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ELECTROCHEMISTRY

MCQs with One Correct Answer

1. Small quantities of solutions of compounds TX, TY and TZ are put into separate test tubes containing X, Y and Z solution. TX does not react with any of these. TY reacts with both X and Z. TZ reacts with X. The decreasing order of state of oxidation of the anions X^-, Y^-, Z^- is
   (a) Y^-, Z^-, X^- (b) Z^-, X^-, Y^-
   (c) Y^-, X^-, Z^- (d) X^-, Z^-, Y^-

2. Following cell has EMF 0.7995V.
   $Pt \mid H_2\,(1\text{ atm}) \mid HNO_3\,(1M) \parallel AgNO_3\,(1M) \mid Ag$
   If we add enough KCl to the Ag cell so that the final Cl^- is 1M. Now the measured emf of the cell is 0.222V. The K_{sp} of AgCl would be –
   (a) $1 \times 10^{-9.8}$ (b) $1 \times 10^{-19.6}$
   (c) 2×10^{-10} (d) 2.64×10^{-14}

3. $Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$ $E° = 0.13$ V
   $Br_2 + 2e^- \longrightarrow 2Br^-$ $E° = 1.08$ V
   Calculate K_{eq} for the cell formed by two electrodes
   (a) 10^{41} (b) 10^{32}
   (c) 10^{-32} (d) 10^{-42}

4. The standard reduction potential for Cu^{2+}/Cu is + 0.34. The reduction potential at pH = 14 for the above couple. ($K_{sp}\,Cu(OH)_2 = 1 \times 10^{-19}$) is:
   (a) -0.22 V (b) $+0.22$ V
   (c) -0.44 V (d) $+0.44$ V

5. The equilibrium constant for the disproportionation reaction
   $$2Cu^+(aq) \longrightarrow Cu\,(s) + Cu^{2+}(aq)$$
   at 25°C ($E°Cu^+ / Cu = 0.52V$,
   $E°Cu^{2+} / Cu = 0.16V$) is
   (a) 6×10^4 (b) 6×10^6
   (c) 1.2×10^6 (d) 1.2×10^{-6}

6. The electrode potentials for
   $Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$
   and $Cu^+(aq) + e^- \longrightarrow Cu\,(s)$
   are + 0.15 V and + 0.50, respectively. The value of $E°_{Cu^{2+}/Cu}$ will be :
   (a) 0.500 V (b) 0.325 V
   (c) 0.650 V (d) 0.150 V

7. Calculate ΔG° for the reaction :
   $Cu^{2+}(aq) + Fe\,(s) \rightleftharpoons Fe^{2+}(aq) + Cu\,(s)$
   Given that : $E°_{Cu^{2+}/Cu} = +0.34$ V,
   $E°_{Fe^{2+}/Fe} = -0.44$ V
   (a) 180.55 kJ (b) 140.35 kJ
   (c) –130.15 kJ (d) –150.54 kJ

8. The e.m.f. of the cell Zn | Zn^{2+} (0.01M) | | Fe^{2+} (0.001M) | Fe at 298 K is 0.2905 then the value of equilibrium for the cell reaction is

(a) $e^{\frac{0.32}{0.0295}}$ (b) $10^{\frac{0.32}{0.0295}}$

(c) $10^{\frac{0.26}{0.0295}}$ (d) $10^{\frac{0.32}{0.0591}}$

9. For a cell reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

$$\Delta_r S^\circ_{298} = -0.32\ kJ/K.$$

What is the value of $\Delta_r S^\circ_{298}(H_2O, l\ ?)$

Given :

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

$$E^\circ = 1.23\ V$$

(a) – 285.07 kJ/mol (b) – 570.14 kJ/mol

(c) 285.07 kJ/mol (d) None of these

10. If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4 cm^{-1}, then its molar conductance in $ohm^{-1}\ cm^2\ mol^{-1}$ is

(a) 10^2 (b) 10^4

(c) 10 (d) 10^3

11. When electric current is passed through acidified water, 112 mL of hydrogen gas at STP collected at the cathode in 965 seconds. The current passed in amperes is

(a) 1.0 (b) 0.5

(c) 0.1 (d) 2.0

12. $\Lambda_{ClCH_2COONa} = 224\ ohm^{-1}cm^2 g\ eq^{-1}$,

$\Lambda_{NaCl} = 38.2\ ohm^{-1}cm^2 g\ eq^{-1}$,

$\Lambda_{HCl} = 203\ ohm^{-1}cm^2 g\ eq^{-1}$,

What is the value of Λ_{ClCH_2COOH}

(a) 288.5 $ohm^{-1}cm^2 g\ eq^{-1}$

(b) 289.5 $ohm^{-1}cm^2 g\ eq^{-1}$

(c) 388.8 $ohm^{-1}cm^2 g\ eq^{-1}$

(d) 59.5 $ohm^{-1}cm^2 g\ eq^{-1}$

13. Equivalent conductance at infinite dilution, λ° of NH_4Cl, NaOH and NaCl are 128.0, 217.8 and 109.3 $ohm^{-1}\ cm^2\ eq^{-1}$ respectively. The equivalent conductance of 0.01 N NH_4OH is 9.30 $ohm^{-1}\ cm^2\ eq^{-1}$, then the degree of ionization of NH_4OH at this temperature would be

