Chapter 15 HW Problems

15-2, 15-5, 15-11, 15-14, 15-15, 15-18, 15-19, 15-24, 15-26, 15-27, 15-29

15-2

a) $Cu^{+} + Ce^{4+} \rightarrow Cu^{2+} + Ce^{3+}$

$E^{0}_{(Cu+/Cu2+)} = 0.161$ V

$E^{0}_{(Ce3+/Ce4+)} = 1.70$ V

b)

$Cu^{2+} + Ag(s) + Cl^{-} \leftrightarrow Cu^{+} + AgCl_{(s)}$

$Ce^{4+} + Ag(s) + Cl^{-} \leftrightarrow Ce^{3+} + AgCl_{(s)}$

c)

$E_{cell} = E^{0}_{(Cu+/Cu2+)} - E_{(Ag/AgClref)} - 0.05916 \log([Cu^{+}]/[Cu^{2+}])$

Or

$E_{cell} = E^{0}_{(Ce3+/Ce4+)} - E_{(Ag/AgClref)} - 0.05916 \log([Ce^{3+}]/[Ce^{4+}])$

d)

It will take 25.0 mL to reach the equivalence point ($M_1V_1 = M_2V_2$)

at 1.00 mL of Cu^{+} added

mmol Ce^{4+} =

(100 mL)(0.0100 M) – (1.00 mL)(0.0400 M) = 0.960 mmol

mmol Ce^{3+} = (1.00 mL)(0.0400 M) = 0.040 mmol

$E_{cell} = E^{0}_{(Ce3+/Ce4+)} - E_{(Ag/AgClref)} - 0.05916 \log([Ce^{3+}]/[Ce^{4+}])$

$= 1.70 - 0.197 - 0.05916 \log(.04/.96)$

$= 1.58$ V

at 12.50 mL of Cu^{+} added (1/2 way!!!!)

mmol Ce^{4+} =

(100 mL)(0.0100 M) – (12.50 mL)(0.0400 M) = 0.500 mmol

mmol Ce^{3+} = (1.00 mL)(0.0400 M) = 0.500 mmol

$E_{cell} = E^{0}_{(Ce3+/Ce4+)} - E_{(Ag/AgClref)} - 0.05916 \log([Ce^{3+}]/[Ce^{4+}])$

$= 1.70 - 0.197 - 0.05916 \log(0.500/0.500)$

$= 1.503$ V

at 25.0 mL of Cu^{+} added (at equiv. pt)

$E_{cell} = \{(E^{0}_{(Cu+/Cu2+)} + E^{0}_{(Ce3+/Ce4+)}) / 2\} – 0.196$ V =
$(0.161 + 1.70)/2 – 0.196$ V
$= 0.734$ V

at 25.50 mL of Cu^{+} added
mmol Cu^{+} =
(0.50 mL)(0.0400 M) = 0.020 mmol
mmol Cu^{2+} = (100 ml)(0.0100 M) = 1.00 mmol

$E_{cell} = E^{0}_{(Cu+/Cu2+)} – E_{(Ag/AgClref)} – 0.05916 \log([Cu^{+}]/[Cu^{2+}])$
$= 0.161 – 0.197 - 0.05916 \log(0.02/1.00)$
$= 0.065$ V

mmol Cu^{+} =
(25.00 ml)(0.0400 M) = 1.00 mmol
mmol Cu^{2+} = (100 ml)(0.0100 M) = 1.00 mmol

$E_{cell} = E^{0}_{(Cu+/Cu2+)} – E_{(Ag/AgClref)} – 0.05916 \log([Cu^{+}]/[Cu^{2+}])$
$= 0.161 – 0.197 - 0.05916 \log(1.00/1.00)$
$= -0.036$ V

15.3
a) $Sn^{2+} + Tl^{3+} \rightarrow Sn^{4+} + Tl^{+}$
$E^{0}_{(Tl+/Tl3+)} = 0.77$ V
$E^{0}_{(Sn2+/Sn4+)} = 0.139$ V

b)
$Sn^{4+} + 2Hg(s) + 2Cl^{-} \leftrightarrow Sn^{2+} + Hg_2Cl_{2(s)}$

$Tl^{3+} + 2Hg(s) + 2Cl^{-} \leftrightarrow Tl^{+} + Hg_2Cl_{2(s)}$

c)

