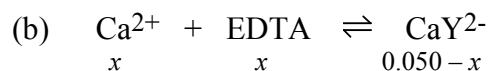


$$\text{S13-1. } \alpha_{Y^{4-}} = \frac{10^{-0.0}10^{-1.5}\dots10^{-10.24}}{(10^{-6.62})^6 + (10^{-6.62})^510^{-0.0} + \dots + 10^{-0.0}10^{-1.5}\dots10^{-10.24}} = 1.78 \times 10^{-4}$$

$$\text{S13-2. (a) } K_f' = \alpha_{Y^{4-}} K_f = 0.36 \times 10^{10.69} = 1.76 \times 10^{10}$$



$$\frac{0.050-x}{x^2} = 1.76 \times 10^{10} \Rightarrow [\text{Ca}^{2+}] = 1.7 \times 10^{-6} \text{ M}$$

$$\text{S13-3. } \frac{[\text{MgY}^{2-}]}{[\text{Mg}^{2+}][\text{Y}^{4-}]} \times \frac{[\text{Na}^+][\text{Y}^{4-}]}{[\text{NaY}^{3-}]} = \frac{K_f(\text{for MgY}^{2-})}{K_f(\text{for NaY}^{3-})} = 1.35 \times 10^7$$

$$[\text{Mg}^{2+}] = \frac{[\text{Na}^+]}{1.35 \times 10^7} \left(\frac{[\text{MgY}^{2-}]}{[\text{NaY}^{3-}]} \right) \quad (1)$$

We know that $[\text{Mg}^{2+}] + [\text{MgY}^{2-}] = 0.0500 \text{ M}$ and $[\text{Na}^+] = [\text{NaY}^{3-}] = 0.100 \text{ M}$. It seems like a good approximation to say that $[\text{Na}^+] = 0.100 \text{ M}$ and $[\text{MgY}^{2-}] = 0.0500 \text{ M}$, since we expect almost all of the Na^+ to be free and almost all of the Mg^{2+} to be bound to EDTA. If the ratio $[\text{MgY}^{2-}]/[\text{NaY}^{3-}]$ is called R , we can say that $[\text{Mg}^{2+}] \approx 0.0500/R$. (To see this, suppose $R = 1/1000$. Then $1/1000$ of the Mg^{2+} will not be bound to EDTA and $[\text{Mg}^{2+}] = (0.0500/1000)$.) In Equation 1 we can set $[\text{Mg}^{2+}] = 0.0500/R$ and $[\text{MgY}^{2-}]/[\text{NaY}^{3-}] = R$.

$$\frac{0.0500}{R} = \frac{[\text{Na}^+]}{1.35 \times 10^7} R \quad (2)$$

Putting the value $[\text{Na}^+] = 0.100$ into Equation 2 gives $R = 2600$. This large value of R confirms the approximations that $[\text{MgY}^{2-}] \approx 0.0500 \text{ M}$ and $[\text{NaY}^{3-}] \approx 0.100 \text{ M}$.

$$\text{S13-4. (a) } (V_e)(0.100 \text{ M}) = (100.0 \text{ mL})(0.0500 \text{ M}) \Rightarrow V_e = 50.0 \text{ mL}$$

$$\text{(b) } [\text{EDTA}] = \left(\frac{1}{2} \right) (0.0500 \text{ M}) \left(\frac{100}{125} \right) = 0.0200 \text{ M}$$

fraction
original
dilution
remaining
concentration
factor

$$\text{(c) } 0.36 \text{ (Table 13-1)}$$

$$\text{(d) } K_f' = (0.36)(10^{8.00}) = 3.6 \times 10^7$$

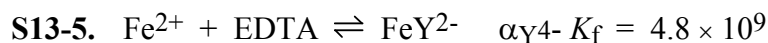
$$(e) [MY^{n-4}] = (0.100 \text{ M}) \left(\frac{100}{150} \right) = 0.0667 \text{ M}$$

$$\frac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \frac{0.0667 - x}{x^2} = 3.6 \times 10^7 \Rightarrow x = [M^{n+}] = 4.3 \times 10^{-5} \text{ M}$$

$$(f) [M^{n+}] = (0.100 \text{ M}) \left(\frac{5.0}{155.0} \right) = 3.23 \times 10^{-3} \text{ M}$$

$$[MY^{n-4}] = (0.0500 \text{ M}) \left(\frac{100.0}{155.0} \right) = 3.23 \times 10^{-2} \text{ M}$$

$$\frac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \frac{(3.23 \times 10^{-2})}{(3.23 \times 10^{-3})[EDTA]} = 3.6 \times 10^7 \Rightarrow [EDTA] = 2.8 \times 10^{-7} \text{ M}$$



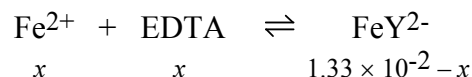
$$V_e = (25.00) \left(\frac{0.02026 \text{ M}}{0.03855 \text{ M}} \right) = 13.14 \text{ mL}$$

$$(a) \underline{12.00 \text{ mL}}: [\text{EDTA}] = \left(\frac{13.14 - 12.00}{13.14} \right) (0.02026 \text{ M}) \left(\frac{25.00}{37.00} \right) = 1.19 \times 10^{-3} \text{ M}$$

$$[\text{FeY}^{2-}] = \left(\frac{12.00}{37.00} \right) (0.03855 \text{ M}) = 1.25 \times 10^{-2} \text{ M}$$

$$[\text{Fe}^{2+}] = \frac{[\text{FeY}^{2-}]}{[\text{EDTA}] K_f} = 2.2 \times 10^{-9} \text{ M} \Rightarrow \text{pFe}^{2+} = 8.66$$

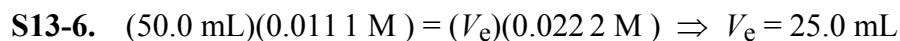
$$(b) \underline{V_e}: \text{Formal concentration of FeY}^{2-} \text{ is } \left(\frac{25.00}{38.14} \right) (0.02026 \text{ M}) = 1.33 \times 10^{-2} \text{ M}$$



$$1.33 \times 10^{-2} - x$$

$$\frac{1.33 \times 10^{-2} x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 1.66 \times 10^{-6} \text{ M} \Rightarrow \text{pFe}^{2+} = 5.78$$

$$(c) \underline{14.00 \text{ mL}}: [\text{Fe}^{2+}] = \left(\frac{14.0 - 13.14}{39.00} \right) (0.03855 \text{ M}) = 8.50 \times 10^{-4} \text{ M} \Rightarrow \text{pFe}^{2+} = 3.07$$



$$\underline{0 \text{ mL}}: \text{pY}^{3+} = -\log(0.0111) = 1.95$$

$$\underline{10.0 \text{ mL}}: [\text{Y}^{3+}] = \left(\frac{25.0 - 10.0}{25.0} \right) (0.0111 \text{ M}) \left(\frac{50.0}{60.0} \right) = 0.00555 \text{ M} \Rightarrow \text{pY}^{3+} = 2.26$$

$$\underline{20.0 \text{ mL}}: [\text{Y}^{3+}] = \left(\frac{25.0 - 20.0}{25.0} \right) (0.0111 \text{ M}) \left(\frac{50.0}{70.0} \right) = 0.00159 \text{ M} \Rightarrow \text{pY}^{3+} = 2.80$$

$$\underline{24.0 \text{ mL}}: [\text{Y}^{3+}] = \left(\frac{25.0 - 24.0}{25.0} \right) (0.0111 \text{ M}) \left(\frac{50.0}{74.0} \right) = 3.00 \times 10^{-4} \text{ M} \Rightarrow \text{pY}^{3+} = 3.52$$

$$\underline{24.9 \text{ mL}}: [\text{Y}^{3+}] = \left(\frac{25.0 - 24.9}{25.0} \right) (0.0111 \text{ M}) \left(\frac{50.0}{74.9} \right) = 2.96 \times 10^{-5} \text{ M} \Rightarrow \text{pY}^{3+} = 4.53$$

$$\begin{aligned} \underline{25.0 \text{ mL}}: \quad & \text{Y}^{3+} + \text{EDTA} \rightleftharpoons \text{Y}(\text{EDTA})^- \quad K_f' = 4.6 \times 10^{11} \\ & x \quad \quad x \quad \quad \frac{50.0}{75.0}(0.0111) - x \\ & \frac{0.00740 - x}{x^2} = 4.6 \times 10^{11} \Rightarrow x = 1.3 \times 10^{-7} \Rightarrow \text{pY}^{3+} = 6.90 \end{aligned}$$

$$\begin{aligned} \underline{25.1 \text{ mL}}: \quad & [\text{EDTA}] = \left(\frac{0.1}{75.1}\right)(0.0222 \text{ M}) = 2.96 \times 10^{-5} \text{ M} \\ & [\text{Y}(\text{EDTA})^-] = \left(\frac{50.0}{75.1}\right)(0.0111 \text{ M}) = 0.00739 \text{ M} \\ & [\text{Y}^{3+}] = \frac{[\text{Y}(\text{EDTA})^-]}{[\text{EDTA}] K_f'} = 5.4 \times 10^{-10} \text{ M} \Rightarrow \text{pY}^{3+} = 9.27 \end{aligned}$$

$$\begin{aligned} \underline{26.0 \text{ mL}}: \quad & [\text{EDTA}] = \left(\frac{1.0}{76.0}\right)(0.0222 \text{ M}) = 2.92 \times 10^{-4} \text{ M} \\ & [\text{Y}(\text{EDTA})^-] = \left(\frac{50.0}{76.0}\right)(0.0111 \text{ M}) = 0.00730 \text{ M} \\ & [\text{Y}^{3+}] = 5.4 \times 10^{-11} \text{ M} \Rightarrow \text{pY}^{3+} = 10.26 \end{aligned}$$

$$\begin{aligned} \underline{30.0 \text{ mL}}: \quad & [\text{EDTA}] = \left(\frac{5.0}{80.0}\right)(0.0222 \text{ M}) = 1.39 \times 10^{-3} \text{ M} \\ & [\text{Y}(\text{EDTA})^-] = \left(\frac{50.0}{80.0}\right)(0.0111 \text{ M}) = 6.94 \times 10^{-3} \text{ M} \\ & [\text{Y}^{3+}] = 1.09 \times 10^{-11} \text{ M} \Rightarrow \text{pY}^{3+} = 10.96 \end{aligned}$$

S13-7. $\text{Cd}^{2+} + \text{Y}^{4-} = \text{CdY}^{2-} \quad K_f = 10^{16.46} = 2.9 \times 10^{16}$
 $\alpha_{\text{Y}^{4-}} = 0.98$ at pH 12.00 (Table 13-1)

For Cd^{2+} and NH_3 , Appendix I gives $K_1 = 10^{2.51}$, $K_2 = 10^{1.96}$,
 $K_3 = 10^{1.30}$ and $K_4 = 10^{0.79}$.

