Chapter 11

1. By convention, we describe an electrochemical cell from left-to-right and from anode-to-cathode; thus

   (a) The anode is the Pt electrode where the oxidation reaction

   $$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

   takes place; the cathode is the Ag electrode with the reduction reaction

   $$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$$

   (b) The anode is the Ag electrode where the oxidation reaction

   $$Ag(s) + Br^-(aq) \rightleftharpoons AgBr(s) + e^-$$

   takes place; the cathode is the Cd electrode with the reduction reaction

   $$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$$

   (c) The anode is the Pb electrode where the oxidation reaction

   $$Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$$

   takes place; the cathode is the PbO_2 electrode with the reduction reaction

   $$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$$

2. (a) The potential is

   $$E = \left(E^\circ_{Ag^+/Ag} - 0.05916\log\frac{1}{a_{Ag^+}}\right) - \left(E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right)$$

   $$E = 0.7996 - 0.05916\log\frac{1}{0.1} - 0.771 + 0.05916\log\frac{0.015}{0.045}$$

   $$E = -0.059\ \text{V}$$

   (b) The potential is

   $$E = \left(E^\circ_{Cd^{2+}/Cd} - \frac{0.05916}{2}\log\frac{1}{a_{Cd^{2+}}}\right) - \left(E^\circ_{AgBr/Ag} - 0.05916\log a_{Br^-}\right)$$

   $$E = -0.4030 - \frac{0.05916}{2}\log\frac{1}{0.05} - 0.071 + 0.05916\log(1.0)$$

   $$E = -0.512\ \text{V}$$

   (c) The potential is

$$E = \left(E^{\circ}_{PbO_2/PbSO_4} - \frac{0.05916}{2}\log\frac{1}{a_{SO_4^{2-}}a_{H^+}^4}\right) - \left(E^{\circ}_{PbSO_4/Pb} - \frac{0.05916}{2}\log a_{SO_4^{2-}}\right)$$

$$E = 1.690 - \frac{0.05916}{2}\log\frac{1}{(2.0)(2.0)^4} + 0.356 + \frac{0.05916}{2}\log(1.5)$$

$$E = +2.10\ \text{V}$$

3. The Nernst equation for the electrochemical cell is

$$E = \left(E^{\circ}_{I_2/I^-} - \frac{0.05916}{2}\log a_{I^-}^2\right) - \left(E^{\circ}_{AgCl/Ag} - 0.05916\log a_{Cl^-}\right)$$

Substituting in known values and solving

$$0.294 = 0.5355 - \frac{0.05916}{2}\log(x)^2 - 0.2223 + 0.05916\log(0.1)$$

$$0.03996 = -\frac{0.05916}{2}\log(x)^2 = -0.05916\log(x)$$

$$-0.6755 = \log(x)$$

gives the activity of I^- as 0.211.

4. In an acidic solution, zinc dissolves as a result of the following oxidation–reduction reaction

$$Zn(s) + 2H^+(aq) \rightleftharpoons H_2(g) + Zn^{2+}(aq)$$

for which the standard state potential is

$$E^{\circ} = E^{\circ}_{H^+/H_2} - E^{\circ}_{Zn^{2+}/Zn} = 0.000\ \text{V} - (-0.7618\ \text{V}) = 0.7618\ \text{V}$$

Because the reaction's potential is positive, we know that the reaction is thermodynamically favorable under standard state conditions. In principle, we expect that any metal with a positive oxidation potential will show similar behavior.

The qualifying phrase "In principle" reminds us that a thermodynamically favorable reaction may not happen if there are kinetic barriers to the reaction; see the last paragraph of Chapter 6 for a brief discussion of this point.

5. To find the selectivity coefficient, we plot potential on the *y*-axis and the concentration of salicylate, expressed logarithmically, on the *x*-axis; Figure SM11.1 shows the resulting plot, which consists of two linear regions. For smaller concentrations of salicylate, the electrode's potential is nearly constant as it responds to the concentration of benzoate in solution. For larger concentrations of salicylate, the electrode's potential is determined by the concentration of salicylate.

Note we use concentration here in place of activity because we assume that maintaining a common matrix for all standards and samples allow us to fold the activity coefficient's into the Nernst equation's constant term; see the text for more details.

