

# 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

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# AVIRAL CLASSES

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MAINS+ADVANCED

TOPIC

ELECTROCHEMISTRY

## SOLUTIONS

## ELECTROCHEMISTRY

## Exercise-I

- (C)**  
In this  $\text{Cl}^-$  will oxidise to give  $\text{Cl}_2$ ,  $\text{Na}^+$  reduction potential has lower potential than water reduction potential so water will reduce to give  $\text{H}_2$ .  
(C) NaCl
- (A)**  
As electron flows from anode to a cathode and so current flows from cathode to anode in outer circuit
- (B)**  
Water oxidation at anode can be represented and  $\text{SO}_4^{2-}$  can't be discharged so  
$$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$$
so ion which will be discharged at anode will be  $\text{OH}^-$ .
- (A)**  
Since to deposit 1 mole of aluminium 3 coulomb of electricity is required, as the valency of silver is + 1 so 3 mole of silver will be deposited by 3C of electricity
- (C)**  
At cathode  
$$4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{H}_2 + 4\text{OH}^-$$
At anode  
$$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$$
Thus at cathode we will get  $\text{H}_2$  whereas at anode we will get  $\text{O}_2$ .
- (A)**  
In electrolysis of a fused salt, the weight deposited on electrode will not depend on temperature.
- (C)**  
In this  $\text{Cl}^-$  will oxidise to give  $\text{Cl}_2$ ,  $\text{Na}^+$  water reduction potential has higher potential than that of water reduction potential, so water will reduce to give  $\text{H}_2$ .
- (B)**  
Cation loses charge at cathode as it gave electron.
- (B)**  
As reduction will take place at cathode so reaction  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  Will take place at cathode
- (B)**  
If mercury is used as cathode in the electrolysis of aqueous NaCl solution then the metal is discharged at mercury to form amalgam.
- (B)**  
 $K = 0.3568 \Omega \text{ cm}^{-1}$   
conductance =  $0.0268 \Omega^{-1}$   
 $K = G \times l/A$   
 $0.3568 = 0.0268 \times l/9$   
 $13.31 \text{ cm}^{-1}$
- (B)**  
 $K = G \cdot L/A$   
 $10^{-3} \times 2.768 = 1/R \times L/A$   
 $L/A = 228.08 \times 10^{-3}$   
 $= 0.2281 \text{ cm}^{-1}$
- (A)**  
$$\wedge = \frac{1000 \times K}{M}$$
On decreasing the value of M will increase but increase will be hyperbolic.

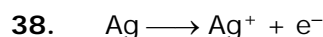
14. (C)  
Higher the dilution higher will be the equivalent conductance
15.  $K = G \frac{L}{A}$   
 $K = \frac{1}{R} \times \frac{L}{A}$   
 $\frac{1}{100} \times 1, K = 10^{-2} \Omega^{-1} \text{ cm}^{-1}$
16. (D)  
 $\lambda_m = \frac{K \times 1000}{M}$   
 $\lambda_m = \frac{0.0110 \times 1000}{0.05}$   
 $= 220 \text{ S cm}^2 \text{ mol}^{-1}$
17. (C)  
L/A is cell constant.  
 $\frac{1.5}{0.75} = 2.0 \text{ cm}^{-1}$
18. (B)  
That electrolyte will be the best electrolyte which has maximum number of ions.
19. (B)  
gm eq. of  $\text{H}_2 = \text{gm eq. of Cu}$   
 $\frac{0.504}{2} \times 2 = \frac{w}{63.5} \times 2$   
 $W = \frac{63.5 \times 0.50R}{2} = 16.0 \text{ gm}$
20. No. of F =  $\frac{it}{96500} = \text{gm eq of Cu}$   
moles of Cu =  $\frac{\text{gmeq. of Cu}}{2}$   
moles of Cu =  $\frac{2.6 \times 380}{96500 \times 2}$   
wt. of Cu =  $\frac{2.6 \times 380}{96500 \times 2} \times 63.5$   
 $= 0.325 \text{ gm}$
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 =  $\frac{8}{96500}$   
 $0.01 = \frac{8}{96500} = 965 \text{ C}$
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 required to generate 1 mole of Mg will be 2 .
26.  $\frac{1.81 \times 10^{22}}{6.02 \times 10^{23}} = \frac{1}{\text{At. mass}} \times 2$   
rxn.  $\text{Mn}^{2+} \longrightarrow \text{Mn}$   
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 =  $\frac{\text{equiv.}}{\text{nf.}}$   
 $\Rightarrow \text{ratio} : \frac{1}{1} ; \frac{1}{2} ; \frac{1}{3}$   
 $\Rightarrow 6 : 3 : 2$
28.  $\frac{2.1}{7} x = \frac{2.7}{27} \times y = \frac{7.2}{48} \times z$   
 $\Rightarrow \text{ratio } x = \frac{y}{3} = \frac{z}{2}$   
If  $x = 1 \Rightarrow y = 3, z = 2$

29. Volume :  $10 \times 10 \times 10^{-2} = 1 \text{ cm}^3$   
 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 =  $\frac{8.94}{63.5} \times 2 \times 96500 \text{ C}$   
 = 27172 C
30. Equivalent of  $\text{H}_2$  = Equivalent of  $\text{O}_2$   
 =  $\frac{2.4}{22.4} \times 4$   
 $\Rightarrow$  mole of  $\text{H}_2$  =  $\frac{2.4}{22.4} \times 4 \times \frac{1}{2}$   
 Volume of  $\text{H}_2$  =  $\frac{2.4 \times 2}{22.4} \times 22.4$   
 = 4.8 L
31. At both electrodes oxidation of Cu & reduction of Cu takes place  
 Anode  $\text{Cu} \longrightarrow \text{Cu}^{2+}$   
 Cathode  $\text{Cu}^{2+} \longrightarrow \text{Cu}$   
 So If 2.5 g deposited at cathode  $\Rightarrow$  2.5 of Cu mass decreased from anode
32.  $\text{Mn}_3\text{O}_4 + 8\text{H}_2\text{O} + 80\text{H}^- \rightarrow 3\text{MnO}_4^{2-} + 16\text{H}^+ + 16\text{OH}^- + 10\text{e}^-$   
 $\text{Mn}_3\text{O}_4 + 16\text{OH}^- \rightarrow 3\text{MnO}_4^{2-} + 8\text{H}_2\text{O} + 10\text{e}^-$   
 nf = 10
33. Cathode  
 $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$   
 Anode  
 $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$
34. LiCl (According to S.R.P.)  
 Cathode  
 $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$   
 Anode  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$   
 $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$   
 At cathode  $(\text{OH}^-) \uparrow$  pOH  $\downarrow$  and pH  $\uparrow$
35. (B)
36.  $E_{\text{cell}} = E^\circ - \frac{0.0591}{n} \log Q_{\text{eq}}$   
 $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2 \quad E^\circ = 0$   
 $Q_{\text{eq}} = \frac{P_{\text{H}_2}}{(\text{H}^+)^2}$

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

$$\Delta E_{\text{cell}} = 0.0591$$

37.  $E^\circ_{\text{cell}} = \frac{0.0591}{2} \log \frac{\text{Sr}^{2+}}{\text{Mg}^{2+}}$   
 =  $\frac{0.0591}{2} \log (2.69 \times 10^{+12}) = 0.3667$



$$E^\circ = -0.799 \quad E_{\text{cell}} = -0.25$$

$$E_{\text{cell}} = -0.25 \quad E^\circ_{\text{cell}} = -0.799$$

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

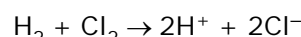
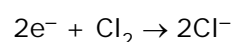
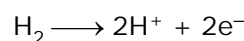
$$-0.25 + 0.799 = -0.0591 \log (\text{Ag}^+)$$

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

$$(\text{Ag}^+) = 5.13 \times 10^{-10}$$

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

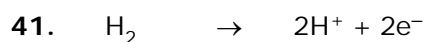
$$= 5.13 \times 10^{-11}$$



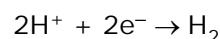
$$[(\text{H}^+)^2 (\text{Cl}^-)^2] = K_{\text{eq}}$$

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

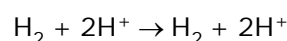
$$= E^\circ - 0.0591 \log [\text{H}^+] [\text{Cl}^-]$$



$$0.4 \text{ atm} \quad 10^{-1}$$



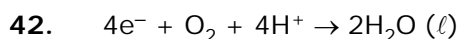
$$10^{-2} \quad 0.1 \text{ atm}$$



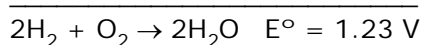
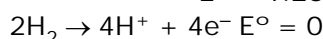
$$0.4 \quad 0.01 \quad 0.1 \quad 0.1 \quad E^\circ = 0$$

