DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

1. **(c)** $CH_3OH\,(l) + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$

$\Delta G_r = \Delta G_f(CO_2,(g)) + 2\Delta G_f(H_2O,(l)) - \Delta G_f(CH_3OH,(l)) - \frac{3}{2}\Delta G_f(O_2,(g))$

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

$= -394.4 - 474.4 + 166.2 = -702.6$ kJ

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

2. **(a)** Given for 0.2 M solution

$R = 50\,\Omega$

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

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

$R = 280\,\Omega$

$\kappa = ?$

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

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

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

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

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

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

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

3. **(b)** Given

$Fe^{3+} + 3e^- \rightarrow Fe$,

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

$Fe^{2+} + 2e^- \rightarrow Fe$,

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

we have to calculate

$Fe^{3+} + e^- \rightarrow Fe^{2+},\ \Delta G = ?$

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

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ ...(iii)

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

Thus for reaction (iii)

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

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

$-nFE^\circ = nFE_2 - nFE_1$

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

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

$\therefore\ E^\circ = -0.770$ V

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

[Stronger reducing agent ⇒ Easy to oxidise
⇓
Lower reduction potential ⇐ higher oxidation potential]

(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 loose 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

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

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

1 mole of Cu deposited ≡ 2 mole of electrons

$Hg^{2+}_{2(aq)} + 2e^- \longrightarrow 2Hg_{(l)}$

1 mole of $Hg_{(l)}$ deposited ≡ 1 mole of electrons

Anode (each cell) :

$2H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$;

1 mole of O_2 ≡ 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.

$$5MnO_4^{2-} + 8H^+ \longrightarrow Mn^{2+} + 4MnO_4^- + 4H_2O$$

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

$$3NO_2 + H_2O \longrightarrow NO + 2NO_3^- + 2H^+$$

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

$$2H^+(aq) + Zn(s) \longrightarrow H_2(g) + Zn^{2+}(aq)$$

Reaction quotient,

$$Q = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2} = \frac{1 \times 0.01}{(0.1)^2} = 1, \ \log Q = 0$$

(b) Cell reaction :

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

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

(c) Cell reaction :

$$2H^+(aq) + Cd(s) \longrightarrow H_2 + Cd^{2+}(aq)$$

$$Q = \frac{P_{H_2} \times [Cd^{2+}]}{[H^+]^2} = \frac{1 \times 0.01}{(0.1)^2} = 1$$

(d) Cell reaction :

$$2H^+(aq) + Zn(s) \longrightarrow H_2 + Zn^{2+}(aq)$$

$$Q = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2} = \frac{1 \times 0.1}{(0.1)^2} = 10$$

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

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

$$K_{sp}(Ag_2C_2O_4) = [Ag^+]_2^2[C_2O_4^{2-}]$$

$$= [Ag^+]_2^2 \times \frac{[Ag^+]_2}{2}$$

or $[Ag^+]_2 = \left[2K_{sp}(Ag_2C_2O_4)\right]^{1/3}$

$$K_{sp}(AgI) = [Ag^+]_1[I^-]$$

$$= [Ag^+]_1^2$$

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

10. **(5)** Let x mole of O_2 is liberated and $3x$ mole of $H_2S_2O_8$ is formed. Reactions at cathode (reduction):

$$2H_2O + 2e^- \rightarrow H_2 + 2\overset{\ominus}{O}H$$

Reactions at anode (oxidation):

i. $2H_2O \rightarrow O_2 + 4H^{\oplus} + 4e^- \begin{bmatrix} 1 \text{ mole } O_2 \equiv 4F \\ x \text{ mole } O_2 = 4xF \end{bmatrix}$

ii. $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \begin{bmatrix} 1 \text{ mole } S_2O_8^{2-} = 2F \\ 3x \text{ mole } S_2O_8^{2-} = 6xF \end{bmatrix}$

Total Faradays at anode = $(4x + 6x)$ F = $10x$ F.

Total Faradays at cathode = 2F ≡ 1 mole H_2.

$10x$ F ≡ Total Faradays at cathode = Total Faradays at anode

∵ 2 F at cathode ≡ 1 mole of H_2.

