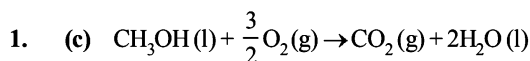


DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC14


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

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

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

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

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

2. (a) Given for 0.2 M solution

$$R = 50 \Omega$$

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

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

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

For 0.5 M solution

$$R = 280 \Omega$$

$$\kappa = ?$$

$$\frac{1}{a} = 50 \times 1.4 \times 10^{-2}$$

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

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

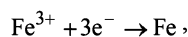
$$= \frac{1}{280} \times 70 \times 10^{-2}$$

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

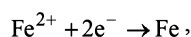
$$\text{Now, } \Lambda_m = \frac{\kappa \times 1000}{M} = \frac{2.5 \times 10^{-3} \times 1000}{0.5}$$

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

3. (b) Given

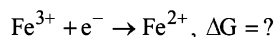


$$E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036 \text{ V} \quad \dots (i)$$



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

we have to calculate



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



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

Thus for reaction (iii)

$$\Delta G = \Delta G_1 - \Delta G_2$$

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

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

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

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

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

4. (a) (i) $\text{Mn}^{n+} + ne^- \rightleftharpoons \text{M}$, for this reaction, high negative value of E° indicates lower reduction potential, that means M will be a good reducing agent.

$$\left[\begin{array}{c} \text{Stronger reducing agent} \Rightarrow \text{Easy to oxidise} \\ \downarrow \\ \text{Lower reduction potential} \Leftarrow \text{higher oxidation potential} \end{array} \right]$$

(ii) Element	F	Cl	Br	I
Reduction potential (E° volt)	+2.87	+1.36	+1.06	+0.54

As reduction potential decreases from fluorine to iodine, oxidising nature also decreases from fluorine to iodine.

- (iii) The size of halide ions increases from F^- to I^- . The bigger ion can lose electron easily. Hence the reducing nature increases from HF to HI.

5. (c) According to Faraday's first law of electrolysis

$$W = \frac{E \times i \times t}{96500}$$

Where E = equivalent weight

$$= \frac{\text{mol. mass of metal (M)}}{\text{oxidation state of metal (x)}}$$

Substituting the value in the formula

$$W = \frac{M}{x} \times \frac{i \times t}{96500}$$

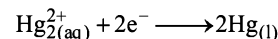
$$\text{or } x = \frac{M}{W} \times \frac{i \times t}{96500} = \frac{10 \times 2 \times 60 \times 60}{96500 \times 0.250} = 3$$

$$\left[\text{Given : no. of moles} = \frac{M}{W} = 0.250 \right]$$

Hence oxidation state of metal is (+3)

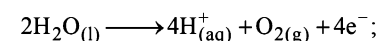
6. (b, c) Cathode : $\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Cu}_{(\text{s})}$

1 mole of Cu deposited \equiv 2 mole of electrons



1 mole of $\text{Hg}_{(\text{l})}$ deposited \equiv 1 mole of electrons

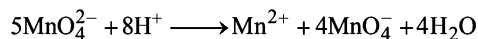
Anode (each cell) :



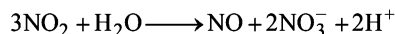
1 mole of $\text{O}_2 \equiv$ 4 mole of electrons

7. (a,c)

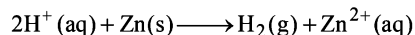
- (a) The MnO_4^{2-} is reduced to Mn^{2+} , so it must also be oxidised to Mn^{7+} MnO_4^- since H^+ is already in its maximum oxidation state.



- (c) NO_2 disproportionates to NO and NO_3^+ . (Oxidation state of N is +5)



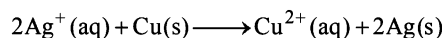
8. (a, b, c) (a) Cell reaction :



Reaction quotient,

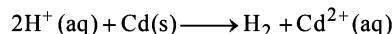
$$Q = \frac{P_{\text{H}_2} \times [\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{1 \times 0.01}{(0.1)^2} = 1, \log Q = 0$$

(b) Cell reaction :



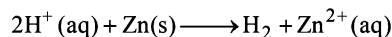
$$Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.25}{(0.5)^2} = 1$$

(c) Cell reaction :



$$Q = \frac{P_{\text{H}_2} \times [\text{Cd}^{2+}]}{[\text{H}^+]^2} = \frac{1 \times 0.01}{(0.1)^2} = 1$$

(d) Cell reaction :



$$Q = \frac{P_{\text{H}_2} \times [\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{1 \times 0.1}{(0.1)^2} = 10$$

9. (b,d) It is the concentration cell in respect to Ag^+ ions.

