Chapter 15 HW Problems

15-2
a) \( \text{Cu}^+ + \text{Ce}^{4+} \rightarrow \text{Cu}^{2+} + \text{Ce}^{3+} \)
\[ E^0_{(\text{Cu}^+/\text{Cu}^{2+})} = 0.161 \text{ V} \]
\[ E^0_{(\text{Ce}^{3+/\text{Ce}^{4+})} = 1.70 \text{ V} \]

b) \( \text{Cu}^{2+} + \text{Ag}(s) + \text{Cl}^- \leftrightarrow \text{Cu}^+ + \text{AgCl}_{(s)} \)
\( \text{Ce}^{4+} + \text{Ag}(s) + \text{Cl}^- \leftrightarrow \text{Ce}^{3+} + \text{AgCl}_{(s)} \)

c) \( E_{\text{cell}} = E^0_{(\text{Cu}^+/\text{Cu}^{2+})} - E_{(\text{Ag}/\text{AgCl}_{\text{ref}})} - 0.05916 \log([\text{Cu}^+]/[\text{Cu}^{2+}]) \)
Or \( E_{\text{cell}} = E^0_{(\text{Ce}^{3+/\text{Ce}^{4+})} - E_{(\text{Ag}/\text{AgCl}_{\text{ref}})} - 0.05916 \log([\text{Ce}^{3+}]/[\text{Ce}^{4+}]) \)

d) It will take 25.0 mL to reach the equivalence point \((M_1V_1 = M_2V_2)\)
at 1.00 mL of \( \text{Cu}^+ \) added
\[
\text{mmol Ce}^{4+} = (100 \text{ mL})(0.0100 \text{ M}) - (1.00 \text{ mL})(0.0400 \text{ M}) = 0.960 \text{ mmol}
\]
\[
\text{mmol Ce}^{3+} = (1.00 \text{ mL})(0.0400 \text{ M}) = 0.040 \text{ mmol}
\]
\[
E_{\text{cell}} = E^0_{(\text{Ce}^{3+/\text{Ce}^{4+})} - E_{(\text{Ag}/\text{AgCl}_{\text{ref}})} - 0.05916 \log([\text{Ce}^{3+}]/[\text{Ce}^{4+}])
 = 1.70 - 0.197 - 0.05916 \log(.04/.96)
 = 1.58 \text{ V}
\]
at 12.50 mL of \( \text{Cu}^+ \) added (1/2 way!!!!)
\[
\text{mmol Ce}^{4+} = (100 \text{ mL})(0.0100 \text{ M}) - (12.50 \text{ mL})(0.0400 \text{ M}) = 0.500 \text{ mmol}
\]
\[
\text{mmol Ce}^{3+} = (1.00 \text{ mL})(0.0400 \text{ M}) = 0.500 \text{ mmol}
\]
\[
E_{\text{cell}} = E^0_{(\text{Ce}^{3+/\text{Ce}^{4+})} - E_{(\text{Ag}/\text{AgCl}_{\text{ref}})} - 0.05916 \log([\text{Ce}^{3+}]/[\text{Ce}^{4+}])
 = 1.70 - 0.197 - 0.05916 \log(.500/0.500)
\]
\[ E_{\text{cell}} = \frac{(E^0_{(Cu+/Cu^{2+})} + E^0_{(Ce^{3+/Ce^{4+})})}}{2} - 0.196 \text{ V} = \frac{(0.161 + 1.70)/2 - 0.196 \text{ V}}{2} = 0.734 \text{ V} \]

at 25.50 mL of Cu\(^+\) added

mmol Cu\(^+\) = 
\[ \text{(25.50 mL)(0.0400 M)} = 0.20 \text{ mmol} \]

mmol Cu\(^{2+}\) = 
\[ \text{(100 ml)(0.0100 M)} = 1.00 \text{ mmol} \]

\[ E_{\text{cell}} = E^0_{(Cu+/Cu^{2+})} - E_{(Ag/AgCl_{\text{ref})}} - 0.05916 \log([Cu^+]/[Cu^{2+}]) \]
\[ = 0.161 - 0.197 - 0.05916 \log(0.02/1.00) \]
\[ = 0.065 \text{ V} \]

