

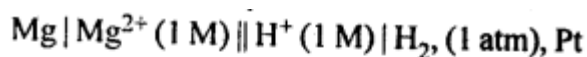
Class 12 Chemistry

NCERT Solutions for Chapter 3 – Electrochemistry

Intext Questions

3.1. How would you determine the standard electrode potential of the system Mg^{2+}/Mg ?

Ans: A cell will be set up consisting of Mg/MgSO_4 (1 M) as one electrode and standard hydrogen electrode Pt, H_2 (1 atm) $|\text{H}^+$ (1 M) as second electrode, measure the EMF of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that e^- s flow from mg electrode to hydrogen electrode, i.e., oxidation takes place on magnesium electrode and reduction on hydrogen electrode. Hence, the cell may be represented as follows :



$$E^\circ_{\text{cell}} = E^\circ_{\text{H}^+ / \frac{1}{2}\text{H}_2} - E^\circ_{\text{Mg}^{2+} / \text{Mg}}$$

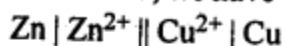
$$\text{Put } E^\circ_{\text{H}^+ / \frac{1}{2}\text{H}_2} = 0$$

$$\therefore E^\circ_{\text{Mg}^{2+} / \text{Mg}} = -E^\circ_{\text{cell}}$$

3.2. Can you store copper sulphate solutions in a zinc pot?

Ans: Zn being more reactive than Cu, displaces Cu from CuSO_4 solution as follows: $\text{Zn} (\text{s}) + \text{CuSO}_4 (\text{aq}) \rightarrow \text{ZnSO}_4 (\text{aq}) + \text{Cu} (\text{s})$

In terms of EMF, we have

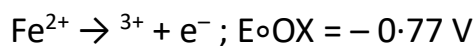


$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{2+} / \text{Cu}} - E^\circ_{\text{Zn}^{2+} / \text{Zn}} \\ &= 0.34 \text{ V} - (-0.76 \text{ V}) \\ &= 1.10 \text{ V} \end{aligned}$$

As E°_{cell} is positive, reaction takes place, i.e., Zn reacts with copper and hence, we cannot store CuSO_4 solution in zinc pot.

3.3. Consult the table on standard electrode potentials and suggest three substances that can oxidise Fe^{2+} ions under suitable conditions.

Ans. The oxidation of Fe^{2+} ions to Fe^{3+} ions proceeds as follows :



Only those substances can oxidise Fe^{2+} ions to Fe^{3+} ions which can accept

electrons released during oxidation or are placed above iron in electrochemical series. These are : $\text{Cl}_2(\text{g})$, $\text{Br}_2(\text{g})$ and $\text{Cr}_2\text{O}_7^{2-}$ ions (in the acidic medium).

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

Ans. For hydrogen electrode, $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$,

Applying Nernst equation,

$$\begin{aligned} E_{\text{H}^+ / \frac{1}{2}\text{H}_2} &= E^\circ_{\text{H}^+ / \frac{1}{2}\text{H}_2} - \frac{0.0591}{n} \log \frac{1}{[\text{H}^+]} \\ &= 0 - \frac{0.0591}{1} \log \frac{1}{10^{-10}} \\ &\quad \left\{ \begin{array}{l} \text{pH} = 10 \\ \Rightarrow [\text{H}^+] = 10^{-10} \text{ M} \end{array} \right\} \\ &= -0.0591 \times 10 \\ &= -0.591 \text{ V} \end{aligned}$$

3.5. Calculate the emf of the cell in which the following reaction takes place: $\text{Ni}(\text{s}) + 2\text{Ag}^+ (0.002 \text{ M}) \rightarrow \text{Ni}^{2+} (0.160 \text{ M}) + 2\text{Ag}(\text{s})$ Given that $E^\circ_{(\text{cell})} = 1.05 \text{ V}$.

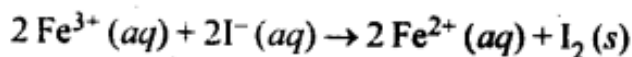
Ans:

Applying Nernst equation,

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \\ &= 1.05 \text{ V} - \frac{0.0591}{2} \log \frac{0.160}{(0.002)^2} \\ &= 1.05 - \frac{0.0591}{2} \log(4 \times 10^4) \\ &= 1.05 - \frac{0.0591}{2} (4.6021) \\ &= 1.05 - 0.14 \text{ V} \\ &= 0.91 \text{ V} \end{aligned}$$

3.6. The cell in which the following reaction occurs: $2\text{Fe}^{3+} (\text{aq}) + 2\text{I}^- (\text{aq}) \rightarrow 2\text{Fe}^{2+} (\text{aq}) + \text{I}_2 (\text{s})$ has $E^\circ_{\text{cell}} = 0.236 \text{ V}$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans:



For the given cell, $n = 2$

$$\begin{aligned} \Delta_r G^\circ &= -nF E^\circ_{\text{cell}} \\ &= -2 \times 96500 \times 0.236 \\ &= -45.55 \text{ kJ mol}^{-1} \end{aligned}$$

Also, $\Delta_r G^\circ = -2.303 RT \log K_C$

$$\begin{aligned} \Rightarrow \log K_C &= \frac{-\Delta_r G^\circ}{2.303RT} \\ &= \frac{-45.55}{2.303 \times 8.314 \times 10^{-3} \times 298} \\ &= 7.983 \end{aligned}$$

$$\begin{aligned} \Rightarrow K_C &= \text{antilog}(7.983) \\ &= 9.616 \times 10^7 \end{aligned}$$

3.7. Why does the conductivity of a solution decrease with dilution?

Ans: The conductivity of a solution is linked with the number of ions present per unit volume. With dilution, these decrease and the corresponding conductivity or specific conductance of the solution decreases.