This means $\beta_1 = K_1 = 3.2 \times 10^2$, $\beta_2 = K_1 K_2 = 3.0 \times 10^4$,
 $\beta_3 = K_1 K_2 K_3 = 5.9 \times 10^5$ and $\beta_4 = K_1 K_2 K_3 K_4 = 3.6 \times 10^6$.

$$\alpha_{\text{Cd}^{2+}} = \frac{1}{1 + \beta_1(0.200) + \beta_2(0.200)^2 + \beta_3(0.200)^3 + \beta_4(0.200)^4} = 8.5 \times 10^{-5}$$

$$K_f' = \alpha_{\text{Y}^{4-}} K_f = 2.8 \times 10^{16}$$

$$K_f'' = \alpha_{\text{Y}^{4-}} \alpha_{\text{Cd}^{2+}} K_f = 2.4 \times 10^{12}$$

Equivalence point = 5.00 mL

(a) At 0 mL, the total concentration of cadmium is $\text{Cd}^{2+} = 0.00100 \text{ M}$ and
 $[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} C_{\text{Cd}^{2+}} = 8.5 \times 10^{-8} \text{ M} \Rightarrow \text{pCd}^{2+} = 7.07$

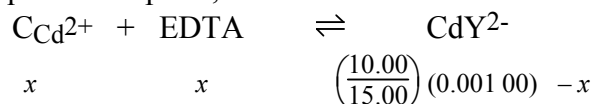
$$(b) \text{ At } 1.00 \text{ mL, } C_{\text{Cd}^{2+}} = \underbrace{\left(\frac{4.00}{5.00}\right)}_{\text{fraction remaining}} \underbrace{(0.00100 \text{ M})}_{\text{original concentration}} \underbrace{\left(\frac{10.00}{11.00}\right)}_{\text{dilution factor}} = 7.27 \times 10^{-4} \text{ M}$$

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} C_{\text{Cd}^{2+}} = 6.2 \times 10^{-8} \text{ M} \Rightarrow \text{pCd}^{2+} = 7.21$$

$$(c) \text{ At } 4.90 \text{ mL, } C_{\text{Cd}^{2+}} = \left(\frac{0.10}{5.00}\right) (0.00100 \text{ M}) \left(\frac{10.00}{14.90}\right) = 1.34 \times 10^{-5} \text{ M}$$

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} C_{\text{Cd}^{2+}} = 1.1 \times 10^{-9} \text{ M} \Rightarrow \text{pCd}^{2+} = 8.94$$

(d) At the equivalence point, we can write



$$\frac{0.000667 - x}{x^2} = 2.4 \times 10^{12} \Rightarrow x = C_{\text{Cd}^{2+}} = 1.7 \times 10^{-8} \text{ M}$$

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} C_{\text{Cd}^{2+}} = 1.4 \times 10^{-12} \text{ M} \Rightarrow \text{pCd}^{2+} = 11.85$$

(e) Past the equivalence point at 5.10 mL, we can say

$$[\text{EDTA}] = \underbrace{\left(\frac{0.10}{15.10}\right)}_{\text{dilution factor}} \underbrace{(0.00200 \text{ M})}_{\text{original concentration}} = 1.3 \times 10^{-5} \text{ M}$$

$$[\text{CdY}^{2-}] = \left(\frac{10.00}{15.10}\right) (0.00100 \text{ M}) = 6.6 \times 10^{-4} \text{ M}$$

$$K'_f = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}][\text{EDTA}]} = \frac{(6.6 \times 10^{-4})}{[\text{Cd}^{2+}](1.3 \times 10^{-5})}$$

$$\Rightarrow [\text{Cd}^{2+}] = 1.8 \times 10^{-15} \text{ M} \Rightarrow \text{pCd}^{2+} = 14.74$$

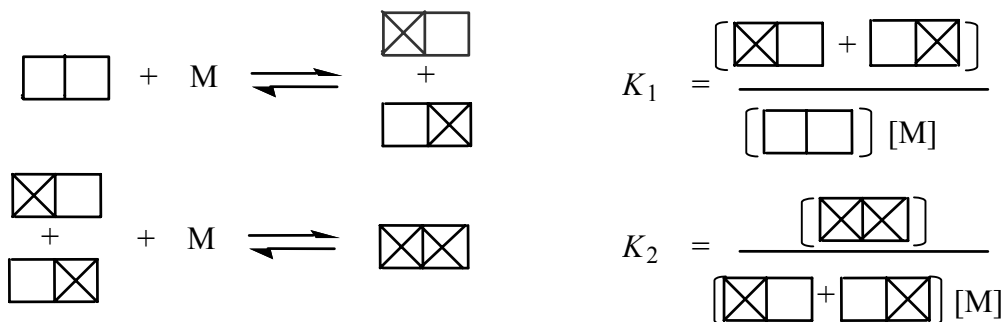
(f) At 6.00 mL,

$$[\text{EDTA}] = \left(\frac{1.00}{16.00}\right) (0.00200 \text{ M}) = 1.2 \times 10^{-4} \text{ M}$$

$$[\text{CdY}^{2-}] = \left(\frac{10.00}{16.00}\right) (0.00100 \text{ M}) = 6.2 \times 10^{-4} \text{ M}$$

$$K'_f = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}][\text{EDTA}]} \Rightarrow [\text{Cd}^{2+}] = 1.8 \times 10^{-16} \text{ M} \Rightarrow \text{pCd}^{2+} = 15.73$$

S13-8. (a) Equations 1 and 2 can be represented as



For noncooperative binding, $\square \square = \square \square = \square \square = \square \square$
 at 50% saturation. Calling each concentration C gives $K_1 = \frac{(C+C)}{(C)[M]}$ and

$$K_2 = \frac{(C)}{(C+C)[M]}, \text{ or } \frac{K_1}{K_2} = \frac{\frac{2C}{CM}}{\frac{C}{2CM}} = 4.$$

S13-9. H_3In^{3-} , yellow, red, violet \rightarrow red

S13-10. $[\text{Fe}^{3+}] = \frac{\text{mmol EDTA} - \text{mmol Mg}^{2+}}{25.00 \text{ mL}} = \frac{0.367 - 0.109}{25.00 \text{ mL}} = 0.0103 \text{ M}$

S13-11. Hardness = 3.2 mM + 1.1 mM = 4.3 mM = 430 mg CaCO_3/L , since the formula mass of CaCO_3 is 100.09 g/mol.

S13-12. Concentration of Ni^{2+} in the standard solution is $\left(\frac{39.3}{30.0}\right)(0.0130 \text{ M}) = 0.0170 \text{ M}$.

The quantity of Ni^{2+} in 25.0 mL is $(25.0 \text{ mL})(0.0170 \text{ M}) = 0.425 \text{ mmol}$.

Excess Ni equals $(10.1 \text{ mL})(0.0130 \text{ M}) = 0.131 \text{ mmol}$.

Therefore $0.425 - 0.131 = 0.294 \text{ mmol}$ of Ni^{2+} reacted with CN^- .

Since each mole of Ni^{2+} reacts with 4 moles of CN^- , there must have been $4(0.294) = 1.176 \text{ mmol}$ of CN^- in 12.7 mL.

$$[\text{CN}^-] = 1.176 \text{ mmol}/12.7 \text{ mL} = 0.0926 \text{ M}.$$

S13-13. Total EDTA used = $(39.98 \text{ mL})(0.04500 \text{ M}) = 1.7991 \text{ mmol}$
 – mmol of Mg^{2+} = $(10.26 \text{ mL})(0.02065 \text{ M}) = 0.2119 \text{ mmol}$
 – mmol of Zn^{2+} = $(15.47 \text{ mL})(0.02065 \text{ M}) = 0.3195 \text{ mmol}$

 mmol of Mn^{2+} = 1.2677 mmol

mg of each metal : Mn^{2+} - 69.64; Mg^{2+} - 5.150; Zn^{2+} - 20.89

$$\text{S13-14. } [\text{Bi}^{3+}] = \frac{\text{mmol EDTA in step 1}}{25.00 \text{ mL}} = \frac{0.1715 \text{ mmol}}{25.00 \text{ mL}} = 6.861 \text{ mM}$$

$$[\text{Ti}^{4+}] = \frac{\text{mmol Zn}^{2+} \text{ in step 3}}{25.00 \text{ mL}} = \frac{0.05385 \text{ mmol}}{25.00 \text{ mL}} = 2.153 \text{ mM}$$

$$[\text{Al}^{3+}] = \frac{\text{mmol Zn}^{2+} \text{ in step 4}}{25.00 \text{ mL}} = \frac{0.3307 \text{ mmol}}{25.00 \text{ mL}} = 13.23 \text{ mM}$$

Color change in steps 3 and 4: yellow \rightarrow red

S13-15. (no solution in manual)

S13-16. Pyrocatechol violet: mean = 2.029₅ standard deviation = 0.020₄

Xylenol orange: mean = 2.047₄ standard deviation = 0.011₅

$$s_{\text{pooled}} = \sqrt{\frac{0.0204^2(6-1) + 0.0115^2(5-1)}{6+5-2}} = 0.017_0$$

$$t = \frac{2.047_4 - 2.029_5}{0.017_0} \sqrt{\frac{6 \cdot 5}{6+5}}$$

$$= 1.74 < 2.262 \text{ (listed for 95\% confidence and 9 degrees of freedom).}$$

The results are not significantly different.

$$\text{S13-17. (a) } z = \frac{x - \mu}{\sigma}. \text{ At } x = 0.1700, z = \frac{0.1700 - 0.1664}{0.0028} = 1.286.$$

$$\text{At } x = 0.1750, z = \frac{0.1750 - 0.1664}{0.0028} = 3.071.$$

Now we interpolate in a table of areas under a Gaussian curve.

From $z = 1.200$ to $z = 1.286$, the area is

$$\begin{array}{l} \text{area between } z = 1.200 \\ \text{and } z = 1.286 \end{array} = \left(\frac{1.286 - 1.200}{1.300 - 1.200} \right) (0.4032 - 0.3849) = 0.0157$$

Fraction of
interval between
 $z = 1.2$ and $z = 1.3$

Area between
 $z = 1.2$ and $z = 1.3$

Area from mean ($z = 0$) to $z = 1.286$ is $0.3849 + 0.0157 = 0.4006$

Similarly, the area from the mean to $z = 3.071$ is 0.4989 .

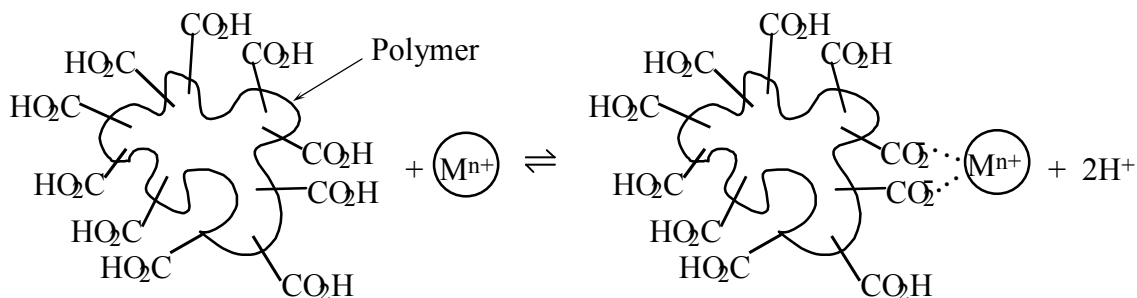
Area from $z = 1.286$ to $z = 3.071$ is $0.4989 - 0.4006 = 0.0983$

9.8% of the measurements are expected for the range 0.1700 to 0.1750 M.