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

$$= -0.041$$



$$E^\circ = 1.23 \text{ V}$$



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

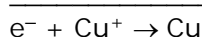
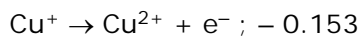
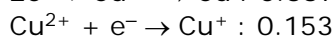
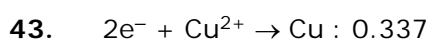
$$= -4 \times 96500 \times 1.23$$

$$= -474.78 \text{ kJ}$$

$$\Delta H^\circ = -285.5 \times 2 \text{ kJ}$$

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

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



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

$$= 0.674 - 0.153$$

$$= 0.521 \text{ V}$$



a

b

$$pH_1 = pK_a + \log a/b ; pH_2 = pK_a + \log b/a$$

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

$$E_1 = -0.0591 \text{ pH}_1 ; E_2 = -0.0591 \text{ pH}_2$$

$$E_1 + E_2 = -0.0591 (\text{pH}_1 + \text{pH}_2)$$

$$E_1 + E_2 = -0.0591 (2pK_a + \log a/2 + \log b/a)$$

$$= -0.0591 \times 2pK_a$$

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

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

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

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

$$= 10^{-2} \times \frac{1000}{0.5} = 20 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 20 \times 10^{-4} \text{ Sm}^2/\text{mol}$$

$$= 0.002 \text{ Sm}^2/\text{mol}^{-1}$$

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

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

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

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

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

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

↓

Molarity of ion

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

$$16 \times 10^{-8} = x^2$$

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

$$K = \frac{380 \times M}{1000} = \frac{380 \times 4 \times 10^{-4}}{1000}$$

$$= 152 \times 10^{-6} \text{ Scm}^{-1}$$

$$= 1.52 \times 10^{-2} \text{ Sm}^{-1}$$

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

$$\Rightarrow N = 6 \times 10^{-5}$$

$$\Rightarrow M = \frac{6 \times 10^{-5}}{3} = 2 \times 10^{-5}$$

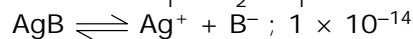
↪ n factor

$$K_{sp} = (3S)^2 (S) = 27S^4 = 27 \times 16 \times 10^{-20}$$

$$= 432 \times 10^{-20} = 4.32 \times 10^{-18}$$



$$S_1 + S_2 \quad S_1$$



$$S_1 + S_2 \quad S_2$$

$$S_1 + S_2 = 2 \times 10^{-7} ; S_1 = 1.5 \times 10^{-7}$$

$$S_2 = 0.5 \times 10^{-7}$$

$$375 \times 10^{-10} = K_{Ag^+} + K_{A^-} + K_{B^-}$$

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

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

$$= 60 (S_1 + S_2) + 80 S_1 + \Lambda_{B^-} S_2$$

After putting value of  $S_1$  &  $S_2$

$$\Lambda_{B^-} = 270$$

## Exercise-II

- $\text{Pb(s)} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$   
 $\text{H}_2\text{SO}_4$  : consumed  
 $\text{H}_2\text{O}$  : produced (volume increases and density decreases)  
 Anode  
 $\text{Pb(s)} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$   
 Cathode  
 $2\text{e}^- + 4\text{H}^+ + \text{PbO}_2 + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$
- (A) At anode oxidation of Cu produce  $\text{Cu}^{2+}$   
 (B) At both electrode oxidation or reduction of hydrogen or  $\text{H}^+$   
 (C) At anode  
 $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$   
 (D) Anode  
 $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$
- Cell reaction  
 $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$   
 $270 \text{ g H}_2\text{O} = \frac{270}{18} \text{ mole} = 15 \text{ mole}$   
 equivalent =  $15 \times 2 = 30$  equivalent  
 (a)  $\text{O}_2$  evolved =  $\frac{15}{2} = 7.5 \text{ mole} = 7.5 \times 22.4 \text{ L} = 168 \text{ L}$   
 (b) Total mole of gas =  $15 \times \frac{3}{2} = \frac{45}{2}$   
 Total volume of gas produced  
 =  $22.4 \times \frac{45}{2} = 504 \text{ L}$   
 (c)  $\text{H}_2$  produced =  $30 \times 22.4 = 336 \text{ L}$   
 at cathode current efficiency = 75%  
 (d) for 30 F electricity consumed  
 will be =  $30 \times \frac{100}{75} = 40 \text{ F}$
- (a) SOP ( $\text{SO}_4^{2-}$ ) = -2.00  
 SOP ( $\text{Cl}^-$ ) = -1.36  
 oxidation of  $\text{SO}_4^{2-}$  will not take place  
 (b) SOP ( $\text{Cl}^-$ ) = -13.6  
 SOP ( $\text{I}^-$ ) = -0.54  
 SOP ( $\text{Br}^-$ ) = -1.09  
 (c) Similarly as (b) option  
 (d)  $\text{Br}^-$  can't be reduced further.
- Cell reaction  
 Anode  
 $\text{Ag(s)} + \text{Cl}^- \rightarrow \text{AgCl(s)} + \text{e}^-$   
 Cathode  
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$   
 $2\text{Ag(s)} + 2\text{Cl}^- + 2\text{H}^+ \rightleftharpoons 2\text{AgCl(s)} + \text{H}_2$

$$E = E^\circ - \frac{0.0591}{2} \log \left\{ \frac{P_{\text{H}_2}}{[\text{Cl}^-]^2 [\text{H}^+]^2} \right\}$$

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

$$\Rightarrow E^\circ = 0.22 \text{ V}$$

$$E_{\text{cell}} = 0.22 - \frac{0.0591}{2} \log \left\{ \frac{P_{\text{H}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right\}$$

$$(a) P_{\text{H}_2} = 2 \Rightarrow E_{\text{cell}} < 0.22$$

$$(b) [\text{Cl}^-] \uparrow \Rightarrow \log \left\{ \frac{P_{\text{H}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right\} = -\text{ve}$$

value

$$\Rightarrow E_{\text{cell}} > 0.22$$

$$(c) [\text{H}^+] \uparrow \Rightarrow E_{\text{cell}} > 0.22$$

$$(d) \text{KCl conc}^n \downarrow \Rightarrow [\text{Cl}^-] \downarrow$$

$$\Rightarrow \log \left\{ \frac{P_{\text{H}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right\} > 0$$

$$\Rightarrow E_{\text{cell}} < 0.22$$

- $\text{H}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O}$   
 $0.015 \text{ V} \quad 0.015 \text{ V} \quad 0.015 \text{ V}$   
 mole mole mole

$$\text{molarity (CH}_3\text{COONa)} = \frac{0.015 \text{ V}}{2 \text{ V}} = \frac{0.015}{2}$$

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

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

- HgO Cathode ; Zn (anode)  
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$   
 $\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$   
 Cell reaction  
 $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$   
 No active species in cell reactions  
 $\Rightarrow$  no change in cell voltage.
- SRP increases  $\Rightarrow$  The tendency to getting reduced increases and the oxidizing power increases.
- We can add only when the net reaction does not contain any electron [E.P. is an intensive property]
- 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 .

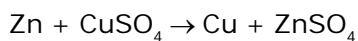
**Statement II** : It is also correct that atomic weight of silver and copper are different but statement II is not the right explanation of I. So answer (B).

11. **Statement I** : is correct because copper lies at higher position in electrochemical series so copper 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



Zinc oxidation takes place and reduction of copper takes place.

**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 explanation 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** : Absolute 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  $\text{H}_2\text{O} = \frac{1}{10000} = C$

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

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

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

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

For C

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

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

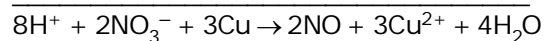
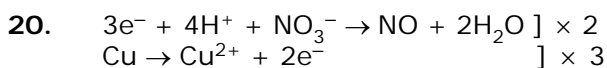
$$C = \frac{1}{8000} - \frac{1}{10000} = \frac{1}{40000}$$

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

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

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

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



$$E_{\text{cell}}^{\circ} = 0.96 - 0.34 = 0.62$$

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

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

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

$$= 0.71 \text{ V}$$



21. C

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

23.  $E = \varepsilon^\circ - \frac{0.591}{n} \log Q.$   
 ef  $KC = Q$   
 $E = 0$   
 Ans. (C)

24.  $\varepsilon = \varepsilon^\circ - \frac{0.591}{n} \log Q.$   
 (A) i.e. straight line

25.  $\varepsilon^\circ = \frac{0.591}{n} \log V_e.$   
 here  $n = 2$

$$0.46 = \frac{0.591}{n} \log K_e$$

Ans. (A)

26.  $\varepsilon^\circ = \frac{0.591}{2} \log V_e$

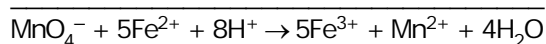
$$1.10 = \frac{0.591}{2} \log K_e$$

Ans. (B)

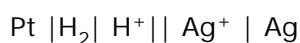
27. (A) At cathode  $H_2$   
 At anode  $O_2$   
 (B) At cathode  $H_2$   
 At anode  $O_2$   
 (C) At cathode  $H_2$   
 At anode  $Cl_2$   
 (D) At cathode Ag  
 At anode  $O_2$

