Chapter 19

19-1 The electrode potential of a system that contains two or more redox couples is the electrode potential of all half-cell processes at equilibrium in the system.

19-2 **(a)** *Equilibrium* is the state that a system assumes after each addition of reagent. *Equivalence* refers to a particular equilibrium state when a stoichiometric amount of titrant has been added.

(b) A *true oxidation/reduction indicator* owes its color change to changes in the electrode potential of the system. A *specific indicator* exhibits its color change as a result of reactions with a particular solute species.

19-3 The electrode potentials for all half-cell processes in an oxidation/reduction system have the same numerical value when the system is at equilibrium.

19-4 For points before equivalence, potential data are computed from the analyte standard potential and the analytical concentrations of the analyte and its reaction product. Post-equivalence point data are based upon the standard potential for the titrant and its analytical concentrations. The equivalence point potential is computed from the two standard potentials and the stoichiometric relation between the analyte and titrant.

19-5 In contrast to all other points on the titration curve, the concentrations of all of the participants in one of the half-reactions or the other cannot be derived from stoichiometric calculations.

19-6 An asymmetric titration curve will be encountered whenever the titrant and the analyte in a ratio that is not 1:1.

19-7 (a)

$$E_{\text{right}} = -0.403 - \frac{0.0592}{2}\log\left(\frac{1}{0.0511}\right) = -0.441\text{ V}$$

$$E_{\text{left}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{1}{0.1393}\right) = -0.151\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.441 - (-0.151) = \underline{\underline{-0.290\text{ V}}}$$

Because E_{cell} is negative, the reaction will not proceed spontaneously in the direction considered and an external voltage source is needed to force this reaction to occur.

(b)

$$E_{\text{right}} = 1.25 - \frac{0.0592}{2}\log\left(\frac{0.0620}{9.06\times10^{-3}}\right) = 1.23\text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.0364}\right) = -0.806\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 1.23 - (-0.806) = \underline{\underline{2.04\text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered.

(c)

$$E_{\text{right}} = -0.250 - \frac{0.0592}{2}\log\left(\frac{1}{0.0214}\right) = -0.299\text{ V}$$

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{765/760}{\left(1.00\times10^{-4}\right)^2}\right) = -0.237\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.299 - (-0.237) = \underline{\underline{-0.0620\text{ V}}}$$

Because E_{cell} is negative, the reaction will not proceed spontaneously in the direction considered and an external voltage source is needed to force this reaction to occur.

(d)

$$E_{\text{right}} = 0.854 - \frac{0.0592}{2}\log\left(\frac{1}{4.59\times10^{-3}}\right) = 0.785\text{ V}$$

$$[Pb^{2+}][I^-]^2 = 7.9\times10^{-9} \text{ and } [Pb^{2+}] = \frac{7.9\times10^{-9}}{[I^-]^2}$$

$$E_{\text{left}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{(0.0120)^2}{7.9\times10^{-9}}\right) = -0.252 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.785 - (-0.252) = \underline{\underline{1.04 \text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered.

(e)

$$\frac{[H_3O^+][NH_3]}{[NH_4{}^+]} = 5.70\times10^{-10} = \frac{[H_3O^+]0.438}{0.379}$$

$$[H_3O^+] = \frac{(5.70\times10^{-10})(0.379)}{0.438} = 4.93\times10^{-10}$$

$$E_{\text{right}} = 0.000 \text{ V}$$

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{1.00}{(4.93\times10^{-10})^2}\right) = -0.551 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.000 - (-0.551) = \underline{\underline{0.551 \text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered.

(f)

$$E_{\text{right}} = 0.359 - 0.0592\log\left(\frac{0.0784}{0.1340(0.0538)^2}\right) = 0.223 \text{ V}$$

$$E_{\text{left}} = 0.099 - 0.0592\log\left(\frac{0.00918}{0.0790(1.47\times10^{-2})^2}\right) = -0.063 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.223 - (-0.063) = \underline{\underline{0.286 \text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered.

19-8 (a)

$$E_{\text{right}} = -0.277 - \frac{0.0592}{2}\log\left(\frac{1}{6.78\times10^{-3}}\right) = -0.341\text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.0955}\right) = -0.793\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.341 - (-0.793) = \underline{\underline{0.452\text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered (oxidation on the left, reduction on the right).

(b)

$$E_{\text{right}} = 0.854 - \frac{0.0592}{2}\log\left(\frac{1}{0.0671}\right) = 0.819\text{ V}$$

$$E_{\text{left}} = 0.771 - \frac{0.0592}{2}\log\left(\frac{0.0681}{0.1310}\right) = 0.788\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.819 - 0.788 = \underline{\underline{0.031\text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered (oxidation on the left, reduction on the right).

(c)

$$E_{\text{right}} = 1.229 - \frac{0.0592}{4}\log\left(\frac{1}{1.12(0.0794)^4}\right) = 1.165\text{ V}$$

$$E_{\text{left}} = 0.799 - 0.0592\log\left(\frac{1}{0.1544}\right) = 0.751\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 1.165 - 0.751 = \underline{\underline{0.414\text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered (oxidation on the left, reduction on the right).

(d)

$$E_{\text{right}} = -0.151 - 0.0592\log(0.1350) = -0.100\text{ V}$$
$$E_{\text{left}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{0.0601}\right) = 0.301\text{ V}$$
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.100 - 0.301 = \underline{\underline{-0.401\text{ V}}}$$

Because E_{cell} is negative, the reaction does not proceed spontaneously in the direction considered (reduction on the left, oxidation on the right).

(e)

$$\frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80\times10^{-4} = \frac{[H_3O^+]0.0764}{0.1302}$$
$$[H_3O^+] = \frac{(1.80\times10^{-4})(0.1302)}{0.0764} = 3.07\times10^{-4}$$

$$E_{\text{right}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{1.00}{(3.07\times10^{-4})^2}\right) = -0.208\text{ V}$$
$$E_{\text{left}} = 0.000\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.208 - 0.000 = \underline{\underline{-0.208\text{ V}}}$$

Because E_{cell} is negative, the reaction does not proceed spontaneously in the direction considered (reduction on the left, oxidation on the right).

(f)

$$E_{\text{right}} = 0.771 - 0.0592\log\left(\frac{0.1134}{0.003876}\right) = 0.684\text{ V}$$
$$E_{\text{left}} = 0.334 - \frac{0.0592}{2}\log\left(\frac{6.37\times10^{-2}}{(7.93\times10^{-3})(1.16\times10^{-3})^4}\right) = -0.040\text{ V}$$
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.684 - (-0.040) = \underline{\underline{0.724\text{ V}}}$$

Because E_{cell} is positive, the reaction proceeds spontaneously in the direction considered (oxidation on the left, reduction on the right).

