Electrochemistry

Case Study Based Questions

Case Study 1

Molar conductivity of a solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Am. The molar conductivity is related to conductivity as:

$$\Lambda_m = \kappa \times V = \frac{1000}{C} \times \kappa. = \kappa \times \frac{1000}{\text{Molarity}}$$

Unity of A$_m$ (molar conductivity) shall be ohm-^{1} cm-^{1}mol-^{1} or Scm^2 mol-1. Thus, knowing molar concentration (C) and conductivity (K), A$_m$ can be calculated. A$_m$ is called molar conductivity at infinite dilution. The molar conductivity of strong electrolytes is found to vary with concentration according to the equation,

Q1. If conductivity of 0.00241 M acetic acid is 7.896 x 10-5 cm-1, the molar conductivity of the solution shall be (in S cm^1 mol-1)

a. 3.276

b. 0.3276

c. 32.76

d. 327.6

Q2. Molar conductivity of a solution is 1.26 x 102 1 cm2 Ω-1. Its molarity is 0.01. Its specific conductivity will be:

a. 1.26 x 10-5

c. 1.26 x 10-4

b. 1.26 x 10-3

d. 12.6 x 10-3

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Q3. The increase in molar conductivity of HCL with dilution is due to:

a. increase in self-ionisation of water

b. hydrolysis of HCL

c. decrease in self-ionisation of water

d. decrease in interionic forces

Q4. Which of the following is wrong about molar conductivity?

a. The solution contains Avogadro number of molecules of the electrolyte.

b. It is the product of specific conductivity and volume of solution in cc containing 1 mole of electrolyte.

c. Its units are ohm-^{1} cm^2 mol-1.

d. Its value for 1 M NaCl is same as that of 1 M glucose solution.

Answers

1. (c) 32.76
2. (b) 1.26 x 10-3
3. (d) decrease in interionic forces
4. (d) Its value for 1 M NaCl is same as that of 1 M glucose solution

Case Study 2

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If Ecell is positive, the reaction is spontaneous and if it is negative, the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu2+. This was first formulated by Faraday in the form of laws of electrolysis. The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by K and it depends upon nature and concentration of electrolyte,

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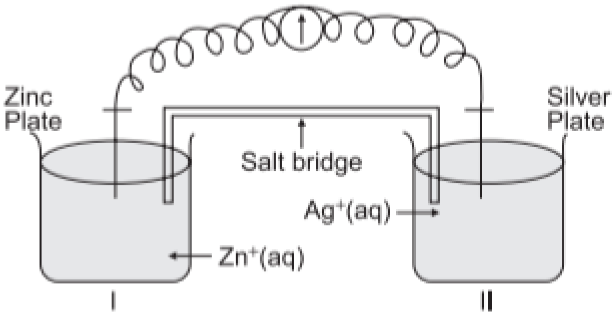
temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



Read the given passage carefully and give the answer of the following questions: (CBSE 2022 Term-2)

Q1. Is silver plate the anode or cathode? What will happen if the salt bridge is removed?

Q2. When does electrochemical cell behaves like an electrolytic cell?

Q3. (i) What will happen to the concentration of Zn2+, and Ag+ when Ecell = 0?
(ii) Why does conductivity of a solution decreases with dilution?

OR

The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol-1. Calculate the conductivity of this solution.

Answers

1. Silver plate is the cathode. No current will flow and the voltage will drop to zero if the salt bridge is removed.

2. An electrochemical cell behaves like an electrolytic cell when Eext> Ecell'

3. (i) When Ecell = 0 (equilibrium is reached), concentration of Zn2+ and Ag+ ions will not change.
(ii) The number of ions per unit volume that carry the current in a solution decreases on dilution. Hence, conductivity decreases.

