CHEMISTRY

For JEE MAIN + JEE ADVANCED

SOLUTIONS BOOKLET

1. ELECTROCHEMISTRY
2. CHEMICAL KINETICS
3. SURFACE CHEMISTRY
4. BIOMOLECULES & POLYMERS
5. S, P-BLOCK ELEMENTS
6. HYDROGEN COMPOUNDS

HEAD OFFICE : World Tower, 99-Rajpur Road, Dehradun (U.K)
BRANCH OFFICE : GMS Road, Near Ballupur Chowk, Dehradun (U.K)
FOUNDATION WING : Imperial Tower, 101-A, Rajpur Road, Dehradun (U.K)
Give Missed Call : 7669-400-400 **Call at : 8881-400-400**

www.aviral.ac.in
www.aviralclasses.com
www.aviralstore.com

JEE-SERIES

CONTENTS

S.No.	Chapter Name	Page No.
	(SOLUTIONS - EXERCISE)	
1.	Electrochemistry	**3 - 25**
2.	Chemical Kinetics	**26 - 48**
3.	Surface Chemistry	**49 - 52**
4.	Biomolecules & Polymers	**53 - 66**
5.	s, p-Block Elements	**67 - 69**
6.	Hydrogen Compounds	**69**

MAINS+ADVANCED

TOPIC

ELECTROCHEMISTRY

SOLUTIONS

ELECTROCHEMSITRY

Exercise-I

1. **(C)**
In this Cl^- will oxidise to give Cl_2 ,Na^+ reduction potential has lower potential than water reduction polenlid so water will reduce to give H_2.
(C) NaCl

2. **(A)**
As electron flows from anode to a cthode and so current flows from cathode to anode in outer drcuit

3. **(B)**
Water oxidation at anode can be represented and SO_4^{2-} can't be discharged so
$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
so ion which will be discharged at anode will be OH^-.

4. **(A)**
Since to deposit 1 mole of aluminium 3 columb of electricity is required, as the alency of silver is + 1 so 3 mole of silver will be deposited by 3C of electricity

5. **(C)**
At cathode
$4H_2O + 4e^- \rightarrow 4H_2 + 4OH^-$
At anode
$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
Thus at cathode we will get H_2 whereas at anode we will get O_2.

6. **(A)**
In electrolysis of a fused salt, the weight deposited on electrode will not depend or temperature.

7. **(C)**
In this Cl^- will oxidise to give Cl_2 Na^+ water reduction potential has higher potential than that of water reduction potential, so water will reduce to give H_2.

8. **(B)**
Cation loses charge at cathode as it gave electron.

9. **(B)**
As reduction will take place at cathode so reaction $Cu^{2+} + 2e \rightarrow Cu$
Will take place at cathode

10. **(B)**
If mercury is used as cathode in the electrolysis of aqueos NaCl solution then the metal is discharged at mercury to from amalgam.

11. **(B)**
$K = 0.3568\ \Omega\ cm^{-1}$
condutance = $0.0268\ \Omega^{-1}$
$K = G \times 1/A$
$0.3568 = 0.0268 \times 1/9$
$13.31\ cm^{-1}$

12. **(B)**
$K = G.\ L/A$
$10^{-3} \times 2.768 = 1/R \times L/A$
$L/A = 228.08 \times 10^{-3}$
$= 0.2281\ cm^{-1}$

13. **(A)**

$$\wedge = \frac{1000 \times K}{M}$$

On decreasing the value of M will increase but increase will be hyberbolic.

14. **(C)**
Higher the dilution higher will be the equivalent conductance

15. $K = G\frac{L}{A}$

$K = \frac{1}{R} \times \frac{L}{A}$

$\frac{1}{100} \times 1$, $K = 10^{-2}\,\Omega^{-1}\,cm^{-1}$

16. **(D)**

$\lambda_m = \frac{K \times 1000}{M}$

$\lambda_m = \frac{0.0110 \times 1000}{0.05}$

$= 220\ S\,cm^2\,mol^{-1}$

17. **(C)**
L/A is cell constant.

$\frac{1.5}{0.75} = 2.0\ cm^{-1}$

18. **(B)**
That electrolyte will be the best electrolyte which has maximum number of ions.

19. **(B)**
gm eq. of H_2 = gm eq. of Cu

$\frac{0.504}{2} \times 2 = \frac{w}{63.5} \times 2$

$W = \frac{63.5 \times 0.50R}{2} = 16.0\ gm$

20. No. of F = $\frac{it}{96500}$ = gm eq of Cu

moles of Cu = $\frac{gm\,eq.of\,Cu}{2}$

moles of Cu = $\frac{2.6 \times 380}{96500 \times 2}$

wt. of Cu = $\frac{2.6 \times 380}{96500 \times 2} \times 63.5$

$= 0.325\ gm$

21. **(B)**
gm equivalent of Al = gm eq. of Cu = gm eq. of Na
3 = 3 = 3
3/3/ = 3/2 = 1
1 : 1.5 : 3

22. **(C)**

gm equivalent = $\frac{8}{96500}$

$0.01 = \frac{8}{96500} = 965\ C$

23. **(B)**
Z = w/it
w in gm
it in columb.
so z = gm/columb

24. **(D)**
Since KCl has the n-factor of 1 so 1 faraday of electricity will liberate one mole of metal from a solution.

25. **(B)**
Since magnesium has the n-factor 2 so the number of faraday rquired to genereate 1 mole of Mg will be 2 .

26. $\frac{1.81 \times 10^{22}}{6.02 \times 10^{23}} = \frac{1}{At.\ mass} \times 2$

rxn. $Mn^{2+} \longrightarrow Mn$
nf = 2

At mass = $\frac{2 \times 6.022 \times 10^{23}}{1.81 \times 10^{22}} = 66.7$

27. Molar ratio
All have the same equivalent

& mole = $\frac{equiv.}{nf.}$

$\Rightarrow$ ratio : $\frac{1}{1}$; $\frac{1}{2}$: $\frac{1}{3}$
$\Rightarrow$ 6 : 3 : 2

28. $\frac{2.1}{7} x = \frac{2.7}{27} \times y = \frac{7.2}{48} \times z$

$\Rightarrow$ ratio $x = \frac{y}{3} = \frac{z}{2}$
If $x = 1 \Rightarrow y = 3, z = 2$

29. Volume : $10 \times 10 \times 10^{-2} = 1\ cm^3$
mass of Cu = 8.94 g

mole of Cu = $\frac{8.94}{63.5}$

EQuivalent of Cu = $\frac{8.94}{63.5} \times 2$

Charge = $\frac{8.94}{63.5} \times 2 \times 96500\ C$
= 27172 C

30. Equivalent of H_2 = Equivalent of O_2

$= \frac{2.4}{22.4} \times 4$

$\Rightarrow$ mole of $H_2 = \frac{2.4}{22.4} \times 4 \times \frac{1}{2}$

Volume of $H_2 = \frac{2.4 \times 2}{22.4} \times 22.4$
= 4.8 L

31. At both electrodes oxidation of Cu & reduction of Cu takes place
Anode $Cu \longrightarrow Cu^{2+}$
Cathode $Cu^{2+} \longrightarrow Cu$
So If 2.5 g deposited at cathode $\Rightarrow$ 2.5 of Cu mass decreased from anode

32. $Mn_3O_4 + 8H_2O + 80H^- \rightarrow 3MnO_4^{2-} + 16H^+ + 16OH^- + 10e^-$
$Mn_3O_4 + 16OH^- \rightarrow 3MnO_4^{2-} + 8H_2O$
nf = 10 $+ 10e^-$

33. Cathode
$2H_2O + 2e^- \rightarrow H_2 + 20H^-$
Anode
$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

34. LiCl (According to S.R.P.)
Cathode
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Anode $2Cl^- \rightarrow Cl_2 + 2e^-$
$2Cl^- \rightarrow Cl_2 + 2e^-$
At cathode $(OH^-) \uparrow$ pOH $\downarrow$ and pH $\uparrow$

35. **(B)**

36. $E_{cell} = E^o - \frac{0.0591}{n} \log Q_{eq.}$
$2H^+ + 2e^- \longrightarrow H_2 \quad E^o = 0$

$Q_{eq.} = \frac{P_{H_2}}{(H^+)^2}$

$E_{cell}\ \frac{-0.0591}{2} \log 100 = -0.0591$
$\Delta E_{cell} = 0.0591$

37. $E^o_{cell} = \frac{0.0591}{2} \log \frac{Sr^{2+}}{Mg^{2+}}$

$= \frac{0.0591}{2} \log (2.69 \times 10^{+12}) = 0.3667$

38. $Ag \longrightarrow Ag^+ + e^-$

$E^o = -0.799 \quad E_{cell} = -0.25$
$E_{cell} = -0.25 \quad E^o_{cell} = -0.799$

$\Rightarrow E_{cell} = E^o_{cell} - \frac{0.0591}{1} \log (Ag^+)$

$-0.25 + 0.799 = -0.0591 \log (Ag^+)$

$\log (Ag^+) = \frac{-0.799 + 0.25}{0.0591}$

$(Ag^+) = 5.13 \times 10^{-10}$
$K_{sp} = (Ag^+)(Cl^-) = 5.13 \times 10^{-10} \times 0.1$
$= 5.13 \times 10^{-11}$

40. Anode
$H_2 \longrightarrow 2H^+ + 2e^-$
Cathode
$2e^- + Cl_2 \rightarrow 2Cl^-$
$H_2 + Cl_2 \rightarrow 2H^+ + 2Cl^-$
$[(H^+)^2 (Cl^-)^2] = K_{eq.}$

$E_{cell} = E^o - \frac{0.0591}{2} \log (H^+)^2 (Cl^-)^2$

$= E^o - 0.0591 \log [H^+] [Cl^-]$

41. $H_2 \rightarrow 2H^+ + 2e^-$
0.4 atm 10^{-1}
$2H^+ + 2e^- \rightarrow H_2$
10^{-2} 0.1 atm

$H_2 + 2H^+ \rightarrow H_2 + 2H^+$
0.4 0.01 0.1 0.1 $E^o = 0$

$E_{cell} = -\frac{0.0591}{2} \log \left(\frac{(0.1)^2 (0.1)}{(0.01)^2 (0.4)} \right)$

$= -0.041$

42. $4e^- + O_2 + 4H^+ \rightarrow 2H_2O\ (\ell)$
$E^o = 1.23\ V$
$2H_2 \rightarrow 4H^+ + 4e^-\ E^o = 0$

$2H_2 + O_2 \rightarrow 2H_2O\quad E^o = 1.23\ V$
$\Delta G^o = -nFE^o$
$= -4 \times 96500 \times 1.23$
$= -474.78\ kg$
$\Delta H^o = -285.5 \times 2\ kJ$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$$

$$= \frac{(-285.5 \times 2) + 474.78}{298} = -0.322$$

43. $2e^- + Cu^{2+} \rightarrow Cu : 0.337$
$Cu^{2+} + e^- \rightarrow Cu^+ : 0.153$
$Cu^+ \rightarrow Cu^{2+} + e^- ; -0.153$