19-9 **(a)**

$$E_{Pb^{2+}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{1}{0.0848}\right) = -0.158 \text{ V}$$

$$E_{Zn^{2+}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.1364}\right) = -0.789 \text{ V}$$

$$E_{cell} = E_{right} - E_{left} = -0.158 - (-0.789) = \underline{\underline{0.631 \text{ V}}}$$

(b)

$$E_{Fe^{3+}} = 0.771 - 0.0592\log\left(\frac{0.0760}{0.0301}\right) = 0.747 \text{ V}$$

$$E_{Fe(CN)_6^{3-}} = 0.36 - 0.0592\log\left(\frac{0.00309}{0.1564}\right) = 0.461 \text{ V}$$

$$E_{cell} = E_{right} - E_{left} = 0.747 - 0.461 = \underline{\underline{0.286 \text{ V}}}$$

(c)

$$E_{SHE} = 0.000 \text{ V}$$

$$E_{TiO^{2+}} = 0.099 - 0.0592\log\left(\frac{0.02723}{(1.46\times10^{-3})(10^{-3})^2}\right) = -0.331 \text{ V}$$

$$E_{cell} = E_{right} - E_{left} = 0.000 - (-0.331) = \underline{\underline{0.331 \text{ V}}}$$

19-10 **(a)** $Zn|\ Zn^{2+}(0.1364\ M)||\ Pb^{2+}(0.0848\ M)|\ Pb$

(b) $Pt|\ Fe(CN)_6^{4-}(0.00309\ M), Fe(CN)_6^{3-}(0.1564\ M)||\ Fe^{3+}(0.0301\ M), Fe^{2+}(0.0760\ M)|\ Pt$

(c) $Pt|\ TiO^{+}(1.46\times10^{-3}M), Ti^{3+}(0.02723\ M), H^{+}(1.00\times10^{-3}M)||\ SHE$

19-11 Note that in these calculations, it is necessary to round the answers to either one or two significant figures because the final step involves taking the antilogarithm of a large number.

(a)

$$Fe^{3+} + V^{2+} \rightleftarrows Fe^{2+} + V^{3+} \quad E^{o}_{Fe^{3+}} = 0.771 \quad E^{o}_{V^{3+}} = -0.256$$

$$0.771 - 0.0592\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) = -0.256 - 0.0592\log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$\frac{0.771-(-0.256)}{0.0592} = \log\left(\frac{[Fe^{2+}][V^{3+}]}{[Fe^{3+}][V^{2+}]}\right) = \log K_{eq} = 17.348$$

$$\frac{[Fe^{2+}][V^{3+}]}{[Fe^{3+}][V^{2+}]} = K_{eq} = 2.23\times10^{17} = \underline{\underline{2.2\times10^{17}}}$$

(b)

$$Fe(CN)_6^{3-}Cr^{2+} \rightleftarrows Fe(CN)_6^{4-}Cr^{3+} \quad E^{o}_{Fe(CN)_6^{3-}} = 0.36 \quad E^{o}_{Cr^{3+}} = -0.408$$

$$0.36 - 0.0592\log\left(\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}\right) = -0.408 - 0.0592\log\left(\frac{[Cr^{2+}]}{[Cr^{3+}]}\right)$$

$$\frac{0.36-(-0.408)}{0.0592} = \log\left(\frac{[Fe(CN)_6^{4-}][Cr^{3+}]}{[Fe(CN)_6^{3-}][Cr^{2+}]}\right) = \log K_{eq} = 12.973$$

$$\frac{[Fe(CN)_6^{4-}][Cr^{3+}]}{[Fe(CN)_6^{3-}][Cr^{2+}]} = K_{eq} = 9.4\times10^{12} = \underline{\underline{9\times10^{12}}}$$

(c)

$$2V(OH)_4^{+} + U^{4+} \rightleftarrows 2VO^{2+} + UO_2^{2+} + 4H_2O \quad E^{o}_{V(OH)_4^{+}} = 1.00 \quad E^{o}_{UO_2^{2+}} = 0.334$$

$$1.00 - \frac{0.0592}{2}\log\left(\frac{[VO^{2+}]^2}{[V(OH)_4^{+}]^2[H^+]^4}\right) = 0.334 - \frac{0.0592}{2}\log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right)$$

$$\frac{(1.00-0.334)\,2}{0.0592} = \log\left(\frac{[VO^{2+}]^2[UO_2^{2+}]}{[V(OH)_4^{+}]^2[U^{4+}]}\right) = \log K_{eq} = 22.50$$

$$\frac{[VO^{2+}]^2[UO_2^{2+}]}{[V(OH)_4^{+}]^2[U^{4+}]} = K_{eq} = 3.2\times10^{22} = \underline{\underline{3\times10^{22}}}$$

(d)

$$Tl^{3+} + 2Fe^{2+} \rightleftarrows Tl^{+} + 2Fe^{3+} \quad E^{o}_{Fe^{3+}} = 0.771 \quad E^{o}_{Tl^{+}} = 1.25$$

$$1.25 - \frac{0.0592}{2}\log\left(\frac{[Tl^+]}{[Tl^{3+}]}\right) = 0.771 - \frac{0.0592}{2}\log\left(\frac{[Fe^{2+}]^2}{[Fe^{3+}]^2}\right)$$

$$\frac{(1.25 - 0.771)\,2}{0.0592} = \log\left(\frac{[Tl^+][Fe^{3+}]^2}{[Tl^{3+}][Fe^{2+}]^2}\right) = \log K_{eq} = 16.18$$

$$\frac{[Tl^+][Fe^{3+}]^2}{[Tl^{3+}][Fe^{2+}]^2} = K_{eq} = 1.5\times10^{16} = \underline{\underline{2\times10^{16}}}$$

(e)

$$2Ce^{4+} + H_3AsO_3 + H_2O \rightleftarrows 2Ce^{3+} + H_3AsO_4 + 2H^+$$

$$E^o_{Ce^{4+}}(\text{in 1 M } HClO_4) = 1.70 \quad E^o_{H_3AsO_4} = 0.577$$

$$1.70 - \frac{0.0592}{2}\log\left(\frac{[Ce^{3+}]^2}{[Ce^{4+}]^2}\right) = 0.577 - \frac{0.0592}{2}\log\left(\frac{[H_3AsO_4]}{[H_3AsO_3][H^+]^2}\right)$$

$$\frac{(1.70 - 0.577)\,2}{0.0592} = \log\left(\frac{[Ce^{3+}]^2[H_3AsO_3][H^+]^2}{[Ce^{4+}]^2[H_3AsO_4]}\right) = \log K_{eq} = 37.94$$

$$\frac{[Ce^{3+}]^2[H_3AsO_3][H^+]^2}{[Ce^{4+}]^2[H_3AsO_4]} = K_{eq} = 8.9\times10^{37} = \underline{\underline{9\times10^{37}}}$$

