

CHAPTER

Electrochemistry

17

- Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is
 (a) Sm mol^{-1} (b) $\text{Sm}^2 \text{mol}^{-1}$ [2002]
 (c) $\text{S}^{-2} \text{m}^2 \text{mol}$ (d) $\text{S}^2 \text{m}^2 \text{mol}^{-2}$.
- EMF of a cell in terms of reduction potential of its left and right electrodes is [2002]
 (a) $E = E_{\text{left}} - E_{\text{right}}$ (b) $E = E_{\text{left}} + E_{\text{right}}$
 (c) $E = E_{\text{right}} - E_{\text{left}}$ (d) $E = -(E_{\text{right}} + E_{\text{left}})$.
- What will be the emf for the given cell [2002]
 $\text{Pt} | \text{H}_2 (\text{P}_1) | \text{H}^+ (\text{aq}) || \text{H}_2 (\text{P}_2) | \text{Pt}$
 (a) $\frac{RT}{F} \log_e \frac{P_1}{P_2}$ (b) $\frac{RT}{2F} \log_e \frac{P_2}{P_1}$
 (c) $\frac{RT}{F} \log_e \frac{P_2}{P_1}$ (d) none of these.
- Which of the following reaction is possible at anode? [2002]
 (a) $2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+$
 (b) $\text{F}_2 \rightarrow 2 \text{F}^-$
 (c) $(1/2) \text{O}_2 + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}$
 (d) none of these.
- When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are [2002]

Cathode	Anode
(a) pure zinc	pure copper
(b) impure sample	pure copper
(c) impure zinc	impure sample
(d) pure copper	impure sample.
- For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be [2003]
 (a) 29.5×10^{-2} (b) 10
 (c) 1×10^{10} (d) 1×10^{-10}
- Standard reduction electrode potentials of three metals A, B & C are respectively +0.5 V, -3.0 V & -1.2 V. The reducing powers of these metals are [2003]
 (a) $A > B > C$ (b) $C > B > A$
 (c) $A > C > B$ (d) $B > C > A$
- When during electrolysis of a solution of AgNO_3 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be [2003]
 (a) 10.8 g (b) 21.6 g
 (c) 108 g (d) 1.08 g
- For the redox reaction : [2003]
 $\text{Zn}(\text{s}) + \text{Cu}^{2+} (0.1 \text{M}) \rightarrow \text{Zn}^{2+} (1 \text{M}) + \text{Cu}(\text{s})$
 taking place in a cell, E_{cell}° is 1.10 volt. E_{cell} for the cell will be $\left(2.303 \frac{RT}{F} = 0.0591 \right)$ [2003]
 (a) 1.80 volt (b) 1.07 volt
 (c) 0.82 volt (d) 2.14 volt
- In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to [2004]
 (a) produce high purity water
 (b) create potential difference between two electrodes
 (c) generate heat
 (d) remove adsorbed oxygen from electrode surfaces
- Consider the following E° values
 $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.77 \text{V}$; $E_{\text{Sn}^{2+}/\text{Sn}}^\circ = -0.14 \text{V}$
 Under standard conditions the potential for the reaction
 $\text{Sn}(\text{s}) + 2 \text{Fe}^{3+} (\text{aq}) \rightarrow 2 \text{Fe}^{2+} (\text{aq}) + \text{Sn}^{2+} (\text{aq})$ is