## 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



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



3.  $E^\circ_{\text{cell}} = E^\circ_{Ce^{4+}/Ce^{3+}} + E^\circ_{Co/Co^{2+}}$

$$1.89 = E^\circ_{Co^{4+}/Co^{3+}} + 0.28$$

$$E^\circ_{Cu^{4+}/Cu^{3+}} = 1.61$$

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

$$-0.15 = 1.20 + E^\circ_{Cl^-/Cl_2}$$

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

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

5.  $E^\circ_{Ag/Ag^+} = -0.80 V$

$$E^\circ_{H_2/H^+} = 0$$

$$\text{Ox. potential of } E^\circ_{H_2/H^+} > E^\circ_{Ag/Ag^+}$$

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

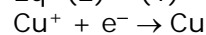
6.  $Cu^{2+} + e^- \rightarrow Cu^{2+} \quad E^\circ = 0.15 V$

....(1)

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^\circ = 0.34 V$$

....(2)

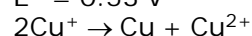
$$\text{Eq}^n (2) - (1)$$



....(3)

$$E^\circ = \frac{(0.34 \times 2) - (0.15)}{1}$$

$$E^\circ = 0.53 V$$



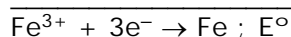
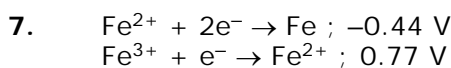
....(4)

$$E^\circ_{\text{disproportionation}}$$

$$\text{Eq}^n (4) = \text{Eq}^n (3) - \text{Eq}^n (1)$$

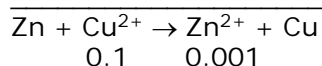
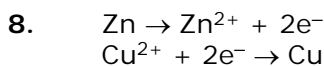
$$E^\circ_{\text{disproportionation}} = 0.53 - 0.15 = 0.38 V$$

Ans : Yes



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

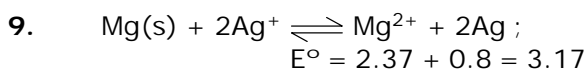
$$E^\circ = -0.367$$



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

$$E = E^\circ - \frac{0.0591}{2} \log \left( \frac{1}{100} \right)$$

$$E = 1.1 + 0.0591 = 1.1591 \text{ V}$$



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

$$3.17 = \frac{0.0591}{2} \log \text{keq}; \Rightarrow \text{keq} = 10^{107.27}$$

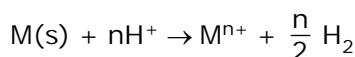
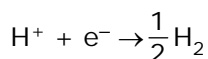
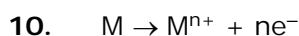
$$\Rightarrow \text{Keq} = 1.862 \times 10^{107}$$

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

$$= -2 \times 96500 \times 3.17 = -611810 \text{ J}$$

$$= -611.81 \text{ J} \Rightarrow \text{max. work} = 611.81$$

kJ



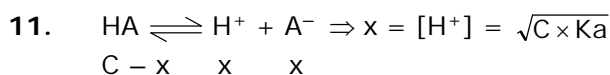
$$E^\circ = 0.76$$

$$E = E^\circ - \frac{0.0591}{n} \log \left[ \frac{(\text{M}^{n+})(\text{P}_{\text{H}_2})^{n/2}}{[\text{H}^+]^n} \right]$$

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

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

$$\Rightarrow n = 2$$



$$\text{pH} = \frac{1}{2} (\text{pK}_a - \log C) ;$$

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

Cell is concentration cell  $\Rightarrow E^\circ = 0$

$$E = -0.0591 [\log (\text{H}^+)_1 - \log (\text{H}^+)_2]$$

$$= 0.0591 [\text{pH}_1 - \text{pH}_2]$$

$$= \frac{1}{2} \times 0.0591 [\text{pK}_{a1} - \text{pK}_{a2} - \log C_1 + \log C_2]$$

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

$$= 0.0591 \text{ V}$$

12.  $E^\circ_{\text{cell}} = 0.14 - 0.13 = 0.01 \text{ V}$

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

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

$$= 0.01 - \frac{0.0591}{2} \times 3$$

$$= -0.07865 \text{ V} \quad \text{Ans.}$$

$$E_{\text{cell}} < 0 \Rightarrow \text{Wrong representation.}$$

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

$$E = 0$$

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

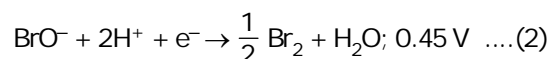
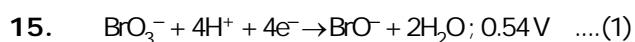
$$\Rightarrow -\frac{0.34 \times 2}{0.059} = \log [\text{Cu}^{2+}]$$

$$\Rightarrow [\text{Cu}^{2+}] = 2.98 \times 10^{-12}$$

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

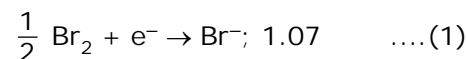
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

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



For resulting reaction  $E^\circ_1 =$

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



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

Resulting  $E^{\circ}_2 =$

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

$$E^{\circ}_2 = 0.613 \text{ V}$$

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

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

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

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

$$E_{\text{cell}} = 0.0295 \text{ V}$$

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

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

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

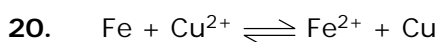
$$\Rightarrow -\log x = \text{pH} = 4 \quad \text{Ans.}$$

$$19. \quad E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V}; E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 \text{ V}]$$

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

$$1.44 - 0.68 = 0.059 \log \text{Keq.}$$

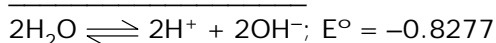
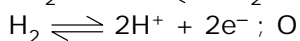
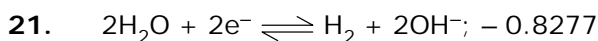
$$\text{Keq.} = 7.6 \times 10^{12}$$



$$E_{\text{cell}} = 0.44 + 0.337 = 0.777$$

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

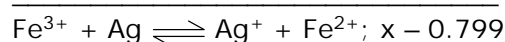
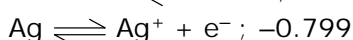
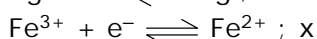
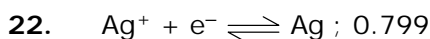
$$\text{Keq.} = 1.97 \times 10^{26}$$



$$-0.8277 = 0.059 \log \text{Keq.}$$

$$\log \text{Keq.} = -14$$

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



$E_{\text{cell}} = 0$  at equilibrium

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

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

$$\Rightarrow x = 0.7827 \text{ V}$$

$$23. \quad \Delta G^{\circ}_{\text{rxn}} = -nFE^{\circ}_{\text{cell}} = -12 \times F \times 2.73 \text{ J}$$

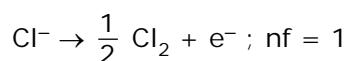
$$\Rightarrow -\frac{12 \times 96500 \times 2.73}{1000} = 4 \times \Delta_f G^{\circ}$$



$$\Rightarrow \Delta_f G^{\circ} [\text{Al}(\text{OH})_4^-] = \frac{-4(-157) - 6(-237.2)}{4} = -1303.13 \text{ kJ}$$

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

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



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

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

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

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

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

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

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

$$25. \quad (\text{a}) \quad 0.25 \text{ mole} = 0.25 \times 3 \text{ equivalents}$$

$$\Rightarrow \text{charge} = 0.25 \times 3 \text{ F}$$

$$(\text{b}) \quad \frac{27.6}{80} \text{ mole} = \frac{27.6}{80} \times 2 \text{ equivalent}$$

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

$$(\text{c}) \quad \text{Equivalent} = 0.5 \times 1.1 \times 2 = 1.1$$

$$\text{Charge} = 1.1 \text{ F}$$

$$26. \quad 0.5 \text{ mole e}^- = 0.5 \text{ F charge by 2}^{\text{nd}} \text{ law}$$

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

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

And

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

27.  $\text{MnO}_2 = \frac{1000}{87} \times 2 \text{ g} \cdot \text{eq.}$   
 where 2 = n factor  
 $\text{Mn}^{2+} \rightarrow \text{Mn}^{4+} + 2\text{e}^-$ ;  $n_f = 2$   
 By using ( $w = \frac{ItE}{96500}$ );  $w = \text{mass}$   
 $E = \text{Eg. wt.}$

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

$$\Rightarrow t = 1.023 \times 10^5 \text{ sec.}$$

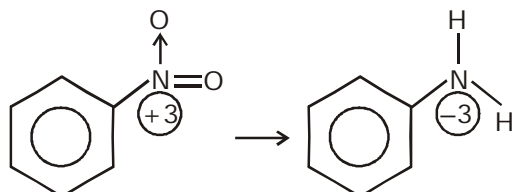
$$\Rightarrow t = 28.43 \text{ hrs.}$$

28.  $\frac{0.224}{22.4} = \frac{1}{100} \text{ mole H}_2$   
 $\Rightarrow \text{Equivalent of H}_2 = \frac{1}{100} \times 2 = \frac{1}{50}$   
 $\Rightarrow \text{O}_2 \text{ produced} = \frac{1}{50} \text{ equivalents}$   
 $= \frac{1}{50} \times \frac{1}{4} = \frac{1}{200} \text{ mole}$   
 $= \frac{1}{200} \times 22.4 = 0.112 \text{ L}$