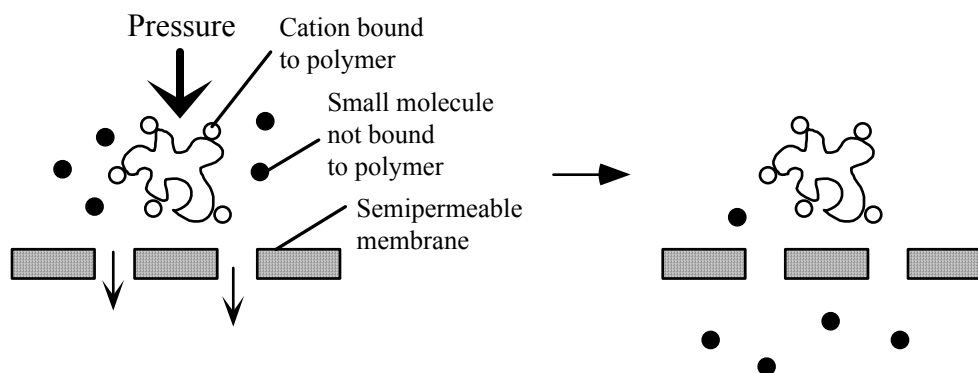
(b) The area from the mean to 0.1750 M was found to be 0.4989 in the part (a). The area beyond 0.1750 M is $0.5000 - 0.4989 = 0.0011$. That is, 0.11% of measurements are expected above 0.1750 M.

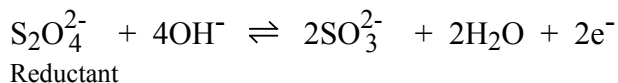
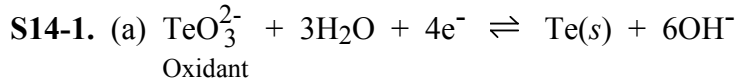
- (c) The warning line needs to be set at $\mu \pm 2\sigma/\sqrt{n}$ and the action line is set at $\mu \pm 3\sigma/\sqrt{n}$, where $n = 4$ is the number of replicate measurements made at each monitoring time. Using $\mu = 0.1664$ M and $\sigma = 0.0028$ M, the warning and action lines should be set at
 warning lines: $0.1664 \pm 2(0.0028)/\sqrt{4} = 0.1692$ and 0.1636 M
 action lines: $0.1664 \pm 3(0.0028)/\sqrt{4} = 0.1706$ and 0.1622 M

S13-18. (a) When polymer is added to the waste, it binds selected cations:



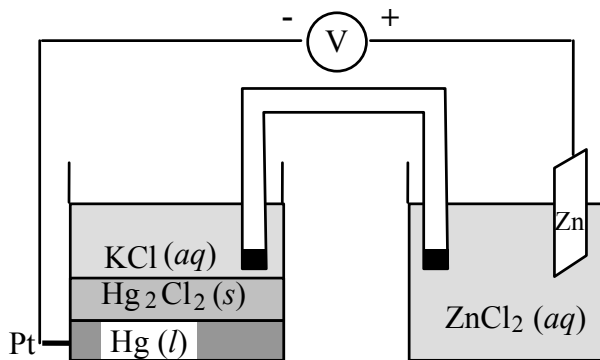
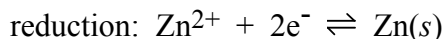
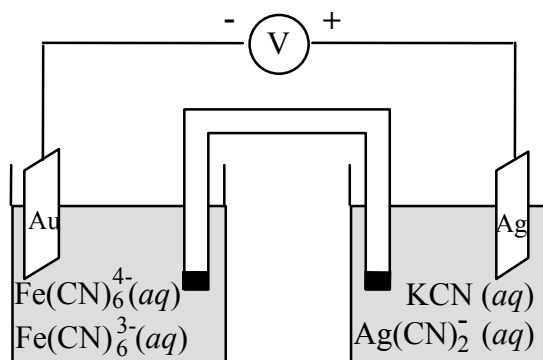
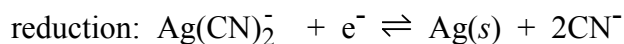
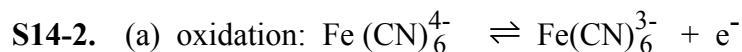
The trick is to choose a polymer and the right conditions to bind the toxic metal ion that you want to remove. When the waste + polymer solution is passed through an ultrafiltration membrane, solvent and other solutes not attached to the polymer pass through the membrane. The small volume of solution that is retained by the membrane contains the toxic cation bound to polymer. To make the process efficient, it is necessary to release the polymer from the cation and to recycle the polymer.





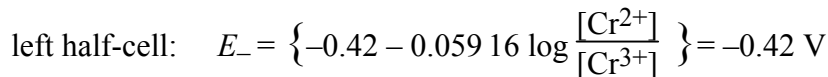
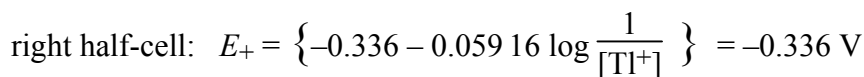
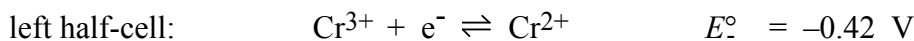
(b) $(1.00 \text{ g Te}) / (127.60 \text{ g/mol}) = 7.84 \text{ mmol}$, which requires $4 \times 7.84 = 31.3 \text{ mmol}$ of electrons
 $(3.13 \times 10^{-2} \text{ mol e}^-)(9.649 \times 10^4 \text{ C/mol}) = 3.02 \times 10^3 \text{ C}$

(c) Current = $(3.02 \times 10^3 \text{ C}) / (3600 \text{ s}) = 0.840 \text{ A}$



S14-3. The calculations below show that the hydrogen-oxygen fuel cell produces the most electricity per kg of reactants and the lead-acid battery produces the least.

$$1 \text{ A}\cdot\text{h} = \frac{(1 \text{ C/s})(3600 \text{ s/h})(1 \text{ h})}{9.649 \times 10^4 \text{ C/mole}^-} = 0.03731 \text{ mol e}^-$$



$$E = E_+ - E_- = -0.336 - (-0.42) = 0.084 \text{ V.}$$

(c) Since the voltage is positive, electrons flow from Pt to Tl and the reaction is $\text{Tl}^+ + \text{Cr}^{2+} \rightleftharpoons \text{Tl}(s) + \text{Cr}^{3+}$

(d) Pt is the anode, since Cr^{2+} is oxidized.

S14-8. Balanced reaction : $\text{HNO}_2 + e^- + \text{H}^+ \rightleftharpoons \text{NO} + \text{H}_2\text{O}$



$$FE_3^\circ = 3F(0.955) - F(0.773) - F(1.108) \quad E_3^\circ = 0.984 \text{ V}$$

S14-9. (a) $\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+ \quad E_+^\circ = 0.161 \text{ V}$



$$\Delta G^\circ = -1FE^\circ = 34.4 \text{ kJ} \quad K = 10^{1E^\circ/0.05916} = 9.2 \times 10^{-7}$$

(b) $2\text{F}_2 + 4e^- \rightleftharpoons 4\text{F}^- \quad E_+^\circ = 2.890 \text{ V}$



$$\Delta G^\circ = -4FE^\circ = -279 \text{ kJ} \quad K = 10^{4E^\circ/0.05916} = 7 \times 10^{48}$$

S14-10. (a) $2\text{IO}_3^- + \text{I}^- + 12\text{H}^+ + 10e^- \rightleftharpoons \text{I}_3^- + 6\text{H}_2\text{O} \quad E_+^\circ = 1.210 \text{ V}$



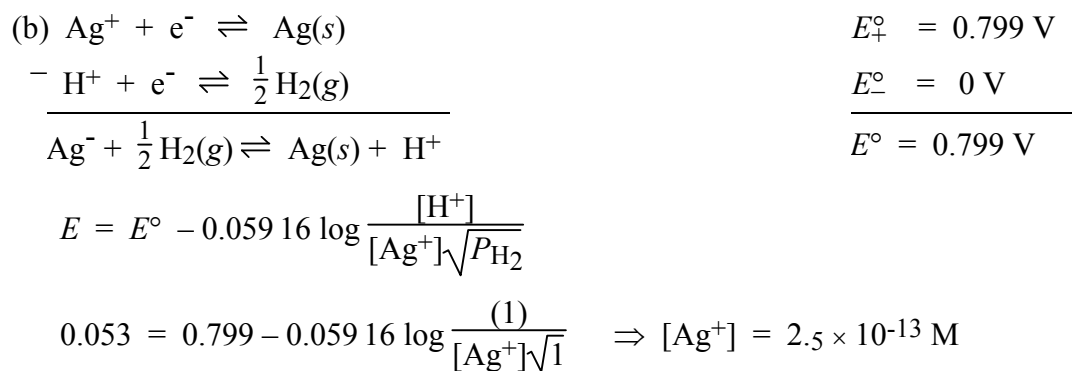
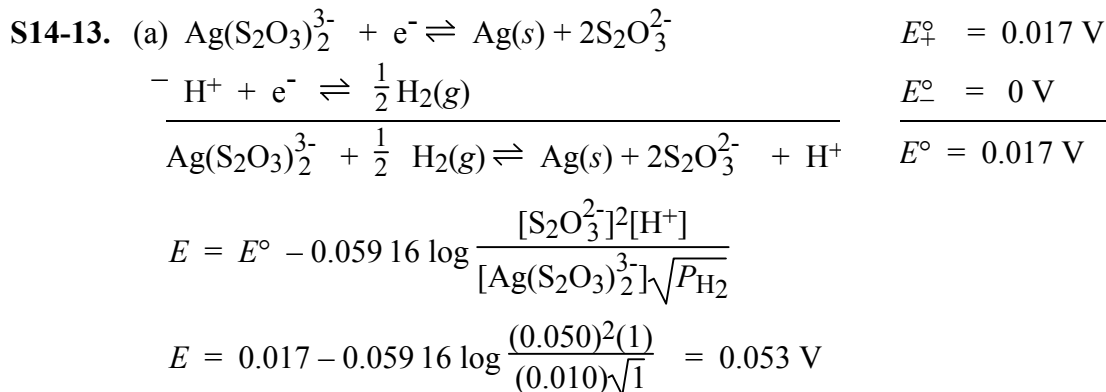
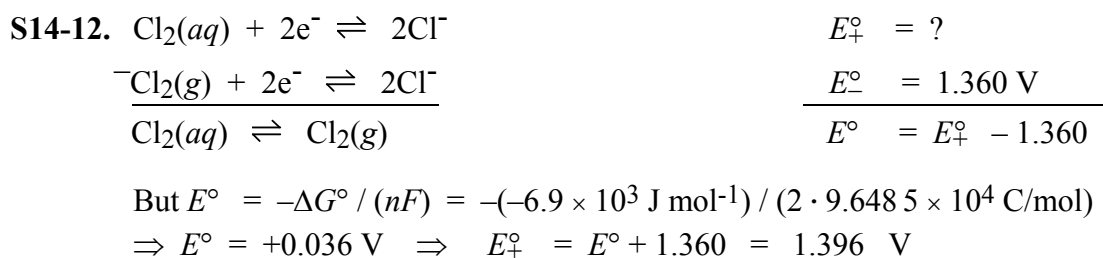
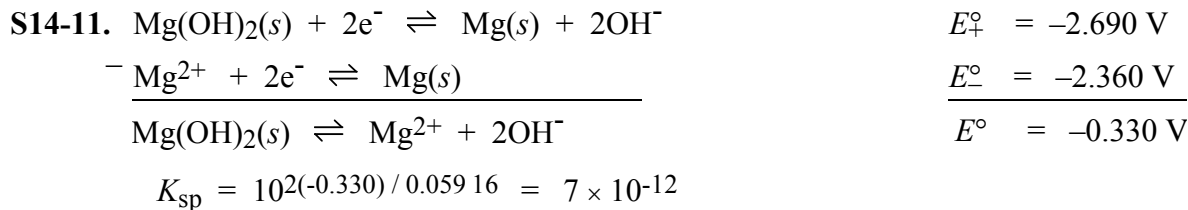
(b) $\Delta G^\circ = -10FE^\circ = -651 \text{ kJ.} \quad K = 10^{10E^\circ/0.05916} = 10^{114}$

$$(c) E = \left\{ 1.210 - \frac{0.05916}{10} \log \frac{[\text{I}_3^-]}{[\text{IO}_3^-]^2[\text{I}^-][\text{H}^+]^{12}} \right\} - \left\{ 0.535 - \frac{0.05916}{10} \log \frac{[\text{I}^-]^{15}}{[\text{I}_3^-]^5} \right\} = 0.178 \text{ V}$$