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OR

$$\text{We know that, } \Lambda_m = \frac{1000 \times \text{Conductivity}}{\text{Molarity}}$$

$$\Rightarrow \quad \text{Conductivity} = \frac{\Lambda_m \times \text{Molarity}}{1000}$$

$$= \frac{138.9 \times 1.5}{1000} = 0.208 \ \text{S cm}^{-1}.$$

Case Study 3

The lead-acid battery represents the oldest rechargeable battery technology. Lead acid batteries can be found in a wide variety of applications including small-scale power storage such as UPS systems, ignition power sources for automobiles, along with large, grid-scale power systems. The spongy lead act as the anode and lead dioxide as the cathode. Aqueous sulphuric acid is used as an electrolyte. The half-reactions during discharging of lead storage cells are:

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$
$\longrightarrow PbSO_4(s) + 2H_2O$

There is no safe way of disposal and these batteries end-up in landfills. Lead and sulphuric acid are extremely hazardous and pollute soil, water as well as air. Irrespective of the environmental challenges it poses, lead-acid batteries have remained an important source of energy. Designing green and sustainable battery systems as alternatives to conventional means remains relevant. Fuel cells are seen as the future source of energy. Hydrogen is considered a green fuel. Problem with fuel cells at present is the storage of hydrogen. Currently, ammonia and methanol are being used as a source of hydrogen for fuel cell. These are obtained industrially, so add to the environmental issues. If the problem of storage of hydrogen is overcome, is it still a 'green fuel'? Despite being the most abundant element in the Universe, hydrogen does not exist on its own so needs to be extracted from the water using electrolysis or separated from carbon fossil fuels. Both of these processes require a significant amount of energy which is currently more than that gained from the hydrogen itself. In addition, this extraction typically requires the use of fossil fuels. More research is being conducted in this field to solve these problems. Despite the problem of no good means to extract Hydrogen, it is a

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uniquely abundant and renewable source of energy, perfect for our future zero-carbon needs. Read the given passage carefully and give the answer of the following questions: (CBSE SQP 2023-24)

Q1. How many coulombs have been transferred from anode to cathode in order to consume one mole of sulphuric acid during the discharging of lead storage cell?

Q2. How much work can be extracted by using lead storage cell if each cell delivers about 2.0 V of voltage? (1 F = 96500 C).

Q3. Do you agree with the statement "Hydrogen is a green fuel." Give your comments for and against this statement and justify your views.

OR

Imagine you are a member of an agency funding scientific research. Which of the following projects will you fund and why?
(i) Safe recycling of lead batteries
(ii) Extraction of hydrogen

Answers

1. 2 mole e (or 2F) have been transferred from anode to cathode to consume 2 mol of H_250, therefore, one mole H_2SO, requires one Faraday of electricity or 96500 coulombs.

2. We have Wmax=-nFE° = -2x 96500 × 2.0 = 386000J of work can be extracted using lead storage cell when the cell is in use.

3. Yes, Hydrogen is a fuel that on combustion gives water as a by product. There are no carbon emissions and no pollutions caused. However, at present the means to obtain hydrogen are electrolysis of water which use electricity obtained from fossil fuels and increase carbon emissions. In spite of the problems faced today in the extraction of hydrogen, we cannot disagree on the fact that hydrogen is a clean source of energy. Further research can help in finding solutions and green ways like using solar energy for extraction of hydrogen. No. It is true that hydrogen is fuel that on combustion gives water as a by product. There are no carbon emissions and no pollutions caused. However, at present the means to obtain hydrogen are electrolysis of water which use electricity obtained from fossil fuels and increase carbon emissions. Hydrogen is no

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doubt a green fuel, but the process of extraction is not green as of today. At present, looking at the process of extraction, hydrogen is not a green fuel.

OR

Both answers will be treated as correct.
(i) Lead batteries are currently the most important and widely used batteries. These are rechargeable. The problem is waste management which needs research and awareness. Currently, these are being thrown into landfills and there is no safe method of disposal or recycling. Research into safer method of disposal will reduce the pollution and health hazards caused to a great extent.
(ii) Fuel cell is a clean source of energy. Hydrogen undergoes combustion to produce water. The need of the hour is green fuel and hydrogen is a clean fuel. The current problem is obtaining hydrogen. Research that goes into this area will help solve the problem of pollution and will be a sustainable solution.

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Solutions for Questions 4 to 12 are Given Below

Case Study 4

Read the passage given below and answer the following questions :
Molar conductivity of ions are given as product of charge on ions to their ionic mobilities and Faraday's constant.