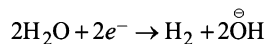
$$\text{Hence, } E_{\text{cell}} = 0.0592 \log \frac{[\text{Ag}^+]_2}{[\text{Ag}^+]_1}$$

$$\begin{aligned} K_{sp}(\text{Ag}_2\text{C}_2\text{O}_4) &= [\text{Ag}^+]_2^2 [\text{C}_2\text{O}_4^{2-}] \\ &= [\text{Ag}^+]_2^2 \times \frac{[\text{Ag}^+]_2}{2} \end{aligned}$$

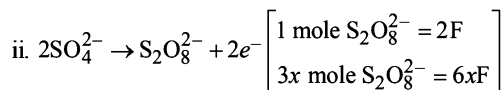
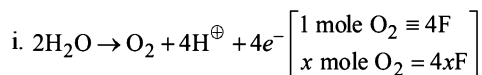
$$\text{or } [\text{Ag}^+]_2 = [2K_{sp}(\text{Ag}_2\text{C}_2\text{O}_4)]^{1/3}$$

$$\begin{aligned} K_{sp}(\text{AgI}) &= [\text{Ag}^+]_1 [\text{I}^-] \\ &= [\text{Ag}^+]_1^2 \end{aligned}$$

$$\text{or } [\text{Ag}^+]_1 = [K_{sp}(\text{AgI})]^{1/2}$$

10. (5) Let x mole of O_2 is liberated and $3x$ mole of $\text{H}_2\text{S}_2\text{O}_8$ is formed. Reactions at cathode (reduction):

Reactions at anode (oxidation):

Total Faradays at anode = $(4x + 6x)\text{F} = 10x\text{F}$.Total Faradays at cathode = $2\text{F} \equiv 1 \text{ mole } \text{H}_2$. $10x\text{F} \equiv \text{Total Faradays at cathode} = \text{Total Faradays at anode}$ $\therefore 2\text{F at cathode} \equiv 1 \text{ mole of } \text{H}_2$.

$$10x\text{F at cathode} \equiv \frac{1}{2\text{F}} \times 10x\text{F} = 5x \text{ mole of } \text{H}_2.$$

$$\text{Ratio} = \frac{\text{Moles of } \text{H}_2 \text{ at cathode}}{\text{Moles of } \text{H}_2\text{S}_2\text{O}_8 \text{ at anode}} = \frac{5x}{3x} = \frac{5}{3}$$

$$\text{Number of moles of } \text{H}_2 = 3 \times \frac{5}{3} = 5$$

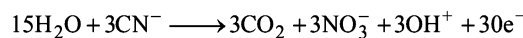
Alternatively

$$\begin{array}{l} \text{Molar ratio of } \text{H}_2\text{S}_2\text{O}_8 : \text{O}_2 \\ (\text{n factor} = 2) \quad (\text{n factor} = 4) \\ = 3 : 1 \end{array}$$

Equivalent ratio = $3 \times 2 : 1 \times 4 = 6 : 4$ Total equivalent of $\text{H}_2\text{S}_2\text{O}_8$ and O_2 at anode = $6 + 4 = 10 \text{ Eq.}$ So total equivalent of H_2 at cathode = 10

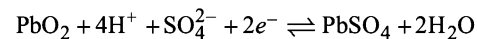
$$\therefore \text{moles of } \text{H}_2 (\text{n factor} = 2) = \frac{10}{2} = 5 \text{ moles}$$

11. (3) Balance the equation.



$$\therefore \text{Number of } e^- \text{ s} = \frac{30}{10} = 3$$

12. (3) Discharging reaction:



$$M_1 = \frac{\% \text{ by weight} \times 10 \times d}{\text{Mw}_2} = \frac{40 \times 1.225 \times 10}{98} = 5 \text{ M}$$

$$M_2 = \frac{\% \text{ by weight} \times 10 \times d}{\text{Mw}_2} = \frac{20 \times 10 \times 0.98}{98} = 2 \text{ M}$$

Change in molarities = $M_1 - M_2 = 5 - 2 = 3 \text{ M}$ 13. (6) Let $x\%$ is the current efficiency of KClO_3 = Number of Faradays.

$$\frac{10\text{g}}{122.5/6} = \frac{2 \times x \times 10.941 \times 3600}{100 \times 96500}$$

$$\therefore x = 60\%$$

$$\therefore \frac{\text{Percentage current efficiency}}{10} = \frac{60}{10} = 6$$

14. (6) Statement (a), (b) and (c) are correct.

Hence, total score = 1 + 2 + 3 = 6.

Statement (a) : pH = 0, means $[H^+] = 1 \text{ M}$

E°_{red} of $\text{MnO}_4^- | \text{Mn}^{2+} > E^\circ_{\text{red}}$ of $\text{Fe}^{3+} | \text{Fe}^{2+}$

So MnO_4^- will undergo reduction and acts as strong oxidant whereas Fe^{2+} undergoes oxidation. Statement (a) is correct.

Statement (b): MnO_4^- titrations in the presence of HCl are unsatisfactory since Cl^- is oxidized to Cl_2 . Statement (b) is correct.

Statement (c):

Since $E^\circ_{\text{red}} \text{Ce}^{4+} | \text{Ce}^{3+} > E^\circ_{\text{red}} \text{MnO}_4^- | \text{Mn}^{2+}$. So Ce^{4+} will reduce to Ce^{3+} . So MnO_4^- cannot oxidize Ce^{3+} to Ce^{4+} . Statement (c) is correct.