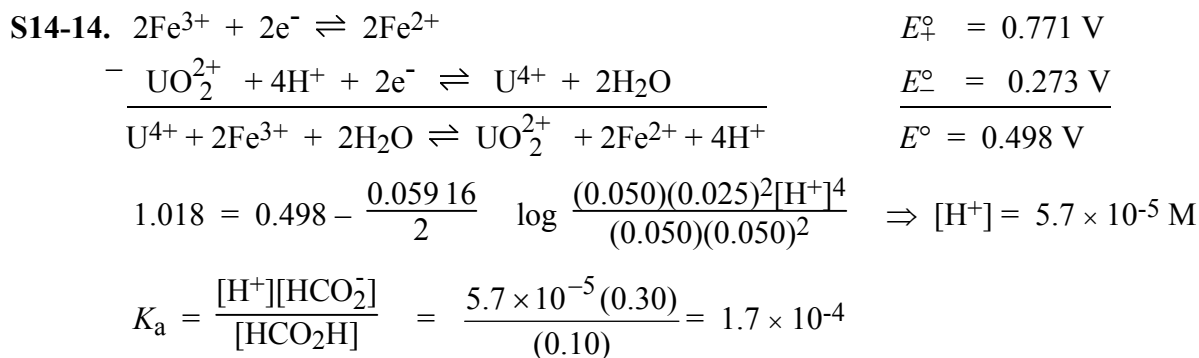
(d) $\Delta G = -10FE = -172 \text{ kJ}$

$$(e) \text{ At equilibrium, } E = 0 \Rightarrow E^\circ = \frac{0.05916}{10} \log \frac{[\text{I}_3]^{-6}}{[\text{IO}_3^-]^2[\text{I}^-]^{16}[\text{H}^+]^{12}} \Rightarrow [\text{H}^+] = 3.1 \times 10^{-9}$$

$$\Rightarrow \text{pH} = 8.51$$



$$(c) K_f = \frac{[\text{Ag(S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2} = \frac{0.010}{(2.5 \times 10^{-13})(0.050)^2} = 1.6 \times 10^{13}$$



S14-15. (a) 25.0 mL of 0.124 M Na_3PO_4 plus 25.0 mL of 0.248 M HClO_4 give 50.0 mL of 0.0620 M H_2PO_4^- , the first intermediate form of the triprotic acid, H_3PO_4 .

$$[\text{H}^+] = \sqrt{\frac{K_1K_2(0.0620) + K_1K_w}{K_1 + 0.0620}} = 2.01 \times 10^{-5} \text{ M}$$

$$[\text{HPO}_4^{2-}] = \frac{K_2[\text{H}_2\text{PO}_4^-]}{[\text{H}^+]} = \frac{(6.23 \times 10^{-8})(0.0620)}{(2.01 \times 10^{-5})} = 1.95 \times 10^{-4} \text{ M}$$

(b) In the left half-cell, $[\text{Pb}^{2+}(\text{left})] = \frac{K_{\text{sp}} \text{ for PbHPO}_4}{[\text{HPO}_4^{2-}]} = \frac{2.0 \times 10^{-10}}{1.95 \times 10^{-4}} = 1.0 \times 10^{-6} \text{ M}$

The net cell reaction is $\text{Pb}^{2+}(\text{left}) \rightleftharpoons \text{Pb}^{2+}(\text{right})$, for which $E^\ominus = 0$ and

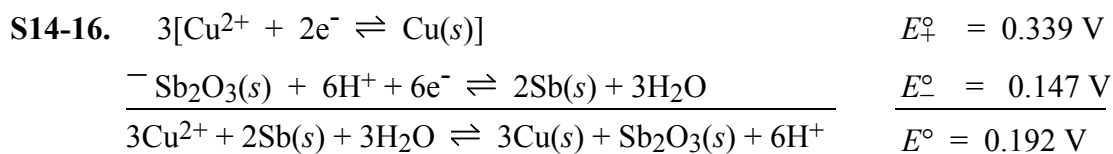
$$E = -\frac{0.05916}{2} \log \frac{[\text{Pb}^{2+}(\text{left})]}{[\text{Pb}^{2+}(\text{right})]}$$

$$0.097 = -\frac{0.05916}{2} \log \frac{1.0 \times 10^{-6}}{[\text{Pb}^{2+}(\text{right})]} \Rightarrow [\text{Pb}^{2+}(\text{right})] = 1.9 \times 10^{-3} \text{ M}$$

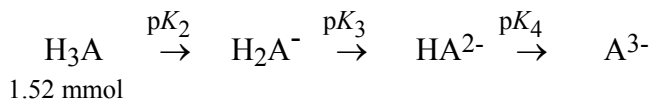
The right half-cell contains exactly twice as many moles of F^- as Pb^{2+} .

Therefore $\text{PbF}_2(\text{s})$ precipitates and in the solution $[\text{F}^-] = 2[\text{Pb}^{2+}]$.

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{F}^-]^2 = (1.9 \times 10^{-3})(3.8 \times 10^{-3})^2 = 2.7 \times 10^{-8}$$



First find $[\text{H}^+]$ in left half-cell:



Addition of 3.50 mmol of NaOH creates 0.46 mmol of A^{3-} plus 1.06 mmol of HA^{2-} .

$$\text{pH} = \text{p}K_4 + \log \frac{[\text{A}^{3-}]}{[\text{HA}^{2-}]} = 10.334 + \log \frac{0.46}{1.06} = 9.97$$

$$E = \left\{ 0.339 - \frac{0.05916}{6} \log \frac{1}{[\text{Cu}^{2+}(\text{right})]^3} \right\} - \left\{ 0.147 - \frac{0.05916}{6} \log \frac{1}{[\text{H}^+(\text{left})]^6} \right\}$$

Inserting $E = 0.418$ V and $[\text{H}^+(\text{left})] = 10^{-9.97}$ gives $[\text{Cu}^{2+}(\text{right})] = 5.02 \times 10^{-13}$ M

Now find $[\text{Y}^{4-}]$ in right half-cell:

	Ca^{2+}	+	EDTA	\rightleftharpoons	CaY^{2-}
initial mmol	2.38		2.22		—
final mmol	0.16		—		2.22

$$K_f(\text{for CaY}^{2-}) = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]}$$

$$4.9 \times 10^{10} = \frac{(2.22 \text{ mmol}/150 \text{ mL})}{(0.16 \text{ mmol}/150 \text{ mL})[\text{Y}^{4-}]} \Rightarrow [\text{Y}^{4-}] = 2.83 \times 10^{-10} \text{ M}$$

$$K_f(\text{for CuY}^{2-}) = \frac{[\text{CuY}^{2-}]}{[\text{Cu}^{2+}][\text{Y}^{4-}]} = \frac{(0.00137)(100/150)}{(5.02 \times 10^{-13})(2.83 \times 10^{-10})} = 6 \times 10^{18}$$

$$\text{S14-17. } E = -0.1038 - \frac{0.05916}{2} \log \frac{P_{\text{CO}}}{P_{\text{CO}_2}[\text{H}^+]^2}$$

$$E = \underbrace{-0.1038 + 0.05916 \log [\text{H}^+]}_{\text{This is } E^\circ \text{ when pH} = 7} - \frac{0.05916}{2} \log \frac{P_{\text{CO}}}{P_{\text{CO}_2}}$$

This is E° when $\text{pH} = 7$

$$E^\circ = -0.1038 + 0.05916 \log (10^{-7.00}) = -0.5179 \text{ V}$$

$$\text{S14-18. } E = E^\circ - \frac{0.05916}{2} \log \frac{[\text{HCO}_2\text{H}]}{P_{\text{CO}_2}[\text{H}^+]^2}$$

Substituting $[\text{HCO}_2\text{H}] = \frac{[\text{H}^+] F_{\text{HCO}_2\text{H}}}{[\text{H}^+] + K_a}$ into the Nernst equation gives

$$E = -0.114 - \frac{0.05916}{2} \log \frac{[\text{H}^+] F_{\text{HCO}_2\text{H}}}{([\text{H}^+] + K_a) P_{\text{CO}_2} [\text{H}^+]^2}$$

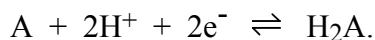
$$E = -0.114 + \underbrace{\frac{0.05916}{2} \log \{([\text{H}^+] + K_a) [\text{H}^+]\}}_{\text{This is } E^\circ \text{ when pH} = 7} - \frac{0.05916}{2} \log \frac{F_{\text{HCO}_2\text{H}}}{P_{\text{CO}_2}}$$

This is E° when $\text{pH} = 7$

Inserting $K_a = 1.8 \times 10^{-4}$ for HCO_2H and $[\text{H}^+] = 10^{-7.00}$ gives

$$E^{\circ'} = -0.114 + \frac{0.05916}{2} \log \{(10^{-7.00} + 1.8 \times 10^{-4})(10^{-7.00})\} = -0.432 \text{ V}$$

S14-19. Calling anthraquinone-2,6-disulfonate A, the reaction may be written



$$E = 0.229 - \frac{0.05916}{2} \log \frac{[H_2A]}{[A][H^+]^2}$$

But $[H_2A] = [H^+]^2 F_{H_2A} / ([H^+]^2 + [H^+]K_1 + K_1K_2)$ and $[A] = F_A$.

Making these substitutions and rearranging the resulting Nernst equation gives

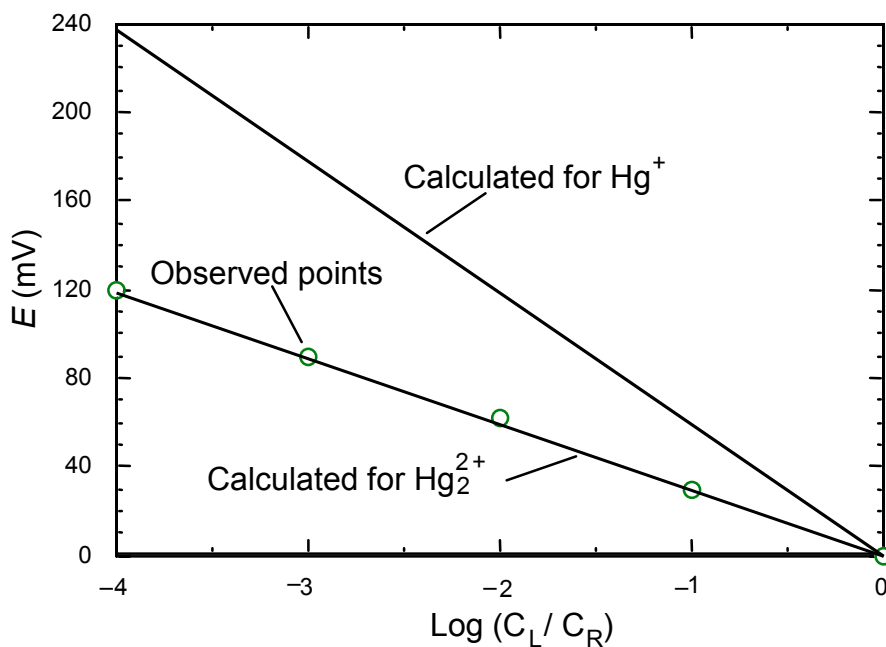
$$E = 0.229 - \frac{0.05916}{2} \log \frac{1}{[H^+]^2 + [H^+]K_1 + K_1K_2} - \frac{0.05916}{2} \log \frac{F_{H_2A}}{F_A}$$

$$\underbrace{\hspace{10em}}_{E^{\circ'} = -0.184 \text{ V}}$$

S14-20. (a) Right: $Hg^+ (C_R) + e^- \rightleftharpoons Hg \quad E^{\circ\ddagger}$
 Left: $Hg^+ (C_L) + e^- \rightleftharpoons Hg \quad E^{\circ} (= E^{\circ\ddagger} \text{ because reactions are the same})$
 $E_+ = E^{\circ\ddagger} - 0.05916 \log (1/C_R); \quad E_- = E^{\circ} - 0.05916 \log (1/C_L)$
 $E = E_+ - E_- = E^{\circ\ddagger} - E^{\circ} - 0.05916 \log (C_L/C_R) = -0.05916 \log (C_L/C_R)$

