_4^{2-}}$$

$$\lambda^0_{Al^{3+}} + \lambda^0_{SO_4^{2-}}$$

Solution:

$$2\lambda^0_{Al^{3+}} + 3\lambda^0_{SO_4^{2-}}$$

Exercises | Q 2.01 | Page 118

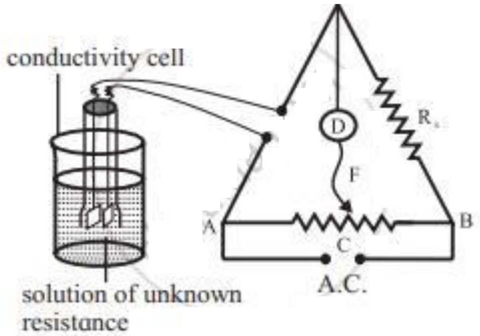
What is a cell constant? What are its units? How is it determined experimentally?

Solution:

For a given cell, the ratio of separation (l) between the two electrodes divided by the area of cross-section (a) of the electrode is called the cell constant.

Cell constant = l/a

The unit of cell constant is m^{-1} (SI unit) or cm^{-1} (C.G.S unit).



1) The cell constant is determined using the 1 M, 0.1 M or 0.01 M KCl solutions. The conductivity of KCl solution is well tabulated at various temperatures.

2) The resistance of KCl solution is measured by Wheatstone bridge as shown in the figure.

3) AB is the uniform wire. R_x is the variable known resistance placed in one arm of Wheatstone bridge. The conductivity cell containing KCl solution of unknown resistance is placed in the other arm of Wheatstone bridge.

4) D is a current detector. F is the sliding contact that moves along AB. A.C. represents the source of alternating current.

5) The sliding contact is moved along AB until no current flows. The detector D shows no deflection. The null point is, thus, obtained at C.

6) According to Wheatstone bridge principle,

$$\frac{R_{(solution)}}{l(AC)} = \frac{R_x}{l(BC)}$$

Hence, $R_{(solution)} = \dfrac{l(AC)}{l(BC)} \times R_x$

7) By measuring lengths AC and BC and knowing R_x , resistance of KCl solution can be calculated.

8) The cell constant is given by

Cell constant = $k_{KCl} \times R_{(solution)}$

The conductivity of KCl solution is known. The cell constant, thus, can be calculated.

Exercises | Q 2.02 | Page 118

Answer the following in one or two sentences.

Write the relationship between conductivity and molar conductivity and hence unit of molar conductivity.

Solution:

1. The molar conductivity of the given solution is related to conductivity as:
   $\wedge = k/c$
2. The SI units of k are S m^{-1} and that of c are mol m^{-3}. Hence, the SI units of $\wedge$ is S m^2 mol^{-1}

Exercises | Q 2.03 | Page 118

Answer the following in one or two sentences.

Write the electrode reactions during electrolysis of molten KCl.

Solution:

Electrode reactions during electrolysis of molten KCl are as follows:

$$2Cl^-_{(l)} \to Cl_{2(g)} + 2e^- \quad \text{(Oxidation half reaction at anode)}$$

$$2K^+_{(l)} + 2e^- \to 2K_{(l)} \quad \text{(Reduction half reaction at cathode)}$$

____

$$2K^+_{(l)} + 2Cl^-_{g} \to 2K_{(l)} + Cl_{2(g)} \quad \text{(Overall cell reaction)}$$

Exercises | Q 2.04 | Page 118

Answer the following in one or two sentences.

Write any two functions of salt bridge.

Solution:

1. It provides electrical contact between two solutions and thereby completes the electrical circuit.
2. It prevents the mixing of two solutions.
3. It maintains electrical neutrality in both the solutions by the transfer of ions.

Exercises | Q 2.05 | Page 118

Answer the following in one or two sentences.

What is standard cell potential for the reaction

$3Ni_{(s)} + 2Al^{3+}$ (1 M) → $3Ni^{2+}$ (1 M) + $2Al_{(s)}$, if E°_{Ni} = - 0.25 V and

E°_{Al} = - 1.66 V?

Solution:

Given: E°_{Ni} = - 0.25 V, E°_{Al} = - 1.66 V

To find: Standard cell potential

Formula: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Calculation: Electrode reactions are

At anode: $Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$

At cathode: $Al^{3+}_{aq} + 3e^- \rightarrow Al_{(s)}$

The standard electrode potential is given by

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = E^\circ_{Al} - E^\circ_{Ni}$

= (- 1.66 V) - (- 0.25 V) = - 1.41 V

The standard cell potential for the reaction is –1.41 V.

Exercises | Q 2.06 | Page 118

Answer the following in one or two sentences.

Write Nernst equation. What part of it represents the correction factor for nonstandard state conditions?

Solution:

1) For any general reaction, aA + bB → cC + dD

Nernst equation is given by

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ OR}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log_{10} \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where n = moles of electrons used in the reaction, F = Faraday = 96500 C,
T = temperature in kelvin,
R = gas constant = 8.314 J K^{-1} mol^{-1}

2) The second term in the Nernst equation is the correction for nonstandard state conditions.

$$\text{Correction factor is } \frac{2.303RT}{nF} \log_{10} \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Exercises | Q 2.07 | Page 118

Answer the following in one or two sentences.