$\lambda_{A^{n+}} = n\mu_{A^{n+}} F$ (here μ is the ionic mobility of A^{n+}).

For electrolytes say A_xB_y, molar conductivity is given by

$\lambda_{m(A_xB_y)} = x_n \mu_{A^{n+}} F + y_m \lambda_{A^{m-}} F$

Ions	**Ionic mobility**
K^+	7.616×10^{-4}
Ca^{2+}	12.33×10^{-4}
Br^-	8.09×10^{-4}
SO_4^{2-}	16.58×10^{-4}

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) At infinite dilution, the equivalent conductance of $CaSO_4$ is
(a) 256×10^{-4} (b) 279 (c) 23.7 (d) 2.0×10^{-8}

(ii) If the degree of dissociation of $CaSO_4$ solution is 10% then equivalent conductance of $CaSO_4$ is
(a) 3.59 (b) 36.9 (c) 27.9 (d) 30.6

OR

The correct order of equivalent conductance at infinite dilution of LiCl, NaCl, KCl is
(a) LiCl = NaCl = KCl (b) LiCl > NaCl > KCl
(c) KCl > LiCl > NaCl (d) KCl > NaCl > LiCl

(iii) What is the unit of equivalent conductivity?
(a) $ohm^{-1}\ cm^2\ eq^{-1}$ (b) $ohm\ cm^2\ eq^{-1}$
(c) $ohm^{-1}\ cm\ eq^{-1}$ (d) $ohm\ cm^{-2}\ eq^{-1}$

(iv) If the molar conductance value of Ca^{2+} and Cl^- at infinite dilution are $118.88 \times 10^{-4}\ m^2\ mho\ mol^{-1}$ and $77.33 \times 10^{-4}\ m^2\ mho\ mol^{-1}$ respectively then the molar conductance of $CaCl_2$ (in $m^2\ mho\ mol^{-1}$) will be
(a) 120.18×10^{-4} (b) 135×10^{-4}
(c) 273.54×10^{-4} (d) 192.1×10^{-4}

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Case Study 5

Read the passage given below and answer the following questions :

Standard electrode potentials are used for various processes :

- It is used to measure relative strengths of various oxidants and reductants.
- It is used to calculate standard cell potential.
- It is used to predict possible reactions.

A set of half-reactions (in acidic medium) along with their standard reduction potential, $E°$ (in volt) values are given below :

$I_2 + 2e^- \longrightarrow 2I^-; \quad E° = 0.54$ V

$Cl_2 + 2e^- \longrightarrow 2Cl^-; \quad E° = 1.36$ V

$Mn^{3+} + e^- \longrightarrow Mn^{2+}; \quad E° = 1.50$ V

$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \quad E° = 0.77$ V

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O; \; E° = 1.23$ V

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following statements is correct?

(a) Cl^- is oxidised by O_2.
(b) Fe^{2+} is oxidised by iodine.
(c) I^- is oxidised by chlorine.
(d) Mn^{2+} is oxidised by chlorine.

(ii) Mn^{3+} is not stable in acidic medium, while Fe^{3+} is stable because

(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2.

(iii) The strongest reducing agent in the aqueous solution is

(a) I^-
(b) Cl^-
(c) Mn^{2+}
(d) Fe^{2+}

(iv) The emf for the following reaction is

$I_2 + KCl \rightleftharpoons 2KI + Cl_2$

(a) –0.82 V
(b) +0.82 V
(c) –0.73 V
(d) +0.73 V

OR

Which of the following statements is correct for the following reaction?

$Fe^{3+} + Mn^{2+} \longrightarrow Fe^{2+} + Mn^{3+}$

(a) The emf of the cell is positive.
(b) Fe^{3+} oxidises Mn^{2+}.
(c) The reaction does not occur.
(d) All are correct.

Case Study 6

Read the passage given below and answer the following questions :

All chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules are present in a few gram of any chemical compound varying with their atomic/molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.