c-78

Chemistry

- (a) 0.91 V (b) 1.40 V [2004]
(c) 1.68 V (d) 0.63 V
12. The standard e.m.f. of a cell involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is ($F = 96,500 \text{ C mol}^{-1}$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)
(a) 1.0×10^{10} (b) 1.0×10^5 [2004]
(c) 1.0×10^1 (d) 1.0×10^{30}
13. The limiting molar conductivities Λ° for NaCl, KBr and KCl are 126, 152 and $150 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The Λ° for NaBr is [2004]
(a) $278 \text{ S cm}^2 \text{ mol}^{-1}$ (b) $176 \text{ S cm}^2 \text{ mol}^{-1}$
(c) $128 \text{ S cm}^2 \text{ mol}^{-1}$ (d) $302 \text{ S cm}^2 \text{ mol}^{-1}$
14. In a cell that utilises the reaction
 $\text{Zn(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
addition of H_2SO_4 to cathode compartment, will [2004]
(a) increase the E and shift equilibrium to the right
(b) lower the E and shift equilibrium to the right
(c) lower the E and shift equilibrium to the left
(d) increase the E and shift equilibrium to the left
15. The $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$ values for Cr, Mn, Fe and Co are -0.41 , $+1.57$, $+0.77$ and $+1.97\text{V}$ respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?
(a) Fe (b) Mn [2004]
(c) Cr (d) Co
16. For a spontaneous reaction the ΔG , equilibrium constant (K) and E°_{Cell} will be respectively [2005]
(a) $-ve, >1, -ve$ (b) $-ve, <1, -ve$
(c) $+ve, >1, -ve$ (d) $-ve, >1, +ve$
17. The highest electrical conductivity of the following aqueous solutions is of [2005]
(a) 0.1 M difluoroacetic acid
(b) 0.1 M fluoroacetic acid
(c) 0.1 M chloroacetic acid
(d) 0.1 M acetic acid
18. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is— $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}^\circ$
- To prepare 5.12 kg of aluminium metal by this method we require [2005]
(a) $5.49 \times 10^1 \text{ C}$ of electricity
(b) $5.49 \times 10^4 \text{ C}$ of electricity
(c) $1.83 \times 10^7 \text{ C}$ of electricity
(d) $5.49 \times 10^7 \text{ C}$ of electricity
19.

Electrolyte:	KCl	KNO_3	HCl	NaOAc	NaCl
$\Lambda^\circ (\text{S cm}^2 \text{ mol}^{-1})$:	149.9	145	426.2	91	126.5
- Calculate $\Lambda^\circ_{\text{HOAc}}$ using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C [2005]
(a) 217.5 (b) 390.7
(c) 552.7 (d) 517.2
20. The molar conductivities $\Lambda^\circ_{\text{NaOAc}}$ and $\Lambda^\circ_{\text{HCl}}$ at infinite dilution in water at 25°C are 91.0 and $426.2 \text{ S cm}^2/\text{mol}$ respectively. To calculate $\Lambda^\circ_{\text{HOAc}}$, the additional value required is [2006]
(a) $\Lambda^\circ_{\text{NaOH}}$ (b) $\Lambda^\circ_{\text{NaCl}}$
(c) $\Lambda^\circ_{\text{H}_2\text{O}}$ (d) $\Lambda^\circ_{\text{KCl}}$
21. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100Ω . The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell when filled with 0.2 M of the same solution is 520Ω . The molar conductivity of 0.2 M solution of electrolyte will be [2006]
(a) $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(b) $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(c) $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(d) $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
22. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below : [2007]
 $\Lambda^\circ_{\text{CH}_3\text{COONa}} = 91.0 \text{ S cm}^2 / \text{equiv.}$
 $\Lambda^\circ_{\text{HCl}} = 426.2 \text{ S cm}^2 / \text{equiv.}$
What additional information/ quantity one needs