$10x$F at cathode $\equiv \frac{1}{2F} \times 10xF = 5x$ mole of H_2.

$$\text{Ratio} = \frac{\text{Moles of } H_2 \text{ at cathode}}{\text{Moles of } H_2S_2O_8 \text{ at anode}} = \frac{5x}{3x} = \frac{5}{3}$$

Number of moles of $H_2 = 3 \times \frac{5}{3} = 5$

Alternatively

Molar ratio of $H_2S_2O_8$: O_2

(n factor = 2) (n factor = 4)

= 3 : 1

Equivalent ratio = 3 × 2 : 1 × 4 = 6 : 4

Total equivalent of $H_2S_2O_8$ and O_2 at anode = 6 + 4 = 10 Eq.

So total equivalent of H_2 at cathode = 10

∴ moles of H_2 (n factor = 2) = $\frac{10}{2}$ = 5 moles

11. **(3)** Balance the equation.

$$15H_2O + 3CN^- \longrightarrow 3CO_2 + 3NO_3^- + 3OH^+ + 30e^-$$

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

12. **(3)** Discharging reaction:

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

$$M_1 = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2} = \frac{40 \times 1.225 \times 10}{98} = 5 \text{ M}$$

$$M_2 = \frac{\% \text{ by weight} \times 10 \times d}{Mw_2} = \frac{20 \times 10 \times 0.98}{98} = 2 \text{ M}$$

Change is molarities = $M_1 - M_2$ = 5 – 2 = 3 M

13. **(6)** Let x % is the current efficiency of $KClO_3$ = Number of Faradays.

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

∴ 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 $[H^+] = 1$ M
E°_{red} of $MnO_4^- \mid Mn^{2+} > E^-_{red}$ of $Fe^{3+} \mid Fe^{2+}$
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 $E^\circ_{red\ Ce^{4+}|Ce^{3+}} > E^\circ_{red\ MnO_4^-|Mn^{2+}}$. 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 ($[H^+] = 1$ M).
Since $E^\circ_{red\ MnO_4^-|Mn^{2+}} > E^\circ_{red\ Fe^{3+}|Fe^{2+}}$
So Fe^{2+} can be oxidized to Fe^{3+} by MnO_4^-.
But Ce^{3+} will not be oxidized to Ce^{4+}.
Since $E^\circ_{red\ Ce^{4+}|Ce^{3+}} > E^\circ_{red\ MnO_4^-|Mn^{2+}}$
So, statement (d) is wrong.

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

$= -0.059(pH_c - pH_a)$

$= -0.059(6-3) = -0.177$ V

$\because E_{cell}$ is – ve, so reaction is Non-spontaneous.

16. (a) $E_{cell} = E_{(Q,2H^+|H_2O)} - E_{SCE}$

Where,

$E_{(Q,2H^+/H_2O)} = E^\circ_{(Q,2H^+/H_2O)} - 0.059\text{ pH}$

$\therefore\ E_{cell} = \left[(E^\circ_{(Q,2H^+/H_2O)} - 0.059\text{ pH}) - E_{SCE}\right]$

$= (0.7 - 0.059\,pH) - (0.24V)$

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

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

17. (b) $E_{cell} = E^\circ - 0.059\,pH$
$= 0.7 - 0.059 \times 2 = 0.582$ 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) $Pb(s) + 2AgCl(s) \rightarrow PbCl_2(s) + 2Ag(s);\ \Delta H_1 = ?$
(2) $Pb(s) + 2AgI(s) \rightarrow PbI_2(s) + 2Ag(s);\ \Delta H_2 = ?$
(1) – (2) gives
$PbI_2(s) + 2AgCl(s) \rightarrow PbCl_2(s) + 2AgI(s)$
$\Delta H = \Delta H_1 - \Delta H_2$

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

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

$= -25183$ cal

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

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

$= -11489$ cal

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

19. (a) The reaction in Daniel's cell is
$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$ (n = 2)
Heat of the reaction may be expressed as

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

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

$= -56187$ cal

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

(A) $2H^+ + 2e^- \longrightarrow H_2$

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

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

Since maximum activity of $H^+ = 1$, So $E_{H^+/H_2} = 0$

(B) $[H^+]_{minimum} = 10^{-14}$ M;

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

(C) For KCl(aq) [1*M*], pH = 7 $[H^+] = 10^{-7}$ M

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

(D) $E = -\frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$

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

$= -0.0591 \times 0.301 = -0.018$ V