

CHAPTER - 3

ELECTROCHEMISTRY INTEXT SOLUTIONS

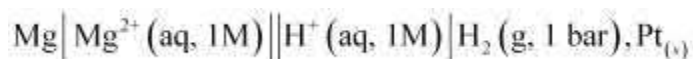
Question 3.1:

How would you determine the standard electrode potential of the system $\text{Mg}^{2+} | \text{Mg}$?

Answer

The standard electrode potential of $\text{Mg}^{2+} | \text{Mg}$ can be measured with respect to the standard hydrogen electrode, represented by $\text{Pt}_{(s)}, \text{H}_{2(g)} (1 \text{ atm}) | \text{H}^+_{(aq)} (1 \text{ M})$.

A cell, consisting of $\text{Mg} | \text{MgSO}_4 (aq, 1 \text{ M})$ as the anode and the standard hydrogen electrode as the cathode, is set up.



Then, the emf of the cell is measured and this measured emf is the standard electrode potential of the magnesium electrode.

$$E^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$$

Here, E_R^{\ominus} for the standard hydrogen electrode is zero.

$$\begin{aligned} \therefore E^{\ominus} &= 0 - E_L^{\ominus} \\ &= -E_L^{\ominus} \end{aligned}$$

Question 3.2:

Can you store copper sulphate solutions in a zinc pot?

Answer

Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.



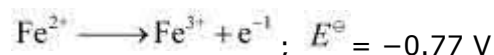
Hence, copper sulphate solution cannot be stored in a zinc pot.

Question 3.3:

Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Answer

Substances that are stronger oxidising agents than ferrous ions can oxidise ferrous ions.



This implies that the substances having higher reduction potentials than $+0.77 \text{ V}$ can oxidise ferrous ions to ferric ions. Three substances that can do so are F_2 , Cl_2 , and O_2 .

Question 3.4:

Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Answer

For hydrogen electrode, $\text{H}^{+} + \text{e}^{-} \longrightarrow \frac{1}{2} \text{H}_2$, it is given that $\text{pH} = 10$

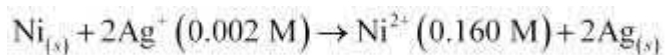
$$\therefore [\text{H}^{+}] = 10^{-10} \text{ M}$$

Now, using Nernst equation:

$$\begin{aligned} E_{\left(\text{H}^{+}/\frac{1}{2}\text{H}_2\right)} &= E^{\ominus}_{\left(\text{H}^{+}/\frac{1}{2}\text{H}_2\right)} - \frac{RT}{nF} \ln \frac{1}{[\text{H}^{+}]} \\ &= E^{\ominus}_{\left(\text{H}^{+}/\frac{1}{2}\text{H}_2\right)} - \frac{0.0591}{1} \log \frac{1}{[\text{H}^{+}]} \\ &= 0 - \frac{0.0591}{1} \log \frac{1}{[10^{-10}]} \\ &= -0.0591 \log 10^{10} \\ &= -0.591 \text{ V} \end{aligned}$$

Question 3.5:

Calculate the emf of the cell in which the following reaction takes place:



Given that

Answer

Applying Nernst equation we have:

$$E_{(\text{cell})}^{\ominus} = 1.05 \text{ V}$$

$$E_{(\text{cell})} = E_{(\text{cell})}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.05 - \frac{0.0591}{2} \log \frac{(0.160)}{(0.002)^2}$$

$$= 1.05 - 0.02955 \log \frac{0.16}{0.000004}$$

$$= 1.05 - 0.02955 \log 4 \times 10^4$$

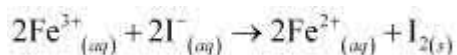
$$= 1.05 - 0.02955 (\log 10000 + \log 4)$$

$$= 1.05 - 0.02955 (4 + 0.6021)$$

$$= 0.914 \text{ V}$$

Question 3.6:

The cell in which the following reactions occurs:



has $E_{\text{cell}}^{\ominus} = 0.236 \text{ V}$ at 298 K.