(a) 0.04 (b) 0.1

(c) 0.39 (d) 0.62

14. Dissociation constant of a weak acid (HA) in terms of Λ_m^∞ and Λ_m is:

(a) $K_a = \frac{c\Lambda_m^\infty}{(\Lambda_m - \Lambda^\infty})$

(b) $K_a = \frac{c\Lambda_m^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m})$

(c) $K_a = \frac{c(\Lambda_m^\infty)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m})$

(d) None of these

15. Given the ionic equivalent conductivities for the following ions:

$\lambda^\circ_{eq}\ K^+ = 73.5\ cm^2\ ohm^{-1}\ eq^{-1}$

$\lambda^\circ_{eq}\ Al^{3+} = 149\ cm^2\ ohm^{-1}\ eq^{-1}$

$\lambda^\circ_{eq}\ SO_4^{2-} = 85.8\ cm^2\ ohm^{-1}\ eq^{-1}$

The Λ°_{eq} for potash alum ($K_2\ SO_4.\ Al_2(SO_4)_3.\ 24H_2O$) is

(a) 215.92 (b) 348.3

(c) 368.2 (d) 108.52

16. On passing a current of 1.0 ampere for 16 min and 5 sec through one litre solution of $CuCl_2$, all copper of the solution was deposited at cathode. The strength of $CuCl_2$ solution was (Molar mass of Cu= 63.5; Faraday constant = 96500 $Cmol^{-1}$)

(a) 0.01 N (b) 0.01 M

(c) 0.02 M (d) 0.2 N

17. Given the following molar conductivities at 25°C:, HCl, 426Ω^{-1} cm^2mol^{-1}; NaCl, 126Ω^{-1} $cm^2\ mol^{-1}$; NaC (sodium crotonate), 83 Ω^{-1} cm^2mol^{-1}. What is the dissociation constant of crotonic acid, if the conductivity of a 0.001 M crotonic acid solution is $3.83 \times 10^{-5}\ \Omega^{-1}cm^{-1}$?

(a) 10^{-5} (b) 1.11×10^{-5}

(c) 1.11×10^{-4} (d) 0.01

18. A lead storage battery containing 5.0 L of (1N) H_2SO_4 solution is operated for 9.65×10^5 s with a steady current of 100 mA. Assuming volume of the solution remaining constant, normality of H_2SO_4 will

(a) remain unchanged (b) increases by 0.20
(c) increase by unity (d) decrease by 0.40

19. In an electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, the amount of copper deposited on the cathode of the second cell and magnitude of the current in amperes is.

(1 faraday = 96,500 coulombs)

(a) 4.95 g, 0.8 A (b) 5.5 g, 0.9 A
(c) 4.76 g, 0.8 A (d) 5.85 g, 0.5 A

20. For the electrochemical cell shown below

$\mathrm{Pt\,|\,H_2}\,(p = 1\text{ atm})\,|\,\mathrm{H^+}\,(\text{aq.}, x\text{ M})\,|$
$|\,\mathrm{Cu^{2+}}\,(aq., 1.0\text{ M})\,|\,\mathrm{Cu}(s)$

The potential is 0.49 V at 298 K. The pH of the solution is closest to:

[Given, standard reduction potential, E° for Cu^{2+}/Cu is 0.34 V.
Gas constant, R is 8.31 J K^{-1} mol^{-1}
Faraday constant, F is 9.65×10^4 J V^{-1} mol^{-1}]

(a) 1.2 (b) 8.3
(c) 2.5 (d) 8.2

Numeric Value Answer

21. What is the standard electrode porential for the reduction of HClO?

$$\mathrm{HClO(aq) + H^+(aq) + 2e^- \longrightarrow Cl^-(aq) + H_2O(l)}$$

Given : $\mathrm{Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-}$, $E^\circ = 0.41$ V

$$\mathrm{HClO(aq) + H^+(aq) + 2Cr^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + Cl^-(aq) + H_2O(l)}, E^\circ = 1.80$$

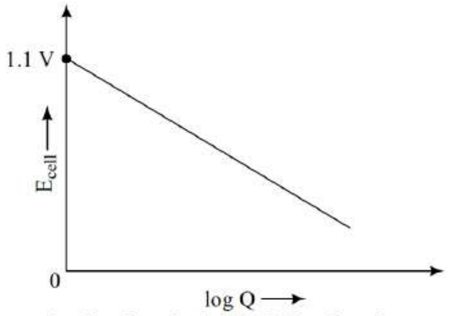
22. What is the potential of an electrode (in V) which originally contained 0.1 M NO_3^- and 0.4 M H^+ and which has been treated by 80% of the cadmium necessary to reduce all the NO_3^- to NO(g) at 1 bar?