(f)

$$2V(OH)_4^+ + H_2SO_3 \rightleftarrows 2VO^{2+} + SO_4^{2-} + 5H_2O \quad E^o_{V(OH)_4^+} = 1.00 \quad E^o_{SO_4^{2-}} = 0.172$$

$$1.00 - \frac{0.0592}{2}\log\left(\frac{[VO^{2+}]^2}{[V(OH)_4^+]^2[H^+]^4}\right) = 0.172 - \frac{0.0592}{2}\log\left(\frac{[H_2SO_3]}{[SO_4^{2-}][H^+]^4}\right)$$

$$\frac{(1.00 - 0.172)\,2}{0.0592} = \log\left(\frac{[VO^{2+}]^2[SO_4^{2-}]}{[V(OH)_4^+]^2[H_2SO_3]}\right) = \log K_{eq} = 27.97$$

$$\frac{[VO^{2+}]^2[SO_4^{2-}]}{[V(OH)_4^+]^2[H_2SO_3]} = K_{eq} = 9.4\times10^{27} = \underline{\underline{9\times10^{27}}}$$

(g)

$$VO^{2+} + V^{2+} + 2H^+ \rightleftarrows 2V^{3+} + H_2O \quad E^o_{VO^{@+}} = 0.359 \quad E^o_{V^{3+}} = -0.256$$

$$0.359 - 0.0592\log\left(\frac{[V^{3+}]}{[VO^{2+}][H^+]^2}\right) = -0.256 - 0.0592\log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$\frac{0.359-(-0.256)}{0.0592} = \log\left(\frac{[V^{3+}]^2}{[VO^{2+}][H^+]^2[V^{2+}]}\right) = \log K_{eq} = 10.389$$

$$\frac{[V^{3+}]^2}{[VO^{2+}][H^+]^2[V^{2+}]} = K_{eq} = \underline{\underline{2.4\times10^{10}}}$$

(h)

$$TiO^{2+} + Ti^{2+} + 2H^+ \rightleftarrows 2Ti^{3+} + H_2O \quad E^o_{TiO^{2+}} = 0.099 \quad E^o_{T^{3+}} = -0.369$$

$$0.099 - 0.0592\log\left(\frac{[Ti^{3+}]}{[TiO^{2+}][H^+]^2}\right) = -0.369 - 0.0592\log\left(\frac{[Ti^{2+}]}{[Ti^{3+}]}\right)$$

$$\frac{0.099-(-0.369)}{0.0592} = \log\left(\frac{[Ti^{3+}]^2}{[TiO^{2+}][H^+]^2[Ti^{2+}]}\right) = \log K_{eq} = 7.9054$$

$$\frac{[Ti^{3+}]^2}{[TiO^{2+}][H^+]^2[Ti^{2+}]} = K_{eq} = \underline{\underline{8.0\times10^{7}}}$$

19-12 (a)

At equivalence, $[Fe^{2+}] = [V^{3+}]$ and $[Fe^{3+}] = [V^{2+}]$

$$E_{eq} = 0.771 - 0.0592\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

$$E_{eq} = -0.256 - 0.0592\log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$2E_{eq} = 0.771 + (-0.256) - 0.0592\log\left(\frac{[Fe^{2+}][V^{2+}]}{[Fe^{3+}][V^{3+}]}\right)$$

$$E_{eq} = \frac{0.771-0.256}{2} = \underline{\underline{0.258\text{ V}}}$$

(b)

At equivalence, $[Fe(CN)_6^{3-}] = [Cr^{2+}]$ and $[Fe(CN)_6^{4-}] = [Cr^{3+}]$

$$E_{eq} = 0.36 - 0.0592 \log\left(\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}\right)$$

$$E_{eq} = -0.408 - 0.0592 \log\left(\frac{[Cr^{2+}]}{[Cr^{3+}]}\right)$$

$$2E_{eq} = 0.36 + (-0.408) - 0.0592 \log\left(\frac{[Fe(CN)_6^{4-}][Cr^{2+}]}{[Fe(CN)_6^{3-}][Cr^{3+}]}\right)$$

$$E_{eq} = \frac{0.36 - 0.408}{2} = \underline{\underline{-0.024\ \text{V}}}$$

(c)

At equivalence, $[VO^{2+}] = 2[UO_2^{2+}]$ and $[V(OH)_4^+] = 2[U^{4+}]$

$$E_{eq} = 1.00 - 0.0592 \log\left(\frac{[VO^{2+}]}{[V(OH)_4^+][H^+]^2}\right)$$

$$2E_{eq} = 2(0.344) - 0.0592 \log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right)$$

$$3E_{eq} = 1.00 + 2(0.344) - 0.0592 \log\left(\frac{[VO^{2+}][U^{4+}]}{[V(OH)_4^+][UO_2^{2+}][H^+]^6}\right)$$

$$3E_{eq} = 1.00 + 2(0.344) - 0.0592 \log\left(\frac{1}{(0.100)^6}\right) = 1.688 - 0.355 = 1.333\ \text{V}$$

$$E_{eq} = \frac{1.333}{3} = \underline{\underline{0.444\ \text{V}}}$$

(d)

At equivalence, $[Fe^{2+}] = 2[Tl^{3+}]$ and $[Fe^{3+}] = 2[Tl^+]$

$$E_{eq} = 0.771 - 0.0592 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

$$2E_{eq} = 2(1.25) - 0.0592 \log\left(\frac{[Tl^+]}{[Tl^{3+}]}\right)$$

$$3E_{eq} = 0.771 + 2(1.25) - 0.0592 \log\left(\frac{[Fe^{2+}][Tl^+]}{[Fe^{3+}][Tl^{3+}]}\right) = 3.27 - 0.0592 \log\left(\frac{2[Tl^{3+}][Tl^+]}{2[Tl^+][Tl^{3+}]}\right)$$

$$E_{eq} = \frac{3.27}{3} = \underline{\underline{1.09\ \text{V}}}$$

(e)

