Electrochemistry

Question 65. (a) Define the term molar conductivity. How is it related to conductivity of the related solution?

(b) One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of a zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.(E^0Zn2+/Zn=−0.76V,E^0Ag+/Ag = + 0.80 V)

Answer:

$$2Al_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$$

$$2Al \longrightarrow 2Al^{3+} + 6e^-$$

or, $$3Cu^{2+} + 6e^- \longrightarrow 3\,Cu$$

Hence, $n = 6$

$$\Delta G^0 = -nFE^0_{Cell}$$

$$\Delta G^0 = -6 \times 96500 \times 2.02 = -1169580 \text{ J mol}^{-1}$$

$$\therefore \quad \Delta G^0 = -116.958 \text{ KJ mol}^{-1}$$

Now, $\Delta G^0 = -2.303\, RT \log K_c$

$$\log K_c = \frac{-\Delta G^0}{2.303RT} = \frac{1169580}{2.308 \times 8.314 \times 298} = \frac{1169580}{5705.84}$$

$$\therefore \quad \log K_c = 205.009$$

(b) Half cell reactions :

At cathode : $2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

At anode : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

The cell can be represented as

$$Zn(s)\ |Zn^{2+}(aq)\ ||\ Ag^+(aq)|\ Ag(s)$$

The cell reaction is

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

$$\therefore \quad E^0_{cell} = E^0_{cathode} - E^\circ_{anode} = 0.80 - (-0.76) = 1.56 \text{ V}$$

$$\because \quad E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Ag^+]}$$

$$1.48 = 1.56 - \frac{0.059}{2} \log \frac{1}{[Ag^+]^2}$$

$$\frac{0.059}{2} \log \frac{1}{[Ag^+]^2} = 1.56 - 1.48 = 0.08$$

$$\log \frac{1}{[Ag^+]^2} = \frac{0.08 \times 2}{0.059}$$

or $$-2 \log [Ag^+] = \frac{0.16}{0.059}$$

$\therefore$ $$\log [Ag^+] = -1.356 = -1 - 0.356 - 1 + 1$$
$$= -2 + (1 - 1.356)$$

$$[Ag^+] = \bar{2}.644$$

$\therefore$ $$\mathbf{[Ag^+] = 4.406 \times 10^{-2}\ M}$$

Question 66 (a) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.

(b) Calculate Λ°_m for acetic acid.

Given that Λ°_m (HCl) = 426 S cm^2 mol^{-1}

Λ°_m (NaCl) = 126 S cm^2 mol^{-1}

Λ°_m (CH3COONa) = 91 S cm^2 mol^{-1}

Answer:

(a) Kohlrausch law of independent migration of ions : The limiting molar conductivity of an electrolyte (i.e. molar conductivity at infinite dilution) is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte

$$\Lambda^{\circ}_m \text{ for } A_xB_y = x\lambda^{\circ}_+ + y\lambda^{\circ}_-$$

For acetic acid Λ° (CH_3COOH)

$$= \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+}$$

$$\Lambda^{\circ}(CH_3COOH) = \Lambda^{\circ}(CH_3COOK) + \Lambda^{\circ}(HCl) - \Lambda^{\circ}(KCl)$$

(*b*) $$\Lambda^{\circ}(CH_3COOH) = \Lambda^{\circ}(CH_3COONa) + \Lambda^{\circ}(HCl) - \Lambda^{\circ}(NaCl)$$

$$= 91 + 426 - 126 = 517 - 126 = 391$$

$$\therefore\ \mathbf{\Lambda^{\circ}(CH_3COOH) = 391\ S\ cm^2\ mol^{-1}}$$

Question 67.

(a) Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery.

(b) A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.

(Given : $E^0_{Ag^+/Ag} = +0.80$ V,

$E^0_{Cu^{2+}/Cu} = +0.34$ V).

Answer:

(a) *At anode :*

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$ (oxidation)

At cathode :

$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$ (Reduction)

Overall reaction :

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

(b) The reaction takes place at anode and cathode in the following ways :

At anode (oxidation) :