The intersection of the two linear regions gives the concentration of salicylate, log[salicylate] = –3 or 1.0×10^{-3} M salicylate, that yields a potential equal to that for a solution of 0.1 M benzoate; the selectivity coefficient, therefore, is

$$K_{A,I} = \frac{[\text{salicylate}]}{[\text{benzoate}]^{z_A/z_I}} = \frac{1.0 \times 10^{-3}}{(0.1)^{-1/-1}} = 0.010$$

To maintain an error of less than 1%, we require that

$$K_{A,I} \times [\text{benzoate}] \leq 0.01 \times [\text{salicylate}]$$

$$(0.01) \times [\text{benzoate}] \leq (0.01)(1 \times 10^{-5}\ \text{M})$$

$$[\text{benzoate}] \leq 1.0 \times 10^{-5}\ \text{M}$$

6. Cocaine is a weak base alkaloid with a pK_a of 8.64 for its conjugate weak acid. Below a pH of 8, cocaine exists primarily in it protonated weak acid form, to which the electrode's membrane is sensitive. Above a pH of 9, cocaine exists primarily in its unprotonated weak base form; apparently the electrode's membrane is not sensitive to this form of cocaine, which explains why the potential declines sharply when the pH exceeds 8.

7. The potential of the pH electrode is

$$E_{\text{cell}} = K + 0.05916 \log a_{H_3O^+}$$

The inner solution of the ammonia electrode, as shown in Table 11.4, contains a fixed concentration of NH_4^+, for which the acid dissociation constant is

$$K_a = \frac{a_{H_3O^+} a_{NH_3}}{a_{NH_4^+}}$$

Solving the K_a expression for $a_{H_3O^+}$ and substituting back into the equation for the pH electrode's potential gives

$$E_{\text{cell}} = K + 0.05916 \log \frac{K_a a_{NH_4^+}}{a_{NH_3}}$$

$$E_{\text{cell}} = K + 0.05916 \log (K_a a_{NH_4^+}) + 0.05916 \log \frac{1}{a_{NH_3}}$$

$$E_{\text{cell}} = K' - 0.05916 \log a_{NH_3}$$

where

$$K' = K + 0.05916 \log (K_a a_{NH_4^+})$$

In the solution between the two membranes, the activity of NH_3 depends on the activity of NH_4^+, which, in turn, depends on the activity of urea in the outer solution; thus

$$E_{\text{cell}} = K'' - 0.05916 \log a_{\text{urea}}$$

where K'' includes the equilibrium constants for the reactions in the outer solution and the pH of the outer solution.

8. The potential of the pH electrode is

$$E_{\text{cell}} = K' + 0.05916 \log a_{H_3O^+} = K' - 0.05916 \times \text{pH}$$

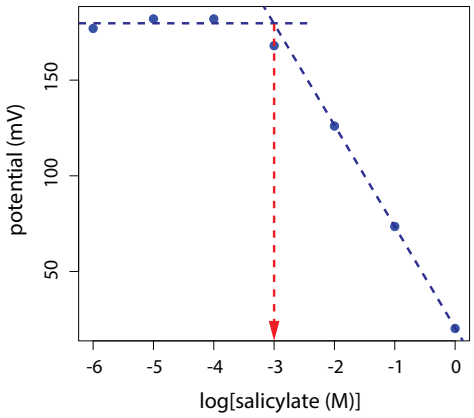

Figure SM11.1 Potential versus concentration data for a salicylate ion-selective electrode in the presence of 0.1 M benzoate. The **blue** dots are the data from Problem 5 and the **blue** dashed lines show the regions where the ISE's potential is determined by the concentration of benzoate or of salicylate. The **red** dashed line shows the concentration of salicylate that yields the same potential as does 0.1 M benzoate.

Solving this equation for pH and substituting into equation 11.15 gives

$$\text{pH} = \frac{K' - E_{\text{cell}}}{0.05916} = Ka_{\text{urea}}$$

which we rearrange to give

$$E_{\text{cell}} = K' - 0.05916Ka_{\text{urea}}$$

What is interesting about this result is that the potential is a linear function of urea's activity when using the membrane electrode in Figure 11.21, but a logarithmic function of urea's activity when using the membrane electrode in Figure 11.20. The potential is a linear function of urea's activity for the membrane electrode in Figure 11.21 because it is related to the kinetics of the enzymatic reaction and the presence within the membrane of a buffer that can maintain a constant buffering strength; see, Ruzicka, J.; Hansen, E. H.; Ghose, A. K.; Mottola, H. A. *Anal. Chem.* **1979**, *51*, 199–203 for further details.