Under what conditions the cell potential is called standard cell potential?

Solution:

The cell potential measured under the standard conditions is called standard cell potential. The standard conditions chosen are 1 M concentration of a solution, 1 atm pressure for gases, solids and liquids in pure form and 25 °C.

Exercises | Q 2.08 | Page 118

Answer the following in one or two sentences.

Formulate a cell from the following electrode reactions:

$$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$$

$$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$$

Solution:

The oxidation half-reaction at the anode is

$$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$$

The reduction half-reaction at cathode is

$$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$$

Notation for anode:	$Mg_{(s)}$	$Mg^{2+}_{(aq)}$
Notation for cathode:	$Au^{3+}_{(aq)}$	$Au_{(s)}$

Cell formula:

$$Mg_{(s)} |Mg^{2+}_{(aq)}| |Au^{3+}_{(aq)}| Au_{(s)}$$

Exercises | Q 2.09 | Page 118

Answer the following in one or two sentences.

How many electrons would have a total charge of 1 coulomb?

Solution:

Charge on I e^- is 1.602×10^{-19} coulomb.

I $e^- \equiv 1.602 \times 10^{-19}$ C

∴ Number of electrons having total charge of 1 coulomb

$$= \frac{1}{1.602 \times 10^{-19}} = 6.242 \times 10^{18}$$

The number of electrons having a total charge of 1 coulomb is 6.242×10^{18}

Exercises | Q 2.1 | Page 118

Answer the following in one or two sentences.

What is the significance of the single vertical line and double vertical line in the formulation galvanic cell?

Solution:

1. A single vertical line placed between two phases in the galvanic cell represents the phase boundary. It indicates direct contact between them.
2. A double vertical line placed between two solutions indicates that they are connected by salt bridge.

Exercises | Q 3.01 | Page 118

Answer the following in brief.

Explain the effect of dilution of the solution on conductivity?

Solution:

1. The electrolytic conductivity is the electrical conductance of unit volume (1 cm^3) of solution. It depends on the number of current-carrying ions present in unit volume of solution.
2. On dilution total number of ions increases as a result of an increased degree of dissociation.
3. An increase in the total number of ions is not in the proportion of dilution. Therefore, the number of ions per unit volume of solution decreases.
4. This results in a decrease of conductivity with a decrease in the concentration of the solution.

Exercises | Q 3.02 | Page 118

Answer the following in brief.

What is a salt bridge?

Solution:

Salt bridge is a U tube containing a saturated solution of an inert electrolyte such as KCl or NH_4NO_3 and 5% agar solution.

Exercises | Q 3.03 | Page 118

Answer the following in brief.

Write electrode reactions for the electrolysis of aqueous NaCl.

Solution:

- **Reduction half-reaction at cathode:**

At cathode, two reduction reactions compete.

i. Reduction of sodium ions.

$$Na^+_{(aq)} + e^- \rightarrow Na_s, E^\circ = -2.71 V$$

ii. Reduction of water to hydrogen gas.

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}, E^\circ = -0.83 V$$

The standard potential for the reduction of water is higher than that for the reduction of Na^+. Hence, water has a much greater tendency to get reduced than the Na^+ ion. Therefore, reduction of water is the cathode reaction when the aqueous NaCl is electrolysed.

- **Oxidation half-reaction at anode:**

At anode, there will be competition between oxidation of Cl^- ion to Cl_2 gas as in the case of molten NaCl and the oxidation of water to O_2 gas.

i. Oxidation of Cl^- ions to chlorine gas

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-, E^\circ_{oxd} = -1.36 V$$

ii. Oxidation of water to oxygen gas.

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 2e^-, E^\circ_{oxd} = -0.4 V$$

The standard electrode potential for the oxidation of water is greater than that of Cl^- ion or water has a greater tendency to undergo oxidation. Hence, an anode half-reaction would be oxidation of water. However, experiments have shown that the gas produced at the anode is Cl_2 and not O_2. This suggests that anode reaction is oxidation of Cl^- to Cl_2 gas. This is because of overvoltage.

- **Net cell reaction:**

  The net cell reaction is the sum of two electrode reactions.

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \qquad \text{(Oxidation half reaction at anode)}$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad \text{(Reductionhalfreactionat cathode)}$$

$$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2OH^-_{(aq)} \qquad \text{(Overall cell reaction)}$$

Exercises | Q 3.04 | Page 118

Answer the following in brief.

How many moles of electrons are passed when 0.8-ampere current is passed for 1 hour through molten $CaCl_2$?