$E_{cell} = E^0_{(Tl+/Tl3+)} – E_{(SCE)} – 0.05916/2 \log([Tl^+]/[Tl^{3+}])$

Or

$E_{cell} = E^0_{(Sn2+/Sn4+)} – E_{(SCE)} – 0.05916 \log([Sn^{2+}]/[Sn^{4+}])$

d)

It will take 5.00 mL to reach the equivalence point ($M_1V_1 = M_2V_2$)

at 1.00 mL of Tl^{3+} added

mmol Sn^{2+} =

(25.0 mL)(0.0100 M) – (1.00 mL)(0.0500 M) = 0.200 mmol

mmol Sn^{4+} = (1.00 mL)(0.0500 M) = 0.0500 mmol

$E_{cell} = E^0_{(Sn2+/Sn4+)} – E_{(SCE)} – 0.05916/2 \log([Sn^{2+}]/[Sn^{4+}])$

= 0.139 – 0.241 - 0.05916/2 log(0.200/.0500)

= -0.120 V

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

mmol Sn^{2+} =

(25.0 mL)(0.0100 M) – (2.50 mL)(0.0500 M) = 0.125 mmol

mmol Sn^{4+} = (2.50 mL)(0.0500 M) = 0.125 mmol

$E_{cell} = E^0_{(Sn2+/Sn4+)} – E_{(SCE)} – 0.05916/2 \log([Sn^{2+}]/[Sn^{4+}])$

= 0.139 – 0.241 - 0.05916/2 log(0.125/0.125)

= -0.102 V

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

$E_{cell} = \{(E^0_{(Sn2+/Sn4+)} + E^0_{(Tl+/Tl3+)}) / 2\} – 0.241 \text{ V} =$

(0.139 + 0.77)/2 – 0.241 V

= 0.21 V

at 5.10 mL of Tl^{3+} added
mmol Tl^{3+} =
(0.10 mL)(0.0500 M) = 0.0050 mmol
mmol Tl^{+} = (25.0 mL)(0.0100 M) = 0.250 mmol

$E_{cell} = E^0_{(Tl+/Tl3+)} – E_{(SCE)} – 0.05916/2 \log([Tl^+]/[Tl^{3+}])$
$= 0.77 – 0.241 - 0.05916/2 \log(0.250/0.005)$
$= 0.49$ V

At 10.00 mL of Tl^{3+} added
mmol Tl^{3+} =
(5.00 mL)(0.0500 M) = 0.250 mmol
mmol Tl^{+} = (25.0 mL)(0.0100 M) = 0.250 mmol

$E_{cell} = E^0_{(Tl+/Tl3+)} – E_{(SCE)} – 0.05916/2 \log([Tl^+]/[Tl^{3+}])$
$= 0.77 – 0.241 - 0.05916/2 \log(0.250/0.250)$
$= 0.53$ 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)
$E_{cell} = E^0_{(A/DA)} – E_{(Ag/AgCl)} – 0.05916/2 \log([A]/[D][H^+]^2)$

$E_{cell} = E^0_{(Fe3+/Fe2+)} – E_{(Ag/AgCl)} – 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$

d) Equiv pt is 20.00 mL
at 5.0 mL of A added
mmol Fe^{3+} =

(10.0 mL)(0.0200 M) – (10.0 mL)(0.010 M) = 0.10 mmol

mmol Fe^{3+} = (10.0 mL)(0.010 M) = 0.10 mmol

$E_{cell} = E^0_{(Fe2+/Fe3+)} - E_{(Ag/AgCl)} - 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$

$= 0.767 - 0.197 - 0.05916 \log(1)$

$= 0.570$ V

At 10.0 mL of A added we are at the equivalence pt

At the equiv. pt.