9. We start with the potential of an electrochemical cell that includes a Ag_2S membrane electrode, with the cell's potential defined in terms of the activity of Ag^+

$$E_{\text{cell}} = K + 0.05916 \log a_{Ag^+}$$

Next, we use the complexation reaction between Ag^+ and CN^-

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$$

and its overall formation constant

$$\beta_2 = \frac{a_{Ag(CN)_2^-}}{a_{Ag^+} a_{CN^-}^2}$$

to rewrite the electrochemical cell's potential in terms of the activity of CN^-

$$E_{\text{cell}} = K + 0.05916 \log \frac{a_{Ag(CN)_2^-}}{\beta_2 (a_{CN^-})^2} = K' - 0.05916 \log (a_{CN^-})^2$$

where K' includes K, β_2, and the activity of $Ag(CN)_2^-$, all of which are constant. Finally, we use the acid-base reaction for HCN

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

and its acid dissociation constant

$$K_a = \frac{a_{H_3O^+} a_{CN^-}}{a_{HCN}}$$

to rewrite the electrochemical cell's potential in terms of the activity of HCN

$$E_{\text{cell}} = K' - 0.05916 \log \frac{(K_a)^2 (a_{HCN})^2}{(a_{H_3O^+})^2}$$

$$E_{cell} = K'' - 2 \times 0.05916 \log a_{HCN}$$

where K'' includes K', K_a, and the activity of H_3O^+, all of which are constant. Our final equation suggests that a 10-fold increase in the activity of HCN will decrease the potential by 0.118 V, or 118 mV. If you examine Figure 2 of US Patent 3859191, you will see that the actual change in potential is approximately –125 mV per 10-fold change in molar concentration, which is in reasonable agreement with our derivation.

10. (a) Figure SM11.2 shows a plot of the data, which is linear for all but the first point and the last point; thus, the linear range is

$$-5.00 \leq \log[\text{penicillin}] \leq -2.70$$

or

$$1.0 \times 10^{-5}\ \text{M} \leq [\text{pencillin}] \leq 2.0 \times 10^{-3}\ \text{M}$$

(b) A linear regression using the data within the calibration curve's linear range gives a calibration equation of

$$E = 331.4\ \text{mV} + 47.76\ \text{mV} \times \log[\text{pencillin}]$$

(c) Substituting the sample's potential into the calibration equation gives log[penicillin] as –3.97 and the concentration of penicillin as 1.1×10^{-4} M.

11. Figure SM11.3 shows the calibration data—note that the *x*-axis is $\log[K^+]$, not $[K^+]$—and the resulting calibration curve, the equation for which is

$$E = 67.56 + 42.36 \times \log[K^+]$$

Substituting the sample's potential into the calibration curve's equation gives $\log[K^+]$ as –0.389 and $[K^+]$ as 0.41 mM. This is the concentration in the sample as analyzed; because the original serum sample was diluted by a factor of 10× (1.00 mL to 10.00 mL), the concentration of K^+ in the original sample is 4.1 mM.

12. Figure SM11.4 shows a plot of the pH electrode's potential on the y-axis versus pH on the x-axis, along with the calibration curve, the equation for which the equation is

$$E = 427.4\ \text{mV} - (65.46\ \text{mV}) \times \text{pH}$$

Substituting into the calibration equation the measured potential for each sample gives the following results:

tomato juice: pH of 4.0

tap water: pH of 6.9

coffee: pH of 4.7

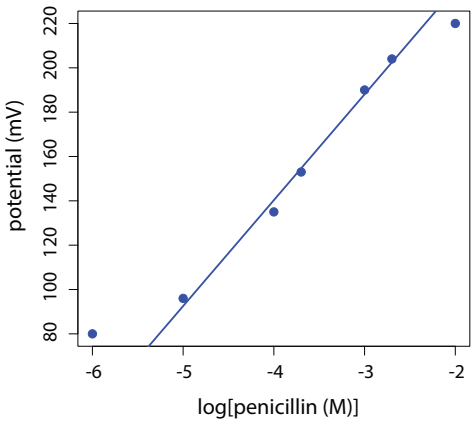

Figure SM11.2 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 10. The calibration curve is restricted to log[penicillin] values between –2.70 and –5.00.

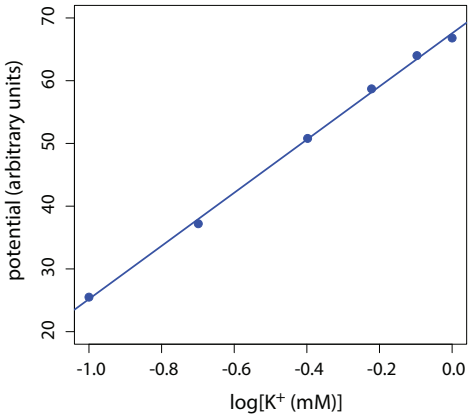

Figure SM11.3 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 11.