Solution:

Given:

Current (I) = 0.8 ampere,
Time (t) = 1 hour = 1× 60 × 60 s = 3600 s

To find:
No. of moles of electrons passed through molten $CaCl_2$

Formulae:

1. Quantity of electricity passed = I(A) × t(s)

2. No. of moles of electrons passed = $\dfrac{Q(C)}{96500(C/\text{mol } e^-)}$

Calculation: Using formula (i),

Quantity of electricity passed = I(A) × t(s)

= 0.8 × 3600 = 2880 C

Using formula (ii),

No. of moles of electrons passed

$$\frac{Q(C)}{96500(C/\text{mol } e^-)} = \frac{2880C}{96500(C/\text{mol } e^-)} = 0.03 \text{ mol } e^-$$

Number of moles of electrons passed through molten $CaCl_2$ is 0.03 mol e^-.

Exercises | Q 3.05 | Page 118

Answer the following in brief.

Construct a galvanic cell from the electrodes Co^{3+} | Co and Mn^{2+}| Mn.

E°_{Co} = 1.82 V, E°_{Mn} = - 1.18 V. Calculate E°_{cell}

Solution:

Given:

E°_{Co} = 1.82 V,

E°_{Mn} = - 1.18 V.

To find: E°_{cell} and cell representation

Formulae: $E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{anode}$

Calculation: Electrode reactions are

At anode: $3\left(Mn_{(s)} \rightarrow Mn^{2+}_{(aq)} + 2e^-\right)$

At cathode: $2\left(Co^{3+}_{(aq)} + 3e^- \rightarrow Co_{(s)}\right)$

The cell is composed of Mn (anode), $Mn_{(s)} \left| Mn^{2+}_{(aq)} \right.$ and $Co(cathode), Co^{3+}_{(aq)} \left| Co_{(s)} \right.$

The cell is represented as:

$Mn_{(s)} \left| Mn^{2+}_{(aq)} \right| \left| Co^{3+}_{(aq)} \right| Co_{(s)}$

The standard electrode potential is given by

$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{anode}$

= 1.82 V - (- 1.18 V)

= 3.00 V

The standard cell potential is 3.00 V.

Exercises | Q 3.06 | Page 118

Answer the following in brief.

Using the relationship ΔG° of cell reaction and the standard potential associated with it, how will you show that the electrical potential is an intensive property?

Solution:

Under standard state conditions, electrical work done in a galvanic cell is given by

$\Delta G° = - nF\ E^{\circ}_{cell}$

ΔG° is an extensive property since its value depends on the amount of substance. If the stoichiometric equation of redox reaction is multiplied by 2, that is, the number of substances oxidized and reduced are doubled, ΔG° doubles. The moles of electrons transferred also doubles.

The ratio,

$E^{\circ}_{cell} = -\frac{\triangle G^{\circ}}{nF}$ then becomes,

$$E^{\circ}_{cell} = -\frac{2 \triangle G^{\circ}}{2nF} = \frac{\triangle G^{\circ}}{nF}$$

Thus, E°_{cell} remains the same by multiplying the redox reaction by 2.

It means E°_{cell} is independent of the amount of substance and is an intensive property.

Exercises | Q 3.07 | Page 118

Answer the following in brief.

Derive the relationship between standard cell potential and equilibrium constant of cell reaction.

Solution:

The relation between standard Gibbs energy change of cell reaction and standard cell potential is given by

$- \Delta G° = - nF\ E^{\circ}_{cell}$ .....(1)

The relation between standard Gibbs energy change of a chemical reaction and its equilibrium constant as given in thermodynamics is:

$\Delta G° = - RT \ln K$ .....(2)

Combining equations (1) and (2), we have

$$- nF\ E^{o}_{cell} = - RT \ln K$$

$$\therefore E^{o}_{cell} = \frac{RT}{nF} \ln K$$

$$= \frac{2.303RT}{nF} \log_{10} K$$

$$= \frac{0.0592}{n} \log_{10} K \text{ at } 25\ °C$$

Exercises | Q 3.08 | Page 118

Answer the following in brief.

It is impossible to measure the potential of a single electrode. Comment.

Solution:

1. Every oxidation reaction needs to be accompanied by a reduction reaction.
2. The occurrence of only oxidation or only reduction is not possible.
3. In galvanic cell oxidation and reduction occur simultaneously.
4. The potential associated with the redox can be experimentally measured. For the measurement of potential two electrodes need to be combined together where the redox reaction occurs.

Hence, it is impossible to measure the potential of a single electrode.

Exercises | Q 3.09 | Page 118

Answer the following in brief.

Why do the cell potential of lead accumulators decrease when it generates electricity?

How the cell potential can be increased?

Solution:

1. The cell potential depends on sulphuric acid concentration (density). As the cell operates to generate current, H_2SO_4 is consumed. Its concentration (density) decreases and the cell potential is decreased.
2. During the recharging process by applying external potential slightly greater than 2 V, H_2SO_4 is regenerated. As a result, its concentration (density) increases and in turn, the cell potential increases.

Exercises | Q 3.1 | Page 118

Answer the following in brief.

Write the electrode reactions and net cell reaction in NICAD battery.