At equivalence, $[Ce^{3+}] = 2[H_3AsO_4]$, $[Ce^{4+}] = 2[H_3AsO_3]$ and $[H^+] = 1.00$

$$E_{eq} = 1.70 - 0.0592\log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

$$2E_{eq} = 2(0.577) - 0.0592\log\left(\frac{[H_3AsO_3]}{[H_3AsO_4][H^+]^2}\right)$$

$$3E_{eq} = 1.70 + 2(0.577) - 0.0592\log\left(\frac{[Ce^{3+}][H_3AsO_3]}{[Ce^{4+}][H_3AsO_4][H^+]^2}\right)$$

$$= 2.854 - 0.0592\log\left(\frac{2[H_3AsO_4][H_3AsO_3]}{2[H_3AsO_3][H_3AsO_4][H^+]^2}\right) = 2.854 - 0.0592\log\left(\frac{1}{(1.00)^2}\right)$$

$$E_{eq} = \frac{2.854}{3} = \underline{\underline{0.951\text{ V}}}$$

(f)

At equivalence, $[V(OH)_4^+] = 2[H_2SO_3]$ and $[VO^{2+}] = 2[SO_4^{2-}]$

$$E_{eq} = 1.00 - 0.0592\log\left(\frac{[VO^{2+}]}{[V(OH)_4^+][H^+]^2}\right)$$

$$2E_{eq} = 2(0.172) - 0.0592\log\left(\frac{[H_2SO_3]}{[SO_4^{2-}][H^+]^4}\right)$$

$$3E_{eq} = 1.00 + 2(0.172) - 0.0592\log\left(\frac{[VO^{2+}][H_2SO_3]}{[V(OH)_4^+][SO_4^{2-}][H^+]^6}\right)$$

$$3E_{eq} = 1.00 + 2(0.172) - 0.0592\log\left(\frac{1}{(0.100)^6}\right) = 1.344 - 0.355 = 9.89\times10^{-1}\text{ V}$$

$$E_{eq} = \frac{9.89\times10^{-1}}{3} = \underline{\underline{0.330\text{ V}}}$$

(g)

At equivalence, $[VO^+] = [V^{2+}]$

$$E_{eq} = 0.359 - 0.0592\log\left(\frac{[V^{3+}]}{[VO^{2+}][H^+]^2}\right)$$

$$E_{eq} = -0.256 - 0.0592\log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$2E_{eq} = 0.359 + (-0.256) - 0.0592\log\left(\frac{[V^{2+}]}{[VO^{+}][H^+]^2}\right) = 0.103 - 0.0592\log\left(\frac{[V^{2+}]}{[V^{2+}][H^+]^2}\right)$$

$$2E_{eq} = 0.103 - 0.0592\log\left(\frac{1}{(0.100)^2}\right) = 0.103 - 0.118 = -0.154\text{ V}$$

$$E_{eq} = \frac{-0.154}{2} = \underline{\underline{-0.008\text{ V}}}$$

(h)

At equivalence, $[Ti^{2+}] = [TiO^{2+}]$

$$E_{eq} = 0.099 - 0.0592\log\left(\frac{[Ti^{3+}]}{[TiO^{2+}][H^+]^2}\right)$$

$$E_{eq} = -0.369 - 0.0592\log\left(\frac{[Ti^{2+}]}{[Ti^{3+}]}\right)$$

$$2E_{eq} = 0.099 + (-0.369) - 0.0592\log\left(\frac{[Ti^{2+}]}{[TiO^{+}][H^+]^2}\right) = 0.103 - 0.0592\log\left(\frac{[Ti^{2+}]}{[Ti^{2+}][H^+]^2}\right)$$

$$2E_{eq} = -0.270 - 0.0592\log\left(\frac{1}{(0.100)^2}\right) = -0.270 - 0.118 = -0.388\text{ V}$$

$$E_{eq} = \frac{-0.388}{2} = \underline{\underline{-0.194\text{ V}}}$$

19-13 **(a)** In the solution to Problem 19-11(a) we find

$$K_{eq} = \frac{[V^{3+}][Fe^{2+}]}{[V^{2+}][Fe^{3+}]} = 2.23\times10^{17}$$

At the equivalence point,

$$[V^{2+}] = [Fe^{3+}] = x$$

$$[V^{3+}] = [Fe^{2+}] = \frac{0.1000}{2} = 0.0500$$

Substituting into the first equation we find

$$2.23\times10^{17} = \frac{(0.0500)^2}{x^2}$$

$$x = \sqrt{\frac{0.00250}{2.23\times10^{17}}} = 1.06\times10^{-10}$$

Thus,

$$[V^{2+}] = [Fe^{3+}] = 1.06\times10^{-10}\ M$$

and

$$[V^{3+}] = [Fe^{2+}] = \underline{\underline{0.0500\ M}}$$

(b) Proceeding in the same way, we find

$$[Fe(CN)_6^{\ 4-}] = [Cr^{3+}] = \underline{\underline{0.0500\ M}}$$

$$[Fe(CN)_6^{\ 3-}] = [Cr^{2+}] = \underline{\underline{1.7\times10^{-8}\ M}}$$

(c) At equivalence

$$[V(OH)_4^{\ +}] = 2[U^{4+}] = x$$

$$[VO_2^{\ 2+}] = 2[UO_2^{\ 2+}] = \frac{2\ (0.1000)}{3} - 2x = \frac{0.2000}{3} = \underline{\underline{0.0667\ M}}$$

$$[UO_2^{\ 2+}] = \frac{0.1000}{3} = \underline{\underline{0.0333\ M}}$$

From the solution for Problem 19-11(c)

$$\frac{[VO_2^{\ 2+}]^2[UO_2^{\ 2+}]}{[V(OH)_4^{\ +}]^2[U^{4+}]} = 3.2\times10^{22} = \frac{(0.0667)^2(0.0333)}{x^2\left(x/2\right)}$$

$$\frac{x^3}{2} = \frac{(0.0667)^2(0.0333)}{3.2\times10^{22}}$$

$$x = \sqrt[3]{2\times\left(4.62\times10^{-27}\right)} = 2.10\times10^{-9}\ M$$

$$[V(OH)_4^{\ +}] = \underline{\underline{2.1\times10^{-9}\ M}} \text{ and } [U^{4+}] = \frac{2.1\times10^{-9}}{2} = \underline{\underline{1.0\times10^{-9}\ M}}$$

(d)

$$[Fe^{2+}] = 2[Tl^{3+}] = x$$

$$[Fe^{3+}] = \underline{\underline{0.0667\ M}} \quad \text{and} \quad [Tl^{+}] = \underline{\underline{0.0333\ M}}$$