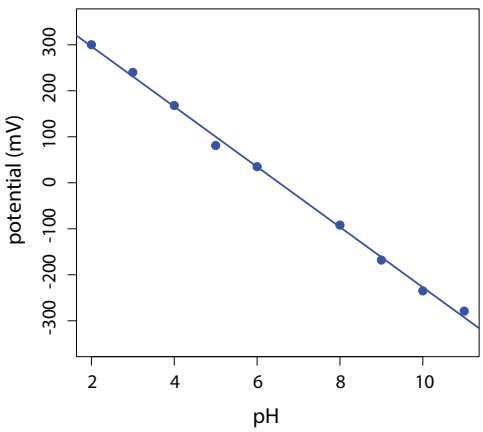

Figure SM11.4 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 12.

13. The following two equations apply to this standard addition

$$0.102 = K - 0.05916\log[NO_2^-]$$

$$0.089 = K - 0.05916\log\left\{\begin{array}{l}[NO_2^-]\times\dfrac{25.00\text{ mL}}{26.00\text{ mL}} + \\ \quad\dfrac{200.0\text{ mg }NO_2^-}{\text{L}}\times\dfrac{1.00\text{ mL}}{26.00\text{ mL}}\end{array}\right\}$$

Subtracting the second equation from the first equation and cleaning up the terms inside the second equation's brackets, leaves us with

$$0.013 = 0.05916\log\left\{\begin{array}{l}0.9615[NO_2^-] + \\ \quad\dfrac{7.692\text{ mg }NO_2^-}{\text{L}}\end{array}\right\} - 0.05916\log[NO_2^-]$$

Finally, solving for $[NO_2^-]$ gives

$$0.013 = 0.05916\log\left\{\frac{0.9615[NO_2^-] + \dfrac{7.692\text{ mg }NO_2^-}{\text{L}}}{[NO_2^-]}\right\}$$

$$1.659 = \frac{0.9615[NO_2^-] + \dfrac{7.692\text{ mg }NO_2^-}{\text{L}}}{[NO_2^-]}$$

$$1.659[NO_2^-] = 0.9615[NO_2^-] + \frac{7.692\text{ mg }NO_2^-}{\text{L}}$$

$$0.6795[NO_2^-] = \frac{7.692\text{ mg }NO_2^-}{\text{L}}$$

$$[NO_2^-] = \frac{11.0\text{ mg }NO_2^-}{\text{L}}$$

14. To determine the concentration of F^- in either the sample of tap water or the sample of toothpaste, we must find an appropriate way to plot the standard additions data. We begin with the Nernst equation

$$E = K - 0.05916\log\left\{C_{\text{samp}}\times\frac{V_{\text{samp}}}{V_{\text{tot}}} + C_{\text{std}}\times\frac{V_{\text{std}}}{V_{\text{tot}}}\right\}$$

where C_{samp} is the concentration of F^- in the original sample, V_{samp} is the volume of the original sample, C_{std} is the concentration of F^- in the standard, V_{std} is the volume of standard, and V_{tot} is the sum of V_{samp} and V_{std}. Rearranging and dividing through by –0.05916 gives

$$\frac{K-E}{0.05916} = \log\left\{C_{\text{samp}}\times\frac{V_{\text{samp}}}{V_{\text{tot}}} + C_{\text{std}}\times\frac{V_{\text{std}}}{V_{\text{tot}}}\right\}$$

Taking the inverse log of both sides of the equation gives

$$10^{\frac{K-E}{0.05916}} = \left\{C_{\text{samp}}\times\frac{V_{\text{samp}}}{V_{\text{tot}}} + C_{\text{std}}\times\frac{V_{\text{std}}}{V_{\text{tot}}}\right\}$$

Expanding the term on the equation's left

$$10^{\frac{K}{0.05916}}\times 10^{\frac{-E}{0.05916}} = \left\{C_{\text{samp}}\times\frac{V_{\text{samp}}}{V_{\text{tot}}} + C_{\text{std}}\times\frac{V_{\text{std}}}{V_{\text{tot}}}\right\}$$

and rearranging leaves us with

$$10^{\frac{-E}{0.05916}} = 10^{\frac{-K}{0.05916}}\left\{C_{\text{samp}} \times \frac{V_{\text{samp}}}{V_{\text{tot}}} + C_{\text{std}} \times \frac{V_{\text{std}}}{V_{\text{tot}}}\right\}$$

$$10^{\frac{-E}{0.05916}} = \frac{10^{\frac{-K}{0.05916}} C_{\text{samp}} V_{\text{samp}}}{V_{\text{tot}}} + \frac{10^{\frac{-K}{0.05916}} C_{\text{std}} V_{\text{std}}}{V_{\text{tot}}}$$

$$V_{\text{tot}} 10^{\frac{-E}{0.05916}} = 10^{\frac{-K}{0.05916}} C_{\text{samp}} V_{\text{samp}} + 10^{\frac{-K}{0.05916}} C_{\text{std}} V_{\text{std}}$$

This last equation is the one we seek as it shows us that a plot of $V_{\text{tot}} \times 10^{-E/0.05916}$ versus V_{std} is a straight-line with a slope, b_1, that is equal to

$$b_1 = C_{\text{std}} \times 10^{-K/0.05916}$$

and a y-intercept, b_0, that is equal to

$$b_0 = C_{\text{samp}} V_{\text{samp}} \times 10^{-K/0.05916}$$

Dividing the equation for b_0 by the equation for b_1 and rearranging gives us a way to determine the concentration of F^- in our original sample

$$C_{\text{samp}} = \frac{b_0 C_{\text{std}}}{b_1 V_{\text{samp}}}$$

Now we can turn our attention to the two sets of data.