$[Fe^{2+}] = [D]$, and $[Fe^{3+}] = [A]$

To calculate E_{cell}, we can make use of this info by adding the following two equations

$E_+ = E^0_{(A/DA)} - 0.05916/2 \log([A]/[D][H^+]^2)$

$E_+ = E^0_{(Fe3+/Fe2+)} - 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$

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

$2E_+ = 2E^0_{(A/DA)} - 0.05916 \log([A]/[D][H^+]^2)$

$+ \quad E_+ = E^0_{(Fe3+/Fe2+)} - 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$

$3E_+ = 2E^0_{(A/DA)} + E^0_{(Fe3+/Fe2+)} -$

$0.05916 \log([A][Fe^{2+}]/[Fe^{3+}][D][H^+]^2)$

$3E_+ = 2(.390) + 0.767 - 0.05916\log(1/[H^+]^2)$

pH = 0.30 $\rightarrow$ $[H^+] = 0.501$ M

$3E_+ = 1.511$ V

$E_+ = 0.504$ V

$E_{cell} = E^+ - E^0_{Ag/AgCl} = 0.504 - 0.197 = 0.307$ V

At 15 mL added
mmol A =
(5.0 mL)(0.010 M) = 0.050 mmol
mmol D =
(10.0 mL Fe^{3+})(0.0200 M Fe^{3+})(1mol D/ 2 mol Fe^{3+}) = 0.100 mmol
(look at stoichiometry of the overall rxn)

$$E_{cell} = E^0_{(A/DA)} - E_{(Ag/AgCl)} - 0.05916/2 \log([A]/[D][H^+]^2)$$
$$= 0.390 - 0.197 - 0.05916/2 \log\{(.05)/(0.100)(.501)^2\}$$
$$= 0.184 \text{ V}$$

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.

$$MnO_4^- + Mo^{3+} \rightarrow Mn^{2+} + MoO_2^{2+}$$

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.

$$3(MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O)$$

$$5(Mo^{3+} + 2H_2O \leftrightarrow MoO_2^{2+} + 4H^+ + 3e^-)$$

$$3MnO_4^- + 4H^+ + 5Mo^{3+} \leftrightarrow 3Mn^{2+} + 5MoO_2^{2+} + 2H_2O$$

Jones reductor

$MoO_4^{2-} + Zn(s) + 8H+ \rightarrow Mo^{3+} + Zn^{2+} + 4H_2O$

$[MoO_4^{2+}] = (16.39 \text{ mL } MnO_4^-)(0.01033 \text{ M } MnO_4^-)*(5 \text{ mmol } MoO_4^{2+}/3 \text{ mmol } MnO_4^-)/(25.00 \text{ mL})$

$= 0.01129 \text{ M } MoO_4^{2+}$

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.

$2(MnO_4^- + 8H^+ + 5e- \leftrightarrow Mn^{2+} + 4H_2O) \quad E^0 = 1.507$

$- \quad 5(O_2 + 2H^+ + 2e- \leftrightarrow H_2O_2) \quad E^0 = 0.695$

$2MnO_4^- + 6H^+ + 5H_2O_2 \leftrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

mmol MnO_4^- = (27.62 mL)(0.02123 M) = 0.5863 mmol MnO_4^-

$[H_2O_2]$dil = (0.5863)*(5 mol H_2O_2/2 mol MnO_4^-)/(25.00 mL)

= 0.05864 M

$[H_2O_2]$ = (0.05864)(250 mL/25 mL) = 0.5864 M

dilution factor

15-18

An aqueous glycerol solution weighing 100.0 mg was treated with 50.0 mL of 0.0837 M Ce^{4+} in 4 M HClO4 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

$C_3H_8O_3 + 3H_2O \leftrightarrow 3HCO_2H + 8H^+ + 8e-$

Write balanced rxn of glycerol with Ce^{4+}

$C_3H_8O_3 + 3H_2O + 8Ce^{4+} \leftrightarrow 8Ce^{3+} + 3HCO_2H + 8H^+$

(8:1 molar ratio)