From the solution for Problem 19-11(d)

$$\frac{[Tl^+][Fe^{3+}]^2}{[Tl^{3+}][Fe^{2+}]^2} = 1.5\times10^{16} = \frac{(0.0333)(0.0667)^2}{\left(x/2\right)x^2}$$

$$\frac{x^3}{2} = \frac{(0.0667)^2(0.0333)}{1.5\times10^{16}}$$

$$x = \sqrt[3]{2\times\left(9.88\times10^{-21}\right)} = \underline{\underline{2.70\times10^{-7}\,\text{M}}} = [Fe^{2+}]$$

$$\frac{x}{2} = \frac{2.70\times10^{-7}}{2} = \underline{\underline{1.4\times10^{-7}\,\text{M}}} = [Tl^{3+}]$$

(e) Proceeding as in part (c), we find

$$\frac{[Ce^{3+}]^2[H_3AsO_4]}{[Ce^{4+}]^2[H_3AsO_3][H^+]^2} = 8.9\times10^{37} = \frac{[Ce^{3+}]^2[H_3AsO_4]}{[Ce^{4+}]^2[H_3AsO_3](1.00)^2} = \frac{(0.0667)^2(0.0333)}{x^3/2}$$

When $x = [Ce^{4+}] = 2[H_3AsO_3]$

$$[Ce^{4+}] = \underline{\underline{6.9\times10^{-14}\,\text{M}}}$$

$$[H_3AsO_3] = \underline{\underline{3.5\times10^{-14}\,\text{M}}}$$

$$[Ce^{3+}] = \underline{\underline{0.067\ \text{M}}}$$

$$[H_3AsO_4] = \underline{\underline{0.033\ \text{M}}}$$

(f) Proceeding as in part (c)

$$[VO^+] = \underline{\underline{0.067\ \text{M}}}$$

$$[SO_4^{\ 2-}] = \underline{\underline{0.033\ \text{M}}}$$

$$[V(OH)_4^{\ +}] = \underline{\underline{3.2\times10^{-11}\,\text{M}}}$$

$$[H_2SO_3] = \underline{\underline{1.6\times10^{-11}\,\text{M}}}$$

(g)

$$x = [V^{2+}] = [VO^{2+}]$$

$$[V^{3+}] = \frac{0.200}{2} = 0.100$$

Assume $[H^+]$ = 0.1000. From the solution to Problem 19-11(g)

$$\frac{[V^{3+}]^2}{[VO^{2+}][V^{2+}][H^+]^2} = 2.4\times10^{10} = \frac{(0.100)^2}{[VO^{2+}][V^{2+}](0.100)^2}$$

$$2.4\times10^{10} = \frac{1.00}{x^2}$$

$$x = [VO^{2+}] = [V^{2+}] = \underline{\underline{6.5\times10^{-6}\text{ M}}}$$

$$[V^{3+}] = \underline{\underline{0.100\text{ M}}}$$

(h) Proceeding as in part (g), we find

$$[Ti^{3+}] = \underline{\underline{0.100\text{ M}}}$$

$$[H^+] = \underline{\underline{0.100\text{ M}}}$$

$$[TiO_2^{\ +}] = [Ti^{2+}] = \underline{\underline{1.1\times10^{-5}\text{ M}}}$$

19-14

	E_{eq}, V	Indicator
(a)	0.258	Phenosafranine
(b)	-0.024	None
(c)	0.444	Indigo tetrasulfonate or Methylene blue
(d)	1.09	1,10-Phenanthroline
(e)	0.951	Erioglaucin A
(f)	0.330	Indigo tetrasulfonate
(g)	-0.008	None
(h)	-0.194	None

19-15 (a)

$$2V^{2+} + Sn^{4+} \rightleftarrows 2V^{3+} + Sn^{2+}$$

At **10.00 mL**,

$$[V^{3+}] = \frac{\left(\frac{0.0500 \text{ mmol } Sn^{4+}}{\text{mL}} \times 10.00 \text{ mL} \times \frac{2 \text{ mmol } V^{3+}}{\text{mmol } Sn^{4+}}\right)}{60.00 \text{ mL}} = 0.0167 \text{ M}$$

$$[V^{2+}] = \frac{\left(\frac{0.1000 \text{ mmol } V^{2+}}{\text{mL}} \times 50.00 \text{ mL}\right)}{60.00 \text{ mL}} - 1.67 \times 10^{-2} \text{ M} = 0.0667 \text{ M}$$

$$E = -0.256 - 0.0592 \log\left(\frac{[V^{2+}]}{[V^{3+}]}\right) = -0.256 - 0.0592 \log\left(\frac{0.0667}{0.0167}\right) = -0.292 \text{ V}$$

The remaining pre-equivalence point data are treated in the same way. The results appear in the spreadsheet that follows.

At **50.00 mL**,

Proceeding as in Problem 19-12, we write

$$E = -0.256 - 0.0592 \log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$2E = 2 \times 0.154 - 0.0592 \log\left(\frac{[Sn^{2+}]}{[Sn^{4+}]}\right)$$

$$3E = -0.256 + (2 \times 0.154) - 0.0592 \log\left(\frac{[V^{2+}][Sn^{2+}]}{[V^{3+}][Sn^{4+}]}\right)$$

At equivalence, $[V^{2+}] = 2[Sn^{4+}]$ and $[V^{3+}] = 2[Sn^{2+}]$. Thus,

$$E_{eq} = \frac{-0.256 + (2 \times 0.154)}{3} - \frac{0.0592 \log(1.00)}{3} = 0.017 \text{ V}$$

At **50.10 mL**,

$$c_{Sn^{2+}} = \frac{\left(\frac{0.1000 \text{ mmol } V^{2+}}{\text{mL}} \times 50.00 \text{ mL} \times \frac{1 \text{ mmol } Sn^{2+}}{2 \text{ mmol } V^{2+}}\right)}{100.10 \text{ mL}} = 0.025 \text{ M} \approx [Sn^{2+}]$$

$$c_{Sn^{4+}} = \frac{\left(\frac{0.0500 \text{ mmol } Sn^{4+}}{\text{mL}} \times 50.10 \text{ mL}\right)}{100.10 \text{ mL}} - 0.025 \text{ M} = 5.0 \times 10^{-5} \text{ M} \approx [Sn^{4+}]$$

$$E = 0.154 - \frac{0.0592}{2} \log\left(\frac{[Sn^{2+}]}{[Sn^{4+}]}\right) = 0.154 - \frac{0.0592}{2} \log\left(\frac{2.5 \times 10^{-2}}{5.0 \times 10^{-5}}\right) = 0.074 \text{ V}$$

The remaining post-equivalence points are obtained in the same way and are found in the table that follows.