(a) To analyze the data for the sample of tap water, we first calculate the average potential for each standard addition and then calculate the y-axis values, $V_{\text{tot}} \times 10^{-E/0.05916}$, expressing volume in liters. Figure SM11.5a shows the calibration data and the calibration curve, for which the calibration equation is

$$V_{\text{tot}} 10^{\frac{-E}{0.05916}} = 1.115\,\text{L} + 4068 V_{\text{std}}$$

Substituting into the equation for C_{samp} gives the concentration of F^- as analyzed as 0.548 ppm, or as 1.10 ppm in the tap water sample.

(b) To analyze the data for the sample of toothpaste, we first calculate the average potential for each standard addition and then calculate the y-axis values, $V_{\text{tot}} \times 10^{-E/0.05916}$, expressing volume in liters. Figure SM11.5b shows the calibration data and the calibration curve, for which the calibration equation is

$$V_{\text{tot}} 10^{\frac{-E}{0.05916}} = 0.1513\,\text{L} + 364.9 V_{\text{std}}$$

Substituting into the equation for C_{samp} gives the concentration of F^- as 2.073 ppm in the sample as analyzed. Accounting for the sample's preparation gives the concentration of F^- in the toothpaste as

$$\frac{2.073\ \text{mg F}^-/\text{L} \times 0.1000\ \text{L} \times \frac{1\ \text{g}}{1000\ \text{mg}}}{0.3619\ \text{g sample}} \times 100 = 0.0573\%\text{w/w F}^-$$

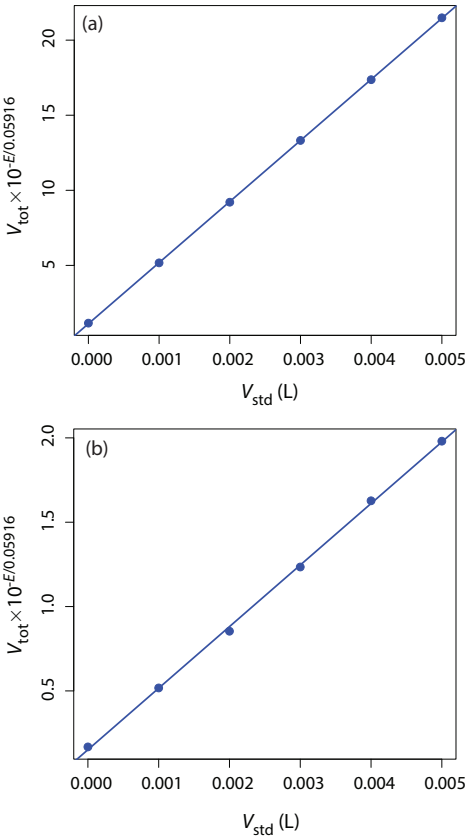

Figure SM11.5 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 14: (a) tap water, and (b) toothpaste.

15. When using external standards, we want to ensure that the matrix of the standards matches the matrix of the samples; thus, we should add sufficient NaCl to each standard solution of KI to match that of the samples. When using internal standards, we prepare a single sample of iodized salt and then spike it with known volumes of a standard solution of KI; there is no need to add NaCl to the standard solution of KI as adding a small volume of the standard to a larger volume of sample will not change significantly the sample's matrix.

16. We can decrease the time needed to oxidize or reduce all the analyte in a sample by (a) increasing the working electrode's surface area, which allows more of the analyte to undergo oxidation or reduction in any unit of time; by (b) using a smaller volume of sample, which means there is less analyte to oxidize or reduce; or by (c) increasing the rate at which we stir the sample as this brings the analyte to the working electrode more quickly and removes more quickly the products of the analyte's oxidation or reduction reaction.

For (c), remember that an oxidation or a reduction reaction takes place at the electrode's surface only.