Solution:

The electrode reactions taking place are:

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \quad \text{(oxidation at anode)}$$

$$NiO_{2(s)} + 2H_2O_l + 2e^- \rightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)} \quad \text{(reduction at cathode)}$$

____

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_l \rightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)} \quad \text{(overall cell reaction)}$$

Exercises | Q 4.01 | Page 118

Answer the following:

What is Kohlrausch law of independent migration of ions? How is it useful in obtaining molar conductivity at zero concentration of a weak electrolyte? Explain with an example.

Solution:

1) Kohlrausch law states that "at infinite dilution each ion migrates independent of co-ion and contributes to total molar conductivity of an electrolyte irrespective of the nature of other ions to which it is associated."

2) Both cation and anion contribute to molar conductivity of the electrolyte at zero concentration and thus $\wedge 0$ is the sum of molar conductivity of cation and that of the anion at zero concentration.

Thus, $\Lambda_0 = n_+\lambda^0_+ + n\_\lambda^0_-$

where λ_+ and $\lambda\_$ are molar conductivities of cation and anion, respectively, n_+ and n_- are the number of moles of cation and anion specified in the chemical formula of the electrolyte.

3) Determination of molar conductivity of weak electrolyte at zero concentration:
The theory is particularly useful in calculating $\wedge 0$ values of weak electrolytes from those of strong electrolytes.

For example, $\wedge_0$ of acetic acid can be calculated by knowing those of HCl, NaCl and CH_3COONa as described below:

Λ_0 (HCl) + Λ_0 (CH_3COONa) - Λ_0 (NaCl)

$$= \lambda^0_{H^+} + \lambda^0_{Cl^-} + \lambda^0_{CH_3COO^-} + \lambda^0_{Na^+} - \lambda^0_{Na^+} - \lambda^0_{Cl^-}$$

$$= \lambda^0_{H^+} + \lambda^0_{CH_3COO\_} = \Lambda_0\ (CH_3COONa)$$

Thus, Λ_0 (CH_3COONa) = Λ_0 (HCl) + Λ_0 (CH_3COONa) - Λ_0 (NaCl).

Because Λ_0 values of strong electrolytes, HCl, CH_3COONa and NaCl, can be determined by extrapolation method, the Λ_0 of acetic acid can be obtained.

Exercises | Q 4.02 | Page 118

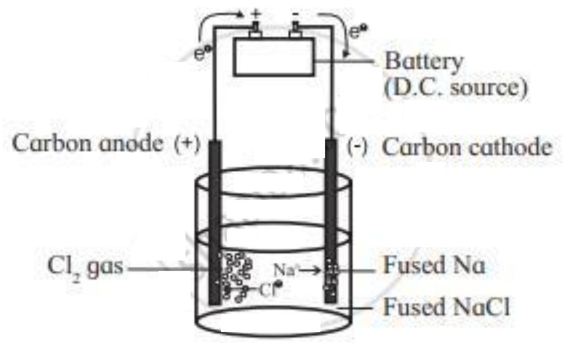
Answer the following:

Explain electrolysis of molten NaCl.

Solution:

1) Construction of cell:

The electrolytic cell consists of a container in which fused NaCl is placed. Two graphite electrodes are immersed in it. They are connected by metallic wires to a source of direct current that is the battery. The carbon electrode connected to the terminal electrode of the battery is an anode and that connected to the negative terminal of the battery is the cathode.



2) Reactions occurring in the cell:

Fused NaCl contains Na^+ and Cl^- ions which are freely mobile. When potential is applied, the cathode attracts Na+ ions and anode attracts Cl^- ions. As these are charged particles, their migration results in an electric current. When these ions reach the respective electrodes, they are discharged according to the following reactions.

i) Oxidation half-reaction at anode:

Cl^- ions migrate to anode. Each Cl^- ion, that reaches anode, gives one electron to anode. It oxidizes to neutral Cl atom in the primary process. Two Cl atoms then combine to form chlorine gas in the secondary process.

$$2Cl^-_{(l)} \rightarrow Cl_{(g)} + Cl_{(g)} + 2e^- \quad \text{(primary process)}$$

$$Cl_{(g)} + Cl_{(g)} \rightarrow Cl_{2(g)} \quad \text{(secondary process)}$$

$$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^- \quad \text{(overall oxidation)}$$

The battery sucks electrons so produced at the anode and pushes them to cathode through a wire in an external circuit. Thus, the battery serves as an electron pump. The electrons from the battery enter into solution through cathode and leave the solution through anode.

ii) Reduction half reaction at cathode:

The electrons supplied by the battery are used in cathodic reduction. Each Na^+ ion, that reaches cathode accepts an electron from the cathode and reduces to metallic sodium.

$$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$$

iii) Net cell reaction:

The net cell reaction is the sum of two electrode reactions.

$$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^- \quad \text{(Oxidation half reaction)}$$

$$2Na^+_{(l)} + 2e^- \rightarrow 2Na_{(l)} \quad \text{(Reduction half reaction)}$$

$$2Na^+_{(l)} + 2Cl^-_{(l)} \rightarrow 2Na_{(l)} + Cl_{2(g)} \quad \text{(Overall cell reaction)}$$

3) Results of electrolysis of molten NaCl:

i) A pale green Cl_2 gas is released at anode.

ii) Molten silvery-white sodium is formed at the cathode.

iii) The decomposition of NaCl into metallic sodium and $Cl_{2(g)}$ is nonspontaneous. The electrical energy supplied by the battery forces the reaction to occur.