15.3

a) \[ \text{Sn}^{2+} + \text{Tl}^{3+} \rightarrow \text{Sn}^{4+} + \text{Tl}^+ \]
\[ E^0_{(Tl^+/Tl^{3+})} = 0.77 \text{ V} \]
\[ E^0_{(Sn^{2+}/Sn^{4+})} = 0.139 \text{ V} \]

b) \[ \text{Sn}^{4+} + 2\text{Hg(s)} + 2\text{Cl}^- \Leftrightarrow \text{Sn}^{2+} + \text{Hg}_2\text{Cl}_2(s) \]
\[ \text{Tl}^{3+} + 2\text{Hg(s)} + 2\text{Cl}^- \Leftrightarrow \text{Tl}^+ + \text{Hg}_2\text{Cl}_2(s) \]
c)

\[ E_{\text{cell}} = E^0_{(\text{Tl}^+/\text{Tl}^3+)} - E_{(\text{SCE})} - 0.05916/2 \log([\text{Tl}^+]/[\text{Tl}^3+]) \]

Or

\[ E_{\text{cell}} = E^0_{(\text{Sn}^{2+/\text{Sn}^4+})} - E_{(\text{SCE})} - 0.05916 \log([\text{Sn}^{2+}]/[\text{Sn}^4+]) \]

d)

It will take 5.00 mL to reach the equivalence point \((M_1 V_1 = M_2 V_2)\)

at 1.00 mL of \(\text{Tl}^3+\) added

mmol \(\text{Sn}^{2+}\) =  
\[
(25.0 \text{ mL})(0.0100 \text{ M}) - (1.00 \text{ mL})(0.0500 \text{ M}) = 0.200 \text{ mmol}
\]

mmol \(\text{Sn}^{4+}\) =  
\[
(1.00 \text{ mL})(0.0500 \text{ M}) = 0.0500 \text{ mmol}
\]

\[ E_{\text{cell}} = E^0_{(\text{Sn}^{2+/\text{Sn}^4+})} - E_{(\text{SCE})} - 0.05916/2 \log([\text{Sn}^{2+}]/[\text{Sn}^4+]) \]

\[ = 0.139 - 0.241 - 0.05916/2 \log(0.200/0.0500) \]

\[ = -0.120 \text{ V} \]

at 2.50 mL of \(\text{Tl}^3+\) added (1/2 way!!!!)

mmol \(\text{Sn}^{2+}\) =  
\[
(25.0 \text{ mL})(0.0100 \text{ M}) - (2.50 \text{ mL})(0.0500 \text{ M}) = 0.125 \text{ mmol}
\]

mmol \(\text{Sn}^{4+}\) =  
\[
(2.50 \text{ mL})(0.0500 \text{ M}) = 0.125 \text{ mmol}
\]

\[ E_{\text{cell}} = E^0_{(\text{Sn}^{2+/\text{Sn}^4+})} - E_{(\text{SCE})} - 0.05916/2 \log([\text{Sn}^{2+}]/[\text{Sn}^4+]) \]

\[ = 0.139 - 0.241 - 0.05916/2 \log(0.125/0.125) \]

\[ = -0.102 \text{ V} \]

at 5.00 mL of \(\text{Tl}^3+\) added (at equiv. pt)

\[ E_{\text{cell}} = \{(E^0_{(\text{Sn}^{2+/\text{Sn}^4+})} + E^0_{(\text{Tl}^+/\text{Tl}^3+)}) / 2\} - 0.241 \text{ V} = \]
\[
(0.139 + 0.77)/2 - 0.241 \text{ V} \]

\[ = 0.21 \text{ V} \]
at 5.10 mL of Tl\(^{3+}\) added

\[
\text{mmol Tl}^{3+} = (0.10 \text{ mL})(0.0500 \text{ M}) = 0.0050 \text{ mmol}
\]

\[
\text{mmol Tl}^+ = (25.0 \text{ mL})(0.0100 \text{ M}) = 0.250 \text{ mmol}
\]

\[
E_{\text{cell}} = E_{(Tl^{3+}/Tl^+)}^0 - E_{(SCE)} - 0.05916/2 \log([Tl^+]/[Tl^{3+}])
\]

\[
= 0.77 - 0.241 - 0.05916/2 \log(0.250/0.005)
\]

\[
= 0.49 \text{ V}
\]

