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+1} Mg?

Ans: A cell will be set up consisting of Mg/$MgSO_4$ (1 M) as one electrode and standard hydrogen electrode Pt, H, (1 atm)H^+/(l 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^{-1} 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 :

$$Mg \mid Mg^{2+}(1\,M) \parallel H^+(1\,M) \mid H_2, (1\,atm), Pt$$

$$E^o_{cell} = E^o_{H^+/\frac{1}{2}H_2} - E^o_{Mg^{2+}/Mg}$$

Put $\quad E^o_{H^+/\frac{1}{2}H_2} = 0$

$$\therefore \quad E^o_{Mg^{2+}/Mg} = -E^o_{cell}$$

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:Zn (s) + $CuSO_4$ (aq) –> $ZnSO_4$(ag)+Cu (s)

In terms of EMF, we have

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

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

As E^o_{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 Fe2+ ions under suitable conditions.

Ans. The oxidation of Fe2+ ions to Fe3+ ions proceeds as follows :

$Fe^{2+} \rightarrow {}^{3+} + e^-$; E∘OX = – 0·77 V

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 : Cl_2(g), Br_2(g) and Cr_2O2-7 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, $H^+ + e^- \longrightarrow 1/2\ H_2$,

Applying Nernst equation,

$$E_{H^+, \frac{1}{2}H_2} = E^\circ_{H^+, \frac{1}{2}H_2} - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}}$$

$$\left\{\begin{array}{l} pH = 10 \\ \Rightarrow [H^+] = 10^{-10} M \end{array}\right\}$$

$$= -0.0591 \times 10$$

$$= -0.591\ V$$

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

Ans:

Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

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

$$= 1.05 - \frac{0.0591}{2}\log(4\times10^4)$$

$$= 1.05 - \frac{0.0591}{2}(4.6021)$$

$$= 1.05 - 0.14\ V$$

$$= 0.91\ V$$

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

Ans:

$$2\,Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

For the given cell, $n = 2$

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

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

$$\Rightarrow \quad \log K_C = \frac{-\Delta_r G^\circ}{2.303RT}$$
$$= \frac{-45.55}{2.303 \times 8.314 \times 10^{-3} \times 298}$$
$$= 7.983$$
$$\Rightarrow \quad K_C = \text{antilog}(7.983)$$
$$= 9.616 \times 10^7$$

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,

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

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

Ans:

$$\Lambda^{o}_{m}(HCOOH) = \lambda^{o}(H^{+}) + \lambda^{o}(HCOO^{-})$$
$$= 349.6 + 54.6$$
$$= 404.2 \text{ S cm}^2 \text{mol}^{-1}$$
$$\Lambda^{C}_{m} = 46.1 \text{ S cm}^2 \text{mol}^{-1}$$

$$\therefore \quad \alpha = \frac{\Lambda^{C}_{m}}{\Lambda^{o}_{m}} = \frac{46.1}{404.2} = 0.114$$

	$HCOOH \rightleftharpoons$	$HCOO^-$ +	H^+
Initial conc.	c	0	0
at equi,	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$\therefore \quad K_a = \frac{c\alpha . c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$= \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}$$

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:

We know, $Q = It$

$$= 0.5 \times (2 \times 60 \times 60)$$
$$= 3600 \text{C}$$

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

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

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

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

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: $Cr_2O_7^{2-}$-+ $14H^+$ + 6e- -> $2Cr_3$+ + $7H_2O$ What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

Ans:

From the reaction, 1 mol of $Cr_2O_7^{2-}$ require 6F

$$= 6 \times 96500 = 579000\,C$$

$\therefore$ 579000 C of electricity are required for reduction of $Cr_2O_7^{2-}$ 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:

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

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

$$\text{Overall Reaction}: Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

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 :

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

In the presence of H^+, iron looses e^{-1}s to form Fe^{3+}. Hence, this spot acts as anode:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

The e^{-1}s released move through the metal to reach another spot where H^+ ions and dissolved oxygen take up these e^{-1} s and reduction occurs. This spot, thus, acts as cathode :

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

The overall reactio nis :

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

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, $Fe_2O_3 . xH_2O$, which is rust.