29.  $x \text{ g Al} = \frac{x}{27} \times 3 \text{ g equivalent Al}$   
 $= \frac{x}{9} \text{ equi. of Al}$   
 $\Rightarrow x \text{ Rs. for } x/9 \text{ equi.}$   
 $\Rightarrow \text{For 1 eq. 9 Rs.}$   
 $x \text{ g Mg} = \frac{x}{24} \times 2 = \frac{x}{12} \text{ Eq. Mg}$   
 For  $\frac{x}{12}$  equi. Mg Rs =  $\frac{x}{12} \times 9 = \frac{3x}{4} \text{ Rs.}$

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)  $\frac{w}{E} = \frac{It}{96500} \Rightarrow \frac{1.5}{\left(\frac{52}{6}\right)} = \frac{12.5 \times 6}{96500}$   
 $\Rightarrow t = 1336.15 \text{ sec}$

31.



nf = 6

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

$$\Rightarrow \text{potential drop} = V = 3$$

$$\text{then energy} = q \times V = 11.58 \times 10^4 \times 3$$

$$J$$

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

$$= 347.4 \text{ kJ}$$

32. Volume of layer =  $80 \times 10^{-4} \text{ m}^2 \times 5 \times 10^{-6} \text{ m}$   
 $= 4 \times 10^{-2} \text{ cm}^3$   
 mass of silver =  $10.8 \times 4 \times 10^{-2}$   
 $= 43.2 \times 10^{-2} \text{ g}$

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

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

$$\Rightarrow t = \frac{0.004 \times 96500}{1} = \frac{0.004 \times 96500}{2}$$

$$\Rightarrow t = 193 \text{ sec.}$$

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

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

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

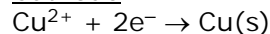
$$\Rightarrow \text{Mol. wt.} = 114.05 \text{ g/mole}$$

For Cu

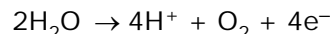
$$\frac{1.95}{63.5} \times 2 = \frac{Q}{96500}$$

$$\Rightarrow Q = 5926.8 \text{ Columb} \quad \text{Ans.}$$

34. g. eq. of  $\text{CuSO}_4 = 0.125$  (taken)  
 more than 0.01 F  
 $\Rightarrow \text{Only } 0.01 \text{ g. eq. CuSO}_4 \text{ will be deposited}$

Cathode

Anode



$$\text{g. eq. of Cu(s)} = 0.01$$

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

$$\Rightarrow \text{Wt. of O}_2 = \frac{0.01}{4} \times 32$$

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

↓

gram of metal

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

from Eqn (1) &amp; (2)

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

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

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

36.  $31.75 \text{ g Cu} = \frac{31.75}{63.5} = \frac{1}{2} \text{ mole}$   
 $= \frac{1}{2} \times 2 = 1 \text{ eq.}$   
 $\Rightarrow 1 \text{ eq. of Na with } 100 \% \text{ yield}$   
 But Eq. of Na =  $1 \times \frac{600}{1000} = 0.6$   
 $\Rightarrow \% \text{ yield} = 60 \%$

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 =  $\frac{30}{965} \times 58.7 = 1.8248 \text{ g}$

38.  $\text{Ni}^{2+}$  solution in Ni electrodes  
Cathode  
 $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$   
Anode  
 $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$   
 No change in molarity  
 Conc<sup>n</sup> = 2M Ans.

39.  $\frac{\ell}{A} = 0.88 \text{ cm}^{-1}$   
 $R = 210 \text{ ohm}$   
 $\Rightarrow C = \frac{1}{210} \text{ mho}$   
 $k = \frac{1}{210} \times 0.88$  by  $k = C \times \frac{\ell}{A}$   
 $\lambda_e = K \times \frac{1000}{N} = \frac{0.88}{210} \times \frac{1000}{0.01}$   
 $= 419 \text{ Scm}^2 \text{ eq}^{-1}$

40.  $\ell_m = k \times \frac{1000}{0.1}$   
 $4.6 = k \times \frac{1000}{0.1}$   
 $\Rightarrow k = 4.6 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$   
 $\rho = \frac{1}{k} = \frac{10^4}{4.6} = 2173.9 \approx 2174$

↓  
Resistivity

41.  $k = 8 \times 10^{-7} \text{ Scm}^{-1}$   
 $k = c \frac{\ell}{A} = C \times \frac{2}{4} = \frac{C}{2}$   
 $C = 2k = 16 \times 10^{-7} \text{ ohm}^{-1}$   
 (i)  $R = \frac{1}{C} = \frac{10^7}{16} = 6.25 \times 10^5 \text{ ohm}$   
 (ii)  $v = IR \Rightarrow I = \frac{V}{R} = \frac{1}{\left(\frac{10^7}{16}\right)}$   
 $\Rightarrow V = 16 \times 10^{-7} \text{ amp.}$
42.  $k = \frac{1}{709.22} = 0.00141 \text{ ohm}^{-1} \text{ cm}^{-1}$   
 $= 0.141 \text{ ohm}^{-1} \text{ m}^{-1}$   
 $\lambda_e = \frac{1}{709.22} \times \frac{1000}{0.01}$   
 $\Rightarrow \lambda_e = 140.99 \approx 141 \text{ mho cm}^2 \text{ eq}^{-1}$   
 $= 141 \times 10^{-4} \text{ mho m}^2 \text{ eq}^{-1}$   
 $= 0.0141 \text{ mho m}^2 \text{ eq}^{-1}$
43.  $\text{BaCl}_2 = \frac{2.08}{137 + 71} = \frac{2.08}{208} = 0.01 \text{ mole}$   
 Molarity =  $\frac{0.01}{400} \times 1000 = \frac{10}{400} = 0.025$   
 M  
 Normality =  $0.025 \times 2 = 0.05 \text{ N}$   
 $\lambda_m = 0.0058 \times \frac{1000}{0.025} = 232$   
 $\lambda_e = 0.0058 \times \frac{1000}{0.05} = 116$
44.  $\lambda [\text{Ba(OH)}_2] = 280 \times 10^{-4} + (248.1 \times 10^{-4}) \times 2$   
 $- 2 \times (126.5 \times 10^{-4})$   
 $= 523.2 \times 10^{-4}$   
 $\lambda_{[\text{Ba(OH)}_2]}^{\circ} = \lambda_{\text{BaCl}_2}^{\circ} + 2\lambda_{\text{NaOH}}^{\circ} - 2\lambda_{\text{NaCl}}^{\circ}$
45.  $\alpha = \frac{112.4}{129.9}$   
 $\alpha = 0.865$
46.  $\Lambda_m^{\circ}(\text{CH}_3\text{COOH}) = \Lambda_m^{\circ}(\text{CH}_3\text{COONa}) + \Lambda_m^{\circ}(\text{HCl})$   
 $- \Lambda_m^{\circ}(\text{NaCl})$   
 $= 91 + 426.1 - 126.5 = 390.6$   
 $\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{48.15}{390.6} = 0.1233$   
 $\% \alpha = 12.33 \%$

47.  $\Lambda_m^\infty(\text{AgBr}) = 133 + 137.4 - 131 = 139.4$   
 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$   
 Specific conductance of saturated AgBr

Solution = specific conductance of AgBr

$$\Rightarrow K_{\text{AgBr}} = \frac{\text{specific conductance of H}_2\text{O}}{139.4} = 8.486 \times 10^{-7} - 7.5 \times 10^{-7} = 0.986 \times 10^{-7}$$

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

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

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

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

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

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

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

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

$$\Rightarrow K_{\text{sp}} = (\text{Ag}^+) (\text{Cl}^-) = N^2$$

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

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.  $\Lambda_m^\infty(\text{H}_2\text{O}) = (3.4982 + 1.98) \times 10^{-2}$   
 $= 5.4782 \times 10^2 \text{ S cm}^2 \text{ mole}^{-1}$

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

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

$$M = 1.04 \times 10^{-7} = [\text{H}^+] = [\text{OH}^-]$$

$$\text{pH} = 6.98$$

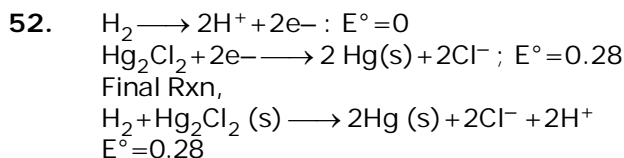
$$K_w = [\text{H}^+] [\text{OH}^-] = 1.08 \times 10^{-14}$$

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

The current would initially deposit Cu till

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} \text{ become } 0.266 \text{ V}$$

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



$$K = \frac{(\text{Cl}^-)^2 (\text{H}^+)^2}{P_{\text{H}_2}}$$

$$0.67 = 0.28 - \frac{0.0591}{2} \log \frac{(\text{Cl}^-)^2 (\text{H}^+)^2}{P_{\text{H}_2}}$$