Exercises | Q 4.03 | Page 118

Answer the following:

What current strength in amperes will be required to produce 2.4 g of Cu from $CuSO_4$ solution in 1 hour? Molar mass of Cu = 63.5 g mol^{-1}.

Solution:

Given:

Mass of Cu = 2.4 g,
Molar mass of Cu = 63.5 g mol^{-1}
1 hours = 1 × 60 × 60 s = 3600 s

To find: Current strength (in amperes)

Formulae:

1) Mole ratio = $\dfrac{\text{Moles of product formed in half reaction}}{\text{Moles of electrons required in half reaction}}$

2) W = $\dfrac{\text{I(A)} \times \text{t(s)}}{96500(\text{C}/\text{mol e}^{-})} \times \text{mole ratio} \times \text{molar mass}$

Calculation:

1) Stoichiometry for the formation of Cu is

$\text{Cu}_{\text{s}}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}_{(\text{s})}$

Using formula (i),

Mole ratio = $\dfrac{1\text{ mole}}{2\text{ mole}}$

2) Using formula (ii),

W = $\dfrac{\text{I(A)} \times \text{t(s)}}{96500(\text{C}/\text{mol e}^{-})} \times \text{mole ratio} \times \text{molar mass}$

$2.4\text{g} = \dfrac{\text{I(A)} \times \text{t(s)}}{96500(\text{C}/\text{mol e}^{-})} \times \dfrac{1\text{ mole}}{2\text{ mole e}^{-1}} \times 63.5\text{g mol}^{-1}$

I(A) = $\dfrac{2.4 \times 96500 \times 2}{63.5 \times 3600}$ = 2.03 A

Current strength in amperes required to produce 2.4 g of Cu from $CuSO_4$ is 2.03 A.

Exercises | Q 4.04 | Page 118

Answer the following:

Equilibrium constant of the reaction,

$2\text{Cu}^{+}_{(\text{aq})} \rightarrow \text{Cu}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})}$ is 1.2×10^{6}.

What is the standard potential of the cell in which the reaction takes place?

Solution:

Given: Equilibrium constant of the reaction (K) = 1.2×10^6.

To find: Standard potential of cell (E°_{cell})

Formulae: $(E^\circ_{cell}) = \frac{0.0592V}{n} \log_{10} K$

Calculation:

For the given reaction, n = 1.

Using formula,

$$(E^\circ_{cell}) = \frac{0.0592}{1} \times \log_{10}(1.2 \times 10^6)$$

$$(E^\circ_{cell}) = 0.0592 \times (6.079) = 0.36 \text{ V}$$

The standard cell potential of cell is 0.36 V.

Exercises | Q 4.05 | Page 119

Answer the following:

Calculate emf of the cell:

$Zn_{(s)} | Zn^{2+} (0.2 \text{ M}) || H^+ (1.6 \text{ M}) | H_2(g, 1.8 \text{ atm}) | Pt$ at 25 °C.

Solution:

Given: $[Zn^{2+}]$ = 0.2 M, $[H^+]$ = 1.6 M, P_{H_2} = 1.8 atm

To find: Emf of the cell (E_{cell})

Formulae:

1) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

2) $E_{cell} = E^{\circ}_{cell} - \frac{0.0592V}{n} \log_{10} \frac{[Product]}{[Reactant]}$

Calculation:

$Zn_{(s)} \rightarrow Zn^{2+}_{(0.2M)} + 2e^{-}$ (oxidation at anode)

$2H^{+}_{(1.6\ M)} + 2e^{-} \rightarrow H_{2(1.8\ atm)}$ (reduction at cathode)

____

$Zn_{(s)} + 2H^{+}_{(1.6\ M)} \rightarrow Zn^{2+}_{(0.2M)} + H_{2(1.8\ atm)}$ (overall reaction)

$E^{\circ}_{H_2} = 0.0V$ and E°_{Zn} = - 0.763 V

Using formula (i),

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$E_{cell} = E^{\circ}_{H_2} - E^{\circ}_{Zn}$

= 0.0 V - (- 0.763 V) = 0.769 V

Using formula (ii),

The cell potential is given by

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592V}{2} \log_{10} \frac{[Product]}{[Reactant]}$$

$$= 0.763 - \frac{0.0592V}{2} \log_{10} \frac{(0.2)(1.8)}{(1.6)^2}$$

= 0.763 + 0.0252 = 0.7882 V

The emf of the cell is 0.7882 V.

Exercises | Q 4.06 | Page 119

Answer the following:

Calculate emf of the cell at 25 °C.