Electrochemistry

c-79

- to calculate Λ° of an aqueous solution of acetic acid?
- Λ° of chloroacetic acid (ClCH_2COOH)
 - Λ° of NaCl
 - Λ° of CH_3COOK
 - the limiting equivalent conductance of H^+ ($\lambda_{\text{H}^+}^\circ$).
23. The cell,
 $\text{Zn} | \text{Zn}^{2+} (1 \text{ M}) || \text{Cu}^{2+} (1 \text{ M}) | \text{Cu}$ ($E^\circ_{\text{cell}} = 1.10 \text{ V}$)
 was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$ is [2007]
- 9.65×10^4
 - antilog (24.08)
 - 37.3
 - $10^{37.3}$
24. Given $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.72 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.42 \text{ V}$. The potential for the cell
 $\text{Cr} | \text{Cr}^{3+} (0.1 \text{ M}) || \text{Fe}^{2+} (0.01 \text{ M}) | \text{Fe}$ is [2008]
- 0.26 V
 - 0.336 V
 - 0.339
 - 0.26 V
25. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is
 $\text{CH}_3\text{OH}(l) + 3/2 \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
 At 298 K standard Gibbs energies of formation for $\text{CH}_3\text{OH}(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are -166.2, -237.2 and -394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be: [2009]
- 87%
 - 90%
 - 97%
 - 80%
26. Given:
 $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{ V}$,
 $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.439 \text{ V}$
 The value of standard electrode potential for the change,
 $\text{Fe}^{3+}(\text{aq}) + e^- \longrightarrow \text{Fe}^{2+}(\text{aq})$ will be: [2009]
- 0.385 V
 - 0.770 V
 - 0.270 V
 - 0.072 V
27. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :
 $\frac{2}{3} \text{Al}_2\text{O}_3 \rightarrow \frac{4}{3} \text{Al} + \text{O}_2$, $\Delta_r G = +966 \text{ kJ mol}^{-1}$
 The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least [2010]
- 4.5 V
 - 3.0 V
 - 2.5 V
 - 5.0 V
28. The correct order of $E^\circ_{\text{M}^{2+}/\text{M}}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is [2010]
- $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$
 - $\text{Cr} < \text{Fe} > \text{Mn} > \text{Co}$
 - $\text{Fe} > \text{Mn} > \text{Cr} > \text{Co}$
 - $\text{Cr} > \text{Mn} > \text{Fe} > \text{Co}$
29. Resistance of 0.2 M solution of an electrolyte is 50 Ω . The specific conductance of the solution is 1.3 S m^{-1} . If resistance of the 0.4 M solution of the same electrolyte is 260 Ω , its molar conductivity is : [2011RS]
- $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 - $625 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 - $62.5 \text{ S m}^2 \text{ mol}^{-1}$
 - $6250 \text{ S m}^2 \text{ mol}^{-1}$
30. The standard reduction potentials for Zn^{2+}/Zn , Ni^{2+}/Ni and Fe^{2+}/Fe are -0.76, -0.23 and -0.44 V respectively.
 The reaction $\text{X} + \text{Y}^{2+} \longrightarrow \text{X}^{2+} + \text{Y}$ will be spontaneous when : [2012]
- $\text{X} = \text{Ni}$, $\text{Y} = \text{Fe}$
 - $\text{X} = \text{Ni}$, $\text{Y} = \text{Zn}$
 - $\text{X} = \text{Fe}$, $\text{Y} = \text{Zn}$
 - $\text{X} = \text{Zn}$, $\text{Y} = \text{Ni}$
31. Given :
 $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$; $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$
 $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$; $E^\circ_{\text{Cl}^-/\text{Cl}_2} = 1.36 \text{ V}$
 Based on the data given above, strongest oxidising agent will be: [2013]
- Cl
 - Cr^{3+}
 - Mn^{2+}
 - MnO_4^-
32. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$ value ? [2013]

c-80

Chemistry

- (a) Cr(Z=24) (b) Mn(Z=25)
(c) Fe(Z=26) (d) Co(Z=27)
33. Resistance of 0.2 M solution of an electrolyte is 50 Ω . The specific conductance of the solution is 1.4 S m⁻¹. The resistance of 0.5 M solution of the same electrolyte is 280 Ω . The molar conductivity of 0.5 M solution of the electrolyte in S m² mol⁻¹ is: [2014]
(a) 5×10^{-4} (b) 5×10^{-3}
(c) 5×10^3 (d) 5×10^2
34. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ , respectively. The correct relationship between λ_C and λ_∞ is given as:
(Where the constant B is positive) [2014]
(a) $\lambda_C = \lambda_\infty + (B)C$
(b) $\lambda_C = \lambda_\infty - (B)C$
(c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$
(d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$
35. Given below are the half-cell reactions:
 $\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}; E^\circ = -1.18 \text{ V}$
- $2(\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}); E^\circ = +1.51 \text{ V}$
- The E° for $3\text{Mn}^{2+} \rightarrow \text{Mn} + 2\text{Mn}^{3+}$ will be: [2014]
(a) -2.69 V; the reaction will not occur
(b) -2.69 V; the reaction will occur
(c) -0.33 V; the reaction will not occur
(d) -0.33 V; the reaction will occur
36. Two Faraday of electricity is passed through a solution of CuSO_4 . The mass of copper deposited at the cathode is
(at. mass of Cu = 63.5 amu) [JEE M 2015]
(a) 2g (b) 127 g
(c) 0 g (d) 63.5 g
37. Given [JEE M 2017]
 $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}, E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V},$
 $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}, E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}.$
Among the following, the strongest reducing agent is
(a) Cr (b) Mn^{2+}
(c) Cr^{3+} (d) Cl^-