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The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The total number of moles of chlorine gas evolved is

(a) 0.5 (b) 1.0 (c) 1.5 (d) 1.9

(ii) If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is

(a) 300 g (b) 446 g (c) 396 g (d) 296 g

OR

The total charge (coulomb) required for complete electrolysis is

(a) 186000 (b) 24125 (c) 48296 (d) 193000

(iii) In the electrolysis, the number of moles of electrons involved are

(a) 2 (b) 1 (c) 3 (d) 4

(iv) In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?

(a) H_2 gas (b) Cl_2 gas (c) O_2 gas (d) None of these

Case Study 7

Read the passage given below and answer the following questions :

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is

$M_{(s)} \mid M^+(\text{aq.; 0.05 molar}) \parallel M^+(\text{aq; 1 molar}) \mid M_{(s)}$

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) For the above cell,

(a) $E_{\text{cell}} < 0 ; \Delta G > 0$ (b) $E_{\text{cell}} > 0 ; \Delta G < 0$ (c) $E_{\text{cell}} < 0 ; \Delta G^\circ > 0$ (d) $E_{\text{cell}} > 0 ; \Delta G^\circ < 0$

OR

If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be

(a) 130 mV (b) 185 mV (c) 154 mV (d) 600 mV

(ii) The value of equilibrium constant for a feasible cell reaction is

(a) < 1 (b) $= 1$ (c) > 1 (d) zero

(iii) What is the emf of the cell when the cell reaction attains equilibrium?

(a) 1 (b) 0 (c) > 1 (d) < 1

(iv) The potential of an electrode change with change in

(a) concentration of ions in solution (b) position of electrodes

(c) voltage of the cell (d) all of these.

Case Study 8

Read the passage given below and answer the following questions :

The electrochemical cell shown below is concentration cell.

$M|M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $\parallel M^{2+}$ (0.001 mol dm^{-3})$|M$

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

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The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The solubility product (K_{sp}, mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.059$)

(a) 2×10^{-15} (b) 4×10^{-15} (c) 3×10^{-12} (d) 1×10^{-12}

(ii) The value of ΔG (in kJ mol^{-1}) for the given cell is (take 1 F = 96500 C mol^{-1})

(a) 3.7 (b) –3.7 (c) 10.5 (d) –11.4

(iii) The equilibrium constant for the following reaction is

$Fe^{2+} + Ce^{4+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

(Given, $E^\circ_{Ce^{4+}/Ce^{3+}} = 1.44$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.68$ V)

(a) 7.6×10^{12} (b) 6.5×10^{10} (c) 5.2×10^{9} (d) 3.4×10^{12}

OR

The solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell

$Ag|Ag^+$ (satd. Ag_2CrO_4 soln) || Ag^+ (0.1 M) | Ag

is 0.164 V at 298 K, is

(a) 3.359×10^{-12} mol^3 L^{-3} (b) 2.287×10^{-12} mol^3 L^{-3}

(c) 1.158×10^{-12} mol^3 L^{-3} (d) 4.135×10^{-12} mol^3 L^{-3}

(iv) To calculate the emf of the cell, which of the following options is correct?

(a) emf = $E_{cathode} - E_{anode}$ (b) emf = $E_{anode} - E_{cathode}$

(c) emf = $E_{anode} + E_{cathode}$ (d) None of these

Case Study 9

Read the passage given below and answer the following questions :

The potential of each electrode is known as electrode potential. Standard electrode potential is the potential when concentration of each species taking part in electrode reaction is unity and the reaction is taking place at 298 K. By convention, the standard electrode potential of hydrogen (SHE) is 0.0 V. The electrode potential value for each electrode process is a measure of relative tendency of the active species in the process to remain in the oxidised/reduced form. The negative electrode potential means that the redox couple is stronger reducing agent than H^+/H_2 couple. A positive electrode potential means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. Metals which have higher positive value of standard reduction potential form the oxides of greater thermal stability.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** An electrochemical cell can be set-up only if the redox reaction is spontaneous.
Reason : A reaction is spontaneous if the free energy change is negative.

(ii) **Assertion :** The standard electrode potential of hydrogen is 0.0 V.
Reason : It is by convention.

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OR

Assertion : The more negative is the standard reduction potential, greater is its ability to displace H_2 from acid.
Reason : Strength of reducing agent increases with the increase in negative value of the standard reduction potential.