(b) Right: $Hg_2^{2+} (C_R) + 2e^- \rightleftharpoons Hg \quad E^{\circ\ddagger}$
 Left: $Hg_2^{2+} (C_L) + 2e^- \rightleftharpoons Hg \quad E^{\circ} (= E^{\circ\ddagger})$
 $E_+ = E^{\circ\ddagger} - \frac{0.05916}{2} \log (1/C_R); \quad E_- = E^{\circ} - \frac{0.05916}{2} \log (1/C_L)$
 $E = E_+ - E_- = -\frac{0.05916}{2} \log (C_L/C_R)$

(c) If Hg(I) is monatomic, the slope of the graph should be -59.16 mV .
 If Hg(I) is diatomic, the slope should be -29.58 mV .



(d)

Cell:	1	2	3	4	5
C_L/C_R :	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}

- (e) The graph above clearly shows that Hg(I) is diatomic.
- (f) Solution B keeps the ionic strength constant. In cell 1, the ionic strength from $\text{Hg}_2(\text{NO}_3)_2$ is 0.15 M and the ionic strength from HNO_3 is 0.16 M, giving a total ionic strength of 0.31 M. In cell 2, the ionic strength from solution A is 0.031 M and the ionic strength from solution B is 0.28 M, giving a total ionic strength of 0.31 M. The ionic strength is 0.31 M in all cells.
- (g) If we do a chemical analysis for mercury and one for nitrate, we could establish that the mole ratio of Hg to nitrate is 1:1. This would establish that the oxidation state of mercury is +1, not +2.

CHAPTER 15: SUPPLEMENTARY SOLUTIONS
ELECTRODES AND POTENTIOMETRY

S15-1. (a) -0.419 V (b) 0.720 V (c) -0.479 V (d) -0.009 V (e) 0.009 V

S15-2. $\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$ $E_+^\circ = 1.098\text{ V}$

$$E_+ = E_+^\circ - \frac{0.05916}{2} \log \frac{[\text{Br}^-]^2}{[\text{Br}_2(\text{aq})]} = 1.098 - \frac{0.05916}{2} \log \frac{[0.234]^2}{[0.00217]} = 1.057\text{ V}$$

$$E = E_+ - E_- = 1.057 - 0.241 = 0.816\text{ V}$$

S15-3. $V_e = 25.0\text{ mL}$. $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) \Rightarrow E_+ = 0.799 - 0.05916 \log \frac{1}{[\text{Ag}^+]}$

$$0.1\text{ mL: } [\text{SCN}^-] = \underbrace{\left(\frac{24.9}{25.0}\right)}_{\substack{\text{Fraction} \\ \text{remaining}}} \underbrace{(0.100\text{ M})}_{\substack{\text{Original} \\ \text{concentration}}} \underbrace{\left(\frac{50.0}{50.1}\right)}_{\substack{\text{Dilution} \\ \text{factor}}} = 0.0994\text{ M}$$

$$[\text{Ag}^+] = K_{\text{sp}}/[\text{SCN}^-] = (1.1 \times 10^{-12})/0.0994 = 1.1 \times 10^{-11}\text{ M}$$

$$E = E_+ - E_- = \left\{ 0.799 - 0.05916 \log \frac{1}{1.1 \times 10^{-11}} \right\} - 0.241 = -0.090\text{ V}$$

$$10.0\text{ mL: } [\text{SCN}^-] = \left(\frac{15.0}{25.0}\right)(0.100\text{ M})\left(\frac{50.0}{60.0}\right) = 0.0500\text{ M}$$

$$[\text{Ag}^+] = K_{\text{sp}}/[\text{SCN}^-] = (1.1 \times 10^{-12})/0.0500 = 2.2 \times 10^{-11}\text{ M}$$

$$E = E_+ - E_- = \left\{ 0.799 - 0.05916 \log \frac{1}{2.2 \times 10^{-11}} \right\} - 0.241 = -0.073\text{ V}$$

$$25.0\text{ mL: } [\text{Ag}^+] = [\text{SCN}^-] \Rightarrow [\text{Ag}^+] = \sqrt{K_{\text{sp}}} = \sqrt{1.1 \times 10^{-12}} = 1.05 \times 10^{-6}\text{ M}$$

$$E = E_+ - E_- = \left\{ 0.799 - 0.05916 \log \frac{1}{1.05 \times 10^{-6}} \right\} - 0.241 = 0.204\text{ V}$$

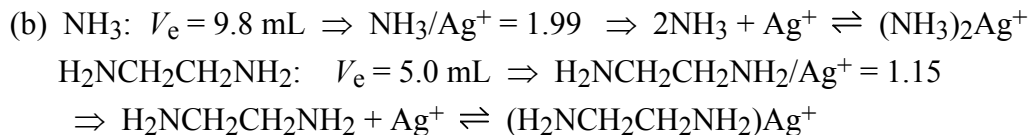
$$30.0\text{ mL: This is } 5.0\text{ mL past } V_e \Rightarrow [\text{Ag}^+] = \left(\frac{5.0}{80.0}\right)(0.200\text{ M}) = 0.0125\text{ M}$$

$$E = E_+ - E_- = \left\{ 0.799 - 0.05916 \log \frac{1}{0.0125} \right\} - 0.241 = 0.445\text{ V}$$

S15-4. (a) $\text{Ag}^+(\text{right}) + \text{e}^- \rightleftharpoons \text{Ag}$ $E_+^\circ = 0.799\text{ V}$
 $-\text{Ag}^+(\text{left}) + \text{e}^- \rightleftharpoons \text{Ag}$ $E_-^\circ = 0.799\text{ V}$

 $\text{Ag}^+(\text{right}) \rightleftharpoons \text{Ag}^+(\text{left})$ $E^\circ = 0$

$$E = -0.05916 \log \frac{[\text{Ag}^+(\text{left})]}{[\text{Ag}^+(\text{right})]}$$



(c) At the equivalence point, $E = -0.15 \text{ V}$ and $[\text{Ag}^+(\text{left})] = 0.100 \text{ M}$.

$$-0.15 = -0.05916 \log \frac{0.100}{[\text{Ag}^+(\text{right})]} \Rightarrow [\text{Ag}^+(\text{right})] \approx 0.03 \text{ M}$$

S15-5. right half-reaction: $\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(s) \quad E^\circ = -0.762 \text{ V}$

$$E = \left\{ -0.762 - \frac{0.05916}{2} \log \frac{1}{[\text{Zn}^{2+}]} \right\} - 0.241$$

$$\text{MgY}^{2-}: K_f = 6.2 \times 10^8; \quad \text{ZnY}^{2-}: K_f = 3.2 \times 10^{16}.$$

When 10 mL of EDTA has been added, $[\text{Mg}^{2+}] = \left(\frac{4}{5}\right)(0.100)\left(\frac{50}{60}\right)$

$$= 0.0667 \text{ M and } [\text{MgY}^{2-}] = \left(\frac{1}{5}\right)(0.100)\left(\frac{50}{60}\right) = 0.0167 \text{ M}.$$

$$\text{But } \frac{[\text{MgY}^{2-}]}{[\text{Mg}^{2+}][\text{Y}^{4-}]} = 6.2 \times 10^8 \Rightarrow [\text{Y}^{4-}] = 4.04 \times 10^{-10} \text{ M}.$$

The concentration of $[\text{ZnY}^{2-}]$ is $(50/60)(1.00 \times 10^{-5}) = 8.33 \times 10^{-6} \text{ M}$.

Because $\frac{[\text{ZnY}^{2-}]}{[\text{Zn}^{2+}][\text{Y}^{4-}]} = 3.2 \times 10^{16}$ and we know $[\text{Y}^{4-}]$ and $[\text{ZnY}^{2-}]$,

we can compute that $[\text{Zn}^{2+}] = 6.44 \times 10^{-13} \text{ M}$.

$$E = \left\{ -0.762 - \frac{0.05916}{2} \log \frac{1}{6.44 \times 10^{-13}} \right\} - 0.241 = -1.364 \text{ V}$$

S15-6. Relative mobilities:

$$\text{H}^+ \rightarrow 36.30 \qquad \text{Cl}^- \rightarrow 7.91$$

$$4.01 \leftarrow \text{Li} \qquad 8.13 \leftarrow \text{Br}^-$$

Anion diffusion from each side is nearly equal, while H^+ diffuses much faster than Li^+ .

Positive charge builds on the right, so the left side will be negative.

S15-7. Velocity = mobility \times field = $(20.50 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})) \times (1000 \text{ V/m})$

$$= 2.05 \times 10^{-4} \text{ m s}^{-1} \text{ for } \text{OH}^- \text{ and } (5.70 \times 10^{-8})(1000) = 5.70 \times 10^{-5} \text{ m s}^{-1} \text{ for } \text{F}^-.$$

To cover 0.0100 m will require $(0.0100 \text{ m})/(2.05 \times 10^{-4} \text{ m s}^{-1}) = 48.8 \text{ s}$ for OH^- and

$$(0.0100)/(5.70 \times 10^{-5}) = 175 \text{ s for } \text{NO}_3^-.$$

S15-8. (a) $E = \text{constant} + \beta \frac{0.05916}{3} \log \mathcal{A}_{\text{La}^{3+}}(\text{outside}).$

(b) If the activity increases by a factor of 10, the potential will increase by $0.05916/3 = 19.7$ mV.

$$(c) E_1 = \text{constant} + (1.00) \frac{0.05916}{3} \log (2.36 \times 10^{-4})$$

$$E_2 = \text{constant} + (1.00) \frac{0.05916}{3} \log (4.44 \times 10^{-3})$$

$$\Delta E = E_2 - E_1 = \frac{0.05916}{3} \log \frac{4.44 \times 10^{-3}}{2.36 \times 10^{-4}} = +25.1 \text{ mV}$$

$$(d) E = \text{constant} + \frac{0.05916}{3} \log \left\{ [\text{La}^{3+}] + \frac{1}{1200} [\text{Fe}^{3+}]^{1/1} \right\}$$

$$0.100 = \text{constant} + \frac{0.05916}{3} \log (1.00 \times 10^{-4}) \Rightarrow \text{constant} = 0.1789 \text{ mV}$$

$$E = 0.1789 + \frac{0.05916}{3} \log \left\{ (1.00 \times 10^{-4}) + \frac{1}{1200} (0.010) \right\} = +100.7 \text{ mV}$$

$$\text{S15-9. } \frac{[\text{ML}]}{[\text{M}][\text{L}]} = 3.6 \times 10^{10} = \frac{0.050}{[\text{M}](0.50)} \Rightarrow [\text{M}] = 2.8 \times 10^{-12} \text{ M}$$