17. The reduction of picric acid to triaminophenol, involves 18 electrons; thus, using Faraday's law, the moles of picric acid in the sample as analyzed is

$$N_A = \frac{Q}{nF} = \frac{21.67\ \text{C}}{\frac{18\ \text{mol e}^-}{\text{mol}} \times \frac{96485\ \text{C}}{\text{mol } e^-}} = 1.248 \times 10^{-5}\ \text{mol}$$

After accounting for the sample's preparation, we find that the original sample's purity is

$$\frac{1.248 \times 10^{-5}\ \text{mol} \times \frac{1000.0\ \text{mL}}{10.00\ \text{mL}} \times \frac{229.10\ \text{g}}{\text{mol}}}{0.2917\ \text{g sample}} \times 100 = 98.0\%\ \text{pure}$$

18. For a coulometric titration, the moles of analyte, N_A, the applied current, i, and the end point time, t_e, are related by the equation

$$it_e = nFN_A$$

where n is the number of electrons in the oxidation-reduction reaction, which, for the coulometric titration of H_2S by I_3^-, is 2 (see Table 11.9 for the titrant's reaction). Solving for N_A, we find that the sample as analyzed contains

Remember that 1 C is equivalent to 1 A•s.

$$N_A = \frac{it_e}{nF} = \frac{(0.0846\ \text{A})(386\ \text{s})}{\frac{2\ \text{mol } e^-}{\text{mol } H_2S} \times \frac{96485\ \text{C}}{\text{mol } e^-}} = 1.692 \times 10^{-4}\ \text{mol } H_2S$$

After accounting for the sample's preparation, we find that the concentration of H_2S in the original sample is

$$\frac{1.692 \times 10^{-4}\ \text{mol } H_2S \times \frac{34.08\ \text{g } H_2S}{\text{mol } H_2S} \times \frac{10^6\ \mu\text{g}}{\text{g}}}{50.00\ \text{mL}} = \frac{115\ \mu\text{g } H_2S}{\text{mL}}$$

19. For this titration to work, the reaction's potential must be positive; thus, we know that under standard-state conditions

$$E^\circ_{rxn} = E^\circ_{I_3^-/I^-} - E^\circ_{H_3AsO_4/H_3AsO_3} = 0.536\text{ V} - 0.559\text{ V} = -0.023\text{ V}$$

the reaction's potential is negative and unfavorable. Because the potential for the H_3AsO_4/H_3AsO_3 half-reaction

$$H_3AsO_4(aq) + 2H^+(aq) + 2e^- \rightleftharpoons H_3AsO_3(aq) + H_2O(l)$$

depends on pH

$$E_{H_3AsO_4/H_3AsO_3} = E^\circ_{H_3AsO_4/H_3AsO_3} - \frac{0.05916}{2}\log\frac{[H_3AsO_3]}{[H_3AsO_4][H^+]^2}$$

it seems likely that the reaction must be more favorable at less acidic pH levels. To demonstrate this, let's assume that the concentrations of H_3AsO_3 and of H_3AsO_4 are equal and at their standard state values so that we can explore the affect on the potential of non-standard state concentrations of H^+ only; under this condition, the potential for the reaction is

$$E^\circ_{rxn} = 0.536\text{ V} - \left\{0.559\,V - \frac{0.05916}{2}\log\frac{1}{[H^+]^2}\right\}$$

$$E^\circ_{rxn} = -0.023\text{ V} - 0.05916\log[H^+]$$

$$E^\circ_{rxn} = -0.023\text{ V} + 0.05916\text{pH}$$

Setting E°_{rxn} to zero and solving for pH shows us that the reaction is favorable for any pH greater than 0.39. For example, the pH of 6 M HCl is approximately –0.8, which means the reaction is unfavorable in a strongly acidic solution. Maintaining a more neutral pH provides for a more positive potential; thus, at a pH of 3 the potential is 0.154 V, but at a pH of 7 the potential is 0.391 V.

20. First we calculate the moles of acrylonitrile in our sample, which is

$$0.594\text{ g} \times \frac{1\text{ mol}}{53.06\text{ g}} \times \frac{1.00\text{ mL}}{1000.0\text{ mL}} = 1.119 \times 10^{-5}\text{ mol}$$

Next, we use Faraday's law to calculate the number of electrons

$$n = \frac{C}{FN_A} = \frac{1.080\text{ C}}{(96485\text{ C/mol }e^-)(1.119 \times 10^{-5}\text{ mol acrylonitrile})}$$

$$n = 1.00\text{ mol }e^-\text{/mol acrylonitrile}$$

21. (a) Let's begin with the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]_{x=0}}{[Fe^{3+}]_{x=0}}$$

using the subscript $x = 0$ to remind us that the potential is determined by the concentrations of Fe^{3+} and Fe^{2+} at the electrode's surface. For

the reduction at the cathode of Fe^{3+}, we know from equation 11.38 that the current is proportional to the difference between its concentration in bulk solution and its concentration at the electrode's surface