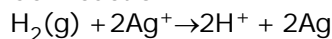
$\Rightarrow$  Normal calomel electrode  $\rightarrow P_{\text{H}_2} = 1$

$$(\text{Cl}^-) = 1$$

$$\Rightarrow -\log(\text{H}^+) = 6.6$$

$$\Rightarrow \text{pH} = 6.6$$

53. Cell reaction

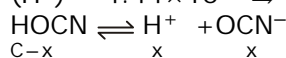


$$E^\circ_{\text{cell}} = 0.8 \text{ V}$$

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

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

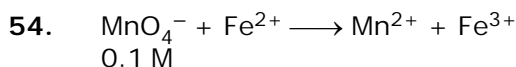
$$\Rightarrow (\text{H}^+)^2 = 4.44 \times 10^{-7} \Rightarrow [\text{H}^+] = 6.66 \times 10^{-4}$$



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

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

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

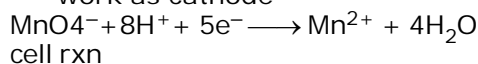


$$\frac{0.1 \times 10}{100} \quad \frac{0.1 \times 90}{100}$$

$$E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} > E^\circ_{\text{H}^+/\text{H}_2}$$



work as cathode



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{5} \log \frac{(\text{Mn}^{2+})}{(\text{H}^+)^8 (\text{MnO}_4^-)}$$

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

$$= 1.41 \text{ V}$$



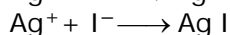
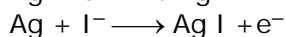
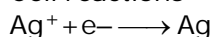
$$E_{\text{cell}} - 0.9 = -0.0591 \log \frac{1}{56} + 0.0591 \log \frac{1}{8}$$

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

$$= 0.0499$$

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

60. Cell reactions



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

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

$$\Rightarrow E^\circ = 0.94 \text{ V}$$

$$\text{Now } E^\circ = 0.0591 \log \frac{1}{K_{\text{sp}}(\text{AgI})}$$

$$\Rightarrow K_{\text{sp}}(\text{AgI}) = 1.16 \times 10^{-16}$$

61. conc. cell

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

$$E_{\text{cell}} = -0.0591 \log$$

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

For  $E_{\text{cell}} = 0$

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

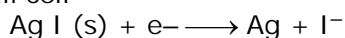
$$\Rightarrow \frac{[\text{Cl}^-]}{[\text{Br}^-]} = \frac{10^{-10}}{5 \times 10^{-13}} = 200$$

62.  $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$

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

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

For Half cell



$$E^\circ = \frac{0.0591}{1} \log (\text{I}^-)$$

$$\frac{E^\circ}{0.0591} = \log (\text{I}^-)$$

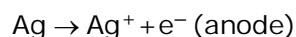
$$\frac{0.7991}{0.0591} - \frac{E^\circ}{0.0591} = -\log (\text{Ag}^+) (\text{I}^-)$$

$$= -\log K_{\text{sp}} = P_{K_{\text{sp}}} = 16.07$$

$$\Rightarrow E^\circ = (16.07 \times 0.0591) - 0.7991$$

$$\Rightarrow E^\circ = -0.15 \text{ V}$$

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



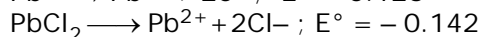
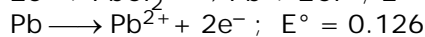
$$= -0.0591 \log \left[ \frac{\left( \frac{2.8 \times 10^{-10}}{0.2} \right)}{\frac{3.3 \times 10^{-13}}{0.001}} \right]$$

$$= -0.0591 \log \left[ \frac{2.85 \times 10^{-13}}{0.66 \times 10^{-13}} \right]$$

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

$$= -0.037$$

64.  $2e^- + \text{PbCl}_2 \longrightarrow \text{Pb} + 2\text{Cl}^-$ ;  $E^\circ = -0.268$

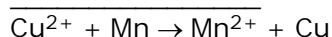
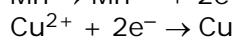


$$E^\circ = \frac{0.059}{2} \log K_{\text{sp}}$$

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

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

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



$$E^\circ = 0.340 + 1.18$$

$$= 1.52$$

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

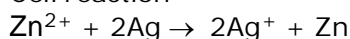
$$= 1.52 - \frac{0.0591}{2} \log \frac{(K_{\text{sp}} / (\text{OH}^-)^2)}{(\text{Cu}^{2+})}$$

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

$$= 1.654 \text{ V}$$



66. Cell reaction



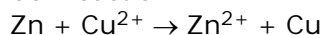
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \left[ \frac{(\text{Ag}^+)^2}{(\text{Zn}^{2+})} \right]$$

$$= E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} + E^{\circ}_{\text{Ag}/\text{Ag}^+} - \frac{0.0591}{2} \log \left[ \frac{\left\{ \frac{K_{\text{sp}}(\text{AgIO}_3)}{[\text{IO}_3^-]} \right\}^2}{(\text{Zn}^{2+})} \right]$$

$$= -0.762 - 0.799 - \frac{0.0591}{2} \log \left[ \frac{\left( \frac{3.02 \times 10^{-8}}{0.3} \right)^2}{0.175} \right]$$

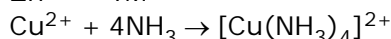
$$= -1.17 \text{ V}$$

67. Cell reaction



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

$$\text{Zn}^{2+} = 1\text{M}$$



$$1\text{M}$$

$$y \quad 2\text{M} \quad 1\text{M}$$

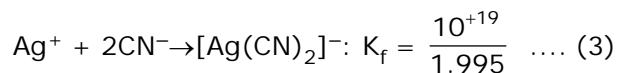
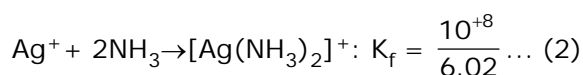
$$K_{\text{p}} = 1 \times 10^{12} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

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

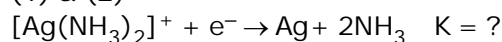
$$y = \frac{10^{-12}}{32} = 3.125 \times 10^{-14}$$

$$E_{\text{cell}} = 1.1 - \frac{0.0591}{2} \log \frac{1}{(3.125 \times 10^{-14})}$$

$$= 0.7 \text{ V}$$

68.  $K_{\text{f}} = 8.227 \times 10^{63}$ 69.  $\text{Ag}^+ + \text{e}^- \rightarrow \bar{\text{Ag}} \quad ; E^{\circ} = 0.7991 \dots (1)$ 

(1) &amp; (2)



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

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

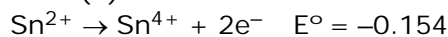
$$K = \frac{10^{13} \times 3.32}{10^8 / 6.02} = 1.99 \times 10^6 = 2 \times 10^6$$

$$E^{\circ} = \frac{0.0591}{1} \log(2 \times 10^6)$$

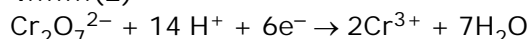
$$= 0.372 \text{ V}$$

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

.....(1)



V.....(2)



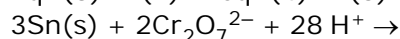
$$E^{\circ} = 1.33 \text{ V} \dots (3)$$

Eq. (1) + (2)



$$E^{\circ} = \frac{(0.136 \times 2) + (-0.154 \times 2)}{4}$$

$$= -0.009 \text{ V}$$

Eq. (3)  $\times$  (2) + eq. (4)  $\times$  (3)

$$E^{\circ} = 1.33 - 0.009$$

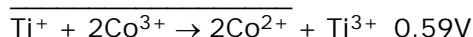
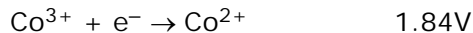
$$E^{\circ} = 1.321$$

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

$$\log K_{\text{eq}}$$

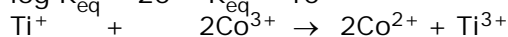
$$\log K_{\text{eq}} = \frac{1.321 \times 12}{0.0591}$$

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

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

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

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



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

$$\text{volume} = 50 \text{ ml}$$

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

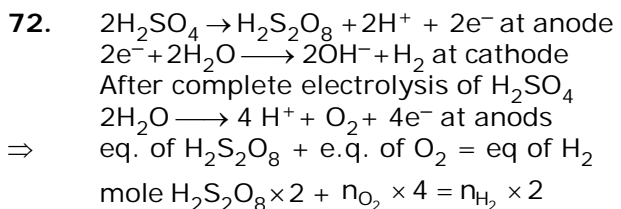
$$= 4y^3 = 5 \times 10^{-24} = y^3 = 1.25 \times 10^{-24}$$

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

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

$$(\text{Ti}^{3+}) = 1.08 \times 10^{-8}$$

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



$$\Rightarrow \text{mole } \text{H}_2\text{S}_2\text{O}_8 \times 2 + \frac{2.35}{22.4} \times 4 = \frac{9.722}{22.4} \times 4$$

$$n_{\text{H}_2\text{S}_2\text{O}_8} = 0.224 \text{ mole}$$

$$\text{mass of } \text{H}_2\text{S}_2\text{O}_8 = 0.224 \times 194 = 43.494 \text{ g}$$

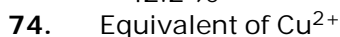
73. Faraday =  $\frac{3 \times 2 \times 3600}{96500} = \frac{216}{965}$  supplied

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

Faraday used  
 current efficiency =

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

$$= 42.2 \%$$



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

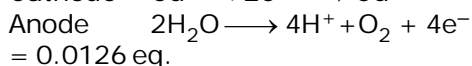
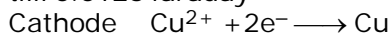
total faraday supplied =

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

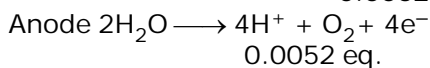
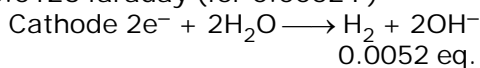
$$= 0.0126 + 0.0052$$

$$= 0.178$$

till 0.0126 faraday



After 0.0126 faraday (for 0.0052 F)



$$\text{total } \text{O}_2 \text{ evolved} = 0.0178 \text{ eq.}$$

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

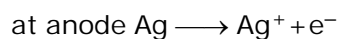
$$\frac{0.0178}{4} \times 22.4 = 0.09968 \text{ L}$$

$$= 99.68 \text{ ml}$$

$$\text{H}_2 \text{ evolved} = 0.0052 \text{ eq.} = \frac{0.0052}{2} \text{ mole}$$

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

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



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

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

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

but it is 95% pure by wt.