$e^- + Cu^+ \rightarrow Cu$

$$E_{Cu^+/Cu} = \frac{2 \times 0.337 - 1 \times 0.153}{1}$$

$= 0.674 - 0.153$
$= 0.521\ V$

44. CH_3COO^- / CH_3COOH
a b
$pH_1 = pK_a + \log a/b$; $pH_2 = pK_a + \log b/a$

$$E_1 = \frac{-0.0591}{2} \log \frac{1}{[H^+]_1^2}$$

$E_1 = -0.591\ pH_1$; $E_2 = -0.0591\ pH_2$
$E_1 + E_2 = -0.0591\ (pH_1 + pH_2)$
$E_1 + E_2 = -0.0591(2pK_a + \log a/2 + \log b/a)$
$= -0.0591 \times 2pKa$

$$pKa = -\frac{(E_1 + E_2)}{0.118}$$

45. $C = \frac{1}{50}$; $\frac{\ell}{a} = \frac{2.2}{4.4} = \frac{1}{2}$

$$K = \frac{C\ell}{a} = \frac{1}{50} \times \frac{1}{2} = 10^{-2}$$

$$\lambda_m = k \times \frac{1000}{M}$$

$$= 10^{-2} \times \frac{1000}{0.5} = 20S\ cm^2\ mol^{-1}$$
$= 20 \times 10^{-4}\ Sm^2/mol$
$= 0.002\ Sm^2/mol^{-1}$

46. $\alpha = \frac{10}{200} = \frac{1}{20}$

$$[H^+] = C\alpha = 0.1 \times \frac{1}{20} = \frac{1}{200}$$

$$pH = -\log \frac{1}{200} = \log 200 = 2.3$$

47. $K = \frac{1}{x}$

$$\wedge = k\,\frac{1000}{M} = \frac{1}{\lambda} \times \frac{1000}{y} = \frac{1000}{xy}$$

48. $380 \times 10^{-4} \times 10^4\ \frac{Scm^2}{mole} = k \times \frac{1000}{M}$
↓
Molarity of ion

$$1.6 \times 10^{-5} = \frac{x^2}{0.01 - x} \Rightarrow 16 \times 10^{-8}$$
$16 \times 10^{-8} = x^2$
$x = 4 \times 10^{-4}$

$$K = \frac{380 \times M}{1000} = \frac{380 \times 4 \times 10^{-4}}{1000}$$
$= 152 \times 10^{-6}\ Scm^{-1}$
$= 1.52 \times 10^{-2}\ Sm^{-1}$

49. $1.5 \times 10^{-4} \times 10^4 = 9 \times 10^{-8} \times \frac{1000}{N}$
$\Rightarrow N = 6 \times 10^{-5}$

$\Rightarrow M = \frac{6 \times 10^{-5}}{3} = 2 \times 10^{-5}$
↳ n factor
K_{sp} $_{20}$ $= (3S)^2\ (S) = 27S^4 = 27 \times 16 \times 10^-$
$= 432 \times 10^{-20} = 4.32 \times 10^{-18}$

50. $AgA \rightleftharpoons Ag^+ + A^- ; 3 \times 10^{-14}$
$S_1 + S_2 \quad S_1$
$AgB \rightleftharpoons Ag^+ + B^- ; 1 \times 10^{-14}$
$S_1 + S_2 \quad S_2$
$S_1 + S_2 = 2 \times 10^{-7}$; $S_1 = 1.5 \times 10^{-7}$
$S_2 = 0.5 \times 10^{-7}$
$375 \times 10^{-10} = K_{Ag^+} + K_{A^-} + K_{B^-}$

$$= \frac{(\Lambda_{Ag^+})(M_{Ag^+})}{1000} + \frac{(\Lambda_{A^-})(M_{A^-})}{1000} +$$

$$\frac{(\Lambda_{B^-})(M_{B^-})}{1000}$$

$= 60\ (S_1 + S_2) + 80\ S_1 + \Lambda_B - S_2$
After putting value of S_1 & S_2
$\Lambda_{B^-} = 270$

Exercise-II

1. $Pb(s) + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_1(s) + 2H_2O$
H_2SO_4 : consumed
H_2O : produced (volume increases and density decreases)
Anode
$Pb\ (S) + SO_4^{2+} \rightarrow PbSO_4 + 2e^-$
Cathode
$2e^- + 4H^+ + PbO_2 + So_4^{2-} \rightarrow PbSO_4\ (s) + 2H_2O$

2. (A) At anode oxidation of Cu produce Cu^{2+}
(B) At both electrode oxidation or reduction of hydrogen or H^+
(C) At anode
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
(D) Anode
$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

3. Cell reaction
$2H_2O \rightleftharpoons 2H_2 + O_2$

$270\ g\ H_2O = \frac{270}{18}$ mole = 15 mole

equivalent = 15 × 2 = 30 equivalent

(a) O_2 evolved = $\frac{15}{2}$ = 7.5 mole = 7.5 × 22.4 L
= 168 L

(b) Total mole of gas = $15 \times \frac{3}{2} = \frac{45}{2}$
Total volume of gas produced

$= 22.4 \times \frac{45}{2}$ = 504 L

(c) H_2 produced = 30 × 22.4 = 336 L
at cathode current efficilency = 75%
(d) for 30 F electricity consumed

will be = $30 \times \frac{100}{75}$ = 40 F

4. (a) SOP (SO_4^{2-}) = –2.00
SOP (Cl^-) = – 1.36
oxidation of SO_4^{2-} will not take place
(b) SOP (Cl^-) = – 13.6
SOP (I^-) = –0.54
SOP (Br^-) = –1.09
(c) Similarly as (b) option
(d) Br^- can't be reduced further.

5. Cell reaction
Anode
$Ag(s) + Cl^{-1} \rightarrow AgCl\ (s) + e^-$
Cathode
$2H^+ + 2e^- \rightarrow H_2$
$2Ag(s) + 2Cl^- + 2H^+ \rightleftharpoons 2AgCl(s) + H_2$

$$E = E^o - \frac{0.0591}{2} \log \left\{ \frac{P_{H_2}}{[Cl^-]^2[H^+]^2} \right\}$$

$$0.22 = E^o - \frac{0.0591}{2} \log \left[\frac{1}{1 \times 1} \right]$$

$\Rightarrow E^o = 0.22$ V

$$E_{cell} = 0.22 - \frac{0.0591}{2} \log \left\{ \frac{P_{H_2}}{[H^+]^2[Cl^-]^2} \right\}$$

(a) $P_{H_2} = 2 \Rightarrow E_{cell} < 0.22$

(b) $[Cl^-] \uparrow \Rightarrow \log \left\{ \frac{P_{H_2}}{[H^+]^2[Cl^-]^2} \right\}$ = –ve value
$\Rightarrow E_{cell} > 0.22$
(c) $[H^+] \uparrow \Rightarrow E_{cell} > 0.22$
(d) KCl $conc^n \downarrow \Rightarrow [Cl^-] \downarrow$

$$\Rightarrow \log \left\{ \frac{P_{H_2}}{[H^+]^2[Cl^-]^2} \right\} > 0$$

$\Rightarrow E_{cell} < 0.22$

6. $H_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$
0.015 V 0.015 V 0.015 V
mole mole mole

molarity $(CH_3COONa) = \frac{0.015V}{2V} = \frac{0.015}{2}$

$$\Lambda_m^o = 6.3 \times 10^{-4} \times \frac{1000}{\left(\frac{0.015}{2}\right)}$$

$$= \frac{6.3 \times 2}{0.15} = 84$$

7. HgO Cathode ; Zn (anode)
$Zn \rightarrow Zn^{2+} + 2e^-$
$Hg^{2+} + 2e^- \rightarrow Hg$
Cell reaction
$Zn + HgO \rightarrow ZnO + Hg$
No active species in cell reactions
$\Rightarrow$ no change in cell voltage.

8. SRP increases $\Rightarrow$ The tendency to getting reduced increases and the oxidizing power increases.

9. We can add only when the net reaction does not contain any electron [E.P. is an intensive property]

10. **Statement I :** is correct as the n factor of both silver and copper are different so

the gm equivalent of electricity required will be different .

Statement II : It is also correct that atomic weight of siliver and copper are different but statement II is not the reight explanation of I. So answer (B).

11. **Statement I :** is correct beause copper lies at higher position in electrichenical sesier so upper will start deposition in vessel.

Statement II : It is false because copper is at higher position so

Ans (C)

12. **Statement I** is correct

because

$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$

Zinc oxidation takes place and reduction of copper take blake.

Statement II : Is also correct and given values are correct

So Ans. (A)

13. **Statement I :** It is correct as gold has higher reduction potential.

Statement II : It is also correct but not the correct explanation of I.

Ans. (B)

14. **Statement I :** It is correct

$\lambda = KV$

$K = \lambda/V$

thus inversely proportional.

Statement II : It is also correct because number of ions per CC decreases and also correct explation of I.

Ans. (A)

15. **Statement I :** It is correct

Statement II : It is correct but not the correct explanation of above

Ans. (B)

16. **Statement I :** Assolute value can't be calculated it is only calculated W.r.t. hydrogen.

Statement II : It is wrong

Ans (C)

17. $200 = k \times \frac{1000}{0.02}$ for KCl

$k = 4 \times 10^{-3}$

for KCl $k = C \frac{\ell}{A}$

$\Rightarrow 4 \times 10^{-3} = \frac{1}{100} \times \frac{\ell}{A}$

$\frac{\ell}{A} = 0.4$

18. Conductance of $H_2O = \frac{1}{10000} = C$

$k = C \frac{\ell}{A} = \frac{1}{10000} \times 0.4$

$k = 4 \times 10^{-5}$

19. For NaCl $125 = k \times \frac{1000}{M}$

$k = C \frac{\ell}{A}$;

For C

$C_{NaCl} + C_{water} = C_{NaCl(solution)}$

$C + \frac{1}{10000} = \frac{1}{8000}$

$C = \frac{1}{8000} - \frac{1}{10000} = \frac{1}{40000}$

$\Rightarrow k = \frac{1}{40000} \times 0.4 = 1 \times 10^{-5}$

$\Rightarrow 125 = 1 \times 10^{-5} \times \frac{1000}{M} \Rightarrow M = 8 \times 10^{-5}$

Mole of NaCl $= \frac{585}{58.5} = 10$ mole

$\Rightarrow$ Volume $= \frac{10}{8 \times 10^{-5}} = 125000$ L

20. $3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O$] $\times 2$

$Cu \rightarrow Cu^{2+} + 2e^-$] $\times 3$

$8H^+ + 2NO_3^- + 3Cu \rightarrow 2NO + 3Cu^{2+} + 4H_2O$

$E^o_{cell} = 0.96 - 0.34 = 0.62$

$E_{cell} = 0.62 - \frac{0.06}{6} \log \frac{(P_{No})^2 (Cu^{2+})^3}{(NO_3^-)^2 (H^+)^8}$

$= 0.62 - 0.01 \log \frac{10^{-6} \times 10^{-3}}{(1)^2 (1)^8}$

$= 0.62 + 0.01 \times 9 = 0.62 + 0.09$

$= 0.71$ V

21. **C**

22. $\Delta W = -nFE$
$82700 = -3 \times 96500$
Ans. (A)

23. $E = \varepsilon° - \frac{0.591}{n} \log Q.$

ef $KC = Q$
$E = O$
Ans. (C)