$Zn_{(s)}$ |Zn^{2+} (0.08 M)| |Cr^{3+} (0.1 M)| |Cr^{3+} (0.1 M)| $Cr_{(s)}$

E°_{Zn} = - 0.76 V, E°_{Cr} = - 0.74 V

Solution:

Given: E°_{Zn} = - 0.76 V, E°_{Cr} = - 0.74 V

To find: Emf of the cell (E_{cell})

Formulae:

1) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

2) $E_{cell} = E^\circ_{cell} - \frac{0.0592V}{n} \log_{10} \frac{[Product]}{[Reactant]}$

Calculation:

$\left[Zn_{(s)} \rightarrow Zn^{2+}_{(0.08M)} + 2e^-\right] \times 3$ (oxidation at anode)

$\left[Cr^{3+}_{(0.1\ M)} + 3e^- \rightarrow Cr_{(s)}\right] \times 2$ (reduction at cathode)

$3Zn_{(s)} + 2Cr^{3+}_{(0.1\ M)} \rightarrow 3Zn^{2+}_{(0.08M)} + Cr_{(s)}$ (overall reaction)

Using formula (i),

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E_{cell} = E^\circ_{Cr} - E^\circ_{Zn}$

= - 0.74 V - (- 0.76 V) = 0.02 V

Using formula (ii),

The cell potential is given by

$E_{cell} = E^\circ_{cell} - \frac{0.0592V}{n} \log_{10} \frac{[Product]}{[Reactant]}$

= 0.02 - $\frac{0.0592V}{6} \log_{10} \frac{(0.08)^3}{(0.1)^2}$

= 0.02 + 0.0127 = 0.0327 V

The emf of the cell is 0.0327 V.

Exercises | Q 4.07 | Page 119

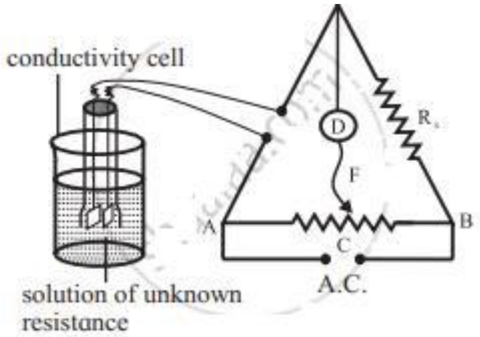
What is a cell constant? What are its units? How is it determined experimentally?

Solution:

For a given cell, the ratio of separation (l) between the two electrodes divided by the area of cross-section (a) of the electrode is called the cell constant.

Cell constant = l/a

The unit of cell constant is m^{-1} (SI unit) or cm^{-1} (C.G.S unit).



1) The cell constant is determined using the 1 M, 0.1 M or 0.01 M KCl solutions. The conductivity of KCl solution is well tabulated at various temperatures.

2) The resistance of KCl solution is measured by Wheatstone bridge as shown in the figure.

3) AB is the uniform wire. R_x is the variable known resistance placed in one arm of Wheatstone bridge. The conductivity cell containing KCl solution of unknown resistance is placed in the other arm of Wheatstone bridge.

4) D is a current detector. F is the sliding contact that moves along AB. A.C. represents the source of alternating current.

5) The sliding contact is moved along AB until no current flows. The detector D shows no deflection. The null point is, thus, obtained at C.

6) According to Wheatstone bridge principle,

$$\frac{R_{(solution)}}{l(AC)} = \frac{R_x}{l(BC)}$$

Hence, $R_{(solution)} = \frac{l(AC)}{l(BC)} \times R_x$

7) By measuring lengths AC and BC and knowing R_x , resistance of KCl solution can be calculated.

8) The cell constant is given by

Cell constant = $k_{KCl} \times R_{(solution)}$

The conductivity of KCl solution is known. The cell constant, thus, can be calculated.

Exercises | Q 4.08 | Page 119

Answer the following:

How will you calculate the moles of electrons passed and mass of the substance produced during electrolysis of a salt solution using reaction stoichiometry?

Solution:

1) Calculation of moles of electrons passed:

Total charge passed is Q(C). The charge of one-mole electrons is 96500 coulombs (C). It is referred to as one faraday (I F). Hence,

$$\text{Moles of electrons actually passed} = \frac{\mathrm{Q(C)}}{96500\left(\mathrm{C/mol\ e^-}\right)}$$

2) Calculation of moles of product formed:

The balanced equation for the half-reaction occurring at the electrode is devised. The stoichiometry of half reaction indicates the moles of electrons passed and the moles of the product formed. From this, we will find the mole ratio, which is given by:

$$\text{Mole ratio} = \frac{\text{Moles of product formed in half-reaction}}{\text{Moles of electrons required in half-reaction}}$$

Moles of product formed = Moles of electrons actually passed × mole ratio

$$= \frac{\mathrm{Q(C)}}{96500\left(\mathrm{C/mol\ e^-}\right)} \times \text{mole ratio}$$

$$= \frac{\mathrm{I(A)} \times \mathrm{t(s)}}{96500\left(\mathrm{C/mol\ e^-}\right)} \times \text{mole ratio}$$

3) Mass of substance produced:

Mass of product (W) can be calculated as given below:

W = moles of product × molar mass of product

$$= \frac{\mathrm{I(A)} \times \mathrm{t(s)}}{96500\left(\mathrm{C/mol\ e^-}\right)} \times \text{mole ratio} \times \text{molar mass of the product}$$

Exercises | Q 4.09 | Page 119

Answer the following:

Write the electrode reactions when lead storage cell generates electricity. What are the anode and cathode and write the electrode reactions during its recharging?