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

$$42.42 \text{ g}$$

$$\text{wt. of anode finally} = 100 - 42.42 = 57.58 \text{ g}$$

76. Wt of water =  $8 \times 10^{12} \text{ lit} = 8 \times 10^{12} \text{ gm}$

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

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

time in years.

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

$$1.9 \text{ million year}$$



volume of solution = 1000 ml

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

$$\text{wt. of } \text{H}_2\text{SO}_4 = 1261 \times \frac{34.6}{100} = 436.306 \text{ g}$$

$$\text{wt. of water} = 1261 - 436.306 = 824.64 \text{ g}$$

After electrolysis

Now during reaction wt. of  $\text{H}_2\text{O}$  formed = x g.

$$\text{mole of } \text{H}_2\text{O} \text{ formed} = \frac{x}{18}$$

$$\text{mole of } \text{H}_2\text{SO}_4 \text{ used} = \frac{x}{18}$$

$$\text{wt. of } \text{H}_2\text{SO}_4 \text{ used} = 98 \times \frac{x}{18} = 5.44x \text{ g.}$$

$$\text{wt. of } \text{H}_2\text{SO}_4 \text{ left} = (436.306 - 5.44x) \text{ g}$$

New wt. of solution = old wt. of solution + wt. of  $\text{H}_2\text{O}$  formed

$$\begin{aligned}
 & - \text{wt. of H}_2\text{SO}_4 \text{ lost} \\
 & = 1261 + x - 5.44x \\
 \text{\% by wt. of new solution} & = \frac{436.306 - 5.44x}{1261 + x - 5.44x} = \frac{27}{100} \\
 x & = 22.59 \text{ g} \\
 \therefore \frac{22.59}{18} & \text{ mole of H}_2\text{O are formed} \\
 \text{Eq. of H}_2\text{O} & = \frac{22.59}{18} \quad (n f = 1) \\
 \text{Faraday} & = \frac{22.59}{18} = 1.255 \text{ faraday} \\
 \text{charge} & = 1.21 \times 10^5 \text{ coulomb}
 \end{aligned}$$

78.  $E^\circ_{\text{cell}} = 0.28 - 0.699 = -0.419 \text{ V.}$

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

cell rxn,  $2e^- + \text{Hg}_2\text{Cl}_2 \longrightarrow 2 \text{Hg Cl} + 2 \text{Cl}^-$   
 $Q \longrightarrow Q \text{H}_2\text{H}^+ + e^-$   
 $2Q + \text{Hg}_2\text{Cl}_2 \longrightarrow 2\text{HgCl} + 2\text{Cl}^- + 2\text{QH}_2\text{H}^+$

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

$$= -0.419 + 0.0591 \text{ pH} = -0.419 + 0.0591 \times 5$$

$$= -0.1235$$

$$E_{\text{cell}} = 0 \Rightarrow \text{pH} = \frac{0.419}{0.0591} = 7.09$$

79.  $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$

$$K_1 = \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]} = 10^{-8}$$

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

$$K_2 = \frac{[\text{S}^{2-}][\text{H}^+]}{[\text{HS}^-]} = 1.1 \times 10^{-13}$$

$$K_1 \cdot K_2 = 1.1 \times 10^{-21} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

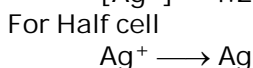
$$\Rightarrow [\text{S}^{2-}] = \frac{1.1 \times 10^{-21} \times 0.1}{(10^{-3})^2}$$

( $\therefore [\text{H}^+] = 10^{-3}$  and  $[\text{H}_2\text{S}] = 0.1 \text{ M}$ )  
 $[\text{S}^{2-}] = 0.11 \times 10^{-15}$

Thus for  $\text{Ag}_2\text{S}$   $K_{\text{sp}} = [\text{Ag}^+]^2[\text{S}^{2-}]$   
 $2 \times 10^{-49} = [\text{Ag}^+]^2 [1.1 \times 10^{-16}]$

$$[\text{Ag}^+]^2 = \frac{2 \times 10^{-49}}{1.1 \times 10^{-16}} = 18.18 \times 10^{-34}$$

$$[\text{Ag}^+] = 4.26 \times 10^{-17} \text{ M}$$



$$\begin{aligned}
 E & = E^\circ - 0.0591 \log \frac{1}{[\text{Ag}^+]} \\
 & = 0.8 + 0.0591 \log [4.26 \times 10^{-17}] \\
 & = -0.1658 \text{ V}
 \end{aligned}$$

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

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

we need R

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

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

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

$$\Rightarrow K = 9.71 \times 10^{-3}$$

$$\Rightarrow C = \frac{9.71 \times 10^{-3}}{(1/3)} = 3 \times 9.7 \times 10^{-3}$$

$$I = 5 \times 3 \times 9.71 \times 10^{-3} = 0.1456 \text{ amp.}$$

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

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

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

$$\frac{73.52}{96500} = \frac{v}{(6/10)} \Rightarrow v = \frac{73.52 \times 0.6}{9600}$$

$$V = 4.57 \times 10^{-4} \text{ cm/s}$$

In 2hrs distance travelled by ion  
 $\Rightarrow 4.56 \times 10^{-4} \times 2 \times 3600 = 3.29 \text{ cm}$

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

$$1.342 = \frac{1}{170.5} \times \frac{l}{1.86 \times 10^{-6} \times 10^{-4}} \text{ (in m}^2\text{)}$$

$$l = 1.342 \times 170.5 \times 1.86 \times 10^{-10}$$

$$l = 4.25 \times 10^{-8} \text{ m}$$

$$l = 4.25 \times 10^{-6} \text{ cm}$$

83.  $K_{\text{SrSO}_4} + K_{\text{water}} = K$  satatal so

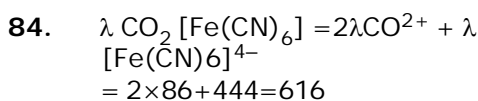
$$K_{\text{SrSO}_4} = 1.482 \times 10^{-4} - 1.5 \times 10^{-6}$$

$$K_{\text{SrSO}_4} = (1.482 - 0.015) \times 10^{-4} = 1.467 \times 10^{-4}$$

$$\begin{aligned}
 \lambda \text{Sr}^{2+} + \lambda \text{SO}_4^{2-} & = \lambda \text{SrSO}_4 = 59.46 + 79.8 \\
 \lambda \text{SrSO}_4 & = 139.26
 \end{aligned}$$

$$139.26 = 1.467 \times 10^{-4} \times \frac{1000}{M}$$

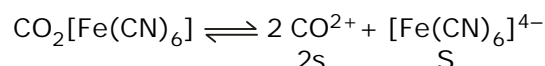
$$M = 0.00105 \text{ mole /L}$$



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

$$616 = (2.06 \times 10^{-6} - 4.1 \times 10^{-7}) \times \frac{1000}{M}$$

$$M = \frac{1.65 \times 10^{-6} \times 1000}{616} = 2.678 \times 10^{-6} = 5$$



$$K_{\text{eq}} = 4s^3$$

$$= 4 \times (2.678 \times 10^{-6})^3$$

$$K_{\text{eq}} = 7.687 \times 10^{-17}$$

85. for aniline

$$(\text{OH}^-) = \sqrt{K_b \times c} = \sqrt{10^{-9} \times 0.5 / 500}$$

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

for HCl

$$\text{pH} = -\log(25/500) = 1.3$$

$$E = +0.0591 (\text{pH}_1 - \text{pH}_2) \quad E^\circ = 0 \text{ conc cell}$$

$$E = 0.0591 (8 - 1.3) = 0.39597 \text{ V}$$

### Exercise-IV

### Level-I

1. LHS half cell  
 $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(1\text{M}) + 2\text{e}^-$   
 RHS half cell  
 $2\text{H}^+(1\text{M}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
- 
- $\text{H}_2(\text{g})\text{P}_1 \rightarrow \text{H}_2(\text{g})\text{P}_2$
- $$E_{\text{Cell}}^0 = 0.00\text{v}, K = \frac{P_2}{P_1}, n = 2$$
- $$E_{\text{Cell}}^0 = E_{\text{Cell}}^0 - \frac{RT}{nF} \ln eV$$
- $$= 0 - \frac{RT}{2F} \ln \frac{P_2}{P_1}$$
- $$\frac{RT}{2F} \ln \frac{P_1}{P_2}$$
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  
 $2 \times (\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-)$   
 At RHS (reduction)  
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- 
- $2\text{Ag} + \text{Cu}^{2+} \rightarrow \text{Cu} + 2\text{Ag}^+, E_{\text{red}} = (y - x)$
- 
- $E^\circ$
- volumes unstant when half cell equation is multiplied / divided.
5. (B)
- $$E_{\text{cell}}^0 = \frac{2.303RT}{nF} \log K_{\text{eq}}$$