24. $\varepsilon = \varepsilon° - \frac{0.591}{n} \log Q.$

(A) i.e. straight line

25. $\varepsilon° = \frac{0.591}{n} \log Ve.$

here n = 2

$0.46 \frac{0.591}{n} \log Ke$

Ans. (A)

26. $\varepsilon° = \frac{0.591}{2} \log Ve$

$1.10 = \frac{0.591}{2} \log Ke$

Ans. (B)

27. (A) At cathode H_2
At anode O_2
(B) At cathode H_2
At anode O_2
(C) At cathode H_2
At anode Cl_2
(D) At cathode Ag
At anode O_2

Exercise-III

1. (a) $2Ag + Cu^{2+} \rightarrow 2Ag^+ + Cu$
(b) $Fe^{2+} \rightarrow Fe^{3+} + e^-$: Anode
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$: Cathode

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

2. (a) $Zn \rightarrow Zn^{2+} + 2e$: Anode
$Ca^{2+} + 2e \rightarrow Cd$: Cathode
$\Rightarrow$ $Zn\ |Zn^{2+}||\ Cd^{2+}\ |\ Cd$
(b) $Ag^+ + e^- \rightarrow Ag$: Cathode
$H_2 \rightarrow 2H^+ + 2e^-$: Anode

$Pt\ |H_2|\ H^+||\ Ag^+\ |\ Ag$

3. $E°_{cell} = E°_{Ce^{4+}/Ce^{3+}} + E°_{Co/Co^{2+}}$

$1.89 = E°_{Co^{4+}/Ce^{3+}} + 0.28$

$E°_{Cu^{4+}/Ce^{3+}} = 1.61$

4. $-0.15 = E°_{Pt^{2+}/Pt} + E°_{Cl^-/Cl_2}$

$-0.15 = 1.20 + E°_{Cl^-/Cl_2}$

$\Rightarrow$ $E°_{Cl^-/Cl_2} = -1.35$

$\Rightarrow$ $E°_{Cl_2/Cl^-} = 1.35$

5. $E°_{Ag/Ag^+} = -0.80$ V

$E°_{H_2/H^+} = 0$

Ox. potential of $E°_{H_2/H^+} > E°_{Ag/Ag^+}$

$\Rightarrow$ $Ag \rightarrow Ag^+ + e^-$ won't take place
Ans. : No.

6. $Cu^{2+} + e^- \rightarrow Cu^{2+}$ $E° = 0.15$ V
....(1)
$Cu^{2+} + 2e^- \rightarrow Cu$ $E° = 0.34$ V
....(2)
Eq^n (2) – (1)
$Cu^+ + e^- \rightarrow Cu$
....(3)
$E° = \frac{(0.34 \times 2) - (0.15)}{1}$
$E° = 0.53$ V
$2Cu^+ \rightarrow Cu + Cu^{2+}$
....(4)
$E°_{disproportion}$
Eq^n (4) = Eq^n (3) – Eq^n (1)
$E°_{disproportion} = 0.53 - 0.15 = 0.38$ V
Ans : Yes

7. $Fe^{2+} + 2e^- \rightarrow Fe$; –0.44 V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$; 0.77 V

$Fe^{3+} + 3e^- \rightarrow Fe$; E^o

$$E^o = \frac{-0.44 \times 2 + 0.77}{3}$$
$E^o = -0.367$

8. $Zn \rightarrow Zn^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
0.1 0.001

$$E = E^o - \frac{0.0591}{2} \log \frac{0.001}{0.1}$$

$$E = E^o - \frac{0.0591}{2} \log \left(\frac{1}{100}\right)$$
$E = 1.1 + 0.0591 = 1.1591$ V

9. $Mg(s) + 2Ag^+ \rightleftharpoons Mg^{2+} + 2Ag$;
$E^o = 2.37 + 0.8 = 3.17$

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

$3.17 = \frac{0.0591}{2} \log keq; \Rightarrow keq = 10^{107.27}$
$\Rightarrow$ Keq = 1.862×10^{107}
$\Delta G^o = -nFE^o$
$= -2 \times 96500 \times 3.17 = -611810$ J
$= -611.81$ J $\Rightarrow$ max. work = 611.81 kJ

10. $M \rightarrow M^{n+} + ne^-$

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

$M(s) + nH^+ \rightarrow M^{n+} + \frac{n}{2} H_2$
$E^o = 0.76$

$$E = E^o - \frac{0.0591}{n} \log \left[\frac{(M^{n+})(P_{H_2})^{n/2}}{[H^+]^n}\right]$$

$$0.81 = 0.76 - \frac{0.0591}{n} \log \left(\frac{0.02 \times (1)^{n/2}}{(1)^n}\right)$$

$$0.81 = 0.76 - \frac{0.0591}{n} \log (0.02)$$
$\Rightarrow$ n = 2

11. $HA \rightleftharpoons H^+ + A^- \Rightarrow x = [H^+] = \sqrt{C \times Ka}$
C – x x x

$$pH = \frac{1}{2} (pKa - \log C) ;$$

$$E = E^o - \frac{0.0591}{1} \log \left[\frac{(H^+)_1}{(H^+)_2}\right]$$

Cell is concentration cell $\Rightarrow E^o = 0$
$E = -0.0591 [\log (H^+)_1 - \log (H^+)_2]$
$= 0.0591 [pH_1 - pH_2]$

$= \frac{1}{2} \times 0.0591 [pKa_1 - pKa_2 - \log C_1 + \log C_2]$

$= \frac{1}{2} \times 0.0591 [5 - 3]$
$= 0.0591$ V

12. $E^o_{cell} = 0.14 - 0.13 = 0.01$V

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log \left[\frac{S_n^{2+}}{Pb^{2+}}\right]$$

$$= 0.01 - \frac{0.0591}{2} \log 10^3$$

$$= 0.01 - \frac{0.0591}{2} \times 3$$
$= -0.07865$ V Ans.
$E_{cell} < 0 \Rightarrow$ Wrong representation.

13. $E = E^o - \frac{0.059}{2} \log [Cu^{2+}]$
$E = 0$

$\Rightarrow E^o = \frac{0.059}{2} \log [Cu^{2+}]$

$\Rightarrow -\frac{0.34 \times 2}{0.059} = \log [Cu^{2+}]$
$\Rightarrow [Cu^{2+}] = 2.98 \times 10^{-12}$

14. $Zn^{2+} = 0.1 \times \frac{20}{100} = 0.02$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.0591}{2} \log \frac{1}{0.02} = -0.81 \text{ V}$$

15. $BrO_3^- + 4H^+ + 4e^- \rightarrow BrO^- + 2H_2O$; 0.54 V ....(1)

$BrO^- + 2H^+ + e^- \rightarrow \frac{1}{2} Br_2 + H_2O$; 0.45 V ....(2)

For resulting reaction E^o_1 =

$$\frac{(0.54 \times 4) + (0.45 \times 1)}{5} = 0.522 \text{ V}$$

$\frac{1}{2} Br_2 + e^- \rightarrow Br^-$; 1.07 ....(1)

After addition of (1) + (2) + (3)

Resulting E^o_2 =

$$\frac{(0.54\times 4)+(0.45)+(1.07)}{6}$$

E^o_2 = 0.613 V

16. $E_{cell} = -\frac{0.0591}{2}\log\left(\frac{0.01}{0.1}\right)$

$= -\frac{0.0591}{2}\log\left(\frac{1}{10}\right)$

$= \frac{0.0591}{2} = 0.0295$ V

17. $E_{cell} = -\frac{0.0591}{2}\log\left(\frac{1}{10}\right)$

E_{cell} = 0.0295 V

18. $0.2364 = \frac{-0.0591}{2}\log\frac{(X)^2}{(1)^2}$

$= \frac{-0.0591}{2}\log(X)^2$

$\Rightarrow \log x = -\frac{0.2364}{0.0591} = -4$

$\Rightarrow$ –logx = pH = 4 Ans.

19. $E^o_{Ce^{4+}/Ce^{3+}} = 1.44$ V; $E^0_{Fe^{3+}/Fe^{2+}} = 0.68$ V]

$E^0_{cell} = 0.0591 \log Keq.$

1.44 – 0.68 = 0.059 log Keq.

Keq. = 7.6×10^{12}

20. $Fe + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu$

E_{cell} = 0.44 + 0.337 = 0.777

$0.777 = \frac{0.0591}{2}\log Keq.$

Keq. = 1.97×10^{26}

21. $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$; – 0.8277

$H_2 \rightleftharpoons 2H^+ + 2e^-$; O

$2H_2O \rightleftharpoons 2H^+ + 2OH^-$; E^o = –0.8277

–0.8277 = 0.059 log Keq.

log Keq. = –14

Keq. = $10^{-14} = K_w$

22. $Ag^+ + e^- \rightleftharpoons Ag$; 0.799

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; x

$Ag \rightleftharpoons Ag^+ + e^-$; –0.799

$Fe^{3+} + Ag \rightleftharpoons Ag^+ + Fe^{2+}$; x – 0.799

E_{cell} = 0 at equilibrium

$\Rightarrow x - 0.799 = \frac{0.0591}{1}\log Keq.$

$\Rightarrow$ x – 0.799 = 0.0591 log [0.531]

$\Rightarrow$ x = 0.7827 V

23. $\Delta G^o_{rxn} = -nFE^o_{cell} = -12 \times F \times 2.73$ J

$\Rightarrow -\frac{12\times 96500\times 2.73}{1000} = 4 \times \Delta_f G^o$

$[Al(OH)_4^-]$

$\Rightarrow \Delta_f G^o [Al(OH)_4^-] = -4(-157) - 6(-237.2)$

$= -1303.13$ kJ

$= -1.3 \times 10^{-6}$ kJ

24. (A) 3.55 g Cl^- = $\frac{1}{10}$ mole Cl^-

$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$; nf = 1

$\Rightarrow$ gm-equivalent = $\frac{1}{10} \times 1 = \frac{1}{10}$

$\Rightarrow$ Faraday = $\frac{1}{10}$ = 0.1

no. of electrons = $0.1 \times 6.022 \times 10^{23}$

(B) 1 gm Cu^{2+} = $\frac{1}{63.5}$ mole Cu^{2+}; nf = 2

$\Rightarrow$ no. of electrons = $\frac{1}{63.5} \times 2 \times 6.022 \times 10^{23}$

(C) 2.7 g Al^{3+} = 0.1 mole Al^{3+}, nf = 3

$\Rightarrow$ no. of electrons = $0.1 \times 3 \times 6.022 \times 10^{23}$

25. (a) 0.25 mole = 0.25 × 3 equivalents

$\Rightarrow$ charge = 0.25 × 3 F

(b) $\frac{27.6}{80}$ mole = $\frac{27.6}{80}$ × 2 equivalent

charge = $\frac{27.6}{40}$ F

(c) Equivalent = 0.5 × 1.1 × 2 = 1.1

Charge = 1.1 F

26. 0.5 mole e^- = 0.5 F charge by 2nd law

0.5 g equivalent of Zn^{2+} & Ag^+

$\Rightarrow \frac{0.5}{2}$ mole of $Zn^{2+} = \frac{0.5}{2} \times 65$ g

And

$\Rightarrow \frac{0.5}{1}$ mole $Ag^+ = 0.5 \times 108$ g

27. $MnO_2 = \frac{1000}{87} \times 2$ g . eq.

where 2 = n factor

$Mn^{2+} \rightarrow Mn^{4+} + 2e^-$; nf = 2

By using (w = ItE/96500) ; ω = mass

E = Eg. wt.