Given : $\mathrm{NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O}$;
$E^\circ = 0.96$ V; log 2 = 0.3

23. On passing current through two cells, connected in series containing solution of $AgNO_3$ and $CuSO_4$, 0.18 g of Ag is deposited. The amount of the Cu (in g) deposited is:

24. $E^o_{cell} = 0.74$ V for the cell,
$\mathrm{Cr\,|\,Cr^{3+}\,(1\,M)\,||\,H^+\,(1\,M)\,|\,Pt\,(H_2)\,(1\,bar)}$ and
$E^o_{cell} = 0.80$ V for the cell $\mathrm{(1\,bar)\,Pt\,(H_2)\,|\,H^+\,(1\,M)\,||\,Ag^+\,(1\,M)\,|\,Ag}$
What is the value of cell EMF for the cell
$\mathrm{Ag\,|\,Ag^+\,(0.1\,M)\,||\,Cr^{3+}\,(0.1\,M)\,|\,Cr}$?

25. For Daniell's cell, the reaction quotient is Q. A variation of E_{cell} with log Q has been plotted. At start, the molar concentration of $CuSO_4$ and $ZnSO_4$ are equal. When concentration of Zn^{2+} increases to 1.5 mol/L, the cell EMF becomes 1.07 V. What is the value of $[Cu^{2+}]$ at this point. Take 2.303 RT/F = 0.06



26. For a hydrazine fuel cell, following data are given at 298 K:

$E^o_{N_2H_4/N_2} = -0.9$ V, $E^o_{\frac{1}{2}O_2/H_2O} = +1.23$ V

Assuming 60% efficiency, what is the maximum amount of energy (in KJ) that can be obtained?

27. During discharging of lead storage battery, the density of 38% H_2SO_4 (w/w) fell from 1.274 g/mL to 1.2 g/mL of 19.6 % (w/w) H_2SO_4. What is the number of faradays that have been exchanged during the discharging process? (vol. of H_2SO_4 in lead storage battery = 2.36 L)

28. The photoelectric current from Na (work function, $w_0 = 2.3$ eV) is stopped by the output voltage of the cell

$Pt(s)|H_2(g, 1\text{ bar})|HCl(aq., pH = 1)|AgCl(s)|Ag(s)$.

The pH of aq. HCl required to stop the photoelectric current from $K(w_0 = 2.25\text{ eV})$, all other conditions remaining the same, is __________ $\times 10^{-2}$ (to the nearest integer).

Given,

$$2.303\frac{RT}{F} = 0.06\text{ V};\ E^0_{AgCl|Ag|Cl^-} = 0.22\text{ V}$$

29. For an electrochemical cell

$Sn(s)|Sn^{2+}\ (aq,\ 1M)\ ||Pb^{2+}\ (aq,\ 1M)|Pb(s)$ the ratio $\frac{[Sn^{2+}]}{[Pb^{2+}]}$ when this cell attains equilibrium is ________.

30. When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of *p*-amino-phenol (in g) produced is _______.

ANSWER KEY																			
1	(a)	**4**	(a)	**7**	(d)	**10**	(d)	**13**	(a)	**16**	(a)	**19**	(c)	**22**	(0.84)	**25**	(0.15)	**28**	(142)
2	(a)	**5**	(c)	**8**	(b)	**11**	(a)	**14**	(b)	**17**	(b)	**20**	(c)	**23**	(0.0529)	**26**	(76.43)	**29**	(2.15)
3	(b)	**6**	(b)	**9**	(a)	**12**	(c)	**15**	(a)	**18**	(d)	**21**	(1.39)	**24**	(1.5)	**27**	(6)	**30**	(9.81)

Hints & Solutions

CHAPTER 17

Electrochemistry

1. **(a)** Oxidising tendency $\propto \frac{1}{\text{Electrode potential}}$

$TX \longrightarrow$ No reaction

$TY \longrightarrow X, Z$

$TZ \longrightarrow X$

$\Rightarrow$ order of electrode potential is

$TY < TZ < TX$

$\Rightarrow$ Order of oxidation of the anion is

$Y^- > Z^- > X^-$

2. **(a)** $2Ag^+ + H_2 \longrightarrow 2H^+ + 2Ag$

$$E = E^\circ - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2} \times [Ag^+]^2}$$

$$0.222 = 0.7995 - \frac{0.0591}{2}\log\frac{1}{[Ag^+]^2}$$

$[Ag^+] = 10^{-9.8}$

$K_{sp} = [Ag^+][Cl^-] = (10^{-9.8}) \times (1) = 10^{-9.8}$

3. **(b)** $Sn^{4+} + 2e^- \longrightarrow Sn^{2+};\ E^\circ = 0.13V$

$Br_2 + 2e^- \longrightarrow 2Br^-;\ E^\circ = 1.08V$

E° value shows Br_2 has higher reduction potential.

