Ch 20 Electrochemistry

37 c) $6e^- + 6H^+_{(aq)} + BrO_3^-{}_{(aq)} \rightarrow Br^-_{(aq)} + 3H_2O_{(l)}$

acidic $3N_2H_{4(g)} \rightarrow 3N_{2(g)} + 4H^+_{(aq)} + 4e^-$

$2BrO_3^-{}_{(aq)} + 3N_2H_{4(g)} \rightarrow 2Br^-_{(aq)} + 6H_2O_{(l)} + 3N_{2(g)}$

39 b) $2e^- + 4H^+_{(aq)} + PbO_{2(s)} + Pb^{+2}_{(aq)} + 2H_2O_{(l)}$

acidic $2I^-_{(aq)} \rightarrow I_{2(s)} + 2e^-$

$4H^+_{(aq)} + PbO_{2(s)} + 2I^-_{(aq)} \rightarrow Pb^{+2}_{(aq)} + 2H_2O_{(l)} + I_{2(s)}$

41 a) $e^- + ClO_{2(aq)} \rightarrow ClO_2^-{}_{(aq)}$

$2OH^-_{(aq)} + H_2O_{2(aq)} \rightarrow O_{2(g)} + (2H^+_{(aq)} + 2OH^-_{(aq)}) + 2e^-$ ($2H_2O_{(l)}$)

Basic $2ClO_{2(aq)} + 2OH^-_{(aq)} + H_2O_{2(aq)} \rightarrow 2ClO_2^-{}_{(aq)} + O_{2(g)} + 2H_2O_{(l)}$

b) $3e^- + [4OH^-_{(aq)} + 4H^+_{(aq)}] + MnO_4^-{}_{(aq)} \rightarrow MnO_{2(s)} + 2H_2O_{(l)} + 4OH^-_{(aq)}$

$4OH^-_{(aq)} + 4H_2O_{(l)} + Al_{(s)} \rightarrow Al(OH)_4^-{}_{(aq)} + [4H^+_{(aq)} + 4OH^-_{(aq)}] + 3e^-$

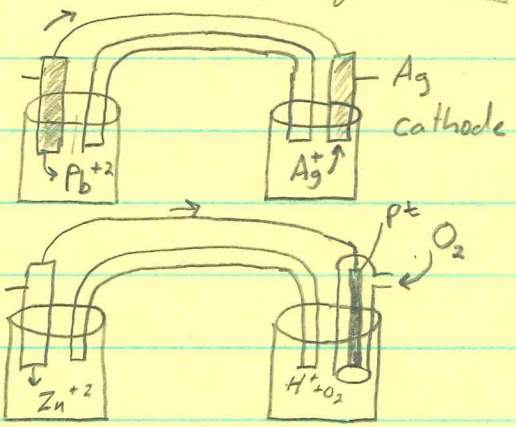
$MnO_4^-{}_{(aq)} + 2H_2O_{(l)} + Al_{(s)} \rightarrow MnO_{2(s)} + Al(OH)_4^-{}_{(aq)}$

45) $2Ag^+_{(aq)} + Pb_{(s)} \rightarrow 2Ag_{(s)} + Pb^{+2}_{(aq)}$

a) red $2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$ $+0.80V$

ox $Pb_{(s)} \rightarrow Pb^{+2}_{(aq)} + 2e$ $+0.13V$

$+0.93V$



c) $O_{2(g)} + 4H^+_{(aq)} + 2Zn_{(s)} \rightarrow 2H_2O_{(l)} + Zn^{+2}_{(aq)}$

red $4e^- + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}$ $+1.93V$

ox $2Zn_{(s)} \rightarrow 2Zn^{+2}_{(aq)} + 4e^-$ $+0.76$

$+1.99V$

Easier!!