(iii) **Assertion :** The negative value of standard reduction potential means that reduction takes place on this electrode with reference to hydrogen electrode.
Reason : The standard electrode potential of a half cell has a fixed value.

(iv) **Assertion :** The absolute value of electrode potential cannot be determined experimentally.
Reason : The electrode potential values are generally determined with respect to SHE.

Case Study 10

Read the passage given below and answer the following questions :

Two types of conductors are generally used, metallic and electrolytic. Free electrons are the current carrier in metallic and in electrolytic conductors, free ions. Specific conductance or conductivity of an electrolytic solution is given by

$$\kappa = C \times \frac{l}{A}$$

where, $C = 1/R$ and $l/A = G^*$ (cell constant)

Molar conductance (Λ_m) and equivalent conductance (Λ_e) of an electrolyte solution are calculated as

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \text{or} \quad \Lambda_e = \frac{\kappa \times 1000}{N}$$

where, M = molarity of solution and N is normality of solution. Molar conductance of strong electrolyte depends on the concentration.

$$\Lambda_m = \Lambda_m^\circ - b\sqrt{C}$$

Λ°_m = molar conductance at infinite dilution, b = constant, C = conc. of solution

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** The molar conductivity of strong electrolyte decreases with increase in concentration.
Reason : At high concentration, migration of ions is slow.

OR

Assertion : The molar conductance of weak electrolyte at infinite dilution is equal to the sum of molar conductance of cations and anions.
Reason : Kohlrausch's law is applicable for strong electrolytes.

(ii) **Assertion :** Equivalent conductance of all electrolytes increases with increasing concentration.
Reason : More number of ions are available per gram equivalent at higher concentration.

(iii) **Assertion :** Specific conductance decreases with dilution whereas equivalent conductance increases.
Reason : On dilution, number of ions per millilitre decreases but total number of ions increases considerably.

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(iv) **Assertion :** The ratio of specific conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.
Reason : Specific conductivity decreases with dilution whereas observed conductance increases with dilution.

Case Study 11

Read the passage given below and answer the following questions :

Electrical work done in unit time is equal to electrical potential multiplied by total charge passed. In order to obtain maximum work from a cell, the charge has to be passed reversibly. The reversible work done by a cell is equal to decrease in its Gibb's energy. Hence, Gibb's energy of reaction is given by

$$\Delta G = -nFE_{cell}$$

Hence, E is the emf of the cell and nF is the amount of energy.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** $\Delta G^\circ = -nFE^\circ$
Reason : E° should be positive for a spontaneous reaction.

(ii) **Assertion :** An electrochemical cell can be set up only if the redox reaction is spontaneous.
Reason : A reaction is spontaneous if free energy change is negative.

OR

Assertion : For an electrochemical cell, $\Delta G < 0$ and $E_{cell} > 0$.
Reason : The given cell is non-spontaneous.

(iii) **Assertion :** Current stops flowing when $E_{cell} = 0$.
Reason : Equilibrium of the cell reaction is attained.

(iv) **Assertion :** E_{cell} should have a positive value for the cell to function.
Reason : $E_{cell} = E_{cathode} - E_{anode}$

Case Study 12

Read the passage given below and answer the following questions :

Nernst equation relates the reduction potential of an electrochemical reaction to the standard potential and activities of the chemical species undergoing oxidation and reduction.

Let us consider the reaction, $M^{n+}_{(aq)} \longrightarrow nM_{(s)}$

For this reaction, the electrode potential measured with respect to standard hydrogen electrode can be given as

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

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(i) **Assertion :** For concentration cell, $\underset{}{Zn_{(s)}}|\underset{C_1}{Zn^{2+}_{(aq)}} \,||\, \underset{C_2}{Zn^{2+}_{(aq)}}\,|\,Zn$

For spontaneous cell reaction, $C_1 < C_2$

Reason : For concentration cell, $E_{cell} = \frac{RT}{nF}\log\frac{C_2}{C_1}$

For spontaneous reaction, $E_{cell} = +ve \Rightarrow C_2 > C_1$

(ii) **Assertion :** For the cell reaction. $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ voltmeter gives zero reading at equilibrium.