At 10.00 mL of Tl\(^{3+}\) added

\[
\text{mmol Tl}^{3+} = (5.00 \text{ mL})(0.0500 \text{ M}) = 0.250 \text{ mmol}
\]

\[
\text{mmol Tl}^+ = (25.0 \text{ mL})(0.0100 \text{ M}) = 0.250 \text{ mmol}
\]

\[
E_{\text{cell}} = E_{(Tl^{3+}/Tl^+)}^0 - E_{(SCE)} - 0.05916/2 \log([Tl^+]/[Tl^{3+}])
\]

\[
= 0.77 - 0.241 - 0.05916/2 \log(0.250/0.250)
\]

\[
= 0.53 \text{ V}
\]

15-4

a) balanced rxn for the titration

\[
H_2O + A + 2Fe^{3+} \leftrightarrow D + 2Fe^{2+} + 2H^+
\]

b) 

\[
DA + 2H^+ + 2Cl^- + 2Ag(s) \leftrightarrow A + H_2O + 2AgCl(s)
\]

Or

\[
Fe^{3+} + Ag(s) + Cl^- \leftrightarrow Fe^{2+} + AgCl_2(s)
\]

c) 

\[
E_{\text{cell}} = E_{(A/DA)}^0 - E_{(Ag/AgCl)} - 0.05916/2 \log([A]/[D][H^+]^2)
\]

\[
E_{\text{cell}} = E_{(Fe^{3+}/Fe^{2+})}^0 - E_{(Ag/AgCl)} - 0.05916 \log([Fe^{2+}]/[Fe^{3+}])
\]
d) Equiv pt is 20.00 mL at 5.0 mL of A added
\[ \text{mmol Fe}^{3+} = (10.0 \text{ mL})(0.0200 \text{ M}) - (10.0 \text{ mL})(0.010 \text{ M}) = 0.10 \text{ mmol} \]
\[ \text{mmol Fe}^{3+} = (10.0 \text{ mL})(0.010 \text{ M}) = 0.10 \text{ mmol} \]

\[ E_{\text{cell}} = E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0 - E_{\text{Ag}/\text{AgCl}} - 0.05916 \log([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) \]
\[ = 0.767 - 0.197 - 0.05916 \log(1) \]
\[ = 0.570 \text{ V} \]

At 10.0 mL of A added we are at the equivalence pt
At the equiv. pt.
\[ [\text{Fe}^{2+}] = [D], \text{ and } [\text{Fe}^{3+}] = [A] \]
To calculate \( E_{\text{cell}} \), we can make use of this info by adding the following two equations

\[ E_+ = E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0 - 0.05916/2 \log([A]/[D][H^+]^2) \]
\[ E_+ = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.05916 \log([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) \]

To effectively combine the log terms of the two equations when we add them, it is convenient to multiply the first equation by a factor of 2

\[ 2E_+ = 2E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0 - 0.05916 \log([A]/[D][H^+]^2) \]
\[ + \frac{E_+ = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.05916 \log([\text{Fe}^{2+}]/[\text{Fe}^{3+}])}{3E_+ = 2E_{\text{Fe}^{2+}/\text{Fe}^{3+}}^0 + E_{\text{Fe}^{3+}/\text{Fe}^{2+}} - 0.05916 \log([A][\text{Fe}^{2+}]/[\text{Fe}^{3+}][D][H^+]^2)} \]
\[ 3E_+ = 2(.390) + 0.767 - 0.05916 \log(1/[H^+]^2) \]
\[ \text{pH} = 0.30 \rightarrow [H^+] = 0.501 \text{ M} \]
\[ 3E_+ = 1.511 \text{ V} \]
\[ E_+ = 0.504 \text{ V} \]
\[ E_{\text{cell}} = E_+ - E_{\text{Ag}/\text{AgCl}} = 0.504 - 0.197 = 0.307 \text{ V} \]
At 15 mL added

\[ \text{mmol A} = (5.0 \text{ mL})(0.010 \text{ M}) = 0.050 \text{ mmol} \]

\[ \text{mmol D} = (10.0 \text{ mL Fe}^{3+})(0.0200 \text{ M Fe}^{3+})(1\text{ mol D}/2 \text{ mol Fe}^{3+}) = 0.100 \text{ mmol} \]