Write equation for the back titration

$Ce^{4+} + Fe^{2+} \leftrightarrow Ce^{3+} + Fe^{3+}$ (1:1 molar ratio)

mmole Ce^{4+} needed to titrate glycerol (G) =

(50.0 mL)(0.0837 M) – (12.11 mL)(0.0448 M) = 3.6425 mmol Ce^{4+}

mmol $C_3H_8O_3$ = (3.6425 mmol Ce^{4+})(1 mmol G/8 mmol Ce^{4+})

= 0.45531 mmol G

mg G = (0.45531 mmol G)(92.0938 mg G/mmol G) = 41.931 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 mL)(0.1186 M) – (31.13 mL)(0.04289 M) =

4.59483 mmol Ce^{4+}

$(\text{mmol } NO_2^-)_{dil}$ =

(4.59483 mmol Ce^{4+})(1 mmol NO_2^-/2 mmol Ce^{4+}) =

2.29742 mmol NO_2^-

$(mmol\ NO_2^-)_{sample}$ =
$(2.29742\ mmol\ NO_2^-)*(500.0/25.00) = 45.94\ mmol\ NO_2^-$

mg G = $(45.94\ mmol\ NO_2^-)*(68.995\ mg\ NaNO_2/mmol\ NO_2^-)$
= 3170.2 mg $NaNO_2$ = 3.1702 g $NaNO_2$

% $NaNO_2$ = (3.1702 g $NaNO_2$)/(4.030 g sample)*100 = 78.67 %

15.25
A potassium iodate solution was prepared by dissolving 1.022 g of KIO_3 (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 H_2SO_4. How many moles of I_3^- are formed?

a. mol IO_3^- = (1.022 g)(1 mol/214.00 g) = 0.004776 mol
Reaction
$IO_3^- + 8I^- \rightarrow 3I_3^- + 3H_2O$
50/500 mL taken or 0.4776 mmol
Thus, 1.433 mmol I_3^- is formed.

b. Titration Reaction

$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$

So… $[S_2O_3^{2-}]$ = (2)(.001433)/(0.03766 L) = 0.07609 M

c.

$A + H_2O \rightarrow DA + 2H^+ + 2e-$ $E^0 = 0.390\ V$

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 0.535\ V$

$A + H_2O + I_3^- \rightarrow DA + 2H^+ + 3I^-$

14.33 mmol I_3^- (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 mmol I_3^- reacted with 0.892 mmol of ascorbic acid.

(0.892 mmol)(176.13 mg/mmol)/1000 = 0.157 g A

Wt % = (0.157/1.223)·100 = 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 I3- with 23.33 mL of 0.04668 M thiosulfate std. Find the weight % of copper in the sample.

$2Cu^{2+} + 5I^- \rightarrow CuI_{(s)} + I_3^-$
$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$

Liberated I_3^- = (23.33 mL)(0.04668 M)/2 = 0.5445 mmol I_3^-

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

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

weight % = (0.6920/3.026)·100 = 11.44 %

15-27

$H_2S \leftrightarrow S(s) + 2H^+ + 2e^-$

$I_3^- + 2e- \leftrightarrow 3I^-$

$H_2S + I_3^- \leftrightarrow S(s) + 2H^+ + 3I^-$

$I_3^- + 2S_2O_3^{2-} \leftrightarrow 3I^- + S_4O_6^{2-}$

$(\text{mmol } I_3^-)_{tot} = (25.00 \text{ mL})(0.01044 \text{ M}) = 0.26100 \text{ mmol } I_3^-$
$(\text{mmol } I_3^-)_{S2O3} = (14.44 \text{ mL})(0.009336 \text{ M})*(1 \text{ mol } I_3^-/2 \text{ mol } S_2O_3^{2-})$
$= 0.067406 \text{ mmol } I_3^-$
$[H_2S] = (0.26100 - 0.067406)*(1 \text{ mol } H_2S/1 \text{ mol } I_3^-)/25.00 \text{ ml}$
$= 0.007744 \text{ M or } 7.744 \text{ mM}$

Since we are titrating a solution that contain I_3^- 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

$I_{2(aq)} + 2e- \leftrightarrow 2I-$ $\Delta G_2^0 = nFE_2^0, E_2^0 = 0.620 \text{ V}$

