

## CHAPTER - 13

# ELECTROCHEMISTRY

1. 3 In the Daniell cell, zinc is the anode and copper is the cathode.  $\text{Cu}^{2+}$  ions move towards copper electrode and is deposited as Cu

2. 2  $E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = -0.44 - (-0.76) = 0.32 \text{ V}$

3. 2 
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}][\text{Cl}^-]^2}{P_{\text{Cl}_2}}$$

Thus,  $E_{\text{cell}}$  increases with decrease in  $[\text{Zn}^{2+}]$  and  $[\text{Cl}^-]$

4. 1 At equilibrium, there is no net reaction occurring in the cell, thus  $E_{\text{cell}} = 0$

5. 4 
$$\log K = \frac{nFE^0}{2.303 RT} = \frac{2 \times 96500 \times 0.295}{2.303 \times 8.314 \times 298}; \text{ Thus } K = 10^{10}$$

6. 3 NaCl and HCl are strong electrolytes, hence straight line plots. Also, conductance of  $\text{H}^+$  is greater than that of  $\text{Na}^+$ .  $\text{NH}_4\text{OH}$  is a weak electrolyte, thus steep variation in  $\wedge_m$  with dilution.

7. 4 
$$\begin{aligned} \wedge_m^0(\text{CH}_3\text{COOH}) &= \wedge_m^0(\text{CH}_3\text{COOK}) + \frac{\wedge_m^0(\text{H}_2\text{SO}_4)}{2} - \frac{\wedge_m^0(\text{K}_2\text{SO}_4)}{2} \\ &= z + \frac{x}{2} - \frac{y}{2} \text{ or } z + \frac{(x-y)}{2} \end{aligned}$$

8. 3  $K_a = \frac{C\alpha^2}{1-\alpha}$  and  $\alpha = \frac{\wedge_m}{\wedge_m^0}$

Thus, 
$$K_a = \frac{c \wedge_m^2}{\wedge_m^0 (\wedge_m^0 - \wedge_m)}$$

9. 3 3F charge can deposit 1 mol Al,  $\frac{3}{2}$  mol Cu and 3 mol Na. Thus, molar ratio of metals deposited is, 1 : 1.5 : 3

10. 3 Substance Products of electrolysis

At anode

dil.  $\text{H}_2\text{SO}_4$        $\text{O}_2$

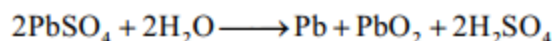
aq.  $\text{AgNO}_3$        $\text{O}_2$

aq.  $\text{CuCl}_2$        $\text{Cl}_2$

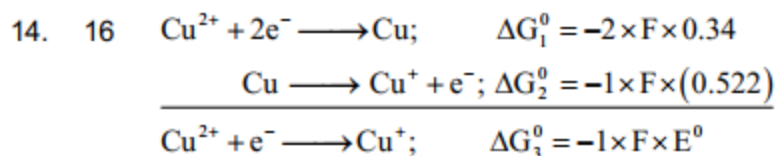
aq.  $\text{CuSO}_4$        $\text{O}_2$

11. 3 At cathode of dry cell,  $\text{MnO}_2$  is reduced to  $\text{MnO}$  (OH). Thus, oxidation number of Mn changes from +4 to +3

12. 2 During recharging, the reaction occurring in the lead acid battery is



13. 147  $E_{\text{cell}} = 1.56 - \frac{0.059}{2} \log \frac{10^{-1}}{10^{-4}} = 1.47 \text{ V or } 147 \times 10^{-2} \text{ V}$



$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

$$E^0 = 2 \times 0.34 - 0.522 = 0.158 \text{ V or } 15.8 \times 10^{-2} \text{ V}$$

15. 266  $\text{Cell constant} = \frac{\text{conductivity}}{\text{conductance}} = \frac{0.152 \times 10^{-3} \text{ Scm}^{-1}}{\left(\frac{1}{1750}\right) \text{ S}} = 266 \times 10^{-3} \text{ cm}^{-1}$

16. 41 For hydrogen electrode,  $E = -0.059 \times \text{pH}$   
 At pH = 0,  $E = 0$ ; At pH = 7,  $E = -0.413$   
 Thus, E decreased by 0.413 V or  $41.3 \times 10^{-2} \text{ V}$