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Answer

Here, $n = 2$, $E_{\text{cell}}^{\ominus} = 0.236 \text{ V}$, $T = 298 \text{ K}$

We know that:

$$\Delta_r G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$$

$$= -2 \times 96487 \times 0.236$$

$$= -45541.864 \text{ J mol}^{-1}$$

$$= -45.54 \text{ kJ mol}^{-1}$$

Again, $\Delta_r G^\ominus = -2.303RT \log K_c$

$$\Rightarrow \log K_c = -\frac{\Delta_r G^\ominus}{2.303 RT}$$

$$= -\frac{-45.54 \times 10^3}{2.303 \times 8.314 \times 298}$$

$$= 7.981$$

$$\therefore K_c = \text{Antilog}(7.981)$$

$$= 9.57 \times 10^7$$

Question 3.7:

Why does the conductivity of a solution decrease with dilution?

Answer

The conductivity of a solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

Question 3.8:

Suggest a way to determine the Λ_m^\ominus value of water.

Answer

Applying Kohlrausch's law of independent migration of ions, the Λ_m^\ominus value of water can be determined as follows:

$$\begin{aligned} \Lambda_{m(\text{H}_2\text{O})}^\ominus &= \lambda_{\text{H}^+}^\ominus + \lambda_{\text{OH}^-}^\ominus \\ &= (\lambda_{\text{H}^+}^\ominus + \lambda_{\text{Cl}^-}^\ominus) + (\lambda_{\text{Na}^+}^\ominus + \lambda_{\text{OH}^-}^\ominus) - (\lambda_{\text{Na}^+}^\ominus + \lambda_{\text{Cl}^-}^\ominus) \end{aligned}$$

$$\Lambda_{m(\text{HCl})}^\ominus + \Lambda_{m(\text{NaOH})}^\ominus - \Lambda_{m(\text{NaCl})}^\ominus$$

$$\Lambda_m^\ominus$$

Hence, by knowing the values of $\Lambda_{m(\text{HCl})}^\ominus$, $\Lambda_{m(\text{NaOH})}^\ominus$, and $\Lambda_{m(\text{NaCl})}^\ominus$, the Λ_m^\ominus value of

water can be determined.

Question 3.9:

The molar conductivity of 0.025 mol L⁻¹ methanoic acid is 46.1 S cm² mol⁻¹.

Calculate its degree of dissociation and dissociation constant. Given $\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$

Answer

$$C = 0.025 \text{ mol L}^{-1}$$

$$\Lambda_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\begin{aligned}\Lambda_m^\circ(\text{HCOOH}) &= \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-) \\ &= 349.6 + 54.6 \\ &= 404.2 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Now, degree of dissociation:

$$\begin{aligned}\alpha &= \frac{\Lambda_m(\text{HCOOH})}{\Lambda_m^\circ(\text{HCOOH})} \\ &= \frac{46.1}{404.2} \\ &= 0.114 \text{ (approximately)}\end{aligned}$$

Thus, dissociation constant:

$$\begin{aligned}K &= \frac{c\alpha^2}{(1-\alpha)} \\ &= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1-0.114)} \\ &= 3.67 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

Question 3.10:

If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Answer I

$$= 0.5 \text{ A}$$

$$t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$$

Thus, $Q = It$

$$= 0.5 \text{ A} \times 7200 \text{ s}$$

$$= 3600 \text{ C}$$

We know that $96487 \text{ C} = 6.023 \times 10^{23}$ number of electrons.

Then,

$$\begin{aligned} 3600 \text{ C} &= \frac{6.023 \times 10^{23} \times 3600}{96487} \text{ number of electrons} \\ &= 2.25 \times 10^{22} \text{ number of electrons} \end{aligned}$$

Hence, 2.25×10^{22} number of electrons will flow through the wire.

Question 3.11:

Suggest a list of metals that are extracted electrolytically.

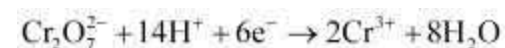
Answer

Metals that are on the top of the reactivity series such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolytically.

Question 3.12:

What is the quantity of electricity in coulombs needed to reduce 1 mol of

$\text{Cr}_2\text{O}_7^{2-}$? Consider the reaction:



Answer

The given reaction is as follows:

$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$, the required quantity of electricity will be:

Therefore, to reduce 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ = 6 F
= 6×96487 C
= 578922 C

Question 3.14:

Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Answer

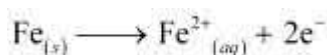
Methane and methanol can be used as fuels in fuel cells.

Question 3.15:

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

Answer

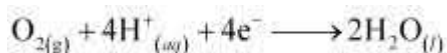
In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,



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,



The overall reaction is:



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 $(\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O})$ i.e., rust.

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