$$i = K_{Fe^{3+}}\{[Fe^{3+}]_{bulk} - [Fe^{3+}]_{x=0}\}$$

with a cathodic limiting current of

$$i_{l,c} = K_{Fe^{3+}}[Fe^{3+}]_{bulk}$$

Combining these two equations and solving for $[Fe^{3+}]_{bulk}$ gives

$$i = i_{l,c} - K_{Fe^{3+}}[Fe^{3+}]_{x=0}$$

$$[Fe^{3+}]_{x=0} = \frac{i_{l,c} - i}{K_{Fe^{3+}}}$$

The minus sign is included here because the cathodic current and the anodic current have opposite signs.

For the oxidation at the anode of Fe^{2+}, a similar treatment gives

$$i = -K_{Fe^{2+}}\{[Fe^{2+}]_{bulk} - [Fe^{2+}]_{x=0}\}$$

$$i_{l,a} = -K_{Fe^{2+}}[Fe^{2+}]_{bulk}$$

$$i = i_{l,a} + K_{Fe^{2+}}[Fe^{2+}]_{x=0}$$

$$[Fe^{2+}]_{x=0} = \frac{i - i_{l,a}}{K_{Fe^{2+}}}$$

Substituting back into the Nernst equation gives

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{\frac{i - i_{l,a}}{K_{Fe^{2+}}}}{\frac{i_{l,c} - i}{K_{Fe^{3+}}}}$$

which we rearrange to arrive at our final equation

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{i - i_{l,a}}{i_{l,c} - i}$$

(b) When the current, i, is zero, the equation for the potential is

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{-i_{l,a}}{i_{l,c}}$$

The cathodic and the anodic limiting currents, as we showed earlier, are related to the bulk concentrations of Fe^{3+} and of Fe^{2+}; thus

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{K_{Fe^{2+}}[Fe^{2+}]_{bulk}}{K_{Fe^{3+}}[Fe^{3+}]_{bulk}}$$

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{K_{Fe^{2+}}}{K_{Fe^{3+}}} - 0.05916\log\frac{[Fe^{2+}]_{bulk}}{[Fe^{3+}]_{bulk}}$$

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]_{bulk}}{[Fe^{3+}]_{bulk}}$$

$$E = 0.771\text{ V} - 0.05916\log\frac{0.050\text{ mM}}{0.100\text{ mM}} = 0.789\text{ V}$$

22. Figure SM11.6 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = 0.1478\,\mu A + (0.01967\mu A/\mu g) \times m_S$$

where m_S is the μg S used to prepare a standard solution. Substituting in the sample's peak current gives a result of 82.5 μg S; as this is the mass of sulfur in the 1.000-mL sample, the concentration of sulfur in the sample is 82.5 μg/mL.

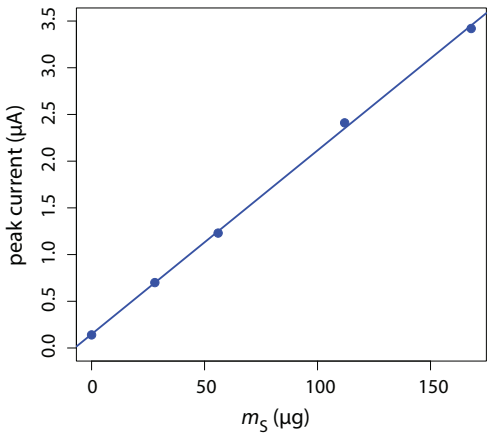

Figure SM11.6 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 22.

23. Figure SM11.7 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = 3.2\mu A + (62.10\,\mu A/M) \times C_{K_3Fe(CN)_6}$$

Substituting in the sample's limiting current gives the concentration of $K_3Fe(CN)_6$ as 7.10 mM as analyzed; the purity of the original sample, therefore, is

$$\frac{\dfrac{7.10 \times 10^{-3}\ \text{mol}}{\text{L}} \times 0.1000\ \text{L} \times \dfrac{329.25\ \text{g}}{\text{mol}}}{0.246\ \text{g sample}} \times 100 = 95.0\%\ \text{pure}$$

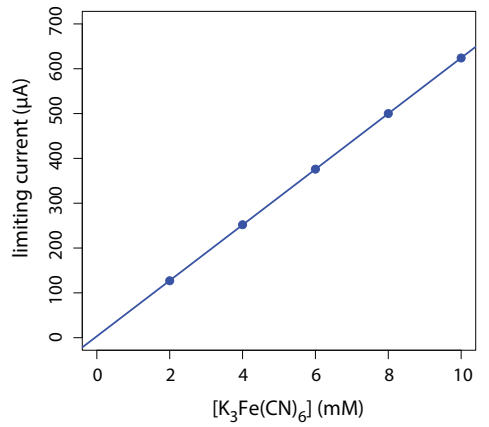

Figure SM11.7 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 23.