Solution:

1) Cell reactions when lead storage cell generates electricity (discharging):

a) Oxidation at anode (–):

When the cell provides current, spongy lead is oxidised to Pb^{2+} ions and negative charge accumulates on lead plates. The Pb^{2+} ions so formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble $PbSO_4$. The net oxidation is the sum of these two processes.

$Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2e^-$ (oxidation)

$Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)}$ (precipitation)

$Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$ .....(1) (overall oxidation)

b) Reduction at cathode (+):

The electrons produced at the anode travel through external circuit and re-enter the cell at the cathode. At cathode, PbO_2 is reduced to Pb^{2+} ions in presence of H^+ ions. Pb^{2+} ions formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble $PbSO_4$ that gets coated on the electrode.

$PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$ (reduction)

$Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)}$ (precipitation)

$$PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \quad .....(2)$$

(overall reduction)

2) During recharging, the anode and cathode are interchanged with PbO2 electrode being anode (+) and lead electrode cathode (–).

3) Cell reactions during recharging:

The potential of the lead accumulator is 2 V. It is recharged when cell potential drops to 1.8 V. To recharge the cell external potential slightly greater than 2 V it is applied across the electrodes. During recharging, the cell functions as an electrolytic cell, and electrolytes are regenerated. The anode and cathode are interchanged with PbO_2 electrode being anode (+) and lead electrode cathode (–).

a) Oxidation at anode (+):

It is reverse of reduction reaction (ii) at cathode that occurs during discharge.

$$PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \quad .....(3)$$

b) Reduction at cathode (–):

It is reverse of oxidation reaction (i) at anode that occurs during discharge.

$$PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO^{2-}_{4(aq)} \quad ...(4)$$

Exercises | Q 4.1 | Page 119

Answer the following:

What are anode and cathode of H_2 - O_2 fuel cell? Name the electrolyte used in it. Write electrode reactions and net cell reaction taking place in the fuel cell.

Solution:

1) The anode and cathode are porous carbon rods containing small amount of finely divided platinum metal that acts as a catalyst.

2) The electrolyte used is hot aqueous solution of KOH.

3) Working (Cell reactions):

i) Oxidation at anode (–):

At anode hydrogen gas is oxidized to H_2O

$$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^- \quad .....(1)$$

ii) Reduction at cathode (+):

The electrons released at anode travel, through external circuit to cathode.

Here O_2 is reduced to OH^-.

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \quad .....(2)$$

iii) Net cell reaction:

The overall cell reaction is the sum of electrode reactions (1) and (2).

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

The overall cell reaction is combustion of H_2 to form liquid water. However, the fuel H_2 gas and the oxidant O_2 do not react directly. The chemical energy released during the formation of O-H bond is directly converted into electrical energy accompanying in above combustion reaction. The cell continues to operate as long as H_2 and O_2 gases are supplied to electrodes.

Exercises | Q 4.11 | Page 119

Answer the following:

What are anode and cathode for Leclanche' dry cell? Write electrode reactions and overall cell reaction when it generates electricity.

Solution:

1) The container of the cell is made of zinc which serves as anode (–) and an inert graphite rod in the centre of the cell immersed in the electrolyte paste (manganese dioxide (MnO_2) and carbon black) serves as cathode (+).

2) Electrode reactions are as follows:

i) Oxidation at anode:

$$Zn_s \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

ii) Reduction at cathode:

$$2NH^+_{4(aq)} + 2MnO_{2(s)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$$

iii) Overall cell reaction:

$$Zn_s + 2NH^+_{4(aq)} + 2MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$$

Exercises | Q 4.12 | Page 119

Answer the following:

Identify oxidising agents and arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.

Al (–1.66V), Al^{3+}(–1.66V), Cl_2 (1.36V), Cd^{2+} (–0.4V), Fe (–0.44V), I_2 (0.54V), Br^- (1.09V).

Solution:

1. The species on the left-hand side of the half-reactions are oxidising agents. Thus, oxidising agents are $Al^{3+}, Cl_2, Cd^{2+},\ \text{and}\ I_2$.
2. Larger the E° value greater is the strength of oxidising agent. Increasing strength of oxidising agents is as follows:

$$Al^{3+}_{(-1.66V)} < Cd^{2+}_{(-0.4V)} < I_{2(0.54V)} < Cl_{2(1.36V)}$$

Exercises | Q 4.13 | Page 119

Answer the following:

Which of the following species are reducing agents? Arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.

K (–2.93V), Br_2(1.09V), Mg(–2.36V), Ce^{3+}(1.61V), Ti^{2+}(–0.37V), Ag^+ (0.8 V), Ni (–0.23V).