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ = 0.80 - (-0.13) = 0.93V$

c) $E^\circ = 1.23V - (-0.76) = 1.99V$

48) anode (−) Pb | Cath (+) $\leftarrow Cl_2$

1M Pb^{+2} | 1M Cl^-

a) $Pb^{+2} + 2e^- \rightarrow Pb$ $-0.13V$ an

$Cl_2 + 2e \rightarrow 2Cl^-$ $+1.36V$ cath

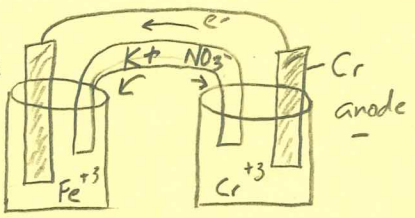
$E^\circ = 1.36 - (-0.13) = 1.49V$

ox $Pb \rightarrow Pb^{+2} + 2e^-$ $+0.13$

red $Cl_2 + 2e^- \rightarrow 2Cl^-$ $+1.36$

$+1.49V$

b) $Pb_{(s)} + Cl_{2(g)} \rightarrow Pb^{+2}_{(aq)} + 2Cl^-_{(aq)}$

47) 

$Fe^{+3}_{(aq)} + 3e^- \rightarrow Fe_{(s)}$ $-0.036V$ cathode

$Cr_{(s)} \rightarrow Cr^{+3}_{(aq)} + 3e^-$ $+0.73V$ anode

$+0.69V$

$Fe^{+3} + Cr \rightarrow Fe + Cr^{+3}$

51) $Sn_{(s)} \mid Sn^{+2}_{(aq)} \parallel NO_{(g)} \mid NO_3^-{}_{(aq)}$

ox red

ox $3Sn_{(s)} \rightarrow 3Sn^{+2} + 2e^-$ $+0.14V$ cathode

red $2NO_3^- + 8H^+ + 3e^- \rightarrow 2NO_{(g)} + 4H_2O$ $+0.96V$ anode

$E^\circ_{cell} = 0.96 - (-0.14V)$

$= 1.10V$ $= 1.10V$

$3Sn_{(s)} + 2NO_3^-{}_{(aq)} + 8H^+_{(aq)} \rightarrow 3Sn^{+2}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$

53a) ox anode
$Ni \rightarrow Ni^{+2} + 2e^-$ $E^\circ_{ox} = +0.23V$ $E^\circ_{cell} = -0.76 - (-0.23) = -0.53V$ nonspontaneous

red cath
$Zn^{+2} + 2e^- \rightarrow Zn$ $E^\circ_{red} = -0.76V$ (Zn more reactive) reverse spontaneous

c) an
$Al \rightarrow Al^{+3} + 3e^-$ $E^\circ_{ox} = +1.66V$ $E^\circ_{cell} = 0.80 - (+1.66) = +2.46V$ spontaneous

cath
$Ag^+ + 1e^- \rightarrow Ag$ $E^\circ_{red} = 0.80V$ (Al more reactive)

$+2.46V$

55) Al is the only metal with a red pot. between Mn + Mg

57) metals with red pot. below H^+ will react in acids Pb + Al are below

$2Al \rightarrow 2Al^{+3} + 6e^-$ $2Al + 6H^+ \rightarrow 2Al^{+3} + 3H_2$ | $Pb \rightarrow Pb^{+2} + 2e^-$ $2H^+ + 2e^- \rightarrow H_2$

$6H^+ + 6e^- \rightarrow 3H_2$ | $Pb + 2H^+ \rightarrow Pb^{+2} + H_2$

61) a) $E^\circ = -1.18V - 0.52V = -1.70V$ Non b) $MnO_2 + 4H^+ \rightarrow Mn^{+2} + 2H_2O$ red $E^\circ_{red} = 1.21$

$Cu \rightarrow Cu^+$ ox $Mn^{+2} \rightarrow Mn$ red $Zn \rightarrow Zn^{+2}$ ox $E^\circ_{ox} = +0.76$

c) $Cl_2 \rightarrow 2Cl^-$ red $E^\circ_{red} = 1.36$ $E^\circ = 1.21 - (-0.76) = +1.97V$ spont $+1.97V$

$2F^- \rightarrow F_2$ ox $E^\circ_{ox} = -2.87$ $E^\circ = 1.36 - 2.87 = -1.51V$ Non

-1.51

63) $Pb^{+2}(a)$ strongest oxidizing agent is one with highest reduction potential

65a) cath
$Pb^{+2} \rightarrow Pb$ $E^\circ_{red} = -0.13$ $E^\circ_{cell} = -2.37 - (0.13)$ $\Delta G^\circ = -nFE^\circ$

an
$Mg \rightarrow Mg^{+2}$ $E_{ox} = +2.37$ $\rightarrow = 2.24V$ $\Delta G^\circ = -2\,mol\,e^- \times \frac{96{,}485C}{mol\,e^-} \times \frac{2.24J}{C} = -432{,}000J$

