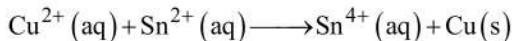


# Electrochemistry

1. The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and  $91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ , respectively at  $25^\circ\text{C}$ . Calculate the equivalent conductance of acetic acid at infinite dilution.
2.  $2F$  of electricity is passed through 20 L of a solution of aqueous solution of KCl. Calculate the pH of the solution.
3. The specific conductivity of a solution containing 1.0g of anhydrous  $\text{BaCl}_2$  in  $200 \text{ cm}^3$  of the solution has been found to be  $0.0058 \text{ S cm}^{-1}$ . Calculate the molar conductivity of the solution. (Molecular wt. of  $\text{BaCl}_2$  = 208).
4. The equivalent conductivities of acetic acid at  $298 \text{ K}$  at the concentrations of  $0.1 \text{ M}$  and  $0.001 \text{ M}$  are  $5.20$  and  $49.2 \text{ S cm}^2 \text{ eq}^{-1}$  respectively. Calculate the degree of dissociation of acetic acid at  $0.001 \text{ M}$  concentration.  
Given that:  $\Lambda^\infty(\text{H}^+)$  and  $\Lambda^\infty(\text{CH}_3\text{COO}^-)$  are  $349.8$  and  $40.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$  respectively.
5. The amount of electricity which releases  $2.0 \text{ g}$  of gold from a gold salt is same as that which dissolves  $0.967 \text{ g}$  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



at  $25^\circ\text{C}$  is represented as  $2.6 \times 10^y$  then find the value of y.

$$(\text{Given: } E^\circ_{\text{Cu}^{2+}|\text{Cu}} = 0.34 \text{ V}; E^\circ_{\text{Sn}^{4+}|\text{Sn}^{2+}} = 0.15 \text{ V})$$

7. If  $\Delta G^\circ$  for the halfcell  $\text{MnO}_4^- | \text{MnO}_2$  in an acid solution is  $xF$  then find the value of x.

$$(\text{Given: } E^\circ_{\text{MnO}_4^-|\text{Mn}^{2+}} = 1.5 \text{ V}; E^\circ_{\text{MnO}_2|\text{Mn}^{2+}} = 1.25 \text{ V})$$

8. The standard reduction potential of a silver chloride electrode (metal-sparingly soluble salt electrode) is  $0.209 \text{ V}$  and for silver electrode is  $0.80 \text{ V}$ . If the moles of  $\text{AgCl}$  that can dissolve in  $10 \text{ L}$  of a  $0.01 \text{ M}$   $\text{NaCl}$  solution is represented as  $10^{-z}$  then find the value of Z.
9. Molar conductivity of aqueous solution of HA is  $200 \text{ S cm}^2 \text{ mol}^{-1}$ , pH of this solution is 4. Calculate the value of  $\text{pK}_a(\text{HA})$  at  $25^\circ\text{C}$ .

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

$$\Lambda_M^\infty(\text{NaCl}) = 125 \text{ Scm}^2 \text{ mol}^{-1}$$

10. A solution containing  $1 \text{ M}$   $\text{XSO}_4$  (aq) and  $1 \text{ M}$   $\text{YSO}_4$  (aq) is electrolysed. If conc. of  $\text{X}^{2+}$  is  $10^{-z} \text{ M}$  when deposition of  $\text{Y}^{2+}$  and  $\text{X}^{2+}$  starts simultaneously, calculate the value of Z.

$$\text{Given: } \frac{2.303RT}{F} = 0.06$$

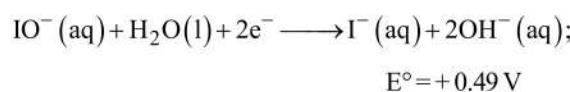
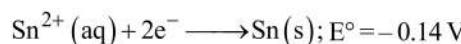
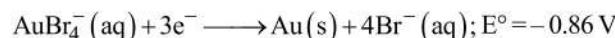
$$E^\circ_{\text{X}^{2+}/\text{X}} = -0.12 \text{ V}; E^\circ_{\text{Y}^{2+}/\text{Y}} = -0.24 \text{ V}$$

11. A solution of  $\text{Ni}(\text{NO}_3)_2$  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  $\text{kJ mol}^{-1}$  at  $298 \text{ K}$   
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$   
 $E^\circ = 2 \text{ V}$  at  $298 \text{ K}$   
 (Faraday's constant,  $F = 96000 \text{ C mol}^{-1}$ )