Hence

$E_{cell} = E_{Br_2/Br^-} - E_{Sn^{+4}/Sn^{+2}}$

$= 1.08 - 0.13 = 0.95$ V

Now $-\Delta G = nF\,E_{cell}$

$n = 2, F = 96500$

$-\Delta G = 2 \times 96500 \times 0.95$ kJ / mol.

Also, $\Delta G = -2.303\,RT\log K_{eq}$

$$\log K_{eq} = -\frac{\Delta G}{2.303 \times R \times T}$$

$$= \frac{-(-2 \times 96500 \times 0.95)}{2.303 \times 8.314 \times 298} = 32.13$$

$K_{eq} = \text{antilog } 32.682 \approx 10^{32}$

4. **(a)** When pH = 14 $[H^+] = 10^{-14}$ and $[OH^-] = 1M$

$K_{sp} = [Cu^{2+}][OH^-]^2 = 10^{-19}$

$$\therefore\quad [Cu^{2+}] = \frac{10^{-19}}{[OH^-]^2} = 10^{-19}$$

The half cell reaction

$Cu^{2+} + 2e^- \longrightarrow Cu$

$$E = E^\circ - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.059}{2}\log\frac{1}{10^{-19}} = -0.22\text{ V}$$

5. **(c)** The reaction

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

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{1}\log\frac{[Cu^{2+}]}{[Cu^+]^2}$$

At equilibrium $E_{cell} = 0$

$\therefore\quad E^\circ_{cell} = 0.059\log K_{eq}$

or, $\log K_{eq} = \frac{0.52 - 0.16}{0.059}$

$\therefore\quad K_{eq} = 1.2 \times 10^6$

6. **(b)** $Cu^{2+} + 1e^- \longrightarrow Cu^+$

$E_1^\circ = 0.15V; \Delta G_1^\circ = -n_1E_1^\circ F$

$Cu^+ + 1e^- \longrightarrow Cu$

$E_2^\circ = 0.50V; \Delta G_2^\circ = -n_2E_2^\circ F$

$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2$

$-nE^\circ F = -1\; n_1 E_1^{o} F + (-1)\; n_2 E_2^{o} F$

$-nE^\circ F = -1\;(n_1 E_1^{o} F + n_2 E_2^{o} F)$

$$E^\circ = \frac{n_1E_1^{o} + n_2E_2^{o}}{n} = \frac{0.15\times1+0.50\times1}{2}$$

$\Rightarrow 0.325$

7. **(d)** The cell reactions are :

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

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

We know that :

$\Delta G^\circ = -nF\ E^\circ_{cell}\ ;\ n = 2$ mol

$E^\circ_{cell} = [E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Fe^{2+}/Fe)}]$

$= (+0.34\ V) - (-0.44\ V) = +0.78\ V$

$F = 96500\ C\ mol^{-1}$

$\therefore\ \Delta G^\circ = -nFE^\circ_{cell}$

$= -(2\ mol)\times(96500\ C\ mol^{-1})\times(+0.78\ V)$

$= -150540\ CV = -150540\ J\ \ (\because\ 1\ CV = 1\ J)$

$= -150.54$ kJ

8. **(b)** For this cell, reaction is;

$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

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

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

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

$$\log K_{eq} = \frac{0.32\times2}{0.0591} = \frac{0.32}{0.0295}$$

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

9. **(a)** We know

$2H_2(g) \longrightarrow 4H^+ + 4e^-;\ E = 0.0\ V$

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l);\ E = 1.23\ V$

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l);\ E^\circ_{cell} = 1.23\ V$

$\Delta G^\circ_{298} = -nFE^\circ = -4\times96500\times1.23 = -474.78$ kJ

$\Delta_f H^\circ_{298} = \Delta_r G^\circ_{298} + T.\Delta_r S^\circ_{298}$

$= (-474.78) + 298\times(-0.32)$

$= -570.14$ kJ/mol

$\therefore\ \ \Delta_f H^\circ_{298} = -285.07$ kJ / mol

10. **(d)** Molarity = 0.01 M ; Resistance = 40 ohm;

Cell constant $\frac{l}{A} = 0.4\,cm^{-1}$.