17. A Given,  $\lambda_{\text{Ag}^+}^0 = 62.3$  and  $\lambda_{\text{Cl}^-}^0 = 67.7 \text{ cm}^2 \text{ mol}^{-1}$   
 So,  $\Lambda_{\text{m(AgCl)}}^0 = 62.3 + 67.7 = 130 \text{ Scm}^2 \text{ mol}^{-1}$

$$\text{Now, } \Lambda_m^\circ = \frac{k \times 10^3}{C} \Rightarrow C \Rightarrow \frac{K \times 10^3}{\Lambda_m^\circ} = \frac{3.4 \times 10^{-6} \times 10^3}{130}$$

$$= 2.6 \times 10^{-5} \text{ mol L}^{-1}$$

18. A On dilution, conductivity of electrolyte decreases whereas molar conductance and equivalent conductance increases

19. C  $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{x^2 \times 1}{1^2 \times 1} = 0 - \frac{0.059}{2} \times 2 \log x$

i.e.,  $-0.059 \log x = 0.295$

$\log x = -5 \Rightarrow x = 10^{-5} \text{ M}$

Now, for HA,  $C\alpha = [H^+] = 10^{-5} \Rightarrow \alpha = \frac{10^{-5}}{0.01} = 10^{-3}$

Thus,  $K_a$  of HA =  $C\alpha^2 = (0.01 \text{ M})(10^{-3})^2 = 10^{-8}$

20. D During electrolysis of  $\text{KNO}_3$ ,  $\text{H}_2\text{O}$  is oxidised at anode and  $\text{H}_3\text{O}^+$  is reduced at cathode. Thus pH of solution remains the same ( $\text{K}^+$  and  $\text{NO}_3^-$  ions are unaffected)

21. B  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$   
 $E = E^\circ - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]}$   
 $\therefore 0.1335 = 0.34 \text{ V} - \left( \frac{0.059 \text{ V}}{2} \right) \log \frac{1}{[\text{Cu}^{2+}]}$   
 $\therefore [\text{Cu}^{2+}] = 10^{-7}$   
 $K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$   
 $\therefore [\text{OH}^-]^2 = \frac{1 \times 10^{-19}}{10^{-7}} = 10^{-12}$   
 $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = 10^{-8}$   
 $\text{pH} = 8$

22. AC  $\text{Cu}^{2+}$  is formed in the cases (A) and (C) (order of reactivity of metals is,  $\text{Zn} > \text{Ni} > \text{Cu} > \text{Ag}$ )

23. BC Chemical equivalent weight of iron in  $\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Fe}(\text{NO}_3)_3$  are  $\frac{M}{2}$ ,  $\frac{M}{3}$  and  $\frac{M}{3}$ , respectively. Thus, amount of Fe deposited in the last two cases will be equal

At the anode, water is oxidised to produce oxygen gas

24. AD  $\Delta G^\circ = -nFE^\circ$

$$\Delta H^\circ - T\Delta S^\circ = -nFE^\circ \Rightarrow E^\circ = \frac{-\Delta H^\circ}{nF} + \frac{T\Delta S^\circ}{nF}$$

$$\left(\frac{\delta E^\circ}{\delta T}\right) = \frac{\Delta S^\circ}{nF} \Rightarrow \Delta S^\circ = nF \times \left[\frac{\delta E^\circ}{\delta T}\right]$$

25. AD Copper has +ve electrode potential whereas tin has -ve electrode potential. Thus,  $\text{Cu}^{2+}$  can be reduced by  $\text{H}_2$  and Sn can be oxidised by  $\text{H}^+$

26. AB Moles of electron transferred =  $\frac{It}{96500} = \frac{2 \times 965}{96500} = 0.02 \text{ mol}$

i.e,  $0.02 \times 6.02 \times 10^{23} = 1.204 \times 10^{22}$  electrons

we know, 96500c deposits  $\frac{63.5}{2} \text{ g Cu}$

$\therefore 2 \times 965 \text{ c}$  deposits 0.635g Cu

27. 10 Cell constant =  $\frac{K}{G} = \frac{4 \times 10^{-3}}{(1/200)} = 8 \times 10^{-1} \text{ cm}^{-1}$

conductivity of  $\text{CuSO}_4 = G \times \text{cell constant}$

$$= \frac{1}{8 \times 10^3} \times 8 \times 10^{-1} = 10^{-4} \text{ scm}^{-1}$$

$$\text{Molar conductivity of } \text{CuSO}_4 = \frac{K \times 1000}{C} = 10 \text{ Scm}^2 \text{ mol}^{-1}$$

28. 4  $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.06}{n} \log Q$

$$0.801 = 0.771 - \frac{0.05}{n} \log 10^{-2} \Rightarrow n = 4$$

29. C
- | Process | Charge required |
|---------|-----------------|
| (I)     | 5F              |
| (II)    | 6F              |
| (III)   | 2F              |
| (IV)    | 3F              |

30. B  $E_{\text{cell}}^\circ = 0$  for all given cells

$E_{\text{cell}}$  is +ve for cells (I) and (II); -ve for cells (III) and (IV)