Answer Key

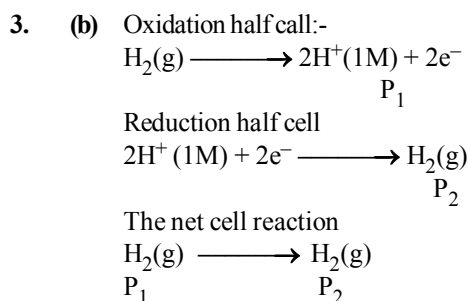
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(b)	(c)	(b)	(a)	(d)	(c)	(d)	(a)	(b)	(b)	(a)	(a)	(c)	(a)	(c)
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
(d)	(a)	(d)	(b)	(b)	(b)	(b)	(d)	(d)	(c)	(b)	(c)	(a)	(a)	(d)
31	32	33	34	35	36	37								
(d)	(d)	(a)	(c)	(a)	(d)	(a)								

SOLUTIONS

1. (b) given $S \propto \frac{\text{area} \times \text{conc}}{\ell} = \frac{\kappa \text{ m}^2 \text{ mol}}{\text{m} \times \text{m}^3}$

$\therefore \kappa = \text{S m}^2 \text{ mol}^{-1}$

2. (c) E_{cell} = Reduction potential of cathode
(right)
- reduction potential of anode (left)
= $E_{\text{right}} - E_{\text{left}}$



$$E^\circ_{\text{cell}} = 0.00 \text{ V} \quad n = 2$$

$$\therefore E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \log_e K$$

$$= 0 - \frac{RT}{nF} \log_e \frac{P_2}{P_1}$$

$$\text{or } E_{\text{cell}} = \frac{RT}{2F} \log_e \frac{P_2}{P_1}$$

4. (a) $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$
O.S. of Cr changes from +3 to +6 by loss of electrons. At anode oxidation takes place.
5. (d) Pure metal always deposits at cathode.
6. (c) The equilibrium constant is related to the standard emf of cell by the expression

$$\log K = E^\circ_{\text{cell}} \times \frac{n}{0.059} = 0.295 \times \frac{2}{0.059}$$

$$\log K = \frac{590}{59} = 10 \text{ or } K = 1 \times 10^{10}$$

7. (d)

A	B	C
+0.5C	-3.0V	-1.2V

NOTE The higher the negative value of reduction potential, the more is the reducing power.
Hence $B > C > A$.

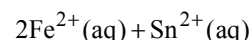
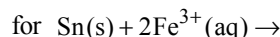
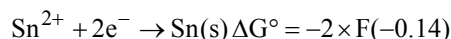
8. (a) When 96500 coulomb of electricity is passed through the electroplating bath the amount of Ag deposited = 108g
 \therefore when 9650 coulomb of electricity is passed deposited Ag.

$$= \frac{108}{96500} \times 9650 = 10.8 \text{ g}$$

9. (b) $E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.059}{n} \log \frac{[\text{Cu}^{+2}]}{[\text{Zn}^{+2}]}$
 $= 1.10 + \frac{0.059}{2} \log [0.1]$
 $= 1.10 - 0.0295 = 1.07 \text{ V}$

10. (b) In $\text{H}_2 - \text{O}_2$ fuel cell, the combustion of H_2 occurs to create potential difference between the two electrodes

11. (a) $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \Delta G^\circ = -1 \times F \times 0.77$