$\frac{1000}{87} \times 2 = \frac{25.5}{96500} \times \frac{85}{100} \times t$

$\Rightarrow$ t = 1.023×10^5 sec.

$\Rightarrow$ t = 28.43 hrs.

28. $\frac{0.224}{22.4} = \frac{1}{100}$ mole H_2

$\Rightarrow$ Equivalent of $H_2 = \frac{1}{100} \times 2 = \frac{1}{50}$

$\Rightarrow$ O_2 produced = $\frac{1}{50}$ equivalents

$= \frac{1}{50} \times \frac{1}{4} = \frac{1}{200}$ mole

$= \frac{1}{200} \times 22.4 = 0.112$ L

29. x g Al $= \frac{x}{27} \times 3$ g equivalent Al

$= \frac{x}{9}$ equi. of Al

$\Rightarrow$ x Rs. for x/9 equi.

$\Rightarrow$ For 1 eq. 9 Rs.

xg Mg $= \frac{x}{24} \times 2 = \frac{x}{12}$ Eq. Mg

For $\frac{x}{12}$ equi. Mg Rs $= \frac{x}{12} \times 9 = \frac{3x}{4}$ Rs.

30. (i) Eq. of Cr $= \frac{24000}{96500} = \frac{240}{965}$

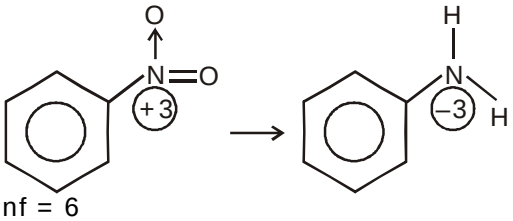
grams of Cr $= \frac{240}{965} \times \frac{1}{6} \times 52$

$= 2.1554$

(ii) $\frac{w}{E} = \frac{It}{96500} \Rightarrow \frac{1.5}{\left(\frac{52}{6}\right)} = \frac{12.5 \times 6}{96500}$

$\Rightarrow$ t = 1336.15 sec

31.



nf = 6

$\Rightarrow \frac{12.3}{123} \times 6$g eq. $= \frac{q}{96500} \times \frac{50}{100}$

$\Rightarrow$ potential drop = V = 3

then energy = q × V = $11.58 \times 10^4 \times 3$ J

= $11.58 \times 10^4 \times 3$J

= 347.4 kJ

32. Volume of layer = 80×10^{-4} $m^2 \times 5 \times 10^{-6}$ m

= 4×10^{-2} cm^3

mass of silver = $10.8 \times 4 \times 10^{-2}$

= 43.2×10^{-2}g

Eq. of silver = $\frac{43.2 \times 10^{-2}}{108} \times 1 = 0.004$

$0.004 = \frac{It}{96500}$

$\Rightarrow$ t = $\frac{0.004 \times 96500}{I} = \frac{0.004 \times 96500}{2}$

$\Rightarrow$ t = 193 sec.

33. Equivalent = $\frac{10 \times 330}{96500} = \frac{33}{965}$

Mole of metal = $\frac{33}{965} \times \frac{1}{2}$

mass = $\frac{33}{965 \times 2} \times$ Mol. wt. = 1.95

$\Rightarrow$ Mol. wt. = 114.05 g/mole

For Cu

$\frac{1.95}{63.5} \times 2 = \frac{Q}{96500}$

$\Rightarrow$ Q = 5926.8 Columb Ans.

34. g. eq. of $CuSO_4$ = 0.125 (taken)

more than 0.01 F

$\Rightarrow$ Only 0.01 g. eq. $CuSO_4$ will be deposited

Cathode

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

Anode

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

g. eq. of Cu(s) = 0.01

wt. of Cu(s) = $\frac{0.01}{2} \times 63.5$

$\Rightarrow$ Wt. of $O_2 = \frac{0.01}{4} \times 32$

35. $(2 + x) \times \frac{88}{100} = 2$ ....(1)

$\downarrow$

gram of metal

$(2 + x) \times \frac{12}{100} = x$ ....(2)

from Eqn (1) & (2)

$x = \frac{12}{44}$

$\Rightarrow \frac{w}{E} = \frac{It}{96500} \Rightarrow \frac{x \times 2\,(\text{n factor})}{112.4}$

$= \frac{5 \times t}{96500} \quad \Rightarrow \quad t = 93.66$ sec.

36. 31.75 g Cu $= \frac{31.75}{63.5} = \frac{1}{2}$ mole

$= \frac{1}{2} \times 2 = 1$ eq.

$\Rightarrow$ 1 eq. of Na with 100 % yield

But Eq. of Na $= 1 \times \frac{600}{1000} = 0.6$

$\Rightarrow$ % yield = 60 %

37. Equivalent $= \frac{It}{96500} = \frac{5 \times 20 \times 60}{96500} = \frac{60}{965}$

Moles of Ni $= \frac{60}{965} \times \frac{1}{2} = \frac{30}{965}$

Mass of Ni $= \frac{30}{965} \times 58.7 = 1.8248$ g

38. Ni^{2+} solution in Ni electrodes

Cathode

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

Anode

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

No change in molarity

Conc^n = 2M Ans.

39. $\frac{\ell}{A} = 0.88\ cm^{-1}$

R = 210 ohm

$\Rightarrow C = \frac{1}{210}$ mho

$k = \frac{1}{210} \times 0.88$ by $k = C \times \frac{\ell}{A}$

$\lambda_e = K \times \frac{1000}{N} = \frac{0.88}{210} \times \frac{1000}{0.01}$

$= 419\ Scm^2\ eq^{-1}$

40. $\ell_m = k \times \frac{1000}{0.1}$

$4.6 = k \times \frac{1000}{0.1}$

$\Rightarrow k = 4.6 \times 10^{-4} ohm^{-1}\ cm^{-1}$

$\rho = \frac{1}{k} = \frac{10^4}{4.6} = 2173.9 \approx 2174$

$\downarrow$

Resistivity

41. $k = 8 \times 10^{-7}\ Scm^{-1}$

$k = c \frac{\ell}{A} = C \times \frac{2}{4} = \frac{C}{2}$

$C = 2k = 16 \times 10^{-7}\ ohm^{-1}$

(i) $R = \frac{1}{C} = \frac{10^7}{16} = 6.25 \times 10^5$ ohm

(ii) $v = IR \Rightarrow I = \frac{v}{R} = \frac{1}{\left(\frac{10^7}{16}\right)}$

$\Rightarrow V = 16 \times 10^{-7}$ amp.

42. $k = \frac{1}{709.22} = 0.00141\ ohm^{-1}\ cm^{-1}$

$= 0.141\ ohm^{-1}\ m^{-1}$

$\lambda_e = \frac{1}{709.22} \times \frac{1000}{0.01}$

$\Rightarrow \lambda_e = 140.99 \approx 141$ mho $cm^2\ eq^{-1}$

$= 141 \times 10^{-4}$ mho $m^2\ eq^{-1}$

$= 0.0141$ mho $m^2\ eq^{-1}$

43. $BaCl_2 = \frac{2.08}{137 + 71} = \frac{2.08}{208} = 0.01$ mole

Molarity $= \frac{0.01}{400} \times 1000 = \frac{10}{400} = 0.025$ M

Normality $= 0.025 \times 2 = 0.05$ N

$\lambda_m = 0.0058 \times \frac{1000}{0.025} = 232$

$\lambda_e = 0.0058 \times \frac{1000}{0.05} = 116$

44. $\lambda\,[Ba(OH)_2] = 280 \times 10^{-4} + (248.1 \times 10^{-4}) \times 2$

$-2 \times (126.5 \times 10^{-4})$

$= 523.2 \times 10^{-4}$

$\lambda^o_{[Ba(OH)_2]} = \lambda^o_{BaCl_2} + 2\lambda^o_{NaOH} - 2\lambda^o_{NaCl}$

45. $\alpha = \frac{112.4}{129.9}$

$\alpha = 0.865$

46. $\Lambda^o_m(CH_3COOH) = \Lambda^o_m(CH_3COONa) + \Lambda^o_m(HCl) - \Lambda^o_m(NaCl)$

$= 91 + 426.1 - 126.5 = 390.6$

$\alpha = \frac{\Lambda_m}{\Lambda^o_m} = \frac{48.15}{390.6} = 0.1233$

% α = 12.33 %

47. Λ_m^∞ (AgBr) = 133 + 137.4 – 131 = 139.4 ohm^{-1} cm^2 mol^{-1}

Specific conductance of saturated AgBr Solution = specific conductance of AgBr + specific conductance of H_2O

$\Rightarrow K_{AgBr} = 8.486 \times 10^{-7} - 7.5 \times 10^{-7}$
$= 0.986 \times 10^{-7}$

$\Rightarrow 139.4 = 0.986 \times 10^{-7} \times \frac{1000}{M}$

$\Rightarrow M = 7.07 \times 10^{-7}$

Solubility = 7.07×10^{-7} mole/ℓ
$= 7.07 \times 10^{-7} \times 188 = 1.329 \times 10^{-4}$ g/ℓ

48. $\Lambda_{Ag^+}^\infty + \lambda_{Cl^-}^\infty = \lambda_{AgCl}^\infty$

$\Rightarrow \lambda_{AgCl}^\infty = 54.3 + 65.5 = 119.8$ ohm^{-1} cm^2 eq^{-1}

$\Rightarrow 119.8 = k \times \frac{1000}{N}$

$\Rightarrow N = \frac{1.12 \times 10^{-6} \times 1000}{119.8}$

$\Rightarrow (Ag^+) = (Cl^-) = N = 9.35 \times 10^{-6}$

$\Rightarrow Ksp = (Ag^+)(Cl^-) = N^2$

$= 8.74 \times 10^{-11} \left(\frac{mole}{\ell}\right)^2$

49. $\alpha = \frac{176.2}{405.2} = 0.435$

$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{0.002(0.435)^2}{1-0.435}$
$= 6.69 \times 10^{-4}$

50. Λ_m^∞ (H_2O) = (3.4982 + 1.98) $\times 10^{-2}$
$= 5.4782 \times 10^2$ S cm^2 mole^{-1}

$M = \frac{k \times 1000}{\lambda_m^\infty}$

$= \frac{5.7 \times 10^{-8} \times 1000}{5.4782 \times 10^2}$

$M = 1.04 \times 10^{-7} = [H^+] = [OH^+]$
pH = 6.98
$K_w = [H^+][OH^-] = 1.08 \times 10^{-14}$

51. $E^\circ_{Bi^{3+}/Bi} = 0.226$; $E^\circ_{Cu^{2+}/Cu} = 0.344$

The current would initially deposit cu till $E^\circ_{Cu^{2+}/CU}$ become 0.266 V

$\Rightarrow 0.226 = 0.344 - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$

