3.53 Solution Outlines to PS 1

1(a) convert $T(°C) \rightarrow T(K)$ & fit $\mathcal{E}^\circ$ vs T and $\mathcal{E}$ vs T

$$\mathcal{E}^\circ = 2288 - 0.4447\,T \text{ mV}$$
$$\mathcal{E} = 2602 - 0.2628\,T \text{ mV}$$

(b) $\Delta G^\circ = -nF\mathcal{E}^\circ = -2F\mathcal{E}^\circ$
$= -4.415\times10^5 + 8.581\times10^1\,T$ J/mol
from which $\Delta H^\circ = -4.415\times10^5$ J/mol
and $\Delta S^\circ = -85.81$ J/mol K

(c) we want ΔG for $MnCl_2$ (pure) $\rightarrow MnCl_2$ (1%)

for which $\Delta G = \overline{G}_{MnCl_2(1\%)} - G^\circ_{MnCl_2(pure)} = \Delta\overline{G}_{MnCl_2}$

we already have these two reactions:
$Mn + Cl_2 = MnCl_2$ (pure) ① $\Delta G_1 = \Delta G^\circ$
$Mn + Cl_2 = MnCl_2$ (1%) ② $\Delta G_2 = \Delta G$

So take $\Delta G_2 - \Delta G_1$ to get $\Delta\overline{G}_{MnCl_2}$

$\therefore \Delta\overline{G}_{MnCl_2} = -2F(\mathcal{E} - \mathcal{E}^\circ)$
$= -2F(314 + 0.1819)/1000$ ← conversion from mV → V
$= -6.059\times10^4 - 35.10\,T$ J/mol

$\therefore \Delta\overline{H}_{MnCl_2} = -6.059\times10^4$ J/mol

$\Delta\overline{S}_{MnCl_2} = +35.10$ J/mol K

(d)(i) $\Delta\bar{G}_{MnCl_2} = RT \ln a_{MnCl_2}$

$\therefore a_{MnCl_2} = \exp \dfrac{\Delta G_{MnCl_2}}{RT}$

650°C 5.463×10^{-6}
750°C 1.182×10^{-5}

$\gamma_{MnCl_2} = a_{MnCl_2} / X_{MnCl_2}$, $X_{MnCl_2} = 0.01$

650°C 5.463×10^{-4}
750°C 1.182×10^{-3}

(ii) $\gamma < 1 \Rightarrow$ negative deviation from ideality

(iii) $\Delta\bar{S}_{ideal} = -R \ln X_{MnCl_2} = 38.29$ J/mol K

$\Delta\bar{S}^{excess}_{MnCl_2} = \Delta\bar{S}_{MnCl_2} - \Delta\bar{S}_{ideal}$

$= 35.10 - 38.29$

$= -3.187$ J/mol K

Since $\Delta\bar{S}_{ideal} > \Delta\bar{S}_{MnCl_2}$, this means that the melt is not fully random $\Rightarrow$ there is evidence of ordering between the various species present $\Rightarrow$ maybe complex formation

(e) $Mn + Cl_2(1\,atm) = MnCl_2$ ①
$Cl_2(1\,atm) = Cl_2(P \neq 1)$ ②

we want $Mn + Cl_2(P \neq 1) = MnCl_2$ ③

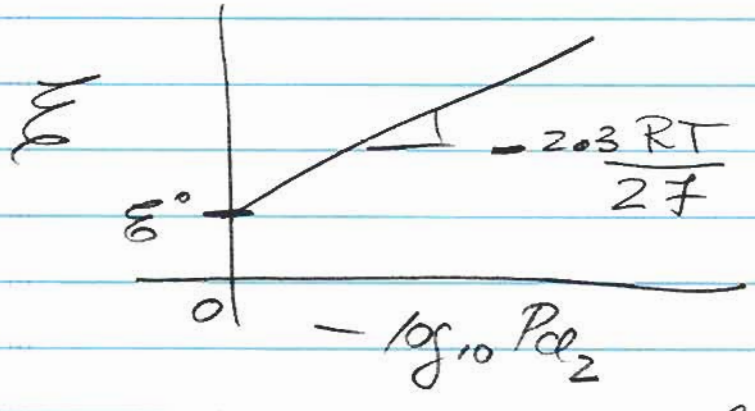
③ = ① − ② $\therefore \mathcal{E}_3 = \mathcal{E}_1 - \mathcal{E}_2$

$$\Delta G_2 = RT \ln P_{Cl_2} \Rightarrow \mathcal{E}_2 = -\frac{RT}{2\mathcal{F}} \ln P_{Cl_2}$$

$\mathcal{E}_1 = \mathcal{E}^\circ$

$$\therefore \mathcal{E}_3 = \mathcal{E}^\circ - \frac{RT}{2\mathcal{F}} \ln P_{Cl_2}$$

$\Rightarrow$ as P_{Cl_2} decreases, $\mathcal{E}_{cell}$ <u>increases</u>



P_{Cl_2}	$\mathcal{E}$ (mV)
1	2346
10^{-3}	2636

(f) analgous to (e): if Mn alloy is used, $a_{Mn} < 1 \Rightarrow \mathcal{E} > \mathcal{E}^\circ$