\therefore Standard potential for the given reaction

$$\text{or } E^\circ_{\text{cell}} = E^\circ_{\text{Sn}/\text{Sn}^{2+}} + E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$$

$$= 0.14 + 0.77 = 0.91 \text{ V}$$

12. (a) $E^\circ_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log K_c$

$$\text{or } 0 = 0.591 - \frac{0.0591}{1} \log K_c$$

$$\text{or } \log K_c = \frac{0.591}{0.0591} = 10 \text{ or } K_c = 1 \times 10^{10}$$

13. (c) $\Lambda^\circ \text{NaCl} = \lambda^\circ \text{Na}^+ + \lambda^\circ \text{Cl}^- \dots \text{(i)}$

$$\Lambda^\circ \text{KBr} = \lambda^\circ \text{K}^+ + \lambda^\circ \text{Br}^- \dots \text{(ii)}$$

$$\Lambda^\circ \text{KCl} = \lambda^\circ \text{K}^+ + \lambda^\circ \text{Cl}^- \dots \text{(iii)}$$

operating (i) + (ii) - (iii)

$$\Lambda^\circ \text{NaBr} = \lambda^\circ \text{Na}^+ + \lambda^\circ \text{Br}^-$$

$$= 126 + 152 - 150 = 128 \text{ S cm}^2 \text{ mol}^{-1}$$

14. (a) $\text{Zn(s)} + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}][\text{H}_2]}{[\text{H}^+]^2}$$

Addition of H_2SO_4 will increase $[\text{H}^+]$ and E_{cell} will also increase and the equilibrium will shift towards RHS

15. (c) The given values show that Cr has maximum oxidation potential, therefore its oxidation will be easiest. (Change the sign to get the oxidation values)

16. (d) **NOTE** For spontaneous reaction ΔG should be negative. Equilibrium constant should be more than one

c-82

Chemistry

($\Delta G = -2.303 RT \log K_c$, If $K_c = 1$ then

$\Delta G = 0$; If $K_c < 1$

then $\Delta G = +ve$). Again $\Delta G = -nFE_{\text{cell}}^{\circ}$.

E_{cell}° must be +ve to have ΔG -ve.

17. (a) Thus difluoro acetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity. The decreasing acidic strength of the carboxylic acids given is
difluoro acetic acid > fluoro acetic acid
> chloro acetic acid > acetic acid.

18. (d) 1 mole of $e^- = 1F = 96500 \text{ C}$
27g of Al is deposited by $3 \times 96500 \text{ C}$
5120 g of Al will be deposited by
$$= \frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7 \text{ C}$$

✚ ALTERNATE SOLUTION

We know, $Q = \frac{mFz}{M}$

$$\therefore Q = \frac{5120 \times 96500 \times 3}{27} = 5.49 \times 10^7 \text{ C}$$

19. (b) $\Lambda_{\text{HCl}}^{\circ} = 426.2$ (i)
 $\Lambda_{\text{AcONa}}^{\circ} = 91.0$ (ii)
 $\Lambda_{\text{NaCl}}^{\circ} = 126.5$ (iii)
 $\Lambda_{\text{AcOH}}^{\circ} = (i) + (ii) - (iii)$
 $= [426.2 + 91.0 - 126.5] = 390.7$

20. (b) $\Lambda_{\text{CH}_3\text{COOH}}^{\circ}$ is given by the following equation

$$\Lambda_{\text{CH}_3\text{COOH}}^{\circ} = (\Lambda_{\text{CH}_3\text{COONa}}^{\circ} + \Lambda_{\text{HCl}}^{\circ}) - (\Lambda_{\text{NaCl}}^{\circ})$$

Hence $\Lambda_{\text{NaCl}}^{\circ}$ is required.

21. (b) $R = 100 \Omega$, $\kappa = \frac{1}{R} \left(\frac{l}{a} \right)$,

$$\frac{l}{a} (\text{cell constant}) = 1.29 \times 100 \text{ m}^{-1}$$

Given, $R = 520 \Omega$, $C = 0.2 \text{ M}$,

μ (molar conductivity) = ?