Statement (d): Fe^{2+} can be titrated against KMnO_4 in acid medium ($[H^+] = 1 \text{ M}$).

Since $E^\circ_{\text{red}} \text{MnO}_4^- | \text{Mn}^{2+} > E^\circ_{\text{red}} \text{Fe}^{3+} | \text{Fe}^{2+}$

So Fe^{2+} can be oxidized to Fe^{3+} by MnO_4^- .

But Ce^{3+} will not be oxidized to Ce^{4+} .

Since $E^\circ_{\text{red}} \text{Ce}^{4+} | \text{Ce}^{3+} > E^\circ_{\text{red}} \text{MnO}_4^- | \text{Mn}^{2+}$

So, statement (d) is wrong.

$$15. (b) \quad E_{\text{cell}} = -\frac{0.059}{1} \log \frac{[H^+]_a}{[H^+]_c}$$

$$= -0.059(\text{pH}_c - \text{pH}_a)$$

$$= -0.059(6 - 3) = -0.177 \text{ V}$$

$\therefore E_{\text{cell}}$ is -ve, so reaction is Non-spontaneous.

$$16. (a) \quad E_{\text{cell}} = E_{(\text{Q}, 2\text{H}^+ | \text{H}_2\text{O})} - E_{\text{SCE}}$$

Where,

$$E_{(\text{Q}, 2\text{H}^+ | \text{H}_2\text{O})} = E^\circ_{(\text{Q}, 2\text{H}^+ | \text{H}_2\text{O})} - 0.059 \text{ pH}$$

$$\therefore E_{\text{cell}} = \left[E^\circ_{(\text{Q}, 2\text{H}^+ | \text{H}_2\text{O})} - 0.059 \text{ pH} \right] - E_{\text{SCE}}$$

$$= (0.7 - 0.059 \text{ pH}) - (0.24 \text{ V})$$

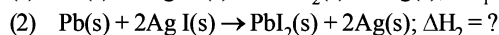
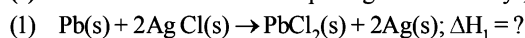
$$= (0.7 - 0.059 \times 10) - (0.24 \text{ V}) = -0.13 \text{ V}$$

$\therefore E_{\text{cell}}$ is -ve, so reaction is endergonic (i.e. $\Delta G = +ve$)

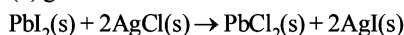
$$17. (b) \quad E_{\text{cell}} = E^\circ - 0.059 \text{ pH} \\ = 0.7 - 0.059 \times 2 = 0.582 \text{ V}$$

Since E_{cell} is +ve, so reaction is exergonic (i.e. $\Delta G = -ve$)

18. (c) The cell reactions for the passage of 2 Faradays, are



(1) - (2) gives



$$\Delta H = \Delta H_1 - \Delta H_2$$

$$\Delta H_1 = nF \left[T \left(\frac{\partial E_1}{\partial T} \right) - E_1 \right]$$

$$= \frac{2 \times 96500 [298 \times (-0.000186) - 0.4902]}{4.18}$$

$$= -25183 \text{ cal}$$

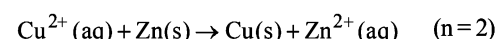
$$\Delta H_2 = nF \left[T \left(\frac{\partial E_2}{\partial T} \right) - E_2 \right]$$

$$= \frac{2 \times 96500 [298 \times (-0.000127) - 0.2111]}{4.18}$$

$$= -11489 \text{ cal}$$

$$\text{Hence, } \Delta H = \Delta H_1 - \Delta H_2 = -25183 - (-11489) \text{ cal} \\ = -13694 \text{ cal.}$$

19. (a) The reaction in Daniel's cell is



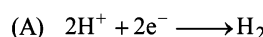
Heat of the reaction may be expressed as

$$\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_p - E \right]$$

$$= 2 \times 96500 \left[\frac{288 \times (-4.28 \times 10^{-4}) - 1.0934}{4.18} \right]$$

$$= -56187 \text{ cal}$$

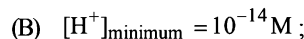
20. A-s; B-r; C-p; D-q



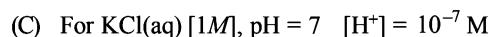
$$E_{\text{H}^+/\text{H}_2} = E^\circ - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[H^+]^2}$$

$$= 0 - \frac{0.0591}{2} \log \frac{1}{[H^+]^2} = 0.0591 \log [H^+]$$

Since maximum activity of $\text{H}^+ = 1$, So $E_{\text{H}^+/\text{H}_2} = 0$



$$E_{\text{minimum}} = 0.0591 \log 10^{-14} = -0.0591 \times (-14) \\ = -0.827 \text{ V}$$



$$\text{Hence, } E = 0.0591 \log 10^{-7} = 0.0591 \times (-7) \\ = -0.414 \text{ V}$$

$$(D) \quad E = -\frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[H^+]^2}$$

$$= \frac{-0.0591}{2} \log \frac{4}{1^2} = -0.0591 \log 2$$

$$= -0.0591 \times 0.301 = -0.018 \text{ V}$$