(look at stoichiometry of the overall rxn)

\[ E_{\text{cell}} = E^0_{(A/DA)} - E_{(Ag/AgCl)} - 0.05916/2 \log([A]/[D][H^+]^2) \]
\[ = 0.390 - 0.197 - 0.05916/2 \log\{(0.05)/(0.100)(0.501)^2\} \]
\[ = 0.184 \text{ V} \]

15-11

The Walden reductor uses the standard Ag/AgCl couple to reduce Fe\(^{3+}\). The standard reduction potential for the Ag/AgCl couple is large enough (0.222 V) that Cr\(^{3+}\) and TiO\(^{2+}\) are not reduced. Where as the reduction potential for the Zn/Zn\(^{2+}\) (Jones reducer) is much less –0.764 V, and Cr\(^{3+}\) and TiO\(^{2+}\) are reduced.

15-14

When 25.00 mL of unknown was passed through a Jones redactor, MoO\(_4^{2-}\) was converted to Mo\(^{3+}\). The filtrate required 16.43 mL of 0.01033 M KMnO\(_4\) to reach an endpoint.

\[ \text{MnO}_4^- + \text{Mo}^{3+} \rightarrow \text{Mn}^{2+} + \text{MoO}_2^{2+} \]

A blank required 0.04 mL. Balance the reaction and find the molarity of moly species in the unknown.

This is not a balanced redox reaction as written. Write two balanced-half reactions and add.

\[ 3(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}) \]
\[ 5(\text{Mo}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{MoO}_2^{2+} + 4\text{H}^+ + 3\text{e}^-) \]
\[ 3\text{MnO}_4^- + 4\text{H}^+ + 5\text{Mo}^{3+} \leftrightarrow 3\text{Mn}^{2+} + 5\text{MoO}_2^{2+} + 2\text{H}_2\text{O} \]
Jones reductor
\[ \text{MoO}_4^{2-} + \text{Zn(s)} + 8\text{H}^+ \rightarrow \text{Mo}^{3+} + \text{Zn}^{2+} + 4\text{H_2O} \]

\[ [\text{MoO}_4^{2+}] = (16.39 \, \text{mL MnO}_4^-)(0.01033 \, \text{M MnO}_4^-)*(5 \, \text{mmol MoO}_4^{2+}/3 \, \text{mmol MnO}_4^-)/(25.00 \, \text{mL}) \]
\[ = 0.01129 \, \text{M MoO}_4^{2+} \]

15-15

A 25.00 mL aliquot of commercial a hydrogen peroxide solution was diluted to 250.0 mL in a volumetric flask. Then 25.00 mL of the diluted solution was mixed with 200 mL of water and 20 mL 3 M H2SO4 and titrated with 0.02123 M KMnO4. The first pink color was observed at 27.66 mL of titrant added. A blank prepared from water in place of the diluted hydrogen peroxide solution required 0.04 mL to give a visible pink color. Find the molarity of the commercial hydrogen peroxide solution.