$\mu = \kappa \times V$ (κ can be calculated as

$$\kappa = \frac{1}{R} \left(\frac{l}{a} \right) \quad \text{now}$$

cell constant is known.)

Hence,

$$\mu = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6} \text{ m}^3$$

$$= 12.4 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

22. (b) **NOTE** According to Kohlrausch's law, molar conductivity of weak electrolyte acetic acid (CH_3COOH) can be calculated as follows:

$$\Lambda_{\text{CH}_3\text{COOH}}^{\circ} = (\Lambda_{\text{CH}_3\text{COONa}}^{\circ} + \Lambda_{\text{HCl}}^{\circ}) - \Lambda_{\text{NaCl}}^{\circ}$$

\therefore Value of $\Lambda_{\text{NaCl}}^{\circ}$ should also be known

for calculating value of $\Lambda_{\text{CH}_3\text{COOH}}^{\circ}$.

23. (d) $E_{\text{cell}} = 0$; when cell is completely discharged.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\text{or } 0 = 1.1 - \frac{0.059}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) = \frac{2 \times 1.1}{0.059} = 37.3$$

$$\therefore \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) = 10^{37.3}$$

24. (d) From the given representation of the cell, E_{cell} can be found as follows.

$$E_{\text{cell}} = E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} - E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

[Nernst-Equ.]

$$= -0.42 - (-0.72) - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

Electrochemistry

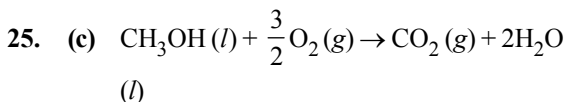
c-83

$$= -0.42 + 0.72 - \frac{0.059}{6} \log \frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}$$

$$= 0.3 - \frac{0.059}{6} \log \frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6} \times 4$$

$$= 0.30 - 0.0393 = 0.26 \text{ V}$$

Hence option (d) is correct answer.



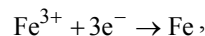
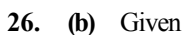
$$\Delta G_r = \Delta G_f(\text{CO}_2, g) + 2\Delta G_f(\text{H}_2\text{O}, l) -$$

$$\Delta G_f(\text{CH}_3\text{OH}, l) - \frac{3}{2} \Delta G_f(\text{O}_2, g)$$

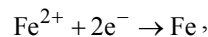
$$= -394.4 + 2(-237.2) - (-166.2) - 0$$

$$= -394.4 - 474.4 + 166.2 = -702.6 \text{ kJ}$$

$$\% \text{ efficiency} = \frac{702.6}{726} \times 100 = 97\%$$

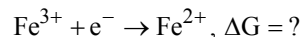


$$E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{ V} \quad \dots \text{(i)}$$

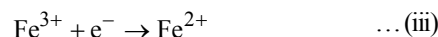


$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.439 \text{ V} \quad \dots \text{(ii)}$$

we have to calculate



To obtain this equation subtract equ (ii) from (i) we get



As we know that $\Delta G = -nFE$

Thus for reaction (iii)

$$\Delta G = \Delta G_1 - \Delta G$$

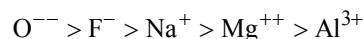
$$-nFE^\circ = -nFE_1 - (-nFE_2)$$

$$-nFE^\circ = nFE_2 - nFE_1$$

$$-1FE^\circ = 2 \times 0.439F - 3 \times 0.036F$$

$$-1FE^\circ = 0.770F$$

$$\therefore E^\circ = -0.770 \text{ V}$$



$$\text{or } E = \frac{\Delta G}{-nF} = \frac{966 \times 10^3}{4 \times 96500} = -2.5 \text{ V}$$

\therefore The potential difference needed for the reduction = 2.5 V.