52. $H_2 \longrightarrow 2H^+ + 2e^-$: $E^\circ = 0$
$Hg_2Cl_2 + 2e^- \longrightarrow 2\,Hg(s) + 2Cl^-$; $E^\circ = 0.28$
Final Rxn,
$H_2 + Hg_2Cl_2\,(s) \longrightarrow 2Hg\,(s) + 2Cl^- + 2H^+$
$E^\circ = 0.28$

$K = \frac{(Cl^-)^2(H^+)^2}{P_{H_2}}$

$0.67 = 0.28 - \frac{0.0591}{2} \log \frac{(Cl^-)^2(H^{+2})}{P_{H_2}}$

$\Rightarrow$ Normal calomel electrodi $\rightarrow PH_2 = 1$
$(Cl^-) = 1$
$\Rightarrow -\log (H^+) = 6.6$
$\Rightarrow$ pH = 6.6

53. Cell reaction
$H_2(g) + 2Ag^+ \rightarrow 2H^+ + 2Ag$
$E^\circ_{cell} = 0.8V$

$0.982 = 0.8 - \frac{0.0591}{2} \log \frac{[H^+]^2}{[Ag^+]^2}$

$\Rightarrow \frac{(0.982 - 0.8) \times 2}{0.0591} = -\log \frac{[H^+]^2}{[0.8]^2}$

$\Rightarrow (H^+)^2 = 4.44 \times 10^{-7} \Rightarrow [H^+] = 6.66 \times 10^{-4}$

$\underset{C-x}{HOCN} \rightleftharpoons \underset{x}{H^+} + \underset{x}{OCN^-}$

$\frac{x^2}{C-x} = K_a$

$K_a = \frac{4.4 \times 10^{-7}}{1.3 \times 10^{-3} - 6.66 \times 10^{-4}}$

$\boxed{K_a = 6.9 \times 10^{-4}}$

54. $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$
0.1 M

$\frac{0.1 \times 10}{100}$ $\frac{0.1 \times 90}{100}$

$E^\circ_{MnO4^-/Mn^{2+}} > E^\circ_{H^+/H_2}$
$\downarrow$
work as cathode
$MnO4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
cell rxn

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{5} \log \frac{(Mn^{2+})}{(H^+)^8(MnO4^-)}$

$= 1.51 - \frac{0.0591}{5} \log \frac{(0.1 \times \frac{90}{100})}{(0.8)^8(0.1 \times \frac{10}{100})}$

$= 1.41$ V

55. Conc. cell $E°_{cell} = 0$
can be represented as
Pt, H_2(1 atm) /H^+/H^+/H_2 (1 atm), Pt
C_1 C_2
Cell rxn
$2H^+ \rightleftharpoons 2H^+$
C_2 C_1

$$E_{cell} = -\frac{0.0591}{2}\log\left(\frac{C_1}{C_2}\right)^2$$

for C_1 $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$0.1-C_1$ C_1 C_1

$$\frac{C_1^2}{0.1} = 1.8\times10^{-5}$$

$C_1^2 = 1.8\times10^{-5}\times0.1 = 1.8\times10^{-6}$
$C_1 = 1.34\times10^{-6}$
For C_2, $NH_4OH \rightleftharpoons OH^- + NH_4^+$
$0.01 - x$ x x

$$\frac{x^2}{0.01} = 1.8\times10^{-5}$$

$(OH^-)^2 = 1.8\times10^{-7}$

$$(H^+)^2 = (C_2)^2 = \frac{(K_w)^2}{(OH^-)^2}$$

$$\Rightarrow \quad (C_2)^2 = \frac{10^{-28}}{1.8\times10^{-7}}$$

$$\Rightarrow \quad E = +\frac{0.0591}{2}\log\frac{10^{-28}/1.8\times10^{-7}}{1.8\times10^{-7}}$$

$= -0.458$ V

56. $Ni_2O_3(s) + H_2O(\ell) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$ $E° = 0.40$
$Fe(s) + 2OH^- \rightleftharpoons FeO(s) + H_2O(\ell) + 2e^-$
$E° = 0.87$
cell reaction
$Ni_2O_3(s) + Fe(s) \rightleftharpoons 2NiO(s) + FeO(s)$
$E° = 1.27$
$E_{cell} = E°_{cell}$ (No active species in cell reaction)
$= 1.27$ V
$\Delta G = -nFE$
$= -2\times96500\times1.27$
$= -245.11$ kJ.

57. $Cu^{2+} + 2e^- \longrightarrow Cu$ $E° = 0.34$
$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2\,OH^-$
$pH = 14 \Rightarrow pOH = 0 \Rightarrow (OH^-) = 1$
$\Rightarrow 1\times10^{-19} = [Cu^{2+}]\,[OH^-]^2$

$$\Rightarrow [Cu^{2+}] = \frac{10^{-19}}{1} = 10^{-19}$$

$$E_{cell} = 0.34 - \frac{0.0591}{2}\log\frac{1}{(Cu^{2+})}$$

$$= 0.34 - \frac{0.0591}{2}\log\left(\frac{1}{Cu^{2+}}\right)$$

$$= 0.34 - \frac{0.0591\times19}{2}$$

$= -0.22$V

58. For given cell
$E°_{cell} = 0$ (conc. cell)

$$E_{cell} = -\frac{0.059}{1}\log\frac{(H^+)anode}{(H^+)cathode}$$

$$-0.188 = -0.059\log\frac{1}{(H^+)cathode}$$

$$\Rightarrow \quad \log(H^+)cathode = -\frac{0.188}{0.059}$$

$(H^+)cathode = 6.51\times10^{-4}$
For Hydrolysis
$C_6H_5NH_3 + H_2O \rightleftharpoons C_6H_5NH_3OH + H^+$
C
C–h h h
$h = 6.51\times10^{-4}$

$$\%\ Hydrolysis = \frac{6.51\times10^{-4}}{(1/32)} = 2.08\times10^{-2}$$

$$K_h = \frac{h^2}{C-h} = \frac{(6.51\times10^{-4})^2}{(1/32 - 6.51\times10^{-4})} = 1.38\times10^{-5}$$

59. $H_2 \longrightarrow 2H^+ + 2e^-$
$Ag^+ + 2e^- \longrightarrow Ag$
$2Ag^+ + H_2 \longrightarrow 2H^+ + Ag$
Initially

$$0.9 = E° - \frac{0.0591}{1}\log\left(\frac{H^+}{Ag^+}\right)$$

$$0.9 = E° - 0.059l\log\left(\frac{0.1}{0.8}\right) =$$

$$E° - 0.059\log\left(\frac{1}{8}\right) \qquad ...(1)$$

After adding NaOH

	H^+	+	OH^-	$\longrightarrow$	H_2O
m.mole	0.1×30		0.05×40		
	3		2		
	1		0		

total volume = 70

remaining $[H^+] = \frac{1}{70}$

$$E_{cell} = E° - 0.0591\log\left(\frac{1/70}{0.8}\right)$$

$$E_{cell} = E° - 0.0591\log\left(\frac{1/70}{0.8}\right) \qquad ....(2)$$

After (2)–(1)

$E_{cell} - 0.9 = -0.0591 \log \frac{1}{56} + 0.0591 \log \frac{1}{8}$

$= 0.0591 \log \left(\frac{56}{8}\right)$

$= 0.0499$

$\Rightarrow \quad E_{cell} = 0.9499 = 0.95\ V$

60. Cell reactions

$Ag^+ + e- \longrightarrow Ag$

$Ag + I^- \longrightarrow Ag\ I + e^-$

$Ag^+ + I^- \longrightarrow Ag\ I$

$0.788 = E° - 0.0591 \log \frac{1}{[Ag^+][I^-]}$

$0.788 = E° - 0.0591 \log \frac{1}{(0.05)(0.05)}$

$\Rightarrow \quad E° = 0.94\ V$

Now $E° = 0.0591 \log \frac{1}{ksp(AgI)}$

$\Rightarrow \quad Ksp\ (AgI) = 1.16 \times 10^{-16}$

61. conc. cell

$E_{cell} = 0.0591 \log \frac{(Ag^+)andoe}{(Ag^+)cathode}$

$E_{cell} = -0.0591 \log$

$\left[\left(\frac{5 \times 10^{-13}}{Br^-}\right) \times \left(\frac{Cl^-}{10^{-10}}\right)\right]$

For $E_{cell} = 0$

$\Rightarrow \quad \frac{5 \times 10^{-13}}{[Br^-]} \times \frac{[Cl^-]}{10^{-10}} = 1$

$\Rightarrow \quad \frac{(Cl^-)}{(Br^-)} = \frac{10^{-10}}{5 \times 10^{-13}} = 200$

62. $Ag^+ + e \longrightarrow Ag$

$0.7991 = \frac{0.0591}{1} \log \frac{1}{(Ag^+)}$

$\Rightarrow \quad \frac{0.7991}{0.0591} = -\log(Ag^+)$

For Half cell

$AgI\ (s) + e- \longrightarrow Ag + I^-$

$E° = \frac{0.0591}{1} \log (I^-)$

$\frac{E°}{0.0591} = \log (I^-)$

$\frac{0.7991}{0.0591} - \frac{E°}{0.0591} = -\log (Ag^+)(I^-)$

$= -\log Ksp = P_{ksp} = 16.07$

$\Rightarrow \quad E° = (16.07 \times 0.0591) - 0.7991$

$\Rightarrow \quad E° = -0.15\ V$

63. $E_{cell} = 0.059 \log \frac{(Ag^+)anode}{(Ag^+)cathode}$

$Ag \rightarrow Ag^+ + e^-\ (anode)$

$= -0.0591 \log \left[\frac{\left(\frac{2.8 \times 10^{-10}}{0.2}\right)}{\frac{3.3 \times 10^{-13}}{0.001}}\right]$

$= -0.0591 \log \left[\frac{2.8510^{-13}}{0.66 \times 10^{-13}}\right]$

$= -0.0591 \log \left[\frac{2.8}{0.66}\right]$

$= -0.037$

64. $2e^- + PbCl_2 \longrightarrow Pb + 2Cl^-\ ; E° = -0.268$

$Pb \longrightarrow Pb^{2+} + 2e^-\ ;\ E° = 0.126$

$PbCl_2 \longrightarrow Pb^{2+} + 2Cl-\ ; E° = -0.142$

$E° = \frac{0.059}{2} \log K_{sp}$

$-\frac{0.142 \times 2}{0.059} = \log k_{sp}$

$K_{sp} = 1.536 \times 10^{-5}\ M^3$

65. $Mn \rightarrow Mn^{2+} + 2e^-$

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

$Cu^{2+} + Mn \rightarrow Mn^{2+} + Cu$

$E^o = 0.340 + 1.18$

$= 1.52$

$E = E^o - \frac{0.0591}{2} \log \frac{Mn^{2+}}{Cu^{2+}}$

$= 1.52 - \frac{0.0591}{2} \log \frac{\left(K_{sp} / (OH^-)^2\right)}{(Cu^{2+})}$

$= 1.52 - \frac{0.0591}{2} \log \left[\frac{\left(\frac{1.9 \times 10^{-13}}{10^{-8}}\right)}{0.675}\right]$

$= 1.654\ V$

66. Cell reaction

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

$= \quad E_{cell} = E^{o}_{cell} - \frac{0.0591}{2} \log \left[\frac{(Ag^{+})^2}{(Zn^{2+})}\right]$