\[ 2(\text{MnO}_4^- + 8\text{H}^+ + 5e^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}) \quad E^0 = 1.507 \]

\[-5(\text{O}_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2\text{O}_2) \quad E^0 = 0.695 \]

\[ 2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \leftrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2 \]

mmol MnO4^- = (27.62 mL)(0.02123 M) = 0.5863 mmol MnO4^-

\[ [\text{H}_2\text{O}_2]\text{dil} = (0.5863)*(5 \, \text{mol H}_2\text{O}_2/2 \, \text{mol MnO}_4^-)/(25.00 \, \text{mL}) \]
\[ = 0.05864 \, \text{M} \]

\[ [\text{H}_2\text{O}_2] = (0.05864)(250 \, \text{mL}/25 \, \text{mL}) = 0.5864 \, \text{M} \]

dilution factor
An aqueous glycerol solution weighing 100.0 mg was treated with 50.0 mL of 0.0837 M Ce\(^{4+}\) in 4 M HClO\(_4\) at 60 °C for 15 min to oxidize the glycerol to formic acid. The excess Ce\(^{4+}\) required 12.11 mL of 0.0448 M Fe\(^{2+}\) to reach a ferroin endpoint. What is the weight percent of glycerol in the unknown?

Write half rxn for the oxidation of glycerol to formic acid
\[ C_3H_8O_3 + 3H_2O \rightleftharpoons 3HCO_2H + 8H^+ + 8e^- \]

Write balanced rxn of glycerol with Ce\(^{4+}\)
\[ C_3H_8O_3 + 3H_2O + 8Ce^{4+} \rightleftharpoons 8Ce^{3+} + 3HCO_2H + 8H^+ \]  
(8:1 molar ratio)

Write equation for the back titration
\[ Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+} \]  
(1:1 molar ratio)

mmole Ce\(^{4+}\) needed to titrate glycerol (G) =
\[ (50.0 \text{ mL})(0.0837 \text{ M}) - (12.11 \text{ mL})(0.0448 \text{ M}) = 3.6425 \text{ mmol Ce}^{4+} \]

\[ \text{mmol C}_3\text{H}_8\text{O}_3 = (3.6425 \text{ mmol Ce}^{4+})(1 \text{ mmol G/8 mmol Ce}^{4+}) \]
\[ = 0.45531 \text{ mmol G} \]

\[ \text{mg G} = (0.45531 \text{ mmol G})(92.0938 \text{ mg G/mmol G}) = 41.931 \text{ mg} \]

wt % G = [(41.931mg G) / (100.0 mg sample)] 100 = 41.9 %

15-19

mmole Ce\(^{4+}\) needed to titrate NO\(_2^-\) =
\[ (50.0 \text{ mL})(0.1186 \text{ M}) - (31.13 \text{ mL})(0.04289 \text{ M}) = 4.59483 \text{ mmol Ce}^{4+} \]

\( (\text{mmol NO}_2^-)_{\text{dil}} = (4.59483 \text{ mmol Ce}^{4+})(1 \text{ mmol NO}_2^-/2 \text{ mmol Ce}^{4+}) = 2.29742 \text{ mmol NO}_2^- \)
(mmol NO₂⁻)_{sample} = 
(2.29742 \text{ mmol NO₂⁻})*(500.0/25.00) = 45.94 \text{ mmol NO₂⁻}

\text{mg G} = (45.94 \text{ mmol NO₂⁻})*(68.995 \text{ mg NaNO₂/mmol NO₂⁻}) 
= 3170.2 \text{ mg NaNO₂} = 3.1702 \text{ g NaNO₂}

\% \text{ NaNO₂} = (3.1702 \text{ g NaNO₂}/(4.030 \text{ g sample})*100 = 78.67 \% 

15.25
A potassium iodate solution was prepared by dissolving 1.022 g of KIO₃ (FM 214.00) in a 500 mL flask. Then 50.00 mL of this solution was pipetted into a flask and treated with 2 g KI and 10 mL of 0.5 M H₂SO₄. How many moles of I₃⁻ are formed?

a. mol IO₃⁻ = (1.022 g)(1 mol/214.00 g) = 0.004776 mol

Reaction

IO₃⁻ + 8I⁻ → 3I₃⁻ + 3H₂O

50/500 mL taken or 0.4776 mmol

Thus, 1.433 mmol I₃⁻ is formed.

b. Titration Reaction

I₃⁻ + 2S₂O₃²⁻ → 3I⁻ + S₄O₆²⁻

So… [S₂O₃²⁻] = (2)(0.01433)/(0.03766 L) = 0.07609 M

c.

\begin{align*}
A + H₂O &\rightarrow DA + 2H^+ + 2e^- & E^0 = 0.390 \text{ V} \\
I₃⁻ + 2e^- &\rightarrow 3I^- & E^0 = 0.535 \text{ V}
\end{align*}

A + H₂O + I₃⁻ → DA + 2H^+ + 3I⁻

14.33 mmol I₃⁻ (or added to the ascorbic acid, 50 out of 500 mL)
(14.22 mL)(0.07609 M) = 1.082 mmol $S_2O_3^{2-}$ added. It will react with 0.5410 mmol $I_3^-$. 