- $$0.295 = \frac{0.0591}{2} \log K_{\text{eq}}$$
- $$\log K_{\text{eq}} = 10$$
6. (C)  
 More (-) ve volume of  $E^\circ$  mean larger reducing power.  
 so,  $B > C > A$
7.  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log Q$   
 $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu}$   
 0.1 M                      1M
- $$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1}{0.1} = 10$$
- $$E_{\text{cell}}^0 = 1.10 - \frac{0.0591}{2} \log 10$$
- $$= 1.10 - 0.0295 = 1.0705 \text{ V}$$
8. (D)  
 Since 96500 C deposits 108 gm of silver  
 so, 9650 C unit 108 gm
9. (C)  
 $\text{Sn}(\text{S}) + 2\text{Fe}^{3+}(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq.}) + \text{Sn}^{2+}(\text{aq.})$
- $$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0$$
- Given  $E_{\text{Sn}^{2+}/\text{Sn}}^0 = -0.014 \text{ V}$
- $$E_{\text{Sn}^{2+}/\text{Sn}}^0 = +0.14$$
- $$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77 \text{ V}$$
- $$E_{\text{cell}}^0 = 0.14 + 0.77 = 0.91 \text{ V}$$

10. (C)

Relation between  $K_{eq}$  and  $E_{cell}^0$  is

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

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

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

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

11. (A)

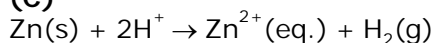
by Kohlrausch's law



$$= 126 + 152 - 150$$

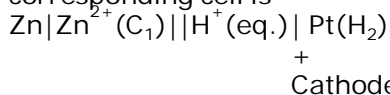
$$= 128 \text{ S cm}^2 \text{ mol}^{-1}$$

12. (C)



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

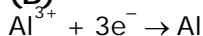
corresponding cell is



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

on addition of  $[\text{H}^+]$   $Q$  decreases due to increase in  $[\text{H}^+]$ .Since equilibrium is displaced toward right and  $E_{cell}$  increases.

13. (B)



$$w = 2Q$$

where

 $w$  = amount of metal

$$= 5.12 \text{ Kg} = 5.12 \times 10^3 \text{ g}$$

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

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

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

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

$$5.49 \times 10^7 \text{ C}$$

14.

$$\begin{aligned} \lambda_{\text{COH}}^\infty &= \lambda_{\text{ACONa}}^\infty + \lambda_{\text{HCl}}^\infty - \lambda_{\text{NaCl}}^\infty \\ &= 91.0 + 426.2 - 126.5 \\ &= 390.7 \end{aligned}$$

15.  $\Delta G^\circ = -2.303 RT \log K_{eq}$

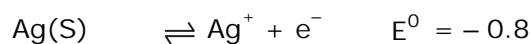
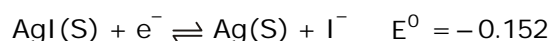
$$\Delta G^\circ = -nF E_{cell}^0$$

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

$$K_{eq} > 1 \text{ and } E_{cell}^0 = +ve$$

thus  $\Delta G^\circ = -ve$ 

16. (C)



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

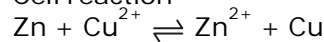
$$-0.952 = \frac{0.059}{1} \log K_{sp}$$

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

17. (C)

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

Cell reaction



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

We know

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

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

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

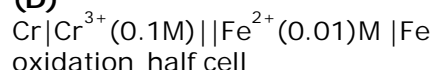
$$\therefore \text{anti log } 37.3$$

18. (A)

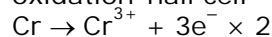
We know from Kohlrausch's law

$$\lambda_{\text{CH}_3\text{COOH}}^0 = \lambda_{\text{CH}_3\text{COONa}}^0 + \lambda_{\text{HCl}}^0 - \lambda_{\text{NaCl}}^0$$

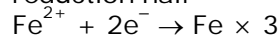
19. (D)



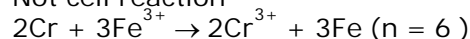
oxidation half cell



reduction half



Not cell reaction



$$E_{cell}^0 = E_{oxid}^0 + E_{red}^0$$

$$= 0.72 - 0.42 = 0.30 \text{ V}$$

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

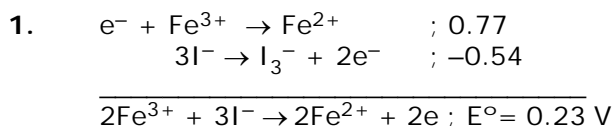
$$= 0.30 - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3}$$

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

$$E_{\text{cell}} = 0.2606 \text{ V}$$

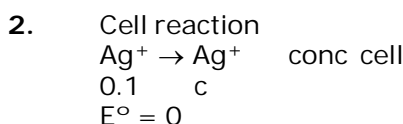
## Exercise-IV

## Level-II



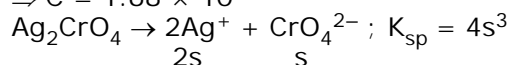
$$E^{\circ} = \frac{0.0591}{2} \log k_{\text{eq}} = 0.23$$

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



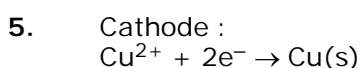
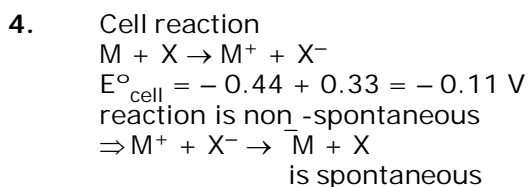
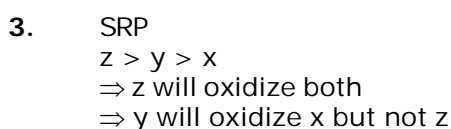
$$\Rightarrow 0.164 = -0.591 \log \frac{c}{0.1}$$

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



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

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



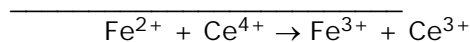
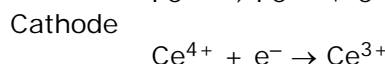
$$\text{Cu g eq.} = \frac{\text{It}}{96500} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500}$$

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

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

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

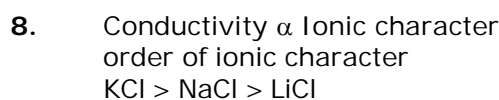
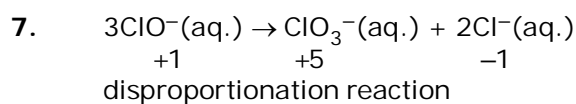
$$= \frac{96 \times 8 \times 10^{-2}}{96500} = 7.95 \times 10^{-5} \text{ M}$$



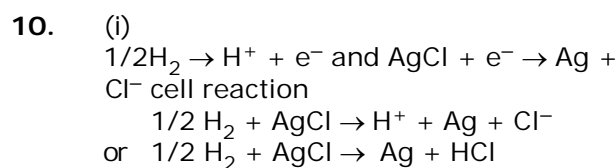
$$E_{\text{cell}}^{\circ} = -0.77 + 1.61$$

= +ve

Current will decrease with time.