Reason : At the equilibrium, there is no change in concentration of Cu^{2+} and Zn^{2+} ions.

(iii) **Assertion :** The Nernst equation gives the concentration dependence of emf of the cell.

Reason : In a cell, current flows from cathode to anode.

(iv) **Assertion :** Increase in the concentration of copper half cell in a cell, increases the emf of the cell.

Reason : $E_{cell} = E^{\circ}_{cell} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$

OR

Assertion : Electrode potential for the electrode Mn^+/Mn with concentration is given by the expression under STP conditions.

$$E = E^{\circ} + \frac{0.059}{n}\log[Mn^+]$$

Reason : STP conditions require the temperature to be 273 K.

HINTS & EXPLANATIONS

4. (i) (b): Equivalent conductance of $CaSO_4$:

$$\Lambda^{\infty}_{CaSO_4} = \lambda^{\infty}_{Ca^{2+}} + \lambda^{\infty}_{SO_4^{2-}}$$

$$\lambda^{\infty}_{Ca^{2+}} = (\mu_{Ca^{2+}})F\,;\,\lambda^{\infty}_{SO_4^{2-}} = (\mu_{SO_4^{2-}})F$$

$\mu_{Ca^{2+}}$ and $\mu_{SO_4^{2-}}$ - are ionic mobilities.

$$\Lambda^{\infty}_{CaSO_4} = F(12.33 + 16.58) \times 10^{-4}$$
$$= 96500 \times 10^{-4} \times 28.91 = 279$$

(ii) (c) : $\alpha = \frac{\Lambda_C}{\Lambda^{\infty}} \Rightarrow 0.1 = \frac{\Lambda_C}{279} \Rightarrow \Lambda_C = 27.9$

OR

(d) : The ions formed are Li^+, Na^+ and K^+, the hydration is maximum in case of Li^+ because of which its mobility is least and has least conductance. Therefore, the correct order is KCl > NaCl > LiCl.

(iii) (a)

(iv) (c) : $\Lambda^{\circ}_{m(CaCl_2)} = \lambda^{\circ}_{Ca^{2+}} + 2\lambda^{\circ}_{Cl^-}$

$$= (118.88 \times 10^{-4}) + 2(77.33 \times 10^{-4})$$
$$= 273.54 \times 10^{-4}\ m^2\ mho\ mol^{-1}$$

5. (i) (c) : The half cell having the higher reduction potential will undergo reduction process.

(ii) (d): Electrode potential of Mn^{3+} is higher than O_2.

(iii) (a) : Due to least electrode potential value.

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(iv) (a) : Half reactions :

$I_2 + 2e^- \longrightarrow 2I^-$ Reduction $E° = 0.54$ V

$2Cl^- \longrightarrow Cl_2 + 2e^-$ Oxidation $E° = -1.36$ V

e.m.f. = –0.82 V

OR

(c) : $Fe^{3+} + Mn^{2+} \longrightarrow Mn^{3+} + Fe^{2+}$

Two half reactions :

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ Reduction $E° = 0.77$ V

$Mn^{2+} \longrightarrow Mn^{3+} + e^-$ Oxidation $E° = -1.50$ V

emf = –0.73 V

Since, emf is negative, the reaction does not occur *i.e.*, Fe^{3+} does not oxidise Mn^{2+}.

6. (i) (b) : $n_{NaCl} = \frac{4\times500}{1000} = 2$ mol

∴ $n_{Cl_2} = 1$ mol

(ii) (b): n_{Na} deposited = 2 mol

∴ n_{Na-Hg} formed = 2 mol

∴ Mass of amalgam formed = 2 × 223 = 446 g

OR

(d) : $2Na^+ + \underset{(2F)}{2e^-} \rightarrow 2Na$

Total charge required = $2F = 2 \times 96500 = 193000$ C

(iii) (a)

(iv) (a)

7. (i) (b) : $\underset{(1\ M)}{M} \longrightarrow \underset{(0.05\ M)}{M^+} + e^-$

For concentration cell, $E_{cell} = -\frac{0.059}{1}\log\frac{0.05}{1}$

$$E_{cell} = -\frac{0.059}{1}\log(5\times10^{-2})$$

$$E_{cell} = -\frac{0.059}{1}[(-2)+\log 5] \quad -0.059(-2 + 0.698)$$

$$= -0.059(-1.302) = 0.0768$$

$\Delta G = -nFE_{cell}$

If E_{cell} is positive, ΔG is negative.