	A	B	C	D	E	F	G
1	**19-15 (a) Titration of 50.00 mL of 0.1000 M V^{2+} with 0.0500 M Sn^{4+}**						
2		Reaction: $2V^{2+} + Sn^{4+} \rightarrow 2V^{3+} + Sn^{2+}$					
3	For V^{3+}/V^{2+}, E^0	-0.256					
4	For Sn^{4+}/Sn^{2+}, E^0	0.154					
5	Initial conc. V^{2+}	0.1000					
6	Conc. Sn^{4+}	0.0500					
7	Volume solution, mL	50.00					
8	**Vol. Sn^{4+}, mL**	**$[V^{3+}]$**	**$[V^{2+}]$**	**$[Sn^{4+}]$**	**$[Sn^{2+}]$**	***E*, V**	
9	10.00	0.0167	0.0667			-0.292	
10	25.00	0.0333	0.0333			-0.256	
11	49.00	0.0495	0.0010			-0.156	
12	49.90	0.0499	0.0001			-0.096	
13	50.00					0.017	
14	50.10			5.00E-05	0.0250	0.074	
15	51.00			4.95E-04	0.0248	0.104	
16	60.00			4.55E-03	0.0227	0.133	
17	**Spreadsheet Documentation**						
18	**B9=$B$6*A9*2/($B$7+A9)**						
19	**C9=($B$5*$B$7-$B$6*A9*2)/($B$7+A9)**						
20	**F9=$B$3-0.0592*LOG10(C9/B9)**						
21	**F13=($B$3+2*$B$4)/3**						
22	**D14=($B$6*A14-$B$5*$B$7/2)/($B$7+A14)**						
23	**E14=$B$7*$B$5/(2*($B$7+A14))**						
24	**F14=$B$4-(0.0592/2)*LOG10(E14/D14)**						
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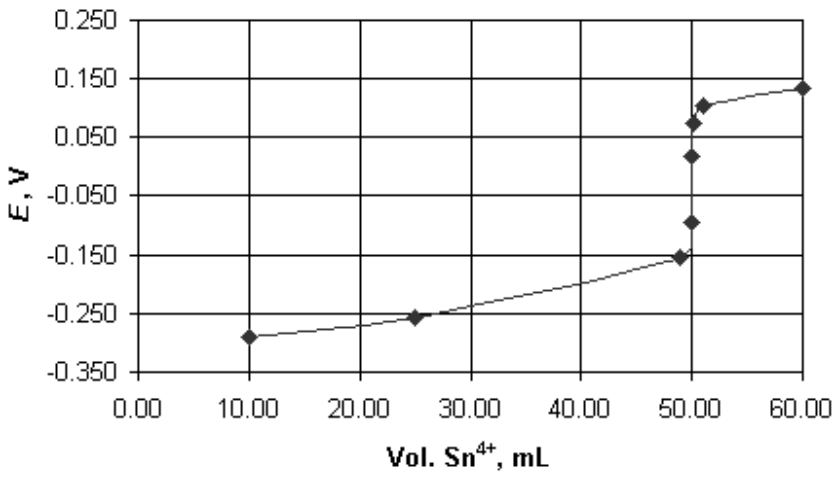

(b)

$$Fe(CN)_6^{3-} + Cr^{2+} \rightleftarrows Fe(CN)_6^{4-} + Cr^{3+}$$

The pre-equivalence point data are obtained by substituting concentrations into the equation

$$E = 0.36 - 0.0592 \log\left(\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}\right)$$

The post-equivalence point data are obtained with the Nernst expression for the Cr^{2+}/ Cr^{3+} system. That is,

$$E = -0.0408 - 0.0592 \log\left(\frac{[Cr^{2+}]}{[Cr^{3+}]}\right)$$

The equivalence point potential is found following the procedure in Problem 19-12. The results for all data points are found in the spreadsheet that follows.

	A	B	C	D	E	F
1	**19-15 (b) Titration of 50.00 mL of 0.1000 M $Fe(CN)_6^{3-}$ with 0.1000 M Cr^{2+}**					
2		Reaction: $Fe(CN)_6^{3-} + Cr^{2+} \rightarrow Fe(CN)_6^{4-} + Cr^{3+}$				
3	For $Fe(CN)_6^{4-}$, E^0	0.36				
4	For Cr^{3+}/Cr^{2+}, E^0	-0.408				
5	Initial conc. $Fe(CN)_6^{3-}$	0.1000				
6	Conc. Cr^{2+}	0.1000				
7	Volume solution, mL	50.00				
8	**Vol. Cr^{2+}, mL**	**[$Fe(CN)_6^{4-}$]**	**[$Fe(CN)_6^{3-}$]**	**[Cr^{3+}]**	**[Cr^{2+}]**	***E*, V**
9	10.00	0.0167	0.0667			0.40
10	25.00	0.0333	0.0333			0.36
11	49.00	0.0495	0.0010			0.26
12	49.90	0.0499	0.0001			0.20
13	50.00					-0.02
14	50.10			0.0500	9.99E-05	-0.248
15	51.00			0.0495	0.0010	-0.307
16	60.00			0.0455	0.0091	-0.367
17	**Spreadsheet Documentation**					
18	**B9=$B$6*A9/($B$7+A9)**					
19	**C9=($B$5*$B$7-$B$6*A9)/($B$7+A9)**					
20	**F9=$B$3-0.0592*LOG10(B9/C9)**					
21	**F13=($B$3+$B$4)/2**					
22	**D14=($B$5*$B$7/($B$7+A14)**					
23	**E14=($B$6*A14-$B$5*$B$7)/($B$7+A14)**					
24	**F14=$B$4-0.0592*LOG10(E14/D14)**					
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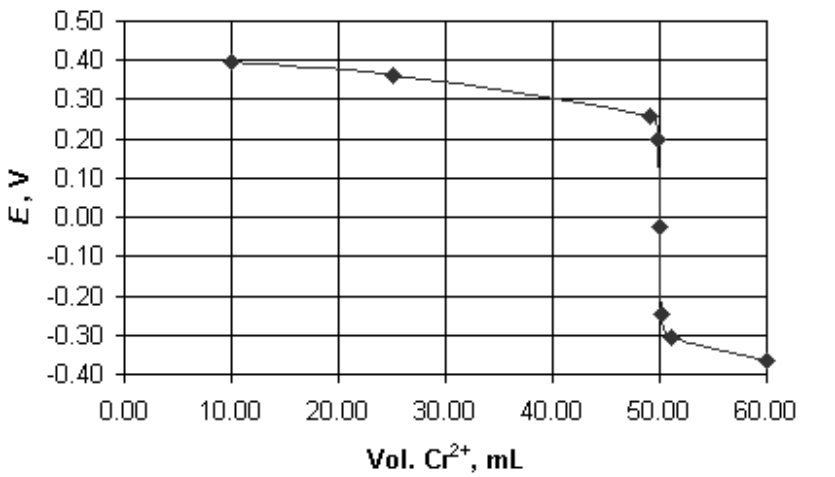

(c) The data points for this titration, which are found in the spreadsheet that follows, are obtained in the same way as those for parts (a) and (b).

