16-2. (a) $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

(b) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^\circ = 0.767$ V

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $\quad E^\circ = 1.70$ V

(c) $$E = \left\{0.767 - 0.059\,16 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}\right\} - \{0.241\} \qquad \text{(A)}$$

$$E = \left\{1.70 - 0.059\,16 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}\right\} - \{0.241\} \qquad \text{(B)}$$

(d) 10.0 mL : Use eq. (A) with $[Fe^{2+}]/[Fe^{3+}] = 40.0/10.0$, since $V_e = 50.0$ mL $\Rightarrow E = 0.490$ V

25.0 mL : $[Fe^{2+}]/[Fe^{3+}] = 25.0/25.0 \Rightarrow E = 0.526$ V

49.0 mL : $[Fe^{2+}]/[Fe^{3+}] = 1.0/49.0 \Rightarrow E = 0.626$ V

50.0 mL : This is V_e, where $[Ce^{3+}] = [Fe^{3+}]$ and $[Ce^{4+}] = [Fe^{2+}]$. Eq. 16-11 gives $E_+ = 1.23$ V and $E = 0.99$ V.

51.0 mL : Use eq. (B) with $[Ce^{3+}]/[Ce^{4+}] = 50.0/1.0 \Rightarrow E = 1.36$ V

60.0 mL : $[Ce^{3+}]/[Ce^{4+}] = 50.0/10.0 \Rightarrow E = 1.42$ V

100.0 mL : $[Ce^{3+}]/[Ce^{4+}] = 50.0/50.0 \Rightarrow E = 1.46$ V

16-3. (a) $Ce^{4+} + Cu^{+} \rightarrow Ce^{3+} + Cu^{2+}$

(b) $Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $\quad E^\circ = 1.70$ V

$Cu^{2+} + e^- \rightleftharpoons Cu^{+}$ $\quad E^\circ = 0.161$ V

(c) $$E = \left\{1.70 - 0.059\,16 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}\right\} - \{0.197\} \qquad \text{(A)}$$

$$E = \left\{0.161 - 0.059\,16 \log \frac{[Cu^{+}]}{[Cu^{2+}]}\right\} - \{(0.197\} \qquad \text{(B)}$$

(d) 1.00 mL : Use eq. (A) with $[Ce^{3+}]/[Ce^{4+}] = 1.00/24.0$, since $V_e = 25.0$ mL $\Rightarrow E = 1.58$ V

12.5 mL : $[Ce^{3+}]/[Ce^{4+}] = 12.5/12.5 \Rightarrow E = 1.50$ V

24.5 mL : $[Ce^{3+}]/[Ce^{4+}] = 24.5/0.5 \Rightarrow E = 1.40$ V

25.0 mL : $E_+ = 1.70 - 0.059\,16 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$

$E_+ = 0.161 - 0.059\,16 \log \frac{[Cu^+]}{[Cu^{2+}]}$

$2E_+ = 1.86_1 - 0.059\,16 \log \frac{[Ce^{3+}][Cu^+]}{[Ce^{4+}][Cu^{2+}]}$

At the equivalence point, $[Ce^{3+}] = [Cu^{2+}]$ and $[Ce^{4+}] = [Cu^+]$.
Therefore the log term above is zero and $E_+ = 1.86_1/2 = 0.930$ V.
$E = 0.930 - 0.197 = 0.733$ V

25.5 mL : Use eq. (B) with $[Cu^+]/[Cu^{2+}] = 0.5/25.0 \Rightarrow E = 0.065$ V

30.0 mL : $[Cu^+]/[Cu^{2+}] = 5.0/25.0 \Rightarrow E = 0.005$ V

50.0 mL : $[Cu^+]/[Cu^{2+}] = 25.0/25.0 \Rightarrow E = -0.036$ V

16-6. Diphenylamine sulfonic acid : colorless → red-violet
Diphenylbenzidine sulfonic acid : colorless → violet
tris (2,2'-bipyridine) iron : red → pale blue
Ferroin : red → pale blue

16-14. $3MnO_4^- + 5Mo^{3+} + 4H^+ \rightarrow 3Mn^{2+} + 5MoO_2^{2+} + 2H_2O$
(16.43 – 0.04) = 16.39 mL of 0.010 33 M $KMnO_4$ = 0.169 3 mmol of MnO_4^- which will react with (5/3)(0.169 3) = 0.282 2 mmol of Mo^{3+}.
$[Mo^{3+}]$ = 0.282 2 mmol/25.00 mL = 0.011 29 M (= original $[MoO_4^{2-}]$).

16-15. $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
(27.66 – 0.04) = 27.62 mL of 0.021 23 M $KMnO_4$ = 0.586 3$_7$ mmol of MnO_4^- which reacts with (5/2)(0.586 3$_7$) = 1.465 9 mmol of H_2O_2 which came from 25.00 mL of diluted solution ⇒ $[H_2O_2]$ = 1.465 9 mmol/25.00 mL = 0.058 64 M in the dilute solution. The original solution was ten times more concentrated = 0.586 4 M.

16-17. $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
18.04 mL of 0.006 363 M $KMnO_4$ = 0.114 8 mmol of MnO_4^- which reacts with (5/2)(0.114 8) = 0.287 0 mmol of $H_2C_2O_4$ which came from (2/3)(0.287 0) = 0.191 3 mmol of La^{3+}. $[La^{3+}]$ = 0.191 3 mmol/50.00 mL = 3.826 mM.

16-18. $C_3H_8O_3 + 3H_2O \rightleftharpoons 3HCO_2H + 8e^- + 8H^+$

glycerol (average oxidation number of C = -2/3)

formic acid (oxidation number of C = +2)

$8Ce^{4+} + 8e^- \rightleftharpoons 8Ce^{3+}$

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

One mole of glycerol requires eight moles of Ce^{4+}.

50.0 mL of 0.083 7 M Ce^{4+} = 4.185 mmol

12.11 mL of 0.044 8 M Fe^{2+} = 0.543 mmol

Ce^{4+} reacting with glycerol = 3.642 mmol

glycerol = (1/8) (3.642) = 0.455_2 mmol = 41.9 mg $\Rightarrow$ original solution = 41.9 wt% glycerol