

- 16-2.** (a) $\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}$
- (b) $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \quad E^\circ = 0.767 \text{ V}$
 $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+} \quad E^\circ = 1.70 \text{ V}$
- (c) $E = \left\{ 0.767 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - \left\{ 0.241 \right\} \quad (\text{A})$
 $E = \left\{ 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - \left\{ 0.241 \right\} \quad (\text{B})$
- (d) 10.0 mL: Use eq. (A) with $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 40.0/10.0$, since $V_e = 50.0 \text{ mL} \Rightarrow E = 0.490 \text{ V}$
25.0 mL: $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 25.0/25.0 \Rightarrow E = 0.526 \text{ V}$
49.0 mL: $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 1.0/49.0 \Rightarrow E = 0.626 \text{ V}$
50.0 mL: This is V_e , where $[\text{Ce}^{3+}] = [\text{Fe}^{3+}]$ and $[\text{Ce}^{4+}] = [\text{Fe}^{2+}]$.
Eq. 16-11 gives $E_+ = 1.23 \text{ V}$ and $E = 0.99 \text{ V}$.
51.0 mL: Use eq. (B) with $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 50.0/1.0 \Rightarrow E = 1.36 \text{ V}$
60.0 mL: $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 50.0/10.0 \Rightarrow E = 1.42 \text{ V}$
100.0 mL: $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 50.0/50.0 \Rightarrow E = 1.46 \text{ V}$
- 16-3.** (a) $\text{Ce}^{4+} + \text{Cu}^+ \rightarrow \text{Ce}^{3+} + \text{Cu}^{2+}$
- (b) $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+} \quad E^\circ = 1.70 \text{ V}$
 $\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+ \quad E^\circ = 0.161 \text{ V}$
- (c) $E = \left\{ 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - \left\{ 0.197 \right\} \quad (\text{A})$
 $E = \left\{ 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \right\} - \left\{ 0.197 \right\} \quad (\text{B})$
- (d) 1.00 mL: Use eq. (A) with $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 1.00/24.0$, since $V_e = 25.0 \text{ mL} \Rightarrow E = 1.58 \text{ V}$
12.5 mL: $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 12.5/12.5 \Rightarrow E = 1.50 \text{ V}$
24.5 mL: $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 24.5/0.5 \Rightarrow E = 1.40 \text{ V}$

$$\underline{25.0 \text{ mL}} : E_+ = 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$E_+ = 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]}$$

$$2E_+ = 1.861 - 0.05916 \log \frac{[\text{Ce}^{3+}][\text{Cu}^+]}{[\text{Ce}^{4+}][\text{Cu}^{2+}]}$$

At the equivalence point, $[\text{Ce}^{3+}] = [\text{Cu}^{2+}]$ and $[\text{Ce}^{4+}] = [\text{Cu}^+]$.

Therefore the log term above is zero and $E_+ = 1.861/2 = 0.930 \text{ V}$.

$$E = 0.930 - 0.197 = 0.733 \text{ V}$$

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

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

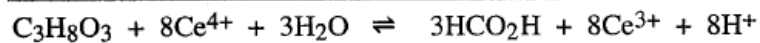
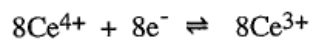
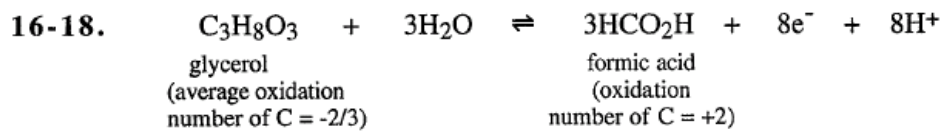
$$\underline{50.0 \text{ mL}} : [\text{Cu}^+]/[\text{Cu}^{2+}] = 25.0/25.0 \Rightarrow E = -0.036 \text{ V}$$

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

- 16-14.** $3\text{MnO}_4^- + 5\text{Mo}^{3+} + 4\text{H}^+ \rightarrow 3\text{Mn}^{2+} + 5\text{MoO}_4^{2-} + 2\text{H}_2\text{O}$
 $(16.43 - 0.04) = 16.39 \text{ mL of } 0.01033 \text{ M KMnO}_4 = 0.1693 \text{ mmol of MnO}_4^-$
 which will react with $(5/3)(0.1693) = 0.2822 \text{ mmol of Mo}^{3+}$.
 $[\text{Mo}^{3+}] = 0.2822 \text{ mmol}/25.00 \text{ mL} = 0.01129 \text{ M (= original } [\text{MoO}_4^{2-}])$.

- 16-15.** $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$
 $(27.66 - 0.04) = 27.62 \text{ mL of } 0.02123 \text{ M KMnO}_4 = 0.58637 \text{ mmol of MnO}_4^-$
 which reacts with $(5/2)(0.58637) = 1.4659 \text{ mmol of H}_2\text{O}_2$ which came from
 25.00 mL of diluted solution $\Rightarrow [\text{H}_2\text{O}_2] = 1.4659 \text{ mmol}/25.00 \text{ mL} =$
 $0.05864 \text{ M in the dilute solution. The original solution was ten times more}$
 concentrated = 0.5864 M.

- 16-17.** $2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$
 $18.04 \text{ mL of } 0.006363 \text{ M KMnO}_4 = 0.1148 \text{ mmol of MnO}_4^-$ which reacts with
 $(5/2)(0.1148) = 0.2870 \text{ mmol of H}_2\text{C}_2\text{O}_4$ which came from $(2/3)(0.2870) =$
 $0.1913 \text{ mmol of La}^{3+}$. $[\text{La}^{3+}] = 0.1913 \text{ mmol}/50.00 \text{ mL} = 3.826 \text{ mM}$.



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

50.0 mL of 0.0837 M Ce^{4+} = 4.185 mmol

12.11 mL of 0.0448 M Fe^{2+} = 0.543 mmol

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

glycerol = (1/8) (3.642) = 0.4552 mmol = 41.9 mg \Rightarrow original solution = 41.9

wt% glycerol