$= E^{0}_{Zn^{2+}/Zn} + E^{0}_{Ag/Ag^{+}} - \frac{0.0591}{2}\log\left[\frac{\left\{\frac{K_{sp}(AgIO_3)}{[IO_3^-]}\right\}^2}{(zn^{2+})}\right]$

$= -0.762 - 0.799 - \frac{0.0591}{2}\log\left[\frac{\left(\frac{3.02\times10^{-8}}{0.3}\right)^2}{0.175}\right]$

$= -1.17$ V

67. Cell reaction

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

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

$Zn^{2+} = 1M$

$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

1M

y 2M 1M

$K_p = 1 \times 10^{12} = \left[\frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}\right]$

$1 \times 10^{12} = \frac{1}{y \times 2^4}$

$y = \frac{10^{-12}}{32} = 3.125 \times 10^{-14}$

$E_{cell} = 1.1 - \frac{0.0591}{2}\log\frac{1}{(3.125\times10^{-4})}$

$= 0.7$ V

68. $K_r = 8.227 \times 10^{63}$

69. $Ag^{+} + e^{-} \rightarrow \bar{A}g \quad ; E^{o} = 0.7991 \ldots (1)$

$Ag^{+} + 2NH_3 \rightarrow [Ag(NH_3)_2]^{+}: K_f = \frac{10^{+8}}{6.02} \ldots (2)$

$Ag^{+} + 2CN^{-} \rightarrow [Ag(CN)_2]^{-}: K_f = \frac{10^{+19}}{1.995} \ldots (3)$

(1) & (2)

$[Ag(NH_3)_2]^{+} + e^{-} \rightarrow Ag + 2NH_3 \quad K = ?$

for (1) reaction $\frac{0.7991}{0.0591} = \log K_{eq}$

$K_{eq} = 3.32 \times 10^{13}$

$K = \frac{10^{13} \times 3.32}{10^{8}/6.02} = 1.99 \times 10^{6} = 2 \times 10^{6}$

$E^{o} = \frac{0.0591}{1}\log(2\times10^{6})$

$= 0.372$ V

70. $Sn(s) \rightarrow Sn^{2+} + 2e^{-} \quad E^{o} = 0.136$ V .....(1)

$Sn^{2+} \rightarrow Sn^{4+} + 2e^{-} \quad E^{o} = -0.154$ V.....(2)

$Cr_2O_7^{2-} + 14\,H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$

$E^{o} = 1.33$ V.....(3)

Eq. (1) + (2)

$Sn(s) \rightarrow Sn^{4+} + 4e- \quad .....(4)$

$E^{o} = \frac{(0.136\times2) + (-0.154\times2)}{4}$

$= -0.009$ V

Eq. (3) × (2) + eq. (4) × (3)

$3Sn(s) + 2Cr_2O_7^{2-} + 28\,H^{+} \rightarrow 4Cr^{4+} + 14\,H_2O + 3Sn^{4+}$

$E^{o} = 1.33 - 0.009$

$E^{o} = 1.321$

$E^{o} = 1.321 = \frac{0.0591}{12}$

$\log K_{eq}$

$\log K_{eq} = \frac{1.321\times12}{0.0591}$

$K_{eq} = 10^{268}$

71. $Ti^{+} \rightarrow Ti^{3+} + 2e^{-} \quad -1.25$V

$Co^{3+} + e^{-} \rightarrow Co^{2+} \quad 1.84$V

$Ti^{+} + 2Co^{3+} \rightarrow 2Co^{2+} + Ti^{3+} \quad 0.59$V

$E^{o} = 0.59 = \frac{0.059}{2}\log K_{eq}$

$\log K_{eq} = 20 = K_{eq} = 10^{20}$

$Ti^{+} + 2Co^{3+} \rightarrow 2Co^{2+} + Ti^{3+}$

mmole 2.5 5mmole

y 2y 5 2.5

$K_{eq} = 10^{20}$ very high

volume = 50 ml

$= 10^{20} = \frac{(Co^{2+})^2(Ti^{3+})}{y.4y^2} = \frac{(0.1)^2(0.05)}{4y^3}$

$= 4y^3 = 5 \times 10^{-24} = y^3 = 1.25 \times 10^{-24}$

$y^3 = 125 \times 10^{-26}$

$y = 1.08 \times 10^{-8}$

$(Ti^{+}) = 1.08 \times 10^{-8}$

$(Co^{3+}) = 2 \times 1.08 \times 10^{-8}$

72. $2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$ at anode

$2e^- + 2H_2O \longrightarrow 2OH^- + H_2$ at cathode

After complete electrolysis of H_2SO_4

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ at anods

$\Rightarrow$ eq. of $H_2S_2O_8$ + e.q. of O_2 = eq of H_2

mole $H_2S_2O_8 \times 2 + n_{O_2} \times 4 = n_{H_2} \times 2$

$\Rightarrow$ mole $H_2S_2O_8 \times 2 + \frac{2.35}{22.4} \times 4 = \frac{9.722}{22.4} \times 4$

$n_{H_2S_2O_8}$ 0.224 mole

mass of $H_2S_2O_8 = 0.224 \times 194 = 43.494$ g

73. Faralay = $\frac{3 \times 2 \times 3600}{96500} = \frac{216}{965}$ supplied

eqvivalent of $Cu^{2+} = \frac{3}{63.5} \times 2 = \frac{6}{63.5}$ =

Faraday used

current efficieny =

$\frac{(6/63.5)}{(216/965)} \times 100 = \frac{6 \times 965}{63.5 \times 216} \times 100$

= 42.2 %

74. Equivalent of Cu^{2+}

$= \frac{0.4}{63.5} \times 2 = \frac{8}{635} = 0.0126$

total faraday supplied =

$\frac{8}{635} + \frac{1.2 \times 7 \times 60}{96500}$

$= 0.0126 + 0.0052$

$= 0.178$

tilll 0.0126 faraday

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

Anode $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

= 0.0126 eq.

After 0.0126 faraday (for 0.0052 F)

Cathode $2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$

0.0052 eq.

Anode $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

0.0052 eq.

total O_2 evolved = 0.0178 eq.

$= \frac{0.0178}{4}$ mole

$\frac{0.0178}{4} \times 22.4 = 0.09968$ L

= 99.68 ml

H_2 evolved = 0.0052 eq. = $\frac{0.0052}{2}$ mole

$= \frac{0.0052}{2} \times 22400 = 58.24$ ml

75. $F = \frac{5 \times 2 \times 3600}{96500} = \frac{360}{965}$

at anode $Ag \longrightarrow Ag^+ + e^-$

Eq. of Ag = $\frac{360}{965}$

$\frac{360}{965} \times 1$ mole of Ag reduced

wt. of Ag reduced = $\frac{360}{965} \times 108 = 42.3$ g.

but it is 95% pure by wt.

$\Rightarrow$ wt. reduced of anode = $\frac{42.3 \times 100}{95}$ =

42.42 g

wt. of anode finally = 100–42.42 = 57.58 g

76. Wt of water = 8×10^{12} lit = 8×10^{12} gm

$\frac{8.2 \times 10^{12}}{18} \times 2 = \frac{it}{96500} = \frac{1.5 \times 10^6 \times t}{96500}$

$t = \frac{8.2 \times 10^{12} \times 96500}{18 \times 1.5 \times 10^6}$ sec.

time in years.

$= \frac{t}{3600 \times 24 \times 365}$ years.

1.9 million year

77. Before elecrolysis

volume of solution = 1000 ml

wt. of solution = $1.261 \times 1000 = 1261$ g

wt. of $H_2SO_4 = 1261 \times \frac{34.6}{100} = 436.306$g

wt. of water = 1261– 436.306 = 824.64 g

After electrolysis

Now during reaction wt. of H_2O formed = x g.

mole of H_2O formed = $\frac{x}{18}$

mole of H_2SO_4 used = $\frac{x}{18}$

wt. of H_2SO_4 used = $98 \times \frac{x}{18} = 5.44x$ g.

wt. of H_2SO_4 left = (436.306–5.44x)g

New wt. of solution = old wt. of solution + wt. of H_2O formed

– wt. of H_2SO_4 lost
= 1261+x–5.44 x
% by wt. of new solution =

$$\frac{436.306-5.44x}{1261+x-5.44x}=\frac{27}{100}$$

x = 22.59 g

$\because$ $\frac{22.59}{18}$ mole of H_2O are formed

Eq. of $H_2O = \frac{22.59}{18}$ (n f=1)

Faraday = $= \frac{22.59}{18} = 1.255$ faraday

charge $= 1.21\times10^5$ columb

78. $E°_{cell} = 0.28 - 0.699 = -0.419$ V.

$$E_{cell} = 0.419 - \frac{0.0591}{n}\log Q$$

cell rxn, $2e^- + Hg_2Cl_2 \longrightarrow 2\,Hg\,Cl + 2\,Cl^-$

$Q \longrightarrow Q\,H_2H^+ + e^-$

$2Q + Hg_2Cl_2 \longrightarrow 2HgCl + 2Cl^- + 2QH_2H^+$

$$E_{Cell} = -0.419 - \frac{0.0591}{2}\log (H^+)^2$$

$= -0.419 + 0.0591$ pH = –0419*
0.0591×5
$= -0.1235$

$$Ecell = 0 \Rightarrow pH = \frac{0.419}{0.0591} = 7.09$$

79. $H_2S \rightleftharpoons HS^- + H^+$

$$K_1 = \frac{[HS^-][H^+]}{[H_2S]} = 10^{-8}$$

$HS^- \rightleftharpoons S^{2-} + H^+$

$$K_2 = \frac{[S^{2-}][H^+]}{[HS^-]} = 1.1\times10^{-13}$$

$$K_1.K_2 = 1.1\times10^{-21} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$\Rightarrow \quad [S^{2-}] = \frac{1.1\times10^{-21}\times0.1}{(10^{-3})^2}$$

($\because [H^+] = 10^{-3}$ and $[H_2S] = 0.1$ M)
$[S^{2-}] = 0.11\times10^{-15}$

Thus for Ag_2S $K_{sp} = [Ag^+]^2[S^{2-}]$

$2\times10^{-49} = [Ag^+]^2\,[1.1\times10^{-16}]$

$$[Ag^+]^2 = \frac{2\times10^{-49}}{1.1\times10^{-16}} = 18.18\times10^{-34}$$

$[Ag^+] = 4.26\times10^{-17}$ M

For Half cell

$Ag^+ \longrightarrow Ag$

$$E = E° - 0.0591\log\frac{1}{[Ag^+]}$$

$= 0.8 + 0.0591\log[4.26\times10^{-17}]$
$= -0.1658$ V

80. $\frac{l}{A} = \frac{0.5}{1.5} = \frac{1}{3}$ cm^{-1}

$I = \frac{V}{R} \Rightarrow I = V\times C$

we need R

$R = \frac{1}{C} \Rightarrow K = C\times\frac{l}{A}$

$\Rightarrow C = \frac{K}{(l/A)}$

Now $\lambda_{eq} = K\times\frac{100}{N} \Rightarrow 97.1 = K\times\frac{1000}{0.1}$

$\Rightarrow K = 9.71\times10^{-3}$

$\Rightarrow C = \frac{9.71\times10^{-3}}{(1/3)} = 3\times9.7\times10^{-3}$

$I = 5\times3\times9.71\times10^{-3} = 0.1456$ amp.