9. (C)



(ii)

$$\Delta G^{\circ}_1 = -F \times 0.23 \text{ at } 15^{\circ}\text{C}$$

$$\Delta G^{\circ}_2 = -F \times 0.21 \text{ at } 35^{\circ}\text{C}$$

$$\text{and } \Delta G^{\circ}_1 = \Delta H^{\circ} - T_1 \Delta S^{\circ}$$

$$\Delta G^{\circ}_2 = \Delta H^{\circ} - T_2 \Delta S^{\circ}$$

$$\Rightarrow \Delta S^{\circ} = -96.5 \text{ KJ} ; \Delta H^{\circ} = 49987 \text{ J}$$

(iii)

For  $20^{\circ}\text{C}$  difference change in

$$E^{\circ} = -0.02$$

$$\Rightarrow E^{\circ}_{25^{\circ}\text{C}} = E^{\circ}_{15^{\circ}\text{C}} - \frac{0.02}{20} = 0.23 - 0.001$$

$$E^{\circ}_{25^{\circ}\text{C}} = 0.229 \text{ V}$$

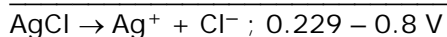
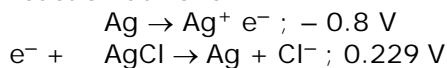
$$\text{cell reaction} = \text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

$$E^{\circ} = \frac{0.0591}{1} \log K_{\text{sp}} = 0.229 - 0.8$$

$$K_{\text{sp}} = 2.18 \times 10^{-10} = S^2$$

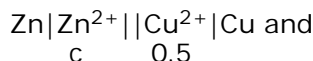
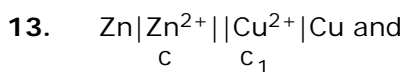
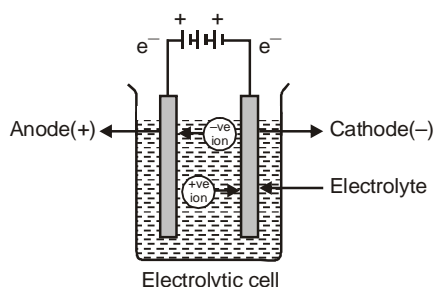
$$S = 1.47 \times 10^{-5} \text{ mole/L}$$

reaction at 25°C



11. If  $\text{MnO}_4^-$  used in aqueous HCl will oxidize  $\text{Cl}^-$  ion also hence it is not suitable for quantitative estimation of  $\text{Fe}(\text{NO}_3)_2$ .

12.



$$E_1 = E^{\circ} - \frac{0.059}{2} \log \left( \frac{c}{0.5} \right)$$

$$E_2 - E_1 = 0.03$$

$$\Rightarrow 0.03 = \frac{0.059}{2} \left[ \log \frac{c}{c_1} - \log \frac{c}{0.5} \right]$$

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

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

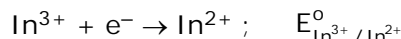
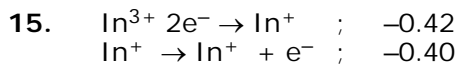
$$0.2905 = E^{\circ} - \frac{0.0591}{2} \log \left( \frac{0.1}{0.01} \right)$$

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

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

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

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



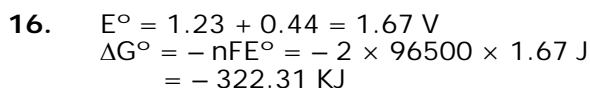
$$E^{\circ}_{\text{In}^{3+}/\text{In}^{2+}} = \frac{-0.42 \times 2 + 0.40}{1} = -0.44$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}^+} + E^{\circ}_{\text{In}^{2+}/\text{In}^{3+}}$$

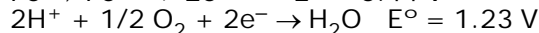
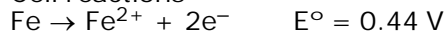
$$= 0.15 + 0.44 = 0.59$$

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

$$K_{\text{eq}} = 10^{10}$$

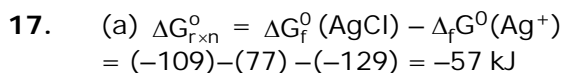


Cell reactions



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$$E^{\circ}_{\text{cell}} = 1.67 \text{ V}$$

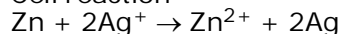


$$E^{\circ} = \frac{\Delta G^{\circ}}{-nF} = \frac{-57 \times 10^3}{-1 \times 96500} = 0.59 \text{ V}$$

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

$$K_{\text{sp}} = 10^{-10} \quad \log K_{\text{sp}} = -10$$

(b) Cell reaction

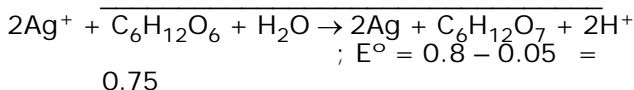
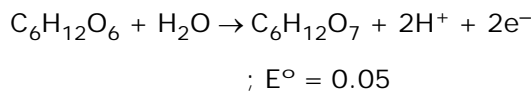
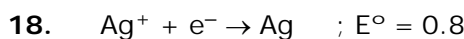


$$E^{\circ}_{\text{cell}} = 0.80 + 0.76 = \frac{0.059}{2} \log \left[ \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right]$$

$$K_{\text{sp}}(\text{AgCl}) = 10^{-10}$$

$$[\text{Ag}^+] = 10^{-5} \text{ M}$$

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



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

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

$$\Rightarrow \ln K = 0.85 \times 2 \times 38.92 = 66.16$$

19. On Increasing the conc. of  $\text{NH}_3$  the concn. of  $\text{H}^+$  ion decreases therefore

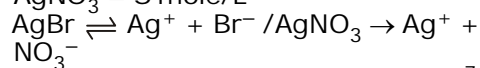
$$E_{\text{red}} = E^\circ - \frac{0.0592}{n} \log[\text{H}^+]^2$$

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

$$E_{\text{red}} = 0.65 \text{ V}$$

20. (D)

21. Suppose the solubility of AgBr in  $10^{-7} \text{ M}$   $\text{AgNO}_3 = S$  mole/L



$$10^{-7} \quad \quad \quad s \quad \quad s \quad \quad \quad 10^{-7}$$

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

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

$$\Rightarrow [\text{Br}^-] = 3 \times 10^{-7} \text{ mole/m}^3$$

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

$$[\text{NO}_3^-] = 10^{-7} \text{ M} = 10^{-4} \text{ mole/m}^3$$

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

$$K_{\text{total}} = K_{\text{Br}} + K_{\text{Ag}^+} + K_{\text{NO}_3^-}$$

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

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

$$\text{Cl}_2 \text{ evolved} = 1 \text{ mole}$$

23. Na – Hg formed  
mole of Na–Hg = mole of Na  
= 2 mole

$$\text{mass of amalgam} = 2 \times 223$$

↓  
mol. mass of Na-Hg

$$= 446 \text{ g}$$

24. Equivalent = charge (F)

$$\text{Charge (F)} = 2 \times 1$$

$$= 2F$$

$$\text{Charge} = 2 \times 26500 \text{ C}$$

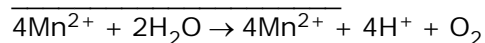
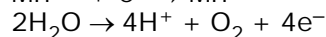
$$= 193000$$

25.  $2\text{I}^- + \text{Cl}_2 \rightarrow \text{I}_2 + 2\text{Cl}^-$

$$E_{\text{cell}}^\circ = 1.36 - 0.54 = 0.82 \text{ V}$$

reaction is feasible

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



$$E_{\text{cell}}^\circ = 1.50 - 1.23$$

$$= 0.27 \text{ V} \quad + \text{ve}$$

27.  $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$

for 0.01 mole  $\text{H}_2$  0.02 mole of electrons are consumed charge required =  $0.02 \times 96500$

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

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

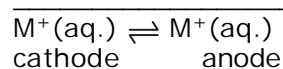
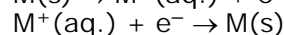
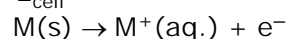
$$= 19.3 \times 10^4 \text{ sec}$$

28. The species having less SRP with respect to  $\text{NO}_3^-$  (0.96) will be oxidized by  $\text{NO}_3^-$  species are V, Fe & Hg

29. (A, B)

30. The given cell is electrolytic conc. cell so

$$E_{\text{cell}}^\circ = 0$$



$$E_{\text{cell}} = \frac{-0.0591}{1} \log \frac{(\text{M}^+)_c}{(\text{M}^+)_a}$$

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

$$= + \text{ve } \Delta G = - \text{ve}$$

31.  $E_{\text{cell}} = E_{\text{cell}}^\circ - 0.0591 \log K$

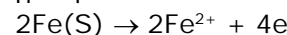
$$E_{\text{cell}}^\circ - \frac{0.0591}{1} \log 0.0025$$

$$= 140 \text{ mV}$$

32.  $2\text{Fe(s)} + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$   $\varepsilon^\circ = 1.67 \text{ V}$

$$\varepsilon_{\text{cell}} = \varepsilon^\circ_{\text{cell}} - \frac{0.591}{n}$$

$$n = 4$$



$$= \varepsilon^\circ_{\text{cell}} - \frac{0.591}{4} \log \left[ \frac{(\text{Fe}^{2+})^2}{(\text{H}^+)^4 (\text{Po}_2)} \right]$$

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

V

Ans. (D)

33.  $\text{M}/\text{M}^{2+}$  (saturated solution )



$$\varepsilon^\circ_{\text{cell}} = 0$$

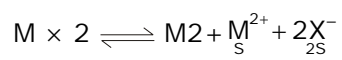
$$\varepsilon_{\text{cell}} = \frac{0.0591}{2} \log \frac{[\text{M}^{2+}]_a}{[\text{M}^{2+}]_c}$$

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



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

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



$$S = 10^{-5}$$

$$K_{sp} = 4S^3$$

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

Ans. (B)

34.  $\Delta G = -nF\varepsilon$   
 $= -2 \times 96500 \times 0.059$   
 $= -11406.3 \text{ J/mole}$   
 $= -11.4 \text{ KJ/mole.}$   
Ans. (D)