24. Letting C_{Sb} represent the concentration of antimony in the vial after soaking the swab in 5.00 mL of 4 M HCl, we have the following two equations for the sample and the standard addition

$$0.38 = k\left\{C_{Sb} \times \frac{4.00\ \text{mL}}{4.10\ \text{mL}}\right\}$$

$$1.14 = k\left\{C_{Sb} \times \frac{4.00\ \text{mL}}{4.20\ \text{mL}} + (5.00 \times 10^2\ \text{ppb}) \times \frac{0.100\ \text{mL}}{4.20\ \text{mL}}\right\}$$

Solving both equations for k and setting them equal to each other gives

$$\frac{0.38}{C_{Sb} \times \dfrac{4.00\ \text{mL}}{4.10\ \text{mL}}} = \frac{1.14}{C_{Sb} \times \dfrac{4.00\ \text{mL}}{4.20\ \text{mL}} + 11.90}$$

which we solve for C_{Sb}

$$0.3619C_{Sb} + 4.522 = 1.112C_{Sb}$$

$$0.7501C_{Sb} = 4.522$$

$$C_{Sb} = 6.03\ \text{ppb Sb}$$

This is the concentration of antimony in the sample as analyzed. The mass of antimony recovered from the suspect's hand is

$$m_{Sb} = \frac{6.03\ \text{ng Sb}}{\text{mL}} \times 5.00\ \text{mL} = 30.2\ \text{ng Sb}$$

25. For the internal standard we have the following relationship between current and concentration

$$\frac{i_{Tl}}{i_{Zn}} = \frac{3.19\,\mu A}{5.71\,\mu A} = K \times \frac{C_{Tl}}{C_{Zn}} = K \times \frac{2.50 \times 10^{-5}\,M}{5.00 \times 10^{-5}\,M}$$

Solving for K gives its value as 1.117. For the sample, we have the following equation that relates current to concentration

$$\frac{20.2\,\mu A}{12.3\,\mu A} = 1.117 \times \frac{C_{Tl}}{5.00 \times 10^{-4}\,M \times \frac{25.00\,mL}{50.00\,mL}}$$

which gives the concentration of thallium as 3.68×10^{-4} M in the sample as analyzed; the concentration of thallium in the original sample, therefore, is

$$\frac{\left\{\frac{3.68 \times 10^{-4}\,mol}{L} \times \frac{50.00\,mL}{25.00\,mL} \times 0.5000\,L \times \frac{204.38\,g}{mol}\right\}}{8.713\,g\ sample} \times 100 = 0.863\%w/w\ Tl$$

26. We begin by letting C_{AA} and C_C represent the concentration of ascorbic acid and the concentration of caffeine, respectively, in the 100-mL volumetric flask. For the analysis of ascorbic acid we have the following two equations for the sample and the standard addition

$$1.40 = k_{AA}\left\{C_{AA} \times \frac{0.500\,mL}{20.50\,mL}\right\}$$

$$2.80 = k_{AA}\left\{C_{AA} \times \frac{0.500\,mL}{21.00\,mL} + (250.0\,ppm) \times \frac{0.500\,mL}{21.00\,mL}\right\}$$

Solving both equations for k_{AA}, setting them equal to each other, and solving for C_{Sb} gives

$$\frac{1.40}{C_{AA} \times \frac{0.500\,mL}{20.50\,mL}} = \frac{2.80}{C_{AA} \times \frac{0.500\,mL}{21.00\,mL} + 5.952}$$

$$0.0333C_{AA} + 8.333 = 0.0683C_{AA}$$

$$0.035C_{AA} = 8.333$$

$$C_{AA} = 238\,ppm$$

This is the concentration of ascorbic acid in the sample as analyzed; the mass of ascorbic acid in the original tablet is

$$\frac{238\,mg\ AA}{L} \times 0.1000\,L \times \frac{0.9183\,g}{0.5630\,g} = 38.8\,mg\ AA$$

For the analysis of caffeine we have the following two equations for the sample and the standard addition

$$3.88 = k_C\left\{C_C \times \frac{0.500\,mL}{20.50\,mL}\right\}$$

$$8.02 = k_C\left\{C_C \times \frac{0.500\text{ mL}}{21.00\text{ mL}} + (200.0\text{ ppm}) \times \frac{0.500\text{ mL}}{21.00\text{ mL}}\right\}$$

Solving both equations for k_C, setting them equal to each other, and solving for C_C gives

$$\frac{3.88}{C_C \times \frac{