Electrochemistry

1. The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm^{-1} cm^2 $equiv^{-1}$, respectively at 25 °C. Calculate the equivalent conductance of acetic acid at infinite dilution.
2. 2F of electricity is passed through 20 L of a solution of aquous solution of KCl. Calculate the pH of the solution.
3. The specific conductivity of a solution containing 1.0g of anhydrous $BaCl_2$ in 200 cm^3 of the solution has been found to be 0.0058 S cm^{-1}. Calculate the molar conductivity of the solution. (Molecular wt. of $BaCl_2 = 208$).
4. The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001M are 5.20 and 49.2 S cm^2 eq^{-1} respectively. Calculate the degree of dissociation of acetic acid at 0.001 M concentration.

   Given that : $\Lambda^{\infty}(H^+)$ and $\Lambda^{\infty}(CH_3COO^-)$ are 349.8 and 40.9 ohm^{-1} cm^2 eq^{-1} respectively.
5. The amount of electricity which releases 2.0 g of gold from a gold salt is same as that which dissolves 0.967g of copper anode during the electrolysis of copper sulphate solution. What is the oxidation number of gold in the gold ion ? (At. mass of Cu = 63.5; Au = 197)
6. If K_c for the reaction

   $$Cu^{2+}(aq) + Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + Cu(s)$$

   at 25°C is represented as 2.6×10^y then find the value of y.

   (Given : $E^{\circ}_{Cu^{2+}|Cu} = 0.34V; E^{\circ}_{Sn^{4+}|Sn^{2+}} = 0.15V$)
7. If ΔG° for the half cell $MnO_4^- \mid MnO_2$ in an acid solution is xF then find the value of x.

   (Given : $E^{\circ}_{MnO_4^-|Mn^{2+}} = 1.5V; E^{\circ}_{MnO_2|Mn^{2+}} = 1.25V$)
8. The standard reduction potential of a silver chloride electrode (metal-sparingly soluble salt electrode) is 0.209 V and for silver electrode is 0.80 V. If the moles of AgCl that can dissolve in 10 L of a 0.01 M NaCl solution is represented as 10^{-Z} then find the value of Z.
9. Molar conductivity of aqueous solution of HA is 200 S cm^2 mol^{-1}, pH of this solution is 4. Calculate the value of pK_a(HA) at 25°C.

   Given : $\Lambda_M^{\infty}(NaA) = 100\ Scm^2mol^{-1}; \Lambda_M^{\infty}(HCl) = 425\ Scm^2mol^{-1};$

   $\Lambda_M^{\infty}(NaCl) = 125\ Scm^2mol^{-1}$
10. A solution containing 1M XSO_4(aq) and 1M YSO_4 (aq) is electrolysed. If conc. of X^{2+} is 10^{-z} M when deposition of Y^{2+} and X^{2+} starts simultaneously, calculate the value of Z.

    Given : $\dfrac{2.303RT}{F} = 0.06$

    $E^{\circ}_{X^{2+}/X} = -0.12V;\ E^{\circ}_{Y^{2+}/Y} = -0.24V$
11. A solution of Ni $(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode?
12. Find the standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K

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

    $E^{\circ} = 2$ V at 298 K

    (Faraday's constant, F = 96000 C mol^{-1})
13. All the energy released from the reaction $X \rightarrow Y$, $\Delta_rG^{\circ} = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E^{\circ} = -0.25$ V

    Under standard conditions, find the number of moles of M^+ oxidized when one mole of X is converted to Y

    [F = 96500 C mol^{-1}]
14. Consider the following half-cell reactions and associated standard half-cell potentials, and determine the maximum voltage that can be obtained by combination resulting in spontaneous processes :

    $$AuBr_4^-(aq) + 3e^- \longrightarrow Au(s) + 4Br^-(aq); E^{\circ} = -0.86\ V$$

    $$Eu^{3+}(aq) + e^- \longrightarrow Eu^{2+}(aq); E^{\circ} = -0.43\ V$$

    $$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s); E^{\circ} = -0.14\ V$$

    $$IO^-(aq) + H_2O(l) + 2e^- \longrightarrow I^-(aq) + 2OH^-(aq);$$

    $$E^{\circ} = +0.49\ V$$
15. The e.m.f. of the cell $Zn \mid Zn^{2+}(0.01M) \mid\mid Fe^{2+}(0.001M) \mid Fe$ at 298 K is 0.2905 then the value of equilibrium constant for the cell reaction 10^x Find x

SOLUTIONS

1. **(390.7)** According to Kohlrausch's law,

$\Lambda^{\circ}_{(eq)CH_3COONa} = \lambda_{CH_3COO^-} + \lambda_{Na^+} = 91.0$ ....(i)

$\Lambda^{\circ}_{(eq)HCl} = \lambda_{H^+} + \lambda_{Cl^-} = 426.16$ ...(ii)

$\Lambda^{\circ}_{(eq)NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} = 126.45$ ....(iii)

Adding equations (i) and (ii) and substracting (iii),

$\lambda_{CH_3COO^-} + \lambda_{Na^+} + \lambda_{H^+} + \lambda_{Cl^-} - \lambda_{Na^+} - \lambda_{Cl^-}$

$= 91.0 + 426.16 - 126.45$

$\lambda_{CH_3COO^-} + \lambda_{H^+} = \Lambda^{\circ}_{(eq)CH_3COOH}$

$= 390.7\ ohm^{-1}\ cm^2\ equiv^{-1}$

2. **(13)** $KCl \xrightarrow{\text{Electrolysis}} \underset{\text{at anode}}{Cl_2(g)} + \underset{\text{at cathode}}{H_2(g)} + \underset{\text{in solution}}{OH^-}$