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

At cathode (reduction) :

$$Cu(s) + 2Ag^{2+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

The complete cell reaction is

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

$\because \quad E^0_{cell} = E^0_{cathode} - E^0_{anode}$

or $\quad E^0_{cell} = +0.80 - (+0.34)$

or $\quad E^0_{cell} = 0.80 - 0.34 = 0.46$ V

Using *Nernst equation*

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2}$$

$$0.422 = 0.46 - \frac{0.059}{2} \log \frac{(0.1)}{[Ag^+]^2}$$

$$0.422 - 0.46 = -\frac{0.059}{2} \log \frac{10^{-1}}{[Ag^+]^2}$$

$$-0.038 = -0.0295 [\log 10^{-1} - \log [Ag^+]^2]$$

$$-0.038 = -0.0295 [-1 - 2 \log [Ag^+]]$$

$$-0.038 = 0.0295 + 0.059 \log [Ag^+]$$

or $\quad -0.059 \log [Ag^+] = 0.038 + 0.0295$

or $\quad -0.059 \log [Ag^+] = 0.0675$

or $\quad -\log [Ag^+] = \dfrac{0.0675}{-0.059}$

or $\quad \log [Ag^+] = 1.14407$

or $\quad [Ag^+] = \text{Antilog } 1.14407$

$\therefore \quad [Ag^+] = \mathbf{13.93\ M}$

Question 68. (a) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for half-cell containing

$0.10\ M\ K_2Cr_2O_7$ (aq), $0.20\ M\ Cr^{3+}$ (aq) and $1.0 \times 10^{-4}\ M\ H^+$ (aq).

The half-cell reaction is

$$Cr_2O_7^{2-}(aq) + 14\ H^+ (aq) + 6e^- \rightarrow 2\ Cr^{3+} (aq) + 7\ H_2O\ (l)$$

and the standard electrode potential is given as $E^0 = 1.33$ V.

Answer:

(a) The lead storage battery is a secondary cell (rechargeable). During discharging the electrode reaction occurs as follows :

At anode :

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

At cathode :

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

Overall reaction :

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2\,SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

(b) E = ? $E^0 = 1.33$ V

E^0_{cell} = 1.33 – 0.05916log[Cr+3]2[Cr2O2−7][H+]14

$$= 1.33 - \frac{0.0591}{6} \log \frac{(0.2)^2}{0.1 \times (10^{-4})^{14}}$$

$$= 1.33 - \frac{0.0591}{6} \log \frac{4 \times 10^{-2}}{10^{-57}}$$

$$= 1.33 - \frac{0.0591}{6} \log 4 \times 10^{55}$$

$$= 1.33 - \frac{(0.0591 \times 55.6020)}{6}$$

$$= 1.33 - 0.5467 = \mathbf{0.783\ volts}$$

Question 69.

(a) How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours? [$Hg(NO_3)_2$ = 200.6 g mol^{-1}]

(b) A voltaic cell is set up at 25 °C with the following half-cells Al^{2+} (0.001 M) and Ni^{2+} (0.50 M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

(Given : E0Ni2+/Ni = – 0.25 V, E0Al3+/Al = – 1.66 V)

Answer:

(a) Quantity of electricity (Q) = I × t = 2 × 3 × 60 × 60 = 21600 C

$Hg^{2+} + 2e^- \rightarrow Hg$

Thus 2F i.e. 2 × 96500 C deposits Hg = 1 mole

$$\therefore \quad 1 \text{ C deposit Hg} = \frac{1}{2 \times 96500}$$

$$\therefore \quad 21600 \text{ C deposit Hg}$$

$$= \frac{1}{2 \times 96500} \times 21600 = \mathbf{0.1119\ mole}$$

(*b*) The cell reaction can be represented as

$$2Al + 3Ni^{2+} \longrightarrow 2Al^{3+} + 3Ni$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.25 - (-1.66) = +1.41 \text{ V}$$

Applying Nernst equation

$$E_{cell} = 1.41 - \frac{0.0591}{6} \log\left[\frac{10^{-6}}{125 \times 10^{-3}}\right]$$

$$= 1.41 - \frac{0.0591}{6} [\log 10^{-3} - \log 125]$$

$$= 1.41 - \frac{0.0591}{6} [-3 - 2.0970]$$

$$= 1.41 + \frac{0.0591}{6} \times 5.0970$$

$$E_{cell} = 1.41 + 0.05 = \mathbf{1.46\ volts}$$

Question 70.

(a) What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it

(b) In the button cell, widely used in watches, the following reaction takes place

$Zn_{(s)} + Ag_2O_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-O_{(aq)}$ Determine E^0 and ΔG^0 for the reaction. (Given E^0Ag+/Ag = +0.80V, E^0Zn2+/Zn = -0.76 V)

Answer: (a) It is a secondary cell.

At anode reaction : $Pb + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$

At cathode reaction : $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Net reaction : $Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

(*b*) $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$$\Rightarrow E^0_{cell} = 0.80 \text{ V} - (-0.76) \text{ V} = +1.56 \text{ V}$$

$$\Delta_r G = -nFE^0_{cell}$$

$$= -2 \times 96500 \text{ C mol}^{-1} \times 1.56 \text{ V}$$

$$= -301080 \text{ J mol}^{-1} = \mathbf{-301.08\ kJ\ mol^{-1}}$$

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