$-432kJ$

67a) $K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-432{,}000J)}{\left(\frac{8.314J}{K \cdot mol}\right)(298K)}} = 5.31 \times 10^{75}$ very spontaneous

65c) cath
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{+2} + 2H_2O$ $E^\circ = 1.21$ $\Delta G^\circ = -2mole^- \times \frac{96{,}485C}{mole^-} \times \frac{0.87J}{C} = -170{,}000J$

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

$E^\circ_{cell} = 1.21 - 0.34 = 0.87V$

67c) $K = e^{\frac{-(-170{,}000J)}{\left(\frac{8.314J}{K \cdot mol}\right)(298K)}} = 6.3 \times 10^{29}$ spontaneous

71) $\Delta G^\circ = -RT\ln K = \left(\frac{-8.314\,J}{mol\cdot K}\right)(298K)(\ln 25) = -7975\,J$

$\Delta G^\circ = -nFE^\circ$ $\quad E^\circ_{cell} = \frac{\Delta G^\circ}{-nF} = \frac{-7975\,J}{(2\,mol\,e^-)\left(\frac{96{,}485\,C}{mol\,e^-}\right)} = 0.041\,\frac{J}{C}$ $\quad 0.041\,V$

73a) $E^\circ = -0.14 + 1.18) = 1.04\,V$

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

b) $E_{cell} = E^\circ - \frac{0.0592V}{n}\ln Q$ $\quad Q = \frac{[Mn^{+2}]}{[Sn^{+2}]} = \frac{2.00M}{0.0100M} = 200$

$E_{cell} = 1.04V - \frac{0.0592V}{2}(200) = 0.97V$ ↓ cell V

c) $Q = \frac{0.0100M}{2.00M} = 0.00500$

$E_{cell} = 1.04V - \frac{0.0592V}{2}(0.00500) = 1.11V$ ↑ cell V

higher conc react shift → $\quad$ higher conc prod shift ←

75) ~~$E^\circ_{cell} = 1.68V + 0.13) = 1.81V$~~ $\quad 3Pb + 2MnO_4^- + 8H^+ \rightarrow 3Pb^{+2} + 2MnO_2 + 4H_2O$ (1.50, 2.0, 0.10)

~~$E_{cell} = 1.81V - \frac{0.0592V}{6}\log\frac{(0.10)^3}{(1.50)^2(2.0)^8} = +1.87V$~~

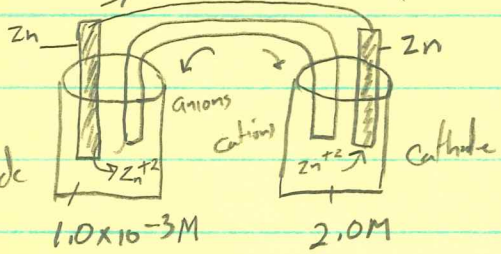
77a) $Zn + Ni^{+2} \rightarrow Zn^{+2} + Ni$: $\quad E_{cell} = 0.53V - \frac{0.0592V}{2}\log\left(\frac{0.100}{1.50}\right) = 0.56V$

$E^\circ_{cell} = -0.23 + 0.76 = 0.53V$

b) $E_{cell} = 0.53V - \frac{0.0592V}{2}\log\frac{1.100}{0.500} = 0.52V$

c) $0.45 = 0.53V - \frac{0.0592V}{2}\log Q$ $\quad \log Q = 2.70$ $\quad Q = 10^{2.70} = 504$

$504 = \frac{[Zn^{+2}]}{1.60M - [Zn^{+2}]}$ $\quad [Zn^{+2}] = 1.60\,M$

79) 

83) alkaline battery

$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

$2MnO_2 + 2H_2O + 2e^- \rightarrow 2MnO(OH) + 2OH^-$

$Zn = 65.38\,g/mol$ $\quad MnO_2$ 86.94_3

$\frac{1\,mol\,Zn}{2\,mol\,MnO_2} = \frac{65.38_3}{86.94_3} = \frac{0.3760\,g\,Zn}{1\,g\,MnO_2}$ or $\frac{1}{1.330}$

85) $\overset{-4\ +1}{CH_4} + 2\overset{0}{O_2} \rightarrow \overset{+4\ -2}{CO_2} + 2H_2O$