13. All the energy released from the reaction  $\text{X} \rightarrow \text{Y}$ ,  $\Delta_f G^\circ = -193 \text{ kJ mol}^{-1}$  is used for oxidizing  $\text{M}^+$  as  $\text{M}^+ \rightarrow \text{M}^{3+} + 2e^-$ ,  $E^\circ = -0.25 \text{ V}$

Under standard conditions, find the number of moles of  $\text{M}^+$  oxidized when one mole of X is converted to Y  
 $[F = 96500 \text{ C mol}^{-1}]$

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 :



15. The e.m.f. of the cell  $\text{Zn} | \text{Zn}^{2+}(0.01 \text{ M}) || \text{Fe}^{2+}(0.001 \text{ M}) | \text{Fe}$  at  $298 \text{ K}$  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,

$$\Lambda_{(\text{eq})\text{CH}_3\text{COONa}}^{\circ} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} = 91.0 \dots (\text{i})$$

$$\Lambda_{(\text{eq})\text{HCl}}^{\circ} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.16 \dots (\text{ii})$$

$$\Lambda_{(\text{eq})\text{NaCl}}^{\circ} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.45 \dots (\text{iii})$$

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

$$\begin{aligned} \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} \\ = 91.0 + 426.16 - 126.45 \\ \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} = \Lambda_{(\text{eq})\text{CH}_3\text{COOH}}^{\circ} \\ = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1} \end{aligned}$$

2. (13)  $\text{KCl} \xrightarrow{\text{Electrolysis}} \text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) + \text{OH}^-$   
at anode at cathode in solution

$1F = 1 \text{ eq of H}_2(\text{g}) = 1 \text{ eq of Cl}_2(\text{g}) \equiv 1 \text{ eq of OH}^- \text{ ions}$   
 $2F = 2 \text{ eq of OH}^-$

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

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

$$\text{pH} = 14 - 1 = 13$$

3. (241.67) Molarity of  $\text{BaCl}_2 = \frac{1 \times 1000}{208 \times 200} = 0.024 \text{ M}$

Also, Normality of  $\text{BaCl}_2 = 0.024 \times 2 = 0.048 \text{ N}$   
( $\because N = M \times \text{Valency factor}$ )

$$\begin{aligned} \text{Now, } \Lambda_m &= \kappa \times \frac{1000}{C_M} = \frac{0.0058 \times 1000}{0.024} \\ &= 241.67 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

4. (12.5) Degree of dissociation is given by

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

- (i) Evaluation of  $\Lambda_{\text{CH}_3\text{COOH}}^{\circ}$

$$\begin{aligned} \Lambda_{\text{CH}_3\text{COOH}}^{\circ} &= \Lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \Lambda_{\text{H}^+}^{\circ} \\ &= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \end{aligned}$$

- (ii) Evaluation of degree of dissociation

At C = 0.001 M,

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

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

$$n_f = 3$$

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

7. (5)  $4\text{H}^+ + \text{MnO}_4^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$

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

$$= -5 \text{ F; } x = 5$$

8. (7)  $E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}^{\circ} = E_{\text{Ag}/\text{Ag}}^{\circ} + \frac{0.0591}{1} \log K_{\text{sp}}$

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

$K_{\text{sp}} = 10^{-10}$ ; 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 =  $10^{-8} \times 10 = 10^{-7}$

$$\begin{aligned} \Lambda_M^{\infty}(\text{HA}) &= \Lambda_M^{\infty}(\text{HCl}) + \Lambda_M^{\infty}(\text{NaA}) - \Lambda_M^{\infty}(\text{NaCl}) \\ &= 425 + 100 - 125 = 400 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

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

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}} = \frac{200}{400} = 0.5;$$

$$K_a = \frac{(C\alpha) \cdot \alpha}{(1-\alpha)} = \frac{10^{-4}(0.5)}{(1-\alpha)} = 10^{-4}; \text{pK}_a = 4$$

$$-0.12 - \frac{0.0591}{2} \log\left(\frac{1}{X}\right) = -0.24$$

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

$$X = 10^{-4}$$

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,

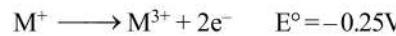


2 F of current deposits = 1 mol

$$\therefore 0.1 \text{ F of current deposits} = 0.05 \text{ mol}$$

12. (-384)  $\Delta G^\circ = -nFE_{\text{cell}}^{\circ}$   
=  $-2 \times (96000) \times 2 \text{ V} = -384000 \text{ J/mol}$   
=  $-384 \text{ kJ/mol}$

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



Hence  $\Delta G^\circ$  for oxidation will be

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

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

48.25 kJ energy oxidises one mole  $\text{M}^+$

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

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

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

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

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

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

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

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

Comparing the value of  $10^x$ ,

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