$+ \quad 3I^- \leftrightarrow 2e- + I_3^-$ $\Delta G_3^0 = nFE_3^0, E_3^0 = -0.535 \text{ V}$

$I_{2(aq)} + I^- \leftrightarrow I_3^-$ $\Delta G_r^0 = (nFE_2^0 + nFE_3^0)$

you can say:
$nFE_r^0 = (nFE_2^0 + nFE_3^0)$, since both half rxns are two electron transfers $\Rightarrow Er^0 = E_2^0 + E_3^0 = 0.085 \text{ V}$
$K = 10^{n(E10 + E30)/0.05916} = 10^{(2*0.085/0.05916)} = 7*10^2$

b)
Subtract the first and last equation

	$I_{2(s)} + 2e- \leftrightarrow 2I-$	$\Delta G_1^0 = nFE_1^0$, $E_1^0 = 0.535$ V
+	$3I^- \leftrightarrow 2e- + I_3^-$	$\Delta G_3^0 = nFE_3^0$, $E_3^0 = -0.535$ V
	$I_{2(s)} + I^- \leftrightarrow I_3^-$	$\Delta G_r^0 = (nFE_1^0 + nFE_3^0)$

$\Delta G^0_{rxn} = (nFE_1^0 + nFE_3^0) = 0 = -RT \ln K_{eq}$
$K_{eq} = 1.0$

$nFE_r^0 = (nFE_1^0 + nFE_3^0)$, since both half rxns are two electron transfers $\Rightarrow$ $Er^0 = E_1^0 + E_3^0 = 0.000$ V

$K = 10^{nF(E10 +E30)} = 1.0$

c)
Subtract the first two equations

	$I_{2(s)} + 2e- \leftrightarrow 2I-$	$\Delta G_1^0 = nFE_1^0$, $E_1^0 = 0.535$ V
+	$2I- \leftrightarrow I_{2(aq)} + 2e-$	$\Delta G_2^0 = nFE_2^0$, $E_2^0 = -0.620$ V
	$I_{2(s)} \leftrightarrow I_{2(aq)}$	$\Delta G_r^0 = (nFE_1^0 + nFE_3^0)$

$nFE_r^0 = (nFE_1^0 + nFE_3^0)$, since both half rxns are two electron transfers $\Rightarrow$ $Er^0 = E_1^0 + E_3^0 = -0.085$ V

$K = 10^{n(E10 + E30)/0.05916} = 10^{(2*-0.085/0.05916)} = 1.338*10^{-3}$

$K = [I_{2(aq)}] = 0.001338$ mol/L $\Rightarrow$ 0.3 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 Br_2 is converted to Br^-, producing I_3^-

$Br_2 + 3I^- \rightarrow 2Br^- + I_3^-$ (this a balanced 2e- transfer redox rxn)

Rxn 4

I_3^- is titrated with $S_2O_3^{2-}$

$I_3^- + 2S_2O_3^{2-} \leftrightarrow 3I^- + S_4O_6^{2-}$

OK!

moles of I_3^- produced from rxn 3 =

(8.83 ml)(0.05113 M)*(1 mol I_3^-/2 mol $S_2O_3^{2-}$) = 0.22574 mmol I_3^-

moles of excess Br_2 left over from rxn 2 =

(0.22574 mmol I_3^-)*(1 mol Br_2/1 mol I_3^-) = 0.22574 mmol Br_2

mmol Br_2 produced from rxn 1 =

(25.00 ml)(0.02000 M)*(3 mol Br_2/1 mol BrO_3^-) = 1.500 mmol Br_2

mol Br_2 reacted with $Al(C_9H_6ON)_3$ =

1.500 mmol – 0.22574 mmol = 1.2743 mmol Br_2

mmol Al^{3+} in unknown =

(1.2743 mmol Br_2)(1 mol C_9H_7ON /2 mol Br_2)*(1 mol Al^{3+}/3 mol C_9H_7ON) = 0.21238 mmol Al^{3+} $\Rightarrow$ 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.