81. $\lambda = 96500\,\mu$
$73.52 = 96500\times\mu$

$\mu = \frac{73.52}{96500}$ (mobility)

$$\mu = \frac{v(\text{speed})}{(\text{potenial gradient})(\text{volt}/\text{cm})}$$

$$\frac{73.52}{96500} = \frac{v}{(6/10)} \Rightarrow v = \frac{73.52\times0.6}{9600}$$

$V = 4.57\times10^{-4}$ cm/s
In 2hrs distance travelled by ion
$\Rightarrow 4.56\times10^{-4}\times2\times3600 = 3.29$ cm

82. $K = C\times\frac{l}{A}$

$$1.342 = \frac{1}{170.5}\times\frac{l}{1.86\times10^{-6}\times10^{-4}}$$ (in m^2)

$I = 1.342\times170.5\times1.86\times10^{-10}$
$I = 4.25\times10^{-8}$ m
$I = 4.25\times10^{-6}$ cm

83. $K_{SrSO_4} + K_{water} = K$ satatal so

$K_{srSo_4} = 1.482\times10^{-4} - 1.5\times10^{-6}$

$$\boxed{K_{srso_4} = (1.482-0.015)\times10^{-4} = 1.467\times10^{-4}}$$

$\lambda\,Sr^{2+} + \lambda SO_4^{2-} = \lambda\,SrSO_4 = 59.46+79.8$
$\lambda SrSO_4 = 139.26$

$139.26 = 1.467\times10^{-4} \times \frac{1000}{M}$

M= 0.00105 mole /L

84. $\lambda\, CO_2\, [Fe(CN)_6] = 2\lambda CO^{2+} + \lambda$ $[Fe(CN)6]^{4-}$

$= 2\times86+444=616$

$\lambda = \frac{K\times1000}{M}$

$616 = (2.06\times10^{-6}–4.1\times10^{-7})\times \frac{1000}{M}$

$M = \frac{1.65\times10^{-6}\times1000}{616} = 2.678\times10^{-6} = 5$

$CO_2[Fe(CN)_6] \rightleftharpoons 2\, CO^{2+} + [Fe(CN)_6]^{4-}$
2s S

$K_{ep} = 4s^3$
$= 4\times(2.678\times10^{-6})^3$
$Kep = 7.687\times10^{-17}$

85. for aniline

$(OH^-) = \sqrt{K_b \times c} = \sqrt{10^{-9}\times0.5/500}$

$(OH^-) = 10^{-6} \Rightarrow pOH = 6 \Rightarrow pH = 8$

for HCl

pH= –log (25/500) = 1.3

$E = +0.0591\,(pH_1–pH_2)$ E° = O conc cell

E = 0.0591 (8–1.3) = 0.39597 V

Exercise-IV Level-I

1. LHS half cell
$H_2(g) \rightarrow 2H^+(1M) + 2e^-$
RHS half cell
$2H^+(1M) + 2e^- \rightarrow H_2(g)$
____
$H_2(g)P_1 \rightarrow H_2(g)\,P_2$

$E^0_{Cell} = 0.00v$, $K = \frac{P_2}{P_1}$, n = 2

$E^0_{Cell} = E^0_{Cell} - \frac{RT}{nF}$ In eV

$= 0 - \frac{RT}{2F}\ \ln\frac{P_2}{P_1}$

$\frac{RT}{2F}\ \ln\frac{P_1}{P_2}$

2. **(B)**
Oxidation takes place at anode (C) & (D).

3. **(C)**
For purification impure gets oxidised (d-electronation) falling into solution with mud, that's why impure at anode.

4. At LHS oxidation
$2\times(Ag \rightarrow Ag^+ + e^-)$
At RHS (reduction)
$Cu^{2+} + 2e^- \rightarrow Cu$
____
$2Ag + Cu^{2+} \rightarrow Cu + 2Ag^+$, $E_{red} = (y – x)$
Eº volumes unstant when half cell equation is multiplied / devided.

5. **(B)**

$E^0_{cell} = \frac{2.303RT}{nF}\log K_{eq}$

$0.295 = \frac{0.0591}{2}\log K_{eq}$

$\log K_{eq} = 10$

6. **(C)**
More (–) ve volume of Eº mean larger reducing power.
so, B > C > A

7. $E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log Q$

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$
0.1 M 1M

$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{0.1} = 10$

$E^0_{cell} = 1.10 - \frac{0.0591}{2}\log 10$

= 1.10 – 0.0295 = 1.0705 V

8. **(D)**
Since 96500 C deposits 108 gm of silver
so, 9650 C unit 108 gm

9. **(C)**
$Sn(S) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq.) + Sn^{2+}(aq.)$

$E^0_{cell} = E^0_{ox} + E^0_{red}$

Given $E^0_{Sn^{2+}/Sn} = -0.014$ V

$E^0_{Sn^{2+}/Sn} = +0.14$

$E^0_{Fe^{3+}/Fe^{2+}} = 0.77$ V

$E^0_{cell} = 0.14 + 0.77 = 0.91$ V

10. (C)

Relation between $K_{eq.}$ and E^0_{cell} is

$$E^0_{cell} = \frac{0.303RT}{nF} \log K_{eq}$$

$$E^0_{cell} = \frac{0.303RT}{n} \log K_{eq}$$

$$0.0591 = \frac{0.0591}{1} \log K_{eq}$$

$\log K_{eq} = 10$

11. (A)

by kohlrausch's law

$\wedge^0 NaBr = \wedge^0 NaCl + \wedge^0 KBr - \wedge^0 KCl$

$= 126 + 152 - 150$

$= 128\ S\ cm^2\ mol^{-1}$

12. (C)

$Zn(s) + 2H^+ \rightarrow Zn^{2+}(eq.) + H_2(g)$

Reaction question $Q = \frac{Zn^{2+}}{(H^+)^2}$

corresponding cell is

$Zn|Zn^{2+}(C_1)||H^+(eq.)|Pt(H_2)$

+

Cathode

$$E^0_{cell} = E^0 - \frac{RT}{2F} \log \frac{[Zn^{2+}]}{[H^+]^2}$$

on addition of $[H^+]$ q decreases due to increase in $[H^+]$.

Since equlibrium is diplaced toward right and E_{cell} increases.

13. (B)

$Al^{3+} + 3e^- \rightarrow Al$

$w = 2\ Q$

where

w = amout of metal

$= 5.12\ Kg = 5.12 \times 10^3\ g$

$$z = \frac{electrichemical equivalent}{96500} = \frac{Atomic\ mass}{electrons \times 96500}$$

$$= \frac{27}{3 \times 96500}$$

$$5.12 \times 10^3 = \frac{27}{3 \times 96500} \times Q$$

$$Q = \frac{5.12 \times 10^3 \times 3 \times 96500}{27}$$

$5.49 \times 10^7\ C$

14. $\wedge^\infty_{ACOH} = \wedge^\infty_{ACONa} + \wedge^\infty_{HCl} - \wedge^\infty_{NaCl}$

$= 91.0 + 426.2 - 126.5$

$= 390.7$

15. $\Delta Cr^o = -2.303\ RT \log K_{eq}$

$\Delta Cr^o = -nFE^0_{cell}$

If a cell reaction is spontaneous (proceeding in forward side) it means

$K_{eq} > 1$ and $E^0_{cell} = +ve$

thus $\Delta Cr^o = -ve$

16. (C)

$AgI(S) + e^- \rightleftharpoons Ag(S) + I^-$ $\quad E^0 = -0.152$

$Ag(S) \rightleftharpoons Ag^+ + e^-$ $\quad E^0 = -0.8$

$AgI(S) \rightarrow Ag^+ + I^-$ $\quad E^0 = -0.952$

$$E^0_{cell} = \frac{0.059}{n} \log K_{sp}$$

$$-0.952 = \frac{0.059}{1} \log K_{sp}$$

$$\log K_{sp} = \frac{-0.952}{0.059} = -16.13$$

17. (C)

Cell is completely discharged, so $E^0_{cell} = 0$

$Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$

Cell reaction

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

We know

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log K_{eq}$$

$$1.10 = E^0_{cell} - \frac{0.0591}{2} \log K_{eq}$$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = anti\ log \frac{2.20}{0.0591}$$

$\therefore$ anti log 37.3

18. (A)

We know from kohlrausch's law

$\lambda^0_{CH_3COOH} = \lambda^0_{CH_3COONa} + \lambda^0_{HCl} - \lambda^0_{NaCl}$

19. (D)

$Cr|Cr^{3+}(0.1M)||Fe^{2+}(0.01)M|Fe$

oxidation half cell

$Cr \rightarrow Cr^{3+} + 3e^- \times 2$

reduction half

$Fe^{2+} + 2e^- \rightarrow Fe \times 3$

Not cell reaction

$2Cr + 3Fe^{3+} \rightarrow 2Cr^{3+} + 3Fe\ (n = 6)$

$E^0_{cell} = E^0_{oxid} + E^0_{red}$

$= 0.72 - 0.42 = 0.30$ V

$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$

$= 0.30 - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3}$

$= 0.30 - \frac{0.0591}{6} \log \frac{10^{-2}}{10^{-6}}$

$E_{cell} = 0.2606$ V

Exercise-IV Level-II

1. $e^- + Fe^{3+} \rightarrow Fe^{2+}$; 0.77
$3I^- \rightarrow I_3^- + 2e^-$; –0.54

$2Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + 2e$; $E^o = 0.23$ V

$E^o = \frac{0.0591}{2} \log k_{eq} = 0.23$

$K_{eq.} = 10^{7.7} = 6.6 \times 10^7$

2. Cell reaction
$Ag^+ \rightarrow Ag^+$ conc cell
0.1 c
$E^o = 0$

$\Rightarrow 0.164 = -0.591 \log \frac{c}{0.1}$

$\Rightarrow C = 1.68 \times 10^{-4}$

$Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4^{2-}$; $K_{sp} = 4s^3$
2s s

$2S = Ag^+ = C = 1.68 \times 10^{-4}$

$K_{sp} = 4 \times \left(\frac{1.68 \times 10^{-4}}{2}\right)^3 = 2.36 \times 10^{-12}$

3. SRP
$z > y > x$
$\Rightarrow$ z will oxidize both
$\Rightarrow$ y will oxidize x but not z

4. Cell reaction
$M + X \rightarrow M^+ + X^-$
$E^o_{cell} = -0.44 + 0.33 = -0.11$ V
reaction is non -spontaneous
$\Rightarrow M^+ + X^- \rightarrow$ M + X is spontaneous

5. Cathode :
$Cu^{2+} + 2e^- \rightarrow Cu(s)$

Cu g eq. $= \frac{It}{96500} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500}$

Cu moles $= \frac{960 \times 2 \times 10^{-3}}{96500 \times 2}$ deposited.

Initially moles of Cu $= \frac{2 \times 960 \times 2 \times 10^{-3}}{96500 \times 2}$

Concentration $= \frac{\left(\frac{96 \times 2 \times 10^{-2}}{96500}\right)}{250} \times 1000$

$= \frac{96 \times 8 \times 10^{-2}}{96500} = 7.95 \times 10^{-5}$ M

6. Anode
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
Cathode
$Ce^{4+} + e^- \rightarrow Ce^{3+}$

$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$
$E^o_{cell} = -0.77 + 1.61$
$= +$ ve
Current will decrease with time.