Solution:

1. The species on the right-hand side of the half-reactions are reducing agents. Thus, reducing agents are K, Mg, Ti^{2+}, Ni
2. The strength of reducing agents increases as E° values decrease. Increasing strength of reducing agents is as follows:

$$\mathrm{Ni}_{(-0.23\mathrm{V})} < \mathrm{Ti}^{2+}_{(-0.37\mathrm{V})} < \mathrm{Mg}_{(-2.36\mathrm{V})} < \mathrm{K}_{(-2.93\mathrm{V})}$$

Exercises | Q 4.14 | Page 119

Answer the following:

Predict whether the following reaction would occur spontaneously under standard state condition.

$$\mathrm{Ca}_{(s)} + \mathrm{Cd}^{2+}_{(aq)} \rightarrow \mathrm{Ca}^{2+}_{(aq)} + \mathrm{Cd}_{(s)}$$

Solution:

$$\mathrm{Ca}_{(s)} + \mathrm{Cd}^{2+}_{(aq)} \rightarrow \mathrm{Ca}^{2+}_{(aq)} + \mathrm{Cd}_{(s)}$$

At anode: $\mathrm{Ca}_{(s)} \rightarrow \mathrm{Ca}^{2+}_{(aq)} + 2e^-$

At cathode: $\mathrm{Ca}^{2+}_{(aq)} + 2e^- \rightarrow \mathrm{Cd}_{(s)}$

From the electrochemical series we have,

E°_{Ca} = - 2.866 V and E°_{Cd} = - 0.403 V

For cell having Ca as anode and Cd as cathode.

$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{Cd}} - E^\circ_{\mathrm{Ca}}$

= - 0.403 V - (- 2.866) V

E°_{cell} = 2.463 V

Emf of cell being positive, the given cell reaction is spontaneous.

Exercises | Q 4.14 | Page 119

Answer the following:

Predict whether the following reaction would occur spontaneously under standard state condition.

$$\mathrm{Ca}_{(s)} + \mathrm{Cd}^{2+}_{(aq)} \rightarrow \mathrm{Ca}^{2+}_{(aq)} + \mathrm{Cd}_{(s)}$$

Solution:

$$Ca_{(s)} + Cd^{2+}_{(aq)} \to Ca^{2+}_{(aq)} + Cd_{(s)}$$

At anode: $Ca_{(s)} \to Ca^{2+}_{(aq)} + 2e^-$

At cathode: $Ca^{2+}_{(aq)} + 2e^- \to Cd_{(s)}$

From the electrochemical series we have,

E°_{Ca} = - 2.866 V and E°_{Cd} = - 0.403 V

For cell having Ca as anode and Cd as cathode.

$$E^\circ_{cell} = E^\circ_{Cd} - E^\circ_{Ca}$$

= - 0.403 V - (- 2.866) V

E°_{cell} = 2.463 V

Emf of cell being positive, the given cell reaction is spontaneous.

Exercises | Q 4.14 | Page 119

Answer the following:

Predict whether the following reaction would occur spontaneously under standard state condition.

$$2Br^-_{(aq)} + Sn^{2+}_{(aq)} \to Br_{2(l)} + Sn_{(s)}$$

Solution:

$$2Br^-_{(aq)} + Sn^{2+}_{(aq)} \to Br_{2(l)} + Sn_{(s)}$$

At anode: $2Br^-_{(aq)} \to Br_{2(l)} + 2e^-$

At cathode: $Sn^{2+}_{(aq)} + 2e^- \to Sn_{(s)}$

From the electrochemical series we have,

$E^\circ_{Br_2}$ = 1.080 V and E°_{Sn} = - 0.136 V

For cell having $Br_{2(l)}$ as anode and Sn as cathode.

$$E^\circ_{cell} = E^\circ_{Sn} - E^\circ_{Br_2}$$

= - 0.136 V - 1.080 V

E°_{cell} = - 1.216 V

Emf of cell being positive, the given cell reaction is nonspontaneous.

Exercises | Q 4.14 | Page 119

Answer the following:

Predict whether the following reaction would occur spontaneously under standard state condition.

$$2\,Ag_{(s)} + Ni^{2+}_{(aq)} \longrightarrow 2\,Ag^{+}_{(aq)} + Ni_{(s)}$$

Solution:

$$2\,Ag_{(s)} + Ni^{2+}_{(aq)} \longrightarrow 2\,Ag^{+}_{(aq)} + Ni_{(s)}$$

At anode: $2\,Ag_{(s)} \longrightarrow 2\,Ag^{+}_{(aq)} + 2\,e^{-}$

At cathode: $Ni^{2+}_{(aq)} + 2\,e^{-} \longrightarrow Ni_{(s)}$

From the electrochemical series we have,

E°_{Ag} = 0.799 V and E°_{Ni} = - 0.257 V

For cell having Ag as anode and Ni as cathode.

$E^{\circ}_{cell} = E^{\circ}_{Ni} - E^{\circ}_{Ag}$

= - 0.257 V - 0.799 V

E°_{cell} = - 1.056 V

Emf of cell being negative, the given cell reaction is nonspontaneous.