OR

(c) : $\frac{E_1}{E_2} = \frac{\log 0.05}{\log 0.0025}$

$\frac{E_1}{E_2} = \frac{\log 5\times10^{-2}}{\log 25\times10^{-4}}$

$E_1 = 0.0768$

$\frac{0.0168}{E_2} = \frac{-1.3}{-2.6} = \frac{1}{2}$ or $E_2 = 154$ mV

(ii) (c) : $K = \text{antilog}\left(\frac{nE°}{0.0591}\right)$

For feasible cell, $E°$ is positive, hence from the above equation, $K > 1$ for a feasible cell reaction.

(iii) (b)

(iv) (a)

8. (i) (b): $0.059 = \frac{+0.059}{2}\log\frac{0.001}{[M^{2+}]}$

$\log\frac{0.001}{[M^{2+}]} = 2$ or $[M^{2+}] = 10^{-5}$

Let solubility of salt be S mol/litre.

Thus, $\underset{S}{MX_2} \longrightarrow \underset{S}{M^{2+}} + \underset{2S}{2X^-}$

∴ $K_{sp} = 4S^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

(ii) (d): $\Delta G = -nFE = -2 \times 96500 \times 0.059$

$= -11387$ J mol^{-1} = –11.4 kJ mol^{-1}

(iii) (a): $E°_{cell} = \frac{0.059}{1}\log K_C$

$E°_{cell} = E°_{Fe^{2+}/Fe^{3+}} + E°_{Ce^{4+}/Ce^{3+}}$

$= -0.68 + 1.44 = 0.76$ V

$\log_{10} K_C = \frac{0.76}{0.059} = 12.88$

$K_C = 7.6 \times 10^{12}$

OR

(b) : $E_{cell} = \frac{0.059}{1}\log\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}$

$0.164 = \frac{0.059}{1}\log\frac{0.1}{[Ag^+]_{LHS}}$

$[Ag^+]_{LHS} = 1.66 \times 10^{-4}$ M

So, $[CrO_4^{2-}] = \frac{1.66\times10^{-4}}{2}$

$K_{sp}(Ag_2CrO_4) = [Ag^+]^2[CrO_4^{2-}]$

$= (1.66\times10^{-4})^2\left(\frac{1.66\times10^{-4}}{2}\right)$

$= 2.287 \times 10^{-12}$ mol^3 L^{-3}

(iv) (a)

9. (i) (b)

(ii) (a)

OR

(a) : More negative is the standard reduction potential, greater is its ability to displace hydrogen from acid.

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(iii) (d): A negative value of standard reduction potential means that oxidation takes place on the electrode with reference to SHE.

(iv) (a)

10. (i) (a)

OR

(c) : $\Lambda^{\infty}_{AB} = \lambda^{\infty}_{A^+} + \lambda^{\infty}_{B^-}$

Kohlrausch's law is applicable for weak electrolytes.

(ii) (d): At higher concentration, mobility of ions decreases. Hence, conductance decreases.

(iii) (c): Total number of ions will increase slightly on dilution (not considerably).

(iv) (b)

11. (i) (b)

(ii) (b): If redox reaction is spontaneous, ΔG is –ve and hence, $E°$ is positive.
$-\Delta G° = nFE°\text{cell}$

OR

(c) : $\Delta G < 0$ and $E_{cell} > 0$; spontaneous.

(iii) (a)

(iv) (b)

12. (i) (a): $\log\left(\frac{C_1}{C_2}\right) < 0$ for spontaneity.

$\therefore \quad C_1 < C_2$

(ii) (a)

(iii) (b)

(iv) (a)

OR

(d) : Nernst equation is measured at 298 K. At STP conditions, temperature to be 273 K.

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