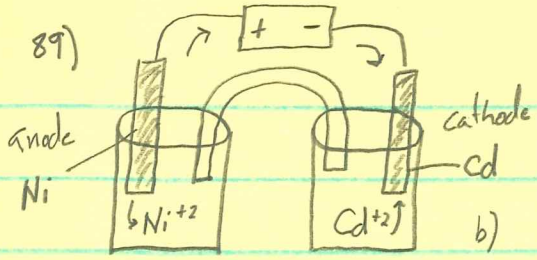
$\Delta G^\circ = [(-394.4) + 2(-228.6)] - [(-50.5) + 2(0)]$

$= -801.1\,KJ$ $\quad n = 8$

$E^\circ_{cell} = \frac{\Delta G^\circ}{-nF} = \frac{-8.011\times10^5\,J}{-8\,mole^- \times \frac{96{,}485\,C}{mol\,e^-}} = 1.038\,\frac{J}{C} \rightarrow V$

87) rust $Fe \rightarrow Fe^{+3}$ for a metal to protect iron it must oxidize more easily (lower red. pot.) Zn + Mn both have higher ox. pot.

89)



a) $Ni \rightarrow Ni^{+2} + 2e^-$ ox $E^\circ_{ox} = +0.23V$

$Cd^{+2} + 2e^- \rightarrow Cd$ red $E^\circ_{red} = -0.40V$

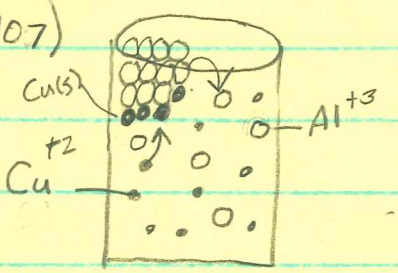
$E^\circ_{cell} = -0.40 - (-0.23V) = -0.17V$

b)

c) a minimum of 0.17 V must be supplied by the battery

99) $325\,mg\,Cu \times \frac{1g\,Cu}{1000\,mg} \times \frac{1\,mol\,Cu}{63.55g} \times \frac{2\,mol\,e^-}{1\,mol\,Cu} \times \frac{96,485C}{1\,mole^-} \times \frac{1\,sec}{5.6C} = 180s$ $\quad A = C/sec$

107)



$Al \rightarrow Al^{+3}$ $E^\circ_{ox} = +1.66V$ $\quad Cu^{+2}$ has higher red pot

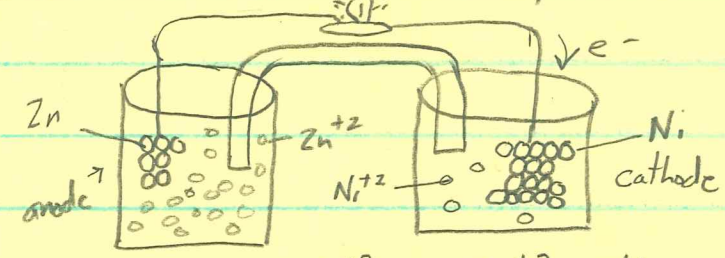
$Cu^{+2} \rightarrow Cu$ $E^\circ_{red} = 0.34V$ $\quad Al^0$ has higher ox pot

$E^\circ_{cell} = 0.34 - (-1.66) = +2.00V$ rxn is spontaneous

108) $Zn^{+2} + 2e \rightarrow Zn$ $E^\circ = +0.76$

$Ni^{+2} + 2e \rightarrow Ni$ $E^\circ = -0.23$ ← higher red. pot.

$E^\circ_{cell} = -0.23 - (0.76) = +0.53V$



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

113) Be wary!

Largest $\Delta E^\circ \rightarrow F_2$ Li^{+1} $E^\circ_{cell} = 2.87 - (-3.04) = 5.91V$

118) $CH_3CH_2OH + O_2^\circ \rightarrow HC_2H_3O_2 + H_2O^{-2}$ $\quad n = 4$ $\quad 324mA = 0.324A$

$10\,sec \times \frac{0.324C}{s} \times \frac{1\,mole^-}{96,485C} \times \frac{1\,mol\,CH_3CH_2OH}{4\,mole^-} = 8.395 \times 10^{-6}\,mol$ ethanol

$$P = \frac{nRT}{V} = \frac{(8.395\times10^{-6}\,mol)\left(0.08206\,\frac{L\cdot atm}{mol\cdot K}\right)(298K)}{0.188L} = 1.092\times10^{-3}\,atm$$

% by vol $\frac{1.092\times10^{-3}\,atm}{1\,atm} \times 100 = 0.109 = 0.1\%$