S15-10. For the pure $[\text{Ca}^{2+}]$ solution we can write

$$E = \text{constant} + \frac{(0.970)(0.05916)}{2} \log (1.00 \times 10^{-3})$$

Putting in $E = 0.3000$ V gives $\text{constant} = 0.3861$ V. For the solution containing the interfering ions we can say that $E = 0.3861 + \frac{(0.970)(0.05916)}{2} \log \left\{ (1.00 \times 10^{-3}) + (0.040)(1.00 \times 10^{-3}) + (0.021)(1.00 \times 10^{-3}) + (0.081)(5.00 \times 10^{-4}) \right\} = 0.3012$ V

At equal concentrations, Zn^{2+} interferes the most.

$$\text{S15-11. } 0.1946 = \text{constant} + \frac{0.0571}{2} \log \left\{ [\text{M}^{2+}]_o + 0.0200 (0.0200) \right\}$$

After making the standard addition, the concentration of M^{2+} is

$$\frac{100.0 [\text{M}^{2+}]_o + 1.00 (0.0307)}{101.0} = (0.9901 [\text{M}^{2+}]_o + 3.04_0 \times 10^{-4}) \text{ M}$$

$$0.2007 = \text{constant} + \frac{0.0571}{2} \log \left\{ (0.9901 [\text{M}^{2+}]_o + 3.04_0 \times 10^{-4}) + 0.0200 (0.0200) \right\}$$

$$= \text{constant} + \frac{0.0571}{2} \log \left\{ 0.9901 [\text{M}^{2+}]_o + 7.04_0 \times 10^{-4} \right\}$$

$$\Delta E = (0.2007 - 0.1946) = \frac{0.0571}{2} \log \frac{(0.9901 [\text{M}^{2+}]_o + 7.04_0 \times 10^{-4})}{[\text{M}^{2+}]_o + 4.00 \times 10^{-4}}$$

$$\Rightarrow [\text{M}^{2+}]_o = 7.7 \times 10^{-5} \text{ M}$$

S15-12. For $\text{Mg}(\text{EDTA})^{2-}$, $K_f = 6.2 \times 10^8$. This solution contains 30% more EDTA than Mg^{2+} .
Therefore, $[\text{EDTA}]/[\text{Mg}(\text{EDTA})^{2-}] = 0.30$

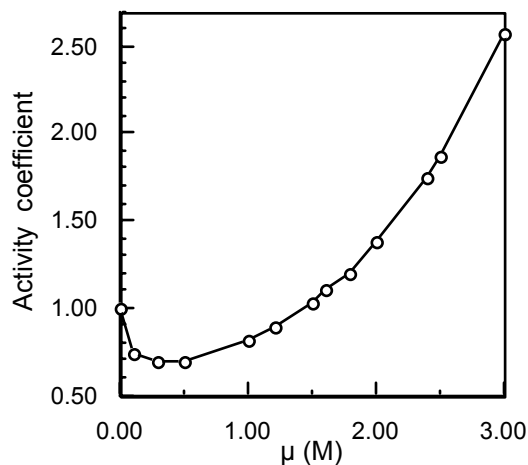
$$\frac{[\text{Mg}(\text{EDTA})^{2-}]}{[\text{Mg}^{2+}][\text{EDTA}]} = \alpha_{Y^{4-}} K_f = 0.36 K_f$$

$$[\text{Mg}^{2+}] = \frac{[\text{Mg}(\text{EDTA})^{2-}]}{[\text{EDTA}]\alpha_{Y^{4-}} K_f} = \frac{1}{(0.30)(0.36)K_f} = 1.49 \times 10^{-8} \text{ M}$$

For $\text{Mn}(\text{EDTA})^{2-}$, $K_f = 7.4 \times 10^{13}$ and $[\text{Mn}^{2+}] = 1.25 \times 10^{-13} \text{ M}$

S15-13. $\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log[\text{H}^+]\gamma_{\text{H}^+} \Rightarrow \gamma_{\text{H}^+} = 10^{-\text{pH}} / [\text{H}^+]$ At $\mu = 0$, we know $\gamma_{\text{H}^+} = 1$

μ (M)	pH	γ_{H^+}	μ (M)	pH	γ_{H^+}
0.10	2.13	0.74	1.60	1.96	1.10
0.30	2.16	0.69	1.80	1.92	1.20
0.50	2.16	0.69	2.00	1.86	1.38
1.00	2.09	0.81	2.40	1.76	1.74
1.20	2.05	0.89	2.50	1.73	1.86
1.50	1.99	1.02	3.00	1.59	2.57



S15-14. The unknown contains x moles of ClO_4^- in 0.050 0 L.

The standard addition adds $(0.001\ 00 \text{ L})(0.050\ 0 \text{ M}) = 5.00 \times 10^{-5} \text{ mol}$ of ClO_4^- .

Therefore, the second solution contains $x + (5.00 \times 10^{-5}) \text{ mol}$ in 0.051 0 L.

We can write a Nernst equation for the first solution:

$$E_1 = \text{constant} - 0.059\ 16 \log[\text{ClO}_4^-]_1$$

and another for the second solution:

$$E_2 = \text{constant} - 0.059\ 16 \log[\text{ClO}_4^-]_2$$

We set $E_1 = 0.3587 \text{ V}$, $E_2 = 0.3461 \text{ V}$, $[\text{ClO}_4^-]_1 = x/0.0500$, and $[\text{ClO}_4^-]_2 = (x + 5.00 \times 10^{-5})/0.0510$.

Now we solve for x by subtracting one equation from the other:

$$\begin{array}{r} 0.3587 = \text{constant} - 0.05916 \log[x/0.0500] \\ - \\ 0.3461 = \text{constant} - 0.05916 \log[(x + 5.00 \times 10^{-5})/0.0510] \\ \hline 0.0126 = -0.05916 \log\left(\frac{x/0.0500}{(x + 5.00 \times 10^{-5})/0.0510}\right) \\ \\ \frac{x/0.0500}{(x + 5.00 \times 10^{-5})/0.0510} = 0.612 \Rightarrow x = 7.51 \times 10^{-5} \text{ mol} \end{array}$$

The original perchlorate concentration was therefore $\frac{7.51 \times 10^{-5} \text{ mol}}{0.0500 \text{ L}} = 1.50 \text{ mM}$

S15-15. (a) For the original solution, we can write

$$[\text{Ag}^+] = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{CN}^-]^2 (7.1 \times 10^{19})} = \frac{[(1.00 \times 10^{-5})]}{(8.0 \times 10^{-6})^2 (7.1 \times 10^{19})} = 2.2 \times 10^{-15} \text{ M}$$

$$E = \text{constant} + 0.05916 \log(2.2 \times 10^{-15}) = 206.3 \text{ mV} \Rightarrow \text{constant} = 1.0734 \text{ V}$$

After addition of CN^- , we can say that

$$[\text{Ag}^+] = \frac{(1.00 \times 10^{-5})}{(12.0 \times 10^{-6})^2 (7.1 \times 10^{19})} = 9.8 \times 10^{-216} \text{ M}$$

$$E = 1.0734 + 0.05916 \log(9.8 \times 10^{-16}) = 185.4 \text{ mV}$$

(b) Let there be x mol of CN^- in 50.0 mL of unknown. After the standard addition, the unknown contains $x + (1.00 \times 10^{-3} \text{ L})(2.50 \times 10^{-4} \text{ M}) = (x + 2.50 \times 10^{-7}) \text{ mol CN}^-$

S15-16. (a) $8.22 \text{ ppm} = 8.22 \times 10^{-6} \text{ g of Cl}^- \text{ per g of solution} = 8.22 \times 10^{-3} \text{ g of Cl}^- \text{ per liter of solution} = 2.32 \times 10^{-4} \text{ M}$.

(b) For a Nernstian electrode we can write $E = \text{constant} - 0.05916 \log [\text{Cl}^-]$

For the first solution, $0.2280 = \text{constant} - 0.05916 \log (2.32 \times 10^{-4})$

$$\Rightarrow \text{constant} = 0.0130 \text{ V}$$

10.0 mL of 100.0 ppm standard contains 2.82×10^{-5} moles of Cl^- .

The original 100.0 mL of solution contains 2.32×10^{-5} moles of Cl^- .

Therefore, the new solution has

$$[\text{Cl}^-] = \frac{(2.32 + 2.82) \times 10^{-5} \text{ mol}}{0.110 \text{ L}} = 4.67 \times 10^{-4} \text{ M}$$

$$E = 0.0130 - 0.05916 \log (4.67 \times 10^{-4}) = 210.0 \text{ mV}$$

(c) A 2 mV change for Cl^- corresponds to a 1 mV change for Ca^{2+} . We could use the table:

ΔE :	0	0.5	1.0	1.5
Q :	1.00	0.696	0.529	0.423

S15-17. (a) Let C_0 = initial concentration of unknown in 100 mL and
 S_0 = initial concentration of standard in 10 mL.

$$\text{Concentration of analyte in diluted sample} = \frac{100}{110} C_0 + \frac{10}{110} S_0 = \frac{10C_0 + S_0}{11}$$

$$\text{Before standard addition : } E_1 = \text{constant} + 0.05916 \log C_0$$

$$\text{After standard addition : } E_2 = \text{constant} + 0.05916 \log \frac{10 C_0 + S_0}{11}$$

$$\Delta E = 0.001 \text{ V} = E_2 - E_1 = 0.05916 \log \frac{10 C_0 + S_0}{11 C_0}$$

$$\text{Solve for } C_0 \Rightarrow C_0 = 0.696 S_0 \Rightarrow Q = 0.696$$

(b) General solution in part a: $Q = C_0/S_0 = 1/(11a - 10)$, where $a = 10^{\Delta E/0.05916}$

	A	B	C
1	DeltaE (mV)	$a = 10^{(\text{DeltaE}/59.16)}$	$Q = 1/(11a-10)$
2	0	1.0000	1.0000
3	1	1.0397	0.6961
4	2	1.0810	0.5290
5	3	1.1239	0.4233
6	4	1.1685	0.3505
7	5	1.2148	0.2973

S15-18. Mean = 1.22₁ standard deviation = 0.05₀

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} = 1.22_1 \pm \frac{(2.17)(0.05_0)}{\sqrt{14}} = 1.22_1 \pm 0.02_9 = 1.19_2 \text{ to } 1.25_0$$

(Student's t was interpolated in Table 4-2 for 13 degrees of freedom.)

The value 1.19 is just barely outside the 95% confidence interval. It is so close to the 95% boundary that I would not say it is outside of "experimental error."

S15-19.	[KF] (M)	Ionic strength (M)	Activity coefficient (γ_{F^-})	Activity (\mathcal{A}_{F^-})
	1.00×10^{-1}	0.100	0.76	0.076
	1.00×10^{-2}	0.0100	0.90	0.0090
	1.00×10^{-3}	0.00100	0.964	0.000964
	1.00×10^{-4}	10^{-4}	close to 1	10^{-4}
	1.00×10^{-5}	10^{-5}	close to 1	10^{-5}
	1.00×10^{-6}	10^{-6}	close to 1	10^{-6}
	1.00×10^{-7}	10^{-7}	close to 1	10^{-7}

The graph of E vs. $\log \mathcal{A}_{F^-}$ is linear for the concentration range 10^{-1} to 10^{-5} with a slope of -57.5 mV. (The linear region extends almost to 10^{-6} M.)