Therefore, $1.433 - 0.5410 = 0.892 \text{ mmol } I_3^-$ reacted with 0.892 mmol of ascorbic acid.

$(0.892 \text{ mmol})(176.13 \text{ mg/mmol})/1000 = 0.157 \text{ g } A$

Wt $\% = (0.157/1.223)\cdot100 = 12.8 \%$

d) must add indicator right before the endpoint.

15-26

A 3.026 g portion of a copper(II) salt was dissolved in a 250 mL volumetric flask. A 50.0 mL aliquot was analyzed by adding 1 g of KI and titrating the liberated $I_3^-$ with 23.33 mL of 0.04668 M thiosulfate std. Find the weight $\%$ of copper in the sample.

$$2\text{Cu}^{2+} + 5\Gamma \rightarrow \text{CuI}_{(s)} + \text{I}_3^-$$

$$\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\Gamma^{-} + \text{S}_4\text{O}_6^{2-}$$

Liberated $I_3^-$ = $(23.33 \text{ mL})(0.04668 \text{ M})/2 = 0.5445 \text{ mmol } I_3^-$

mmol Cu$^{2+}$ in 50.00 mL aliquot = $(0.5445)(2/1) = 1.089 \text{ mmol } \text{Cu}^{2+}$

mass Cu$^{2+}$ in sample = $(1.089 \text{ mmol})(63.546 \text{ mg/mmol Cu})(250/50)(1 \text{ g}/1000 \text{ mg}) = 0.3460 \text{ g}$

weight $\% = (0.6920/3.026)\cdot100 = 11.44 \%$
H₂S ↔ S(s) + 2H⁺ + 2e⁻

I₃⁻ + 2e⁻ ↔ 3I⁻

H₂S + I₃⁻ ↔ S(s) + 2H⁺ + 3I⁻

I₃⁻ + 2S₂O₃²⁻ ↔ 3I⁻ + S₄O₆²⁻

(mmol I₃⁻)_{tot} = (25.00 mL)(0.01044 M) = 0.26100 mmol I₃⁻

(mmol I₃⁻)_{S₂O₃} = (14.44 mL)(0.009336 M)*(1 mol I₃⁻/2 mol S₂O₃²⁻)

= 0.067406 mmol I₃⁻

[H₂S] = (0.26100 - 0.067406)*(1 mol H₂S/1 mol I₃⁻)/25.00 ml

= 0.007744 M or 7.744 mM

Since we are titrating a solution that contain I₃⁻ before the equivalence point it is important that we wait until just before the equivalence point to add the starch indicator.

15-28

a) Subtract the second and last equation

I₂(aq) + 2e⁻ ↔ 2I⁻  \hspace{1cm} \Delta G_2^0 = nFE_2^0, \hspace{0.5cm} E_2^0 = 0.620 V

+ 3I⁻ ↔ 2e⁻ + I₃⁻  \hspace{1cm} \Delta G_3^0 = nFE_{3}^0, \hspace{0.5cm} E_3^0 = -0.535 V

I₂(aq) + I⁻ ↔ I₃⁻  \hspace{1cm} \Delta G_r^0 = (nFE_2^0 + nFE_{3}^0)

you can say:

nFE_r^0 = (nFE_2^0 + nFE_{3}^0), since both half rxns are two electron transfers  \Rightarrow Er^0 = E_2^0 + E_3^0 = 0.085 V