Specific conductivity (κ)

$$= \frac{\text{cell constant}}{\text{resistance}} = \frac{0.4}{40} = 0.01\ ohm^{-1}\ cm^{-1}$$

$$\text{Molar conductance } (\wedge_m) = \frac{1000\kappa}{\text{Molarity}}$$

$$= \frac{1000\times0.01}{0.01} = 10^3\ ohm^{-1}\ cm^2\ mol^{-1}$$

11. **(a)** $2H^+ + 2e^- \longrightarrow H_2$

$$E_H\,(\text{Eq. wt}) = \frac{2}{2} = 1\ g$$

$$= \frac{22400}{2} = 11200\ mL\ (STP)$$

$$\text{Total charge passed} = \frac{96500\times112}{11200} = 965$$

$Q = It = 965$

$$I = \frac{965}{965} = 1\ amp.$$

12. **(c)** $ClCH_2COONa + HCl \rightarrow ClCH_2COOH + NaCl$

$\Lambda_{ClCH_2COONa} + \Lambda_{HCl} = \Lambda_{ClCH_2COOH} + \Lambda_{NaCl}$

$224 + 203 = \Lambda_{ClCH_2COOH} + 38.2$

$\Lambda_{ClCH_2COOH} = 427 - 38.2$

$= 388.8\ ohm^{-1}cm^2 g\ eq^{-1}$

13. **(a)** $\Lambda^\infty_{eq}(NH_4OH) = \Lambda^\infty_{eq}(NH_4Cl) + \Lambda^\infty_{eq}(NaOH) - \Lambda^\infty_{eq}(NaCl)$

$= 129.8 + 217.8 - 109.3 = 238.3\ ohm^{-1}cm^2eq^{-1}$

$$\alpha = \frac{\Lambda_{eq}}{\Lambda^\infty_{aq}} = \frac{9.30}{238.3} = 0.04$$

14. **(b)** $$\underset{c(1-\alpha\ )}{HA(aq)} \rightleftharpoons \underset{c\alpha}{H^+(aq)} + \underset{c\alpha}{A^-(aq)}$$

$$K_a = \frac{c\alpha^2}{1-\alpha};\ \text{where } \alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

$$\therefore \quad K_a = \frac{c\left(\frac{\Lambda_m}{\Lambda_m^\infty}\right)^2}{\left(1-\frac{\Lambda_m}{\Lambda_m^\infty}\right)}$$

$$= \frac{c\Lambda_m^2}{\Lambda_m^\infty\left(\Lambda_m^\infty - \Lambda_m\right)}$$

15. **(a)** (Eq. = Charge on the ion/Total charge)

$$[K^+] = \frac{1}{8}\text{ mole} \times 2 = \frac{1}{4}\text{ mole} = \frac{1}{4}\text{ Eq.}$$

$$[Al^{3+}] = \frac{6}{8} = \frac{3}{4}\text{Eq.}$$

$$[SO_4^{2-}] = \frac{8}{8} = 1\text{ Eq.}$$

$$\Lambda_{eq}{}^\circ\ K_2SO_4.Al_2(SO_4)_3.24H_2O$$
$$= \lambda_{eq}{}^\circ(K^+) + \lambda_{eq}{}^\circ(Al^{3+}) + \lambda_{eq}{}^\circ(SO_4{}^{2-})$$
$$= \frac{1}{4} \times 73.5 + 149 \times \frac{3}{4} + 85.8 \times 1$$
$$= 18.375 + 111.75 + 85.8 = 215.92$$

16. **(a)** By Faraday's Ist law of electrolysis,

$$\frac{W}{E} = \frac{Q}{96500} \qquad (\text{where } Q = it = \text{charge of ion})$$

We know that no. of gram equivalent

$$= \frac{W}{E} = \frac{it}{96500} = \frac{1\times965}{96500} = \frac{1}{100}$$

(where i = 1 A, t = 16 × 60 + 5 = 965 sec.)

Since, we know that

$$\text{Normality} = \frac{\text{No. of gram equivalent}}{\text{Volume (in litre)}} = \frac{\frac{1}{100}}{1}$$

=0.01 N

17. **(b)** The molar conductivity of the dissociated form of crotonic acid is

$$\Lambda_m(HC) = \Lambda_m(HCl) + \Lambda_m(NaC) - \Lambda_m(NaCl)$$
$$= (426 + 83 - 126)\ \Omega^{-1}\ cm^2mol^{-1}$$
$$= 383\ \Omega^{-1}\ cm^2mol^{-1}$$

The molar conductivity of HC,

$$\Lambda_m(HC) = \frac{\kappa}{C} = \frac{3.83\times10^{-5}\Omega^{-1}cm^{-1}}{0.001}\times1000$$
$$= 38.3\ \Omega^{-1}\ cm^2mol^{-1}$$

The degree of dissociation,

$$\alpha = \frac{\Lambda_m(HC)}{\Lambda_m^\infty(HC)} = \frac{\left(38.3\Omega^{-1}cm^2mol^{-1}\right)}{\left(383\Omega^{-1}cm^2mol^{-1}\right)} = 0.1$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{\left(10^{-3}\right)(0.1)^2}{1-0.1} = 1.11\times10^{-5}$$

18. **(d)**

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

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

The reaction indicates that 2 moles of H_2SO_4 corresponds to 2 × 96500 C and 2 mol H_2SO_4 $\equiv$ 4 equiv. of H_2SO_4.