	A	B	C	D	E	F
1	**19-15 (c) Titration of 50.00 mL of 0.1000 M $Fe(CN)_6^{4-}$ with 0.0500 M Tl^{3+}**					
2		Reaction: $2Fe(CN)_6^{4-} + Tl^{3+} \rightarrow 2Fe(CN)_6^{3-} + Tl^{+}$				
3	For $Fe(CN)_6^{4-}$, E^0	0.36				
4	For Tl^{3+}/Tl^{+}, E^0	1.25				
5	Initial conc. $Fe(CN)_6^{4-}$	0.1000				
6	Conc. Tl^{3+}	0.0500				
7	Volume solution, mL	50.00				
8	**Vol. Tl^{3+}, mL**	**$[Fe(CN)_6^{4-}]$**	**$[Fe(CN)_6^{3-}]$**	**$[Tl^{3+}]$**	**$[Tl^{+}]$**	***E*, V**
9	10.00	0.0667	0.0167			0.32
10	25.00	0.0333	0.0333			0.36
11	49.00	0.0010	0.0495			0.46
12	49.90	0.0001	0.0499			0.52
13	50.00					0.95
14	50.10			5.00E-05	0.0250	1.17
15	51.00			4.95E-04	0.0248	1.20
16	60.00			4.55E-03	0.0227	1.23
17	**Spreadsheet Documentation**					
18	**B9=($B$5*$B$7-$B$6*A9*2)/($B$7+A9)**					
19	**C9=$B$6*A9*2/($B$7+A9)**					
20	**F9=$B$3-0.0592*LOG10(B9/C9)**					
21	**F13=($B$3+2*$B$4)/3**					
22	**D14=($B$6*A14-$B$5*$B$7/2)/($B$7+A14)**					
23	**E14=($B$5*$B$7/2)/($B$7+A14)**					
24	**F14=$B$4-(0.0592/2)*LOG10(E14/D14)**					
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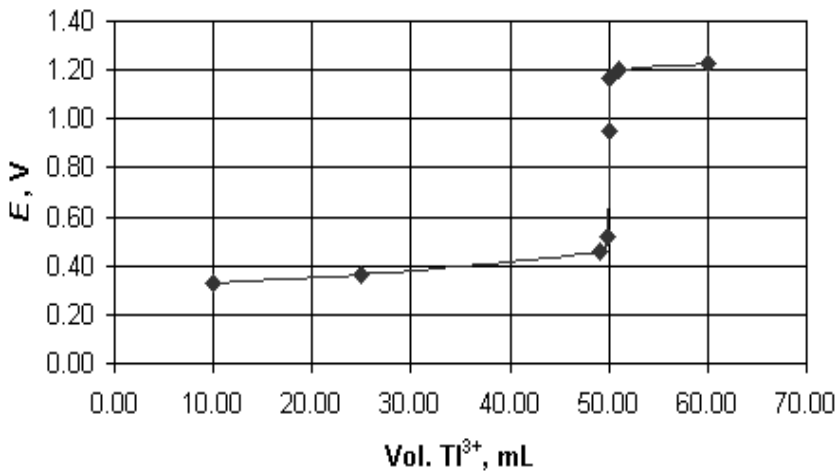

(d) The data points for this titration, which are found in the spreadsheet that follows, are obtained in the same way as those for parts (a) and (b).

	A	B	C	D	E	F
1	**19-15 (d) Titration of 0.1000 M Fe^{3+} with Sn^{2+}**					
2		Reaction: $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$				
3	For Fe^{3+}/Fe^{2+} E^0	0.771				
4	For Sn^{4+}/Sn^{2+}, E^0	0.154				
5	Initial conc. Fe^{3+}	0.1000				
6	Conc. Sn^{2+}	0.0500				
7	Volume solution, mL	50.00				
8	**Vol. Sn^{2+}, mL**	**[Fe^{3+}]**	**[Fe^{2+}]**	**[Sn^{4+}]**	**[Sn^{2+}]**	***E*, V**
9	10.00	0.0667	0.0167			0.807
10	25.00	0.0333	0.0333			0.771
11	49.00	0.0010	0.0495			0.671
12	49.90	0.0001	0.0499			0.611
13	50.00					0.360
14	50.10			0.0250	5.00E-05	0.234
15	51.00			0.0248	4.95E-04	0.204
16	60.00			0.0227	4.55E-03	0.175
17	**Spreadsheet Documentation**					
18	**B9=($B$5*$B$7-$B$6*A9*2)/($B$7+A9)**					
19	**C9=$B$6*A9*2/($B$7+A9)**					
20	**F9=$B$3-0.0592*LOG10(B9/C9)**					
21	**F13=($B$3+2*$B$4)/3**					
22	**D14=(($B$5*$B$7/2)/($B$7+A14)**					
23	**E14=($B$6*A14-$B$5*$B$7/2)/($B$7+A14)**					
24	**F14=$B$4-(0.0592/2)*LOG10(E14/D14)**					
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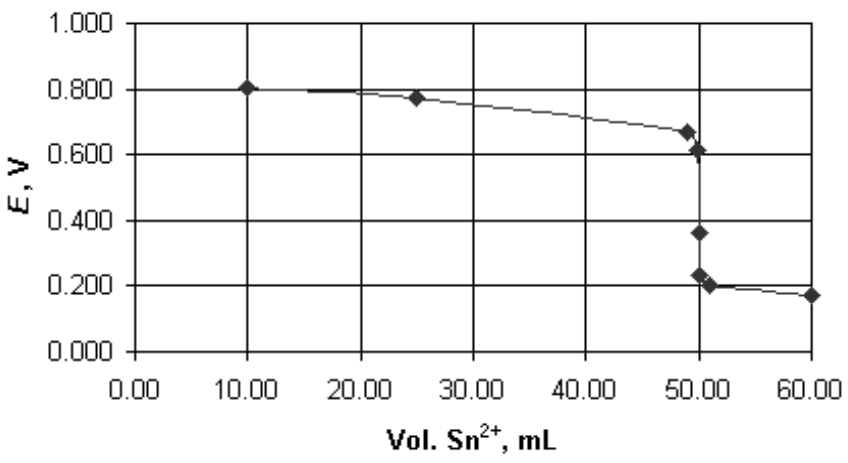