7. $3ClO^-(aq.) \rightarrow ClO_3^-(aq.) + 2Cl^-(aq.)$
+1 +5 –1
disproportionation reaction

8. Conductivity α Ionic character
order of ionic character
KCl > NaCl > LiCl

9. **(C)**

10. (i)
$1/2H_2 \rightarrow H^+ + e^-$ and $AgCl + e^- \rightarrow Ag + Cl^-$ cell reaction
$1/2\ H_2 + AgCl \rightarrow H^+ + Ag + Cl^-$
or $1/2\ H_2 + AgCl \rightarrow Ag + HCl$

(ii)
$\Delta G^o_1 = -F \times 0.23$ at 15°C
$\Delta G^o_2 = -F \times 0.21$ at 35°C
and $\Delta G^o_1 = \Delta H^o - T_1\ \Delta S^o$
$\Delta G^o_2 = \Delta H^o - T_2\ \Delta S^o$
$\Rightarrow \Delta S^o = -96.5$ KJ : $\Delta H^o = 49987$ J
(iii)
For 20°C difference change in
$E^o = -0.02$

$\Rightarrow E^0_{25^oC} = E^0_{15^oC} - \frac{0.02}{20} = 0.23 - 0.001$

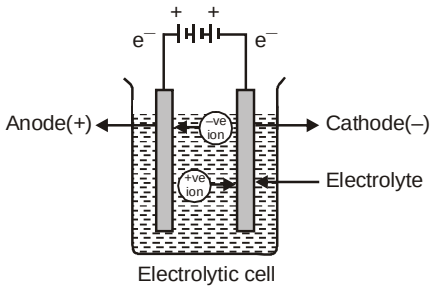
$E^0_{25^oC}$ = 0.229 V
cell reaction = $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

$E^o = \frac{0.0591}{1} \log K_{sp} = 0.229 - 0.8$
$K_{sp} = 2.18 \times 10^{-10} = S^2$
$S = 1.47 \times 10^{-5}$ mole/L
reaction at 25°C
$Ag \rightarrow Ag^+ e^-$; – 0.8 V
$e^- + AgCl \rightarrow Ag + Cl^-$; 0.229 V

$AgCl \rightarrow Ag^+ + Cl^-$; 0.229 – 0.8 V

11. If MnO_4^- used in aqueous HCl if will oxidize Cl^- ion also hence it is not suitable for quantitative estimation of $Fe(NO_3)_2$.

12.



13. $Zn|\underset{c}{Zn^{2+}}||\underset{c_1}{Cu^{2+}}|Cu$ and
$Zn|\underset{c}{Zn^{2+}}||\underset{0.5}{Cu^{2+}}|Cu$

$E_1 = E^o - \frac{0.059}{2} \log\left(\frac{c}{0.5}\right)$
$E_2 - E_1 = 0.03$
$\Rightarrow 0.03 \frac{0.059}{2}\left[\log\frac{c}{c_1} - \log\frac{c}{0.5}\right]$

$\Rightarrow 1 = \log \frac{0.5}{c_1} = c_1 = 0.05$

14. $E = E^o - \frac{0.0591}{2} \log Q$

$0.2905 = E^o - \frac{0.0591}{2} \log\left(\frac{0.1}{0.01}\right)$

$E^o = 0.2905 + \frac{0.0591}{2} = 0.32$

$E^o = 0.32 = \frac{0.0591}{2} \log K_{eq}$

$\log K_{eq} = \frac{0.32}{0.0295}$
$K_{eq} = 10^{0.32/0.0295}$

15. $In^{3+} 2e^- \rightarrow In^+$; –0.42
$In^+ \rightarrow In^+ + e^-$; –0.40

$In^{3+} + e^- \rightarrow In^{2+}$; $E^o_{In^{3+}/In^{2+}}$

$E^o_{In^{3+}/In^{2+}} = \frac{-0.42 \times 2 + 0.40}{1} = -0.44$

$E^0_{cell} = E^0_{Cu^{2+}/Cu^+} + E^0_{In^{2+}/In^{3+}}$
$= 0.15 + 0.44 = 0.59$

$E^0_{cell} = 0.59 = \frac{0.059}{1} \log K_{eq}$
$K_{eq} = 10^{10}$

16. $E^o = 1.23 + 0.44 = 1.67$ V
$\Delta G^o = -nFE^o = -2 \times 96500 \times 1.67$ J
$= -322.31$ KJ
Cell reactions
$Fe \rightarrow Fe^{2+} + 2e^-$ $E^o = 0.44$ V
$2H^+ + 1/2\ O_2 + 2e^- \rightarrow H_2O$ $E^o = 1.23$ V

$E^o_{cell} = 1.67$ V

17. (a) $\Delta G^o_{r\times n} = \Delta G^0_f(AgCl) - \Delta_f G^0(Ag^+)$
$= (-109) - (77) - (-129) = -57$ kJ

$E^o = \frac{\Delta G^0}{-nF} = \frac{-57 \times 10^3}{-1 \times 96500} = 0.59$ V

$-\log K_{sp} = nE^o/0.0591 = \frac{1 \times 0.59}{0.059} = 10$
$K_{sp} = 10^{-10}$ $\log K_{sp} = -10$

(b) Cell reaction
$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$E^o_{cell} = 0.80 + 0.76 = \frac{0.059}{2} \log\left[\frac{(Zn^{2+})}{(Ag^+)^2}\right]$

$K_{sp}(AgCl) = 10^{-10}$
$(Ag^+) = 10^{-5}$ M

In 100 ml $[Ag^+]$mole $= \frac{10^{-5}}{1000} \times 100 =$
10^{-6}

18. $Ag^+ + e^- \rightarrow Ag$; $E^o = 0.8$

$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H^+ + 2e^-$
; $E^o = 0.05$

$2Ag^+ + C_6H_{12}O_6 + H_2O \rightarrow 2Ag + C_6H_{12}O_7 + 2H^+$
; $E^o = 0.8 - 0.05 = 0.75$

$E^o = \frac{0.059}{2} \log K = 0.85 \frac{RT}{2F} \ln K$

$\Rightarrow \ln K = \frac{0.85 \times 2F}{RT}$
$\Rightarrow \ln K = 0.85 \times 2 \times 38.92 = 66.16$

19. On Increasing the conc. of NH_3 the concn. of H^+ ion decreases therefore

$$E_{red} = E^o - \frac{0.0592}{n}\log[H^+]^2$$

$$= \frac{0.0592}{n} \times 2 \times \log 10^{-11}$$

$E_{red} = 0.65$ V

20. **(D)**

21. Suppose the solubility of AgBr in 10^{-7} M $AgNO_3$ = S mole/L

$AgBr \rightleftharpoons Ag^+ + Br^- / AgNO_3 \rightarrow Ag^+ + NO_3^-$

s s 10^{-7} 10^{-7}

$K_{sp}(AgBr) = (S + 10^{-7})S = 12 \times 10^{-14}$

$\Rightarrow S = 3 \times 10^{-7}$ M

$\Rightarrow [Br^-] = 3 \times 10^{-4}$ mole/m^3

$[Ag^+] = 4 \times 10^{-7}$ M $= 4 \times 10^{-4}$ mole/m^3

$[NO_3^-] = 10^{-7}$ M $= 10^{-4}$ mole/m^3

Calculate K for each ion by $K = \lambda \times C$

$K_{total} = K_{Br} + K_{Ag^+} + K_{NO_3^-}$

$= 55 \times 10^{-7}\ Sm^{-1}\ mole^{-1}$

22. mole of $Cl^- = 4 \times \frac{500}{1000} = 2$ mole

Cl_2 evolved = 1 mole

23. Na – Hg formed

mole of Na–Hg = mole of Na

= 2 mole

mass of amalgam = 2×223 ↓ mol.mass of Na-Hg

= 446 g

24. Equivalents = charge (F)

Charge (F) = 2×1

= 2F

Charge = 2×26500 C

= 193000

25. $2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$

$E^0_{cell} = 1.36 - 0.54 = 0.82$ V

reaction is feasible

26. $Mn^{3+} + e^- \rightarrow Mn^{2+}$

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

$4Mn^{2+} + 2H_2O \rightarrow 4Mn^{2+} + 4H^+ + O_2$

$E^0_{cell} = 1.50 - 1.23$

$= 0.27$ V + ve

27. $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

for 0.01 mole H_2 0.02 mole of electrons are consumed charge required = 0.02×96500

$\Rightarrow 0.02 \times 96500 = I \times t$

$$t = \frac{0.02 \times 96500}{10 \times 10^{-3}}$$

$= 19.3 \times 10^4$ sec

28. The species having less SRP with respect to NO_3^- (0.96) will be oxidized by NO_3^- species are

V, Fe & Hg

29. **(A, B)**

30. The given cell is electrolytic conc. cell so

$E^0_{cell} = 0$

$M(s) \rightarrow M^+(aq.) + e^-$

$M^+(aq.) + e^- \rightarrow M(s)$

$M^+(aq.) \rightleftharpoons M^+(aq.)$

cathode anode

$$E_{cell} = \frac{-0.0591}{1}\log\frac{(M^+)c}{(M^+)a}$$

$$= -0.0591 \log\left(\frac{0.05}{1}\right)$$

= + ve ΔG = – ve

31. $E_{cell} = E^0_{cell} - 0.0591 \log K$

$$E^0_{cell} - \frac{0.0591}{1}\log 0.0025$$

= 140 mV

32. $2Fe(S) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O\ (\ell)$ $\varepsilon° = 1.67$ V

$$\varepsilon \text{ cell} = \varepsilon° \text{ cell} - \frac{0.591}{n}$$

n = 4

$2Fe(S) \rightarrow 2Fe^{2+} + 4e$

$$= \varepsilon° \text{ cell} - \frac{0.591}{4}\log\left[\frac{(Fe^{2+})^2}{(H^+)^4(Po_2)}\right]$$

$$= 1.67 - \frac{0.0591}{4}\log\frac{(10^{-3})^2}{0.1 \times (10^{-3})^4} = 1.57$$ V

Ans. (D)

33. M/M^{2+} (saturated solution) $||M^{2+}(0.001)|M$

$\varepsilon°$ cell = O

$$\varepsilon \text{ cell} = \frac{0.0591}{2}\log\frac{[M^{2+}]_a}{[M^{2+}]_c}$$

$$0.0591 = \frac{0.0591}{2}\log\left[\frac{(M^{2+})_a}{0.001}\right]$$

$2 = \log \frac{(M^{2+})_a}{0.001}$

$(M^{2+})_2 = 10^{-5}$

$M \times 2 \rightleftharpoons M2 + \underset{S}{M^{2+}} + \underset{2S}{2X^-}$

$S = 10^{-5}$

$Ksp = 4S^3$

$= 4 \times 10^{-15}$

Ans. (B)

34. $\Delta G = -nF\varepsilon$

$= -2 \times 96500 \times 0.059$

$= -11406.3$ J/mole

$= -11.4$ KJ/mole.

Ans. (D)