K = 10^{n(E_{10} + E_{30})/0.05916} = 10^{(2*0.085)/0.05916} = 7*10^2
b) Subtract the first and last equation

\[
\begin{align*}
I_{2(s)} + 2e^- & \leftrightarrow 2I^- & \Delta G_1^0 = nFE_1^0, & E_1^0 = 0.535 \text{ V} \\
+ 3I^- & \leftrightarrow 2e^- + I_3^- & \Delta G_3^0 = nFE_3^0, & E_3^0 = -0.535 \text{ V}
\end{align*}
\]

\[
I_{2(s)} + I^- \leftrightarrow I_3^- & \quad \Delta G_r^0 = (nFE_1^0 + nFE_3^0)
\]

\[
\Delta G_{\text{rxn}}^0 = (nFE_1^0 + nFE_3^0) = 0 = -RT \ln K_{eq}
\]

\[K_{eq} = 1.0\]

\[nFE_r^0 = (nFE_1^0 + nFE_3^0), \text{ since both half rxns are two electron transfers} \Rightarrow E_r^0 = E_1^0 + E_3^0 = 0.000 \text{ V}\]

\[K = 10^{n(F(E_1^0 + E_3^0)/0.05916)} = 1.0\]

c) Subtract the first two equations

\[
\begin{align*}
I_{2(s)} + 2e^- & \leftrightarrow 2I^- & \Delta G_1^0 = nFE_1^0, & E_1^0 = 0.535 \text{ V} \\
+ 2I^- & \leftrightarrow I_{2(aq)} + 2e^- & \Delta G_2^0 = nFE_2^0, & E_2^0 = -0.620 \text{ V}
\end{align*}
\]

\[
I_{2(s)} \leftrightarrow I_{2(aq)} & \quad \Delta G_r^0 = (nFE_1^0 + nFE_3^0)
\]

\[nFE_r^0 = (nFE_1^0 + nFE_3^0), \text{ since both half rxns are two electron transfers} \Rightarrow E_r^0 = E_1^0 + E_3^0 = -0.085 \text{ V}\]

\[K = 10^{n(F(E_1^0 + E_3^0)/0.05916)} = 10^{(2*(-0.085/0.05916))} = 1.338*10^{-3}\]

\[K = [I_{2(aq)}] = 0.001338 \text{ mol/L} \Rightarrow 0.3 \text{ g/L}\]
15-31

WoW!!! This is a fun one!!!! You must break it down into steps.

There are four different reactions that are occurring in this experiment; the first two are given, the last two are not.

Let us write the last two out
Rxn 3
The excess Br₂ is converted to Br⁻, producing I₃⁻
Br₂ + 3I⁻ → 2Br⁻ + I₃⁻ (this a balanced 2e- transfer redox rxn)

Rxn 4
I₃⁻ is titrated with S₂O₃²⁻
I₃⁻ + 2S₂O₃²⁻ ↔ 3I⁻ + S₄O₆²⁻

OK!

moles of I₃⁻ produced from rxn 3 =
(8.83 ml)(0.05113 M)*(1 mol I₃⁻/2 mol S₂O₃²⁻) = 0.22574 mmol I₃⁻

moles of excess Br₂ left over from rxn 2 =
(0.22574 mmol I₃⁻)*(1 mol Br₂/1 mol I₃⁻) = 0.22574 mmol Br₂

mmol Br₂ produced from rxn 1 =
(25.00 ml)(0.02000 M)*(3 mol Br₂/1 mol BrO₃⁻) = 1.500 mmol Br₂

mol Br₂ reacted with Al(C₉H₆ON)₃ =
1.500 mmol − 0.22574 mmol = 1.2743 mmol Br₂

mmol Al³⁺ in unknown =
(1.2743 mmol Br₂)( 1 mol C₉H₆ON /2 mol Br₂)*(1 mol Al³⁺/3 mol C₉H₆ON) = 0.21238 mmol Al³⁺ ⇒ 5.730 mg Al
In order to eliminate rounding errors it is important that you keep as many figures as we can in each of the intermediate calculations. Then, for the final answer you must go back through each step starting from the first one to determine the correct sig. figs that carry through to the answer.