3.8. Suggest a way to determine the value of water.

Ans:

By using Kohlrausch's law, Λ°_m for H_2O can be calculated, we can write,

$$\Lambda^\circ_m = \Lambda^\circ_m (\text{HCl}) + \Lambda^\circ_m (\text{NaOH}) - \Lambda^\circ_m (\text{NaCl})$$

Being strong electrolytes, Λ°_m values of HCl, NaOH and NaCl are known. By substituting their values, we can obtain Λ°_m for H_2O .

3.9. The molar conductivity of 0.025 mol L^{-1} methanoic acid is $46.1 \text{ S cm}^2 \text{ mol}^{-1}$.

1. Calculate its degree of dissociation and dissociation constant Given

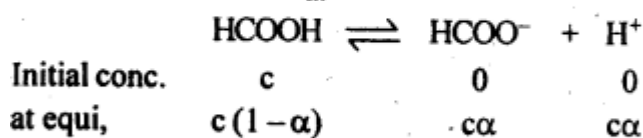
$$\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1} \text{ and } \lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

Ans:

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

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

$$\therefore \alpha = \frac{\Lambda_m^C}{\Lambda_m^\circ} = \frac{46.1}{404.2} = 0.114$$



$$\begin{aligned}\therefore K_a &= \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \\ &= \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}\end{aligned}$$

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?

Ans:

$$\begin{aligned}\text{We know, } Q &= It \\ &= 0.5 \times (2 \times 60 \times 60) \\ &= 3600 \text{ C}\end{aligned}$$

$$1F \Rightarrow 96500\text{C} \Rightarrow 1 \text{ mole of } e^{-1} \text{ s}$$

$$\Rightarrow 6.02 \times 10^{23} e^{-1} \text{ s}$$

\therefore 3600 C is equivalent to the flow of e^{-1} s

$$\begin{aligned}&= \frac{6.02 \times 10^{23}}{96500} \times 3600 \\ &= 2.246 \times 10^{22} e^{-1} \text{ s}\end{aligned}$$

3.11. Suggest a list of metals which can be extracted electrolytically.

Ans: The highly reactive metals having large -ve E° values, which can themselves act as powerful reducing agents can be extracted electrolytically. The process is known as electrolytic reduction. For details, consult Unit-6. For example, sodium, potassium, calcium, magnesium etc.

3.12. Consider the reaction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$?

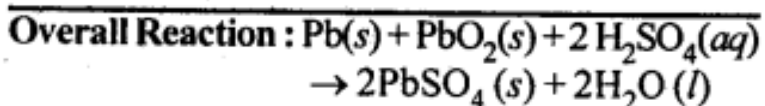
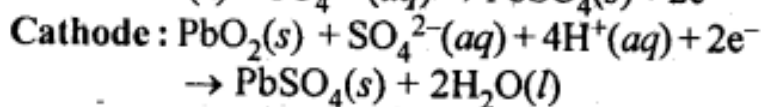
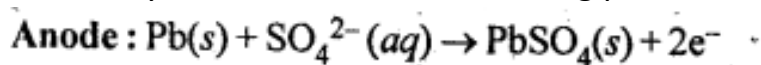
Ans:

From the reaction, 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ require $6F$
 $= 6 \times 96500 = 579000 \text{ C}$

\therefore 579000 C of electricity are required for reduction of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+}

3.13. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Ans: A lead storage battery consists of anode of lead, cathode of a grid of lead packed with lead dioxide (PbO_2) and 38% H_2SO_4 solution as electrolyte. When the battery is in use, the reaction taking place are:



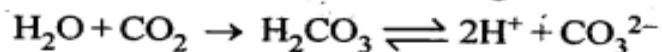
On charging the battery, the reverse reaction takes place, i.e., PbSO_4 deposited on electrodes is converted back to Pb and PbO_2 and H_2SO_4 is regenerated.

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

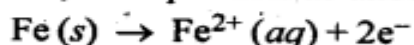
Ans: Methane (CH_4) and methanol (CH_3OH) can also be used as fuels in place of hydrogen in the fuel cells.

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

Ans: The water present on the surface of iron dissolves acidic oxides of air like CO_2 , SO_2 , etc. to form acids which dissociate to give H^+ ions :

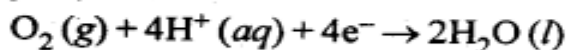


In the presence of H^+ , iron loses e^- s to form Fe^{2+} . Hence, this spot acts as anode:

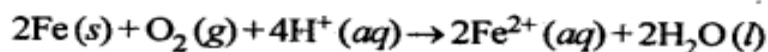


The e^- s released move through the metal to reach another spot where H^+ ions and dissolved oxygen take up these e^- s and reduction occurs.

This spot, thus, acts as cathode :



The overall reaction is :



Thus, an electrochemical cell is set up on the surface.

Ferrous ions are further oxidised by atmospheric oxygen to ferric ions which combine with water to form hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, which is rust.

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