28. (a) The value of $E^\circ_{\text{M}^{2+}/\text{M}}$ for given metal ions are

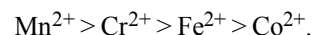
$$E^\circ_{\text{Mn}^{2+}/\text{Mn}} = -1.18 \text{ V},$$

$$E^\circ_{\text{Cr}^{2+}/\text{Cr}} = -0.9 \text{ V},$$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V} \text{ and}$$

$$E^\circ_{\text{Co}^{2+}/\text{Co}} = -0.28 \text{ V}.$$

The correct order of $E^\circ_{\text{M}^{2+}/\text{M}}$ values without considering negative sign would be



29. (a) $k = \frac{1}{R} \times \frac{\ell}{A}$

$$1.3 = \frac{1}{50} \times \frac{\ell}{A}$$

$$\frac{\ell}{A} = 65 \text{ m}^{-1}$$

$$\Lambda = \frac{k \times 1000}{\text{molarity}}$$

[molarity is in moles/litre but 1000 is used to convert liter into cm^3]

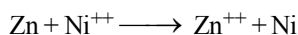
$$= \frac{\left(\frac{1}{260} \times 65 \text{ m}^{-1} \right) \times 1000 \text{ cm}^3}{0.4 \text{ moles}}$$

$$= \frac{650 \text{ m}^{-1}}{260 \times 4 \text{ mol}} \times \frac{1}{1000} \text{ m}^3$$

$$= 6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

30. (d) For a spontaneous reaction ΔG must be -ve
Since $\Delta G = -nFE^\circ$

Hence for ΔG to be -ve ΔE° has to be positive. Which is possible when $X = \text{Zn}$, $Y = \text{Ni}$



$$E^\circ_{\text{Zn}/\text{Zn}^{2+}} + E^\circ_{\text{Ni}^{2+}/\text{Ni}}$$

$$= 0.76 + (-0.23) = +0.53 \quad (\text{positive})$$

31. (d) Higher the value of standard reduction potential, stronger is the oxidising agent, hence MnO_4^- is the strongest oxidising agent.

32. (d) $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0.41 \text{ V}$ $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$

$$E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} = +1.57 \text{ V},$$

$$E^\circ_{\text{Co}^{3+}/\text{Co}^{2+}} = +1.97 \text{ V}$$

33. (a) Given for 0.2 M solution

$$R = 50 \Omega$$

$$\kappa = 1.4 \text{ S m}^{-1} = 1.4 \times 10^{-2} \text{ S cm}^{-1}$$

$$\text{Now, } R = \rho \frac{\ell}{a} = \frac{1}{\kappa} \times \frac{\ell}{a}$$

$$\Rightarrow \frac{\ell}{a} = R \times \kappa = 50 \times 1.4 \times 10^{-2}$$

For 0.5 M solution

$$R = 280 \Omega$$

$$\kappa = ?$$

$$\frac{\ell}{a} = 50 \times 1.4 \times 10^{-2}$$

$$\Rightarrow R = \rho \frac{\ell}{a} = \frac{1}{\kappa} \times \frac{\ell}{a}$$

$$\Rightarrow \kappa = \frac{1}{280} \times 50 \times 1.4 \times 10^{-2}$$

$$= \frac{1}{280} \times 70 \times 10^{-2}$$

$$= 2.5 \times 10^{-3} \text{ S cm}^{-1}$$

$$\text{Now, } \Lambda_m = \frac{\kappa \times 1000}{M}$$

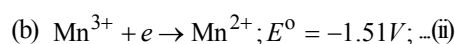
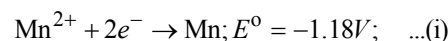
$$= \frac{2.5 \times 10^{-3} \times 1000}{0.5}$$

$$= 5 \text{ S cm}^2 \text{ mol}^{-1} = 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

34. (c) According to Debye Huckle onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

35. (a) (a)



Now multiplying equation (ii) by two and subtracting from equation (i)



$$E^\circ = E_{\text{Ox.}} + E_{\text{Red.}}$$

$$= -1.18 + (-1.51) = -2.69 \text{ V}$$

(-ve value of EMF (i.e. $\Delta G = +ve$) shows that the reaction is non-spontaneous)

36. (d) $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$
2F i.e. $2 \times 96500 \text{ C}$ deposit $\text{Cu} = 1 \text{ mol} = 63.5 \text{ g}$

37. (a) $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$

$$E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$$

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$$

$$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74$$

Since Cr^{3+} is having least reducing potential, so Cr is the best reducing agent.