Assuming that the temperature was 25°C , the theoretical slope would be -59.16 mV, so the value of β is $57.5 / 59.16 = 0.972$. If you chose to fit the data down to 10^{-6} M (which is not unreasonable), the slope is -56.0 mV and β is 0.947.

S15-20. (a) We want the fractional composition equations for ethylenediamine:

$$\text{fraction in the form enH}^+ = \alpha_{\text{HA}^-} = \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\text{fraction in the form enH}_2^{2+} = \alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\text{fraction in the form en} = \alpha_{\text{A}^{2-}} = \frac{K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

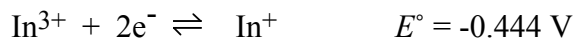
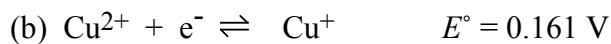
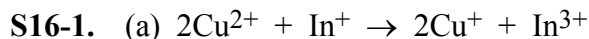
(b) There are 4 equilibrium constants. There is no charge balance because the pH was fixed.

We can write two mass balances, one for Cu^{2+} and one for en:

$$\text{Cu}_{\text{total}} = 0.00100 \text{ M} = [\text{Cu}^{2+}] + [\text{Cu(en)}^{2+}] + [\text{Cu(en)}_2^{2+}]$$

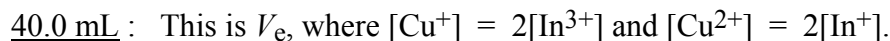
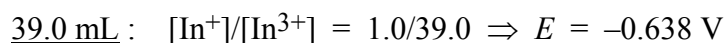
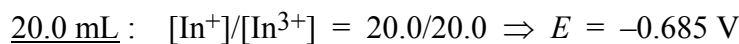
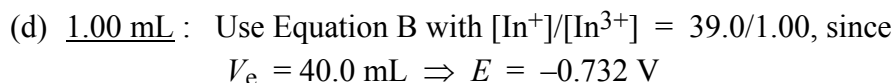
$$\text{en}_{\text{total}} = 0.0150 \text{ M} = [\text{en}] + [\text{enH}^+] + [\text{enH}_2^{2+}] + [\text{Cu(en)}^{2+}] + 2[\text{Cu(en)}_2^{2+}]$$

REDOX TITRATIONS



(c) $E = \left\{ 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \right\} - \left\{ 0.241 \right\} \quad (\text{A})$

$E = \left\{ -0.444 - \frac{0.05916}{2} \log \frac{[\text{In}^+]}{[\text{In}^{3+}]} \right\} - \left\{ 0.241 \right\} \quad (\text{B})$



Adding the two Nernst equations gives

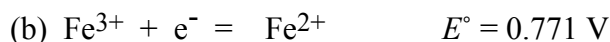
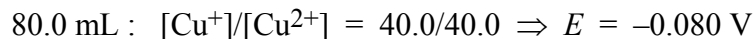
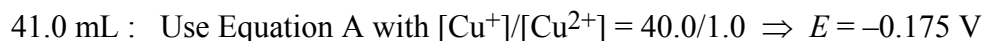
$$E_+ = 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]}$$

$$2E_+ = -0.888 - 0.05916 \log \frac{[\text{In}^+]}{[\text{In}^{3+}]}$$

$$3E_+ = -0.727 - 0.05916 \log \frac{[\text{In}^+][\text{Cu}^+]}{[\text{In}^{3+}][\text{Cu}^{2+}]}$$

$$3E_+ = -0.727 - 0.05916 \log \frac{[\text{In}^+]2[\text{In}^{3+}]}{[\text{In}^{3+}]2[\text{In}^+]}$$

$$\Rightarrow E_+ = -0.242 \text{ V and } E = -0.483 \text{ V.}$$



(c) $E = \left\{ 0.771 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - \left\{ 0.197 \right\} \quad (\text{A})$

$E = \left\{ 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \right\} - \left\{ 0.197 \right\} \quad (\text{B})$

(d) 1.0 mL : Use Equation A with $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 1.0/24.0$, since $V_e = 25.0 \text{ mL} \Rightarrow E = 0.656 \text{ V}$

12.5 mL : $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 12.5/12.5 \Rightarrow E = 0.574 \text{ V}$

24.5 mL : $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 24.5/0.5 \Rightarrow E = 0.474 \text{ V}$

25.0 mL : This is V_e , where $[\text{Cu}^{2+}] = [\text{Fe}^{2+}]$ and $[\text{Cu}^+] = [\text{Fe}^3]$.

Adding the two Nernst equations gives

$$E_+ = 0.771 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

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

$$2E_+ = 0.932 - 0.05916 \log \frac{[\text{Fe}^{2+}][\text{Cu}^+]}{[\text{Fe}^{3+}][\text{Cu}^{2+}]}$$

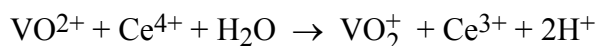
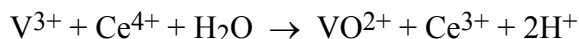
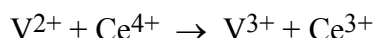
$$2E_+ = 0.932 - 0.05916 \log \frac{[\text{Fe}^{2+}][\text{Fe}^{3+}]}{[\text{Fe}^{3+}][\text{Fe}^{2+}]}$$

$$\Rightarrow E_+ = 0.466 \text{ V and } E = 0.269 \text{ V.}$$

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

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

S16-3. Titration reactions:

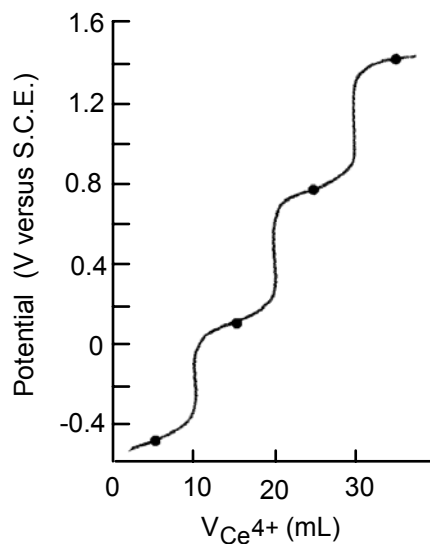


At 5.0 mL: $E_+ = -0.255 - 0.05916 \log \frac{[\text{V}^{2+}]}{[\text{V}^{3+}]} \Rightarrow E = -0.496 \text{ V}$

At 15.0 mL: $E_+ = 0.337 - 0.05916 \log \frac{[\text{V}^{3+}]}{[\text{VO}^{2+}](1.00)^2} \Rightarrow E = 0.096 \text{ V}$

At 25.0 mL: $E_+ = 1.001 - 0.05916 \log \frac{[\text{VO}^{2+}]}{[\text{VO}_2^+](1.00)^2} \Rightarrow E = 0.760 \text{ V}$

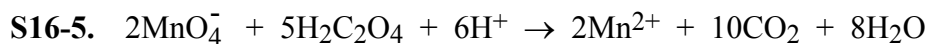
At 35.0 mL: $E_+ = 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} = 1.70 - 0.05916 \log \left(\frac{30.0}{5.0} \right) \Rightarrow E = 1.41 \text{ V}$



$$(22.11 - 0.07) = 22.04 \text{ mL of } 0.01234 \text{ M KMnO}_4 = 0.2720 \text{ mmol of MnO}_4^-$$

which will react with $(5/3)(0.2720) = 0.4533 \text{ mmol of Mo}^{3+}$.

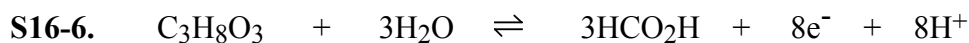
$$[\text{Mo}^{3+}] = 0.4533 \text{ mmol}/50.00 \text{ mL} = 9.066 \text{ mM.}$$



12.34 mL of 0.004321 M $\text{KMnO}_4 = 0.05332 \text{ mmol of MnO}_4^-$ which reacts with

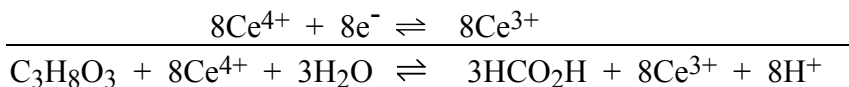
$$(5/2)(0.05332) = 0.1333 \text{ mmol of H}_2\text{C}_2\text{O}_4 \text{ which came from}$$

$$(2/3)(0.1333) = 0.08887 \text{ mmol of La}^{3+}. [\text{La}^{3+}] = 0.08887 \text{ mmol}/25.00 \text{ mL} = 3.555 \text{ mM.}$$



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

formic acid
(oxidation number
of C = +2)



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

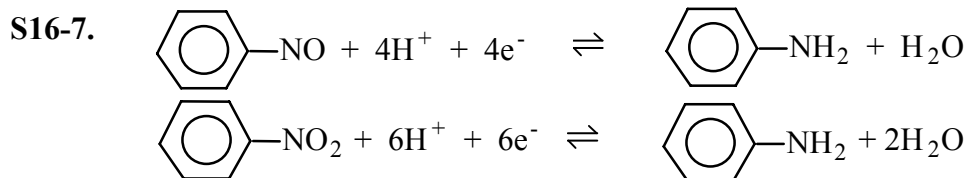
$$50.0 \text{ mL of } 0.0899 \text{ M Ce}^{4+} = 4.495 \text{ mmol}$$

$$10.05 \text{ mL of } 0.0437 \text{ M Fe}^{2+} = 0.439 \text{ mmol}$$

$$\text{Ce}^{4+} \text{ reacting with glycerol} = 4.056 \text{ mmol}$$

$$\text{glycerol} = (1/8)(4.056) = 0.5070 \text{ mmol} = 46.7 \text{ mg}$$

$$\Rightarrow \text{original solution} = 30.5 \text{ wt \% glycerol}$$



One mole of nitrosobenzene reacts with 4 moles of Cr^{2+} and one mole of nitrobenzene reacts with 6 moles of Cr^{2+} . Let $x = \text{mg}$ of $\text{C}_6\text{H}_5\text{NO}$ and $24.43 - x = \text{mg}$ of $\text{C}_6\text{H}_5\text{NO}_2$.

We can write

$$\frac{4x}{107.112} + \frac{6(24.43 - x)}{123.111} = \text{mmol of Cr}^{2+} = (21.57)(0.05000)$$

$$x = 9.84 \text{ mg} = 40.3\%$$

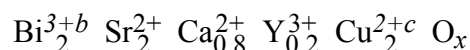
S16-8. 0.1392 g of $\text{KBrO}_3 = 0.8335 \text{ mmol}$ of BrO_3^- which generates $3(0.8335) = 2.501 \text{ mmol}$ of Br_2 according to the reaction $\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$

One mole of excess Br_2 generates one mole of I_2 by the reaction $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$

The I_2 requires 19.18 mL of $0.05000 \text{ M S}_2\text{O}_3^{2-} = 0.9590 \text{ mmol}$ of $\text{S}_2\text{O}_3^{2-}$. Therefore, there must have been $(1/2)(0.9590) = 0.4795 \text{ mmol}$ of $\text{I}_2 = 0.4795 \text{ mmol}$ of excess Br_2 .

The Br_2 that reacted with acetoacetanilide must have been $2.501 - 0.4795 = 2.021 \text{ mmol}$ of Br_2 . Since one mole of Br_2 reacts with one mole of acetoacetanilide there must have been 2.021 mmol of acetoacetanilide, or $(1/2)(2.021) = 1.010 \text{ mmol}$ of $\text{Be}^{2+} = 9.107 \text{ mg}$ of Be .