2 × 96500 C consumed 4 equiv. of H_2SO_4

and $100\times10^{-3}\ \times\ 9.65\times10^5$ C consumed

$$= \frac{4\times100\times10^{-3}\times9.65\times10^5}{2\times96500} = 2\text{ equiv. } H_2SO_4$$

$$\therefore \quad \text{Decrease in normality} = \frac{2}{5} = 0.40$$

19. **(c)** Gold deposited in the first cell = 9.85 g

At. wt. of Gold = 197, Oxidation number of gold = +3

$$\text{Eq. Wt. of Gold} = \frac{197}{3}$$

W = Zit

(where W stands for the weight of ions deposited, i for current and t for time and Z for electro-chemical equivalent of the electrolyte.)

∵ Charge required to deposit 1 g eq. of gold = 1F = 96,500 C

∴ Charge required to deposit 9.85 g of gold or

$$\frac{9.85}{197/3}\text{ g eq. of gold} = \frac{96{,}500\times9.85\times3}{197}\text{ C}$$

= 14475 C

According to Faraday's second law,

$$\frac{\text{Wt. of Cu}}{\text{Eq. wt. of Cu}} = \frac{\text{Wt. of Gold}}{\text{Eq. wt. of Gold}}$$

$\Rightarrow$ Wt. of Cu deposited

$$= \frac{9.85 \times 3}{197} \times \frac{63.5}{2} = 4.76\,\text{g}$$

$$\text{Current} = \frac{Q}{t} = \frac{14475}{5 \times 3600}\ \text{A} = \frac{193}{240}\ \text{A} = 0.80\,\text{A}$$

20. **(c)** $\mathrm{Cu^{2+}(aq) + H_2 \rightleftharpoons 2H^+ + Cu(s)}$

For the given electrochemical cell

$\mathrm{Pt \mid H_2}\,(p = 1\ \text{atm}) \mid$

$\mathrm{H^+}$ (aq. xM) $\|$ $\mathrm{Cu^{2+}}$ (aq. 1.0 M) $\mid$ Cu(s)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\mathrm{H^+}]^2}{[\mathrm{Cu^{2+}}]}$$

$$0.49 = 0.37 - \frac{0.0591}{2} \log \frac{x^2}{1}$$

$$0.49 = 0.37 - \frac{0.0591}{2} \times 2 \log x$$

$0.15 = -0.0591 \times \log x$

$2.54 = -\log x$

Also, $-\log[\mathrm{H^+}] = \text{pH}$

$\therefore\ \text{pH} = -\log x$

$\Rightarrow\ \text{pH} = 2.54 \approx 2.5$

21. **(1.39)** $\mathrm{Cr^{2+}(aq) \longrightarrow Cr^{3+}\ aq(\ +e^-, E^\circ = 0.41\ V}$ ...(i)

$\mathrm{HClO(aq) + H^+(aq) + 2Cr^{2+}(aq) \longrightarrow}$

$\mathrm{2Cr^{3+}(aq) + Cl^-\ (aq\ ) + H_2O(l), E^\circ = 1.8V}$ ...(ii)

[Reaction (i)] $\times -2$ + [Reaction (ii)] we get.

$$\mathrm{HClO(aq) + H^+(aq) + 2e^- \longrightarrow Cl^-(aq) + H_2O(l)}$$

$$\Delta G^\circ = -2FE^\circ - 2(-1 \times FE^\circ)$$

$$-2FE^\circ = -2F(1.8) + 2F(0.41)$$

$E^\circ = +1.8 - 0.41 = 1.39\ \text{V}$

22. **(0.84)** After addition of Cd and its oxidation into $\mathrm{Cd^{2+}}$.

$$\mathrm{NO_3^-(aq) + 4H^+\ (aq\ ) + 3e^- \longrightarrow NO(g) + 2H_2O(l)}$$

$0.1 - x \quad 0.4 - 4x;$

where $x = 0.08$

$[\mathrm{NO_3^-}]$ remaining $= 0.02$ M; $[\mathrm{H^+}]$ remaining $= 0.08$M

$$E_{\mathrm{NO_3^-|NO}} - E^\circ_{\mathrm{NO_3^-|NO}} - \frac{0.0591}{3} \log \frac{1}{[\mathrm{NO_3^{0-}}][\mathrm{H^+}]^4}$$

$$= 0.96 - \frac{0.0591}{3} \log \frac{1}{(0.02)(0.08\ ^4)} = 0.84\ \text{V}$$

23. **(0.0529)** Using Faraday's second law of electrolysis,

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equ. wt. of Cu}}{\text{Equ. wt. of Ag}}$$

$$\Rightarrow \frac{w_{\text{Cu}}}{0.18} = \frac{63.5}{2} \times \frac{1}{108}$$

$$\Rightarrow w_{\text{Cu}} = \frac{63.5 \times 18}{2 \times 108 \times 100} = 0.0529\ \text{g.}$$