$1F = 1$ eq of $H_2(g) = 1$ eq of $Cl_2(g) \equiv 1$ eq of OH^- ions

$2F = 2$ eq of OH^-

$[OH^-] = \dfrac{2\,eq}{\text{Volume in L}} = \dfrac{2}{20\,L} = 10^{-1}$ N or M

$\therefore$ $pOH = -\log(10^{-1}) = 1$

$pH = 14 - 1 = 13$

3. **(241.67)** Molarity of $BaCl_2 = \dfrac{1 \times 1000}{208 \times 200} = 0.024$ M

Also, Normality of $BaCl_2 = 0.024 \times 2 = 0.048$ N

($\because$ N = M × Valency factor)

Now, $\Lambda_m = \kappa \times \dfrac{1000}{C_M} = \dfrac{0.0058 \times 1000}{0.024}$

$= 241.67\ S\ cm^2\ mol^{-1}$

4. **(12.5)** Degree of dissociation is given by

$\alpha = \dfrac{\Lambda^c}{\Lambda^\infty}$

(i) Evaluation of $\Lambda^{\infty}_{CH_3COOH}$

$\Lambda^{\infty}_{CH_3COOH} = \Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{H^+}$

$= 40.9 + 349.8 = 390.7\ ohm^{-1}\ cm^2\ eq^{-1}$

(ii) Evaluation of degree of dissociation

At C = 0.001 M,

$\alpha = \dfrac{\Lambda^c}{\Lambda^\infty} = \dfrac{49.2}{390.7} = 0.125$ i.e., 12.5%

5. **(3)** $\dfrac{0.967}{63.5} \times 2 = \dfrac{2}{197} \times n_f$

$n_f = 3$

6. **(6)** $K_c = 10^{\frac{2(0.34-0.15)}{0.0591}} = 2.6 \times 10^6$

7. **(5)** $4H^+ + MnO_4^- \rightleftharpoons MnO_2 + 2H_2O$

$\Delta G^\circ = -3 \times F \times \left(\dfrac{1.5 \times 5 - 2 \times 1.25}{3}\right)$

$= -5\,F;\ x = 5$

8. **(7)** $E^{\circ}_{Cl^-/AgCl/Ag} = E^{\circ}_{Ag/Ag} + 1\dfrac{0.0591}{1}\log K_{sp}$

$0.209 = 0.80 + \dfrac{0.0591}{1}\log K_{sp}$

$K_{sp} = 10^{-10}$; Let solubility of AgCl in 0.01 M solution is x

$10^{-10} = x\,(x + 0.01)$

$x = 10^{-8}$

$\therefore$ Moles of AgCl dissolved in 10L $= 10^{-8} \times 10 = 10^{-7}$

9. **(4)** $\Lambda^{\infty}_{M}(HA) = \Lambda^{\infty}_{M}(HCl) + \Lambda^{\infty}_{M}(NaA) - \Lambda^{\infty}_{M}(NaCl)$

$= 425 + 100 - 125 = 400\ S\ cm^2 mol^{-1}$

$pH = 4$, $[H^+] = 10^{-4} = \alpha C$

$\alpha = \dfrac{\Lambda_m}{\Lambda^{\infty}_m} = \dfrac{200}{400} = 0.5;$

$K_a = \dfrac{(C\alpha)\cdot\alpha}{(1-\alpha)} = \dfrac{10^{-4}(0.5)}{(1-\alpha)} = 10^{-4}; pK_a = 4$

10. **(4)** $-0.12 - \dfrac{0.0591}{2}\log\left(\dfrac{1}{X}\right) = -0.24$

$\log\dfrac{1}{X} = \dfrac{0.12 \times 2}{0.06} = 4$

$X = 10^{-4}$

11. **(0.05)** According to the Faraday's law of electrolysis, nF of current is required for the deposition of 1 mole. According to the reaction,

$Ni(NO_3)_2 \longrightarrow Ni^{2+} + 2NO_3^-$

2 F of current deposits = 1 mol

$\therefore$ 0.1 F of current deposits = = 0.05 mol

12. **(–384)** $\Delta G^\circ = -nFE^\circ_{cell}$

$= -2 \times (96000) \times 2\ V = -384000$ J/mol

$= -384$ kJ/mol

13. **(4)** $X \longrightarrow Y$; $\Delta G^\circ = -193\ kJ\ mol^{-1}$

$M^+ \longrightarrow M^{3+} + 2e^-$ $\quad E^\circ = -0.25V$

Hence ΔG° for oxidation will be

$\Delta G^\circ = -nFE^\circ$

$= -2 \times 96500 \times (-0.25) = 48250\ J = 48.25\ kJ$

48.25 kJ energy oxidises one mole M^+

$\therefore$ 193 kJ energy oxidises $\dfrac{193}{48.25}$ mole $M^+ = 4$ mole M^+

14. **(1.35)** Maximum voltage $E^\circ = 0.49 + 0.86 = 1.35$ V

15. **(10.85)** For this cell, reaction is; $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

$E = E^\circ - \dfrac{0.0591}{n}\log\dfrac{c_1}{c_2};\ E^\circ = E + \dfrac{0.0591}{n}\log\dfrac{c_1}{c_2}$

$$E^\circ = 0.2905 + \frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}} = 0.32 \text{ V.}$$

$$\mathrm{E}^\circ = \frac{0.0591}{2}\log \mathrm{K_{eq}}$$

$$\log \mathrm{K_{eq}} = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$$\therefore \mathrm{K_{eq}} = 10^{\frac{0.32}{0.0295}}$$

Comparing the value of 10^x,

$$x = \frac{0.32}{0.0295} = 10.847 \approx 10.85$$