S16-9. Denote the average oxidation number of Bi as $3+b$ and the average oxidation number of Cu as $2+c$.



$$\text{Positive charge} = 6 + 2b + 4 + 1.6 + 0.6 + 4 + 2c = 16.2 + 2b + 2c$$

$$\text{The charge must be balanced by O}^{2-} \Rightarrow x = 8.1 + b + c$$

$$\text{The formula mass of the superconductor is } 760.37 + 15.9994(8.1+b+c).$$

$$\text{One gram contains } 1/[770.14 + 15.9994(8.1+b+c)] \text{ moles.}$$

Experiment A: Initial $\text{Cu}^+ = 0.1000 \text{ mmol}$; final $\text{Cu}^+ = 0.0522 \text{ mmol}$. Therefore 110.6 mg of superconductor consumed 0.0478 mmol Cu^+ .

$$2 \times \text{mmol Bi}^{5+} + \text{mmol Cu}^{3+} \text{ in } 110.6 \text{ mg superconductor} = 0.0478.$$

Experiment B: Initial $\text{Fe}^{2+} = 0.0500 \text{ mmol}$; final $\text{Fe}^{2+} = 0.0213 \text{ mmol}$. Therefore 143.9 mg of superconductor consumed $0.0287 \text{ mmol Fe}^{2+}$.

$$2 \times \text{mmol Bi}^{5+} \text{ in } 143.9 \text{ mg superconductor} = 0.0287.$$

Normalizing to 1 gram of superconductor gives

Expt A: $2(\text{mmol Bi}^{5+}) + \text{mmol Cu}^{3+}$ in 1 g superconductor = 0.432 2

Expt B: $2(\text{mmol Bi}^{5+})$ in 1 g superconductor = 0.199 4

It is easier not to get lost in the arithmetic if we suppose that the oxidized bismuth is Bi^{4+} and equate one mole of Bi^{5+} to two moles of Bi^{4+} .

Therefore we can rewrite the two equations above as

$$\text{mmol Bi}^{4+} + \text{mmol Cu}^{3+} \text{ in 1 g superconductor} = 0.433 2 \quad (1)$$

$$\text{mmol Bi}^{4+} \text{ in 1 g superconductor} = 0.199 4 \quad (2)$$

Subtracting Equation 2 from Equation 1 gives

$$\text{mmol Cu}^{3+} \text{ in 1 g superconductor} = 0.233 8 \quad (3)$$

Equations 2 and 3 tell us that the stoichiometric relationship in the formula of the superconductor is $b/c = 0.199 4/0.233 8 = 0.852 9$.

Since 1 g of superconductor contains 0.789 4 mmol Cu^{3+} , we can say

$$\frac{\text{mol Cu}^{3+}}{\text{mol solid}} = 2c$$

$$\frac{\text{mol Cu}^{3+} / \text{mol solid}}{\text{gram solid} / \text{mol solid}} = \frac{2c}{760.37 + 15.999 4(8.1 + b + c)}$$

$$\frac{\text{mol Cu}^{3+}}{\text{gram solid}} = \frac{2c}{770.14 + 15.999 4(8.1 + b + c)} = 2.338 \times 10^{-4} \quad (4)$$

Substituting $b = 0.852 9c$ in the denominator of Equation 4 allows us to solve for c :

$$\frac{2c}{770.14 + 15.999 4(8.1 + 1.852 9c)} = 2.338 \times 10^{-4} \Rightarrow c = 0.105_5$$

$$\Rightarrow b = 0.852 9c = 0.090_0$$

The average oxidation numbers are $\text{Bi}^{+3.090_0}$ and $\text{Cu}^{+2.105_5}$ and the formula of the compound is $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8.295_5}$, since the oxygen stoichiometry derived at the beginning of the solution is $x = 8.1 + b + c$.

S16-10. Coefficients of the balanced equations are :

(a) 1, 1 \rightarrow 1

(f) 1, 1 \rightarrow 1, 1, 1

(b) 2, 1, 2 \rightarrow 1, 2, 5

(g) 1, 1 \rightarrow 2, 1, 2

(c) 1, 24, 24 \rightarrow 6, 6, 42, 48, 1

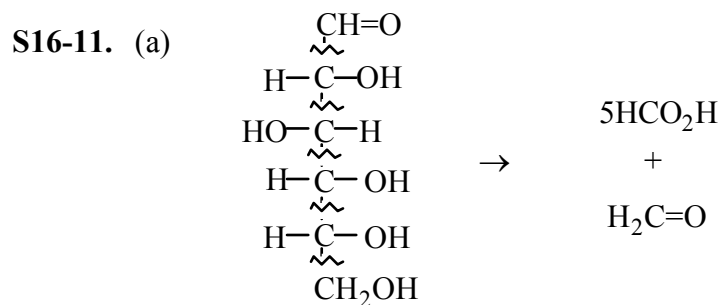
(h) 1, 5, 6 \rightarrow 3, 3

(d) 1, 1, 1 \rightarrow 1, 1

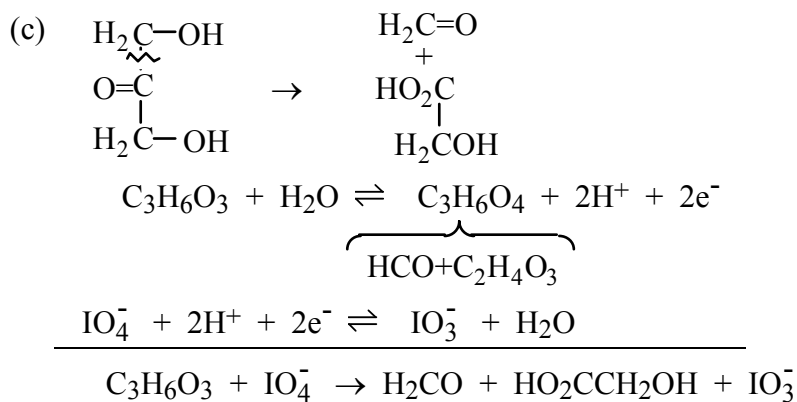
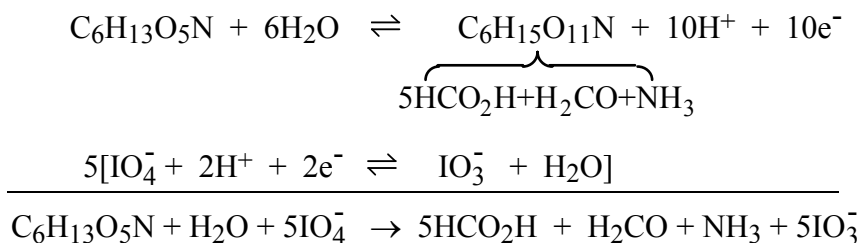
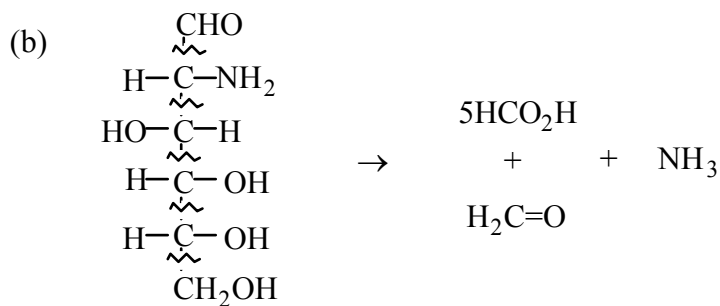
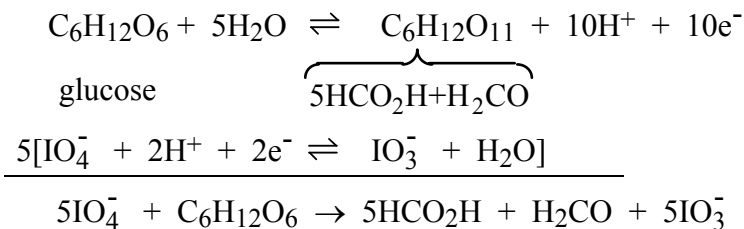
(i) 1, 2, 1 \rightarrow 1, 1, 1

(e) 3, 1, 3 \rightarrow 1, 6, 6

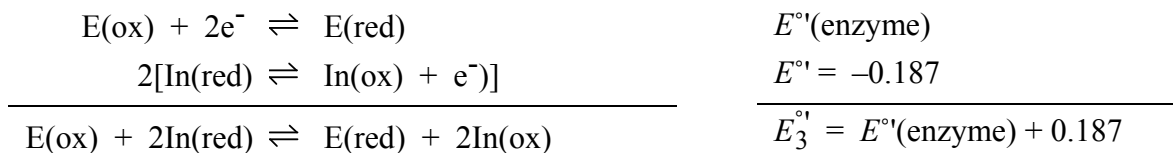
One mole of Be^{3+} requires 228 moles of thiosulfate.



To balance this reaction we can write



S16-12. For the equilibrium between enzyme (E) and indicator (In) we can write



For the net reaction,

$$K = \frac{[\text{E(red)}][\text{In(ox)}]^2}{[\text{E(ox)}][\text{In(red)}]^2} = \frac{(1.80 \times 10^{-5})(3.9 \times 10^{-5})^2}{(4.2 \times 10^{-5})(5.5 \times 10^{-5})^2} = 0.215$$

$$E_3^{\circ'} = \frac{0.05916}{2} \log K = -0.0197 \text{ V}. \quad E^{\circ'}(\text{enzyme}) = E_3^{\circ'} - 0.187 = -0.207 \text{ V}.$$

S16-13. Titration reaction: $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$

0.02046 m KMnO_4 (FM 158.03) contains 0.02046 mol KMnO_4

(= 3.2333 g KMnO_4) per kg of H_2O .

0.933 g of this titrant contains

$$(0.933 \text{ g solution}) \left(\frac{3.2333 \text{ g KMnO}_4}{1003.2 \text{ g solution}} \right) = 3.007 \text{ mg KMnO}_4 = 19.03 \text{ } \mu\text{mol KMnO}_4.$$

The concentration of excess, unreacted KMnO_4 in the pink solution at the end of the titration is given by Beer's law: $[\text{KMnO}_4] = A/(\epsilon l)$, where A is the absorbance (0.018), ϵ is the molar absorptivity ($2.45 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), and l is the cuvet pathlength (1.000 cm).

Using these numbers gives $[\text{KMnO}_4] = 7.35 \text{ } \mu\text{M}$.

If the volume of titrated solution is 500.9 mL, the quantity of unreacted KMnO_4 is

$$(7.35 \text{ } \mu\text{M})(0.5009 \text{ L}) = 3.68 \text{ } \mu\text{mol}.$$

The quantity of KMnO_4 consumed by H_2O_2 is therefore $(19.03 - 3.68) = 15.35 \text{ } \mu\text{mol}$.

From the stoichiometry of the titration reaction, the quantity of H_2O_2 in the unknown is

$$(5/2)(15.35 \text{ } \mu\text{mol}) = 38.38 \text{ } \mu\text{mol}.$$

The concentration of unknown is $38.38 \text{ } \mu\text{mol} / 0.5000 \text{ L} = 76.8 \text{ } \mu\text{M}$.

You could lower the detection limit by using a lower concentration of standard KMnO_4 and a cuvet with a longer pathlength. This allows less KMnO_4 to be delivered and less excess KMnO_4 to be detected. It might be necessary to withdraw aliquots of the titrated solution near the end point and measure the absorbance to find out when the end point has been reached. That is, the reagents could be so dilute that you will not see the color, even though the spectrophotometer will see absorbance with a sufficiently long pathlength cuvet.