(e) $2MnO_4^- + 5U^{4+} + 2H_2O \rightleftarrows 2Mn^{2+} + 5UO_2^{2+} + 4H^+$

At **10.00 mL**,

$$\frac{0.02000 \text{ mmol } MnO_4^-}{\text{mL}} \times 10.00 \text{ mL } MnO_4^- = 0.2000 \text{ mmol } MnO_4^-$$

$$\frac{0.05000 \text{ mmol } U^{4+}}{\text{mL}} \times 50.00 \text{ mL } U^{4+} = 2.500 \text{ mmol } U^{4+}$$

$$c_{UO_2^{2+}} = [UO_2^{2+}] = \frac{\left(0.2000 \text{ mmol } MnO_4^- \times \frac{5 \text{ mmol } UO_2^{2+}}{2 \text{ mmol } MnO_4^-}\right)}{60.00 \text{ mL solution}} = 8.33 \times 10^{-3} \text{ M } UO_2^{2+}$$

$$c_{U^{4+}} = [U^{4+}] = \frac{(2.5000 \text{ mmol } U^{4+})}{60.00 \text{ mL}} - 8.33 \times 10^{-3} = 0.0333 \text{ M } U^{4+}$$

$$E = 0.334 - \frac{0.0592}{2}\log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right) = 0.334 - \frac{0.0592}{2}\log\left(\frac{3.33 \times 10^{-2}}{([8.33 \times 10^{-3}])(1.00)^4}\right) = 0.316 \text{ V}$$

Additional pre-equivalence point data, obtained in the same way, are given in the spreadsheet that follows.

At **50.00 mL**,

$$5E_{eq} = 5 \times 1.51 - 0.0592\log\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right)$$

$$2E_{eq} = 2 \times 0.334 - 0.0592\log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right)$$

Adding the two equations gives

$$7E_{eq} = (5 \times 1.51) + (2 \times 0.334) - 0.0592\log\left(\frac{[Mn^{2+}][U^{4+}]}{[MnO_4^-][UO_2^{2+}][H^+]^{12}}\right)$$

At equivalence, $[MnO_4^-] = 2/5[U^{4+}]$ and $[Mn^{2+}] = 2/5[UO_2^{2+}]$

Substituting these equalities and $[H^+] = 1.00$ into the equation above gives

$$E_{eq} = \frac{8.218}{7} - \frac{0.0592\log(1.00)}{7} = \frac{8.218}{7} = 1.17 \text{ V}$$

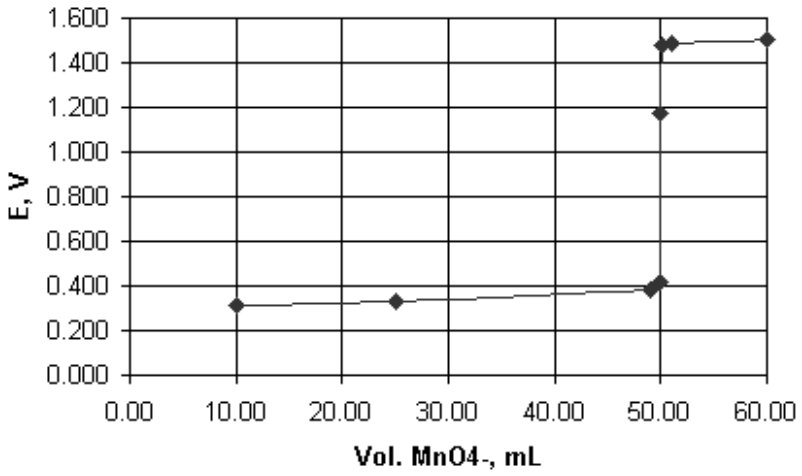
At **50.10 mL**,

$$\text{mmol } MnO_4^- \text{ added} = \frac{0.02000 \text{ } MnO_4^-}{\text{mL}} \times 50.10 \text{ mL } MnO_4^- = 1.0020 \text{ } MnO_4^-$$

$$\text{mmol } Mn^{2+} \text{ formed} = \frac{0.05000 \text{ mmol } U^{4+}}{\text{mL}} \times 50.00 \text{ mL } U^{4+} \times \frac{2 \text{ mmol } Mn^{2+}}{5 \text{ mmol } U^{4+}} = 1.000 \text{ mmol } Mn^{2+}$$

$$\text{mmol } MnO_4^- \text{remaining} = 1.0020 - 1.000 = 2.0 \times 10^{-3} \text{mmol } MnO_4^-$$

$$E = 1.51 - \frac{0.0592}{5} \log\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right) = 1.51 - \frac{0.0592}{5} \log\left(\frac{(1.000/100.10)}{(1.0020/100.10)(1.00)^8}\right) = 1.48 \text{ V}$$

The remaining post equivalence point data are derived in the same way and are given in the spreadsheet that follows.

	A	B	C	D	E	F	G
1	**19-15 (e) Titration of 50.00 mL 0.05000 M U^{4+} with 0.02000 M MnO_4^-**						
2		Reaction: $2MnO_4^- + 5U^{4+} + 2H_2O \rightarrow 2Mn^{2+} + 5UO_2^{2+} + 4H^+$					
3	For U^{4+}/UO_2^{2+}, E^0	0.334					
4	For MnO_4^-, E^0	1.51					
5	Initial conc. U^{4+}	0.0500					
6	Conc. MnO_4^-	0.0200					
7	Volume solution, mL	50.00					
8	**Vol. MnO_4^-, mL**	**$[U^{4+}]$**	**$[UO_2^{2+}]$**	**$[MnO_4^-]$**	**$[Mn^{2+}]$**	**$[H^+]$**	***E*, V**
9	10.00	0.0333	0.0083			1.00	0.316
10	25.00	0.0167	0.0167			1.00	0.334
11	49.00	0.0005	0.0247			1.00	0.384
12	49.90	0.0001	0.0250			1.00	0.414
13	50.00					1.00	1.17
14	50.10			2.00E-05	0.0100	1.00	1.48
15	51.00			0.0002	0.0099	1.00	1.49
16	60.00			0.0018	0.0091	1.00	1.50
17	**Spreadsheet Documentation**						
18	**B9=$B$5*$B$7-$B$6*A9*5/2)/($B$7+A9)**						
19	**C9=($B$6*A9*5/2)/($B$7+A9)**						
20	**F9=1.00 (entry)**						
21	**G9=$B$3-(0.0592/2)*LOG10(B9/(C9*F9^4))**						
22	**G13=((5*$B$4+2*$B$3)/7)-(0.0592/7)*LOG10(F13)**						
23	**D14=($B$6*A14-$B$5*$B$7*2/5)/($B$7+A14)**						
24	**E14=($B$5*$B$7*2/5)/($B$7+A14)**						
25	**G14=$B$4-(0.0592/5)*LOG10(E14/(D14*F14^8))**