24. **(1.5)**

For the cell:

(anode) (cathode)

$\mathrm{Cr \mid Cr^{3+}}$ (1 M) $\|$ $\mathrm{H^+}$ (1 M) $\mid$ Pt $\mathrm{(H_2)}$ (1 bar)

$$E^\circ_{\text{cell}} = E^\circ_{\mathrm{H^+/H_2}} - E^\circ_{\mathrm{Cr^{3+}/Cr}}$$

$$0.74 = 0 - E^\circ_{\mathrm{Cr^{3+}/Cr}}$$

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

For the cell:

(anode) (cathode)

(1 bar) Pt $\mathrm{(H_2)}$ $\mid$ $\mathrm{H^+}$ (1 M) $\|$ $\mathrm{Ag^+}$ (1 M) $\mid$ Ag

$$E^\circ_{\text{cell}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}}$$

$$0.80 = E^\circ_{\mathrm{Ag^+/Ag}} - 0$$

$$E^\circ_{\mathrm{Ag^+/Ag}} = +0.80\ \text{V}$$

For the cell:

(anode) (cathode)

$\mathrm{Ag \mid Ag^+}$ (0.1 M) $\|$ $\mathrm{Cr^{3+}}$ (0.1 M) $\mid$ Cr

Reduction at cathode:

(i) $\mathrm{Cr^{3+} + 3e^- \rightarrow Cr};\ E^\circ_{\mathrm{Cr^{3+}/Cr}} = -0.74\ \text{V}$

Oxidation at anode:

(ii) $\mathrm{Ag \rightarrow Ag^+ + e^-};\ E^\circ_{\mathrm{Ag^+/Ag}} = +0.80\ \text{V}$

eq. (i) + 3 × eq. (ii)

$Cr^{3+} + 3\,Ag \rightarrow Cr + 3\,Ag^{+}; n = 3$

$$E^{o}_{cell} = E^{o}_{Cr^{3+}/Cr} - E^{o}_{Ag^{+}/Ag}$$

$$E^{o}_{cell} = -0.74 - 0.80 = -1.54\ V$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Ag^{+}]^{3}}{[Cr^{3+}]}$$

$$= -1.54 - \frac{0.06}{3}\log\frac{(0.1)^{3}}{(0.1)} = -1.54 - \frac{0.06}{3}\times(-2)$$

$$= -1.5\ V$$

25. **(0.15)**

Cell reaction for Daniell's cell:

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

Reaction quotient $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

At start, $Q = 1$ as $[Zn^{2+}] = [Cu^{2+}]$

also $\log Q = 0$ at point O for $Q = 1$

This is the maximum EMF, the cell can generate. As the reaction proceeds, $[Zn^{2+}]$ will increase and $[Cu^{2+}]$ will decrease. Thus, the value of Q will increase and the cell EMF will decrease.

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.07\ V,\ E^{o}_{cell} = 1.10\ V, n = 2$$

$$1.07 = 1.10 - \frac{0.06}{2}\log\frac{1.5}{[Cu^{2+}]}$$

$$0.03 = 0.03\log\frac{1.5}{[Cu^{2+}]}$$

$$\log\frac{1.5}{[Cu^{2+}]} = 1$$

$$\Rightarrow \quad \frac{1.5}{[Cu^{2+}]} = 10$$

$$\Rightarrow \quad [Cu^{2+}] = 0.15\ mol/L$$

26. **(76.43)**

Reduction at cathode:

$$\overset{o}{O}_2 \rightarrow 2H_2\overset{-2}{O}$$

$$O_2 + 4\,H^{+} + 4e^{-} \rightarrow 2\,H_2O,\ E^{o} = +1.23\ V$$

Oxidation at anode:

$$\overset{-2}{N}_2H_4 \rightarrow \overset{o}{N}_2$$

$$N_2H_4 \rightarrow N_2 + 4\,H^{+} + 4e^{-}\ \overset{o}{E}, = -0.9\ V$$

Overall cell reaction:

$N_2H_4\,(aq) + O_2(g) \rightarrow N_2(g) + 2H_2O\ (l); n = 4$

$$E^{o}_{cell} = E^{o}_{\frac{1}{2}O_2/H_2O} - E^{o}_{N_2/N_2H_4}$$

$$= (1.23 - 0.9)V = +0.33\ V$$

Maximum available potential $E^{o}_{cell} = 0.33\ V$

Maximum amount of energy $= -\Delta G$

$$= nF\,E^{o} = 4\times 96500\times 0.33\ J = 1{,}27{,}380\ J$$

Assuming 60% efficiency

$$W_{max} = 127380\times\frac{60}{100}\ J = 76.43\ KJ$$

27. **(6)** Molecular mass of $H_2SO_4 = 98$ g/mol

Molarity of initial solution

$$= \frac{\%W/W\times 10\times d}{\text{moleculer mass}} = \frac{38\times 10\times 1.274}{98} = 4.94$$

Molarity of final solution

$$= \frac{19.6\times 10\times 1.2}{98} = 2.4\ M$$

Decrease in amount of H_2SO_4 during this discharging process

$= (4.94 - 2.4)\times 98\times 2.36\ g = 6\times 98\ g$

Overall reaction during discharging

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \rightarrow$
$2PbSO_4(s) + 2H_2O(l); n = 2$

$\therefore$ For 1 mole of H_2SO_4 +1 F is required

6×98 g $H_2SO_4 = 6$ moles of H_2SO_4

Thus, number of Faradays required = 6

28. **(142)**

Sodium metal :

$E = E_0 + (KE)_{max};\ E^{0}_{cell} = 0.22\ V$

Cell reaction

Cathode : $AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{-}(aq)$

Anode : $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

Overall :

$$AgCl(s) + \frac{1}{2}H_2(g) \longrightarrow Ag(s) + H^+(aq) + Cl^-(aq)$$

$$E_{cell} = E^0_{cell} - \frac{0.06}{1}\log[H^+][Cl^-]$$

$$E_{cell} = 0.22 - \frac{0.06}{1}\log[10^{-1}][10^{-1}]$$

$$= 0.22 + 0.12 = 0.34\ V$$

$(KE)_{max} = E_{cell} = 0.34\ eV$

So, $E = 2.3 + 0.34 = 2.64\ eV$ = Energy of photon incident

For potassium metal :

$E = E_0 + (KE)_{max}$

$2.64 = 2.25 + (KE)_{max}$

$(KE)_{max} = 0.39 = E_{cell}$

Cell reaction

Cathode : $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$

Anode : $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

Overall : $AgCl(s) + \frac{1}{2}H_2(g) \longrightarrow$

$$Ag(s) + H^+(aq) + Cl^-(aq)$$

$$E_{cell} = E^0_{cell} - \frac{0.06}{1}\log[H^+][Cl^-]$$

$0.39 = 0.22 - 0.06\log[H^+]^2$

$0.39 = 0.22 - 0.12\log[H^+]$

$0.17 = 0.12 \times pH$

$pH = 17/12 = 1.4166 \simeq 1.42 = 142 \times 10^{-2}$

29. **(2.15)**

At equilibrium state $E_{cell} = 0$; $E^0_{cell} = 0.01\ V$

$$Sn + Pb^{2+} \longrightarrow Sn^{2+} + Pb$$

$$E = E^0_{cell} - \frac{0.06}{n}\log\frac{[P]}{[R]}$$

$$0 = 0.01 - \frac{0.06}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$$-0.01 = -\frac{0.06}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]}$$

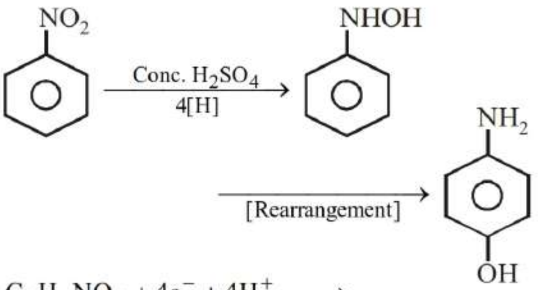
$$\frac{1}{3} = \log\frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$$\frac{[Sb^{2+}]}{[Pb^{2+}]} = 10^{1/3} = 2.15$$

30. **(9.81)** 9.65 ampere current was passed for 1.0 hour (3600 seconds)

Number of moles of electrons passed

$$= \frac{I(A) \times t(s)}{96500} = \frac{9.65A \times 3600s}{96500} = 0.36\ \text{moles}$$



$$C_6H_5NO_2 + 4e^- + 4H^+ \longrightarrow$$

$$p\text{-Aminophenol} + H_2O$$

∵ 4 moles of electrons reduces 1 mole of nitrobenzene to *p*-aminophenol.

∴ 0.36 moles of electrons will reduce $\frac{0.36}{4} = 0.09$ moles of nitrobenzene to *p*-aminophenol.

p-aminophenol molar mass = 109.14 g/mol

Mass of *p*-aminophenol obtained

= 109.14 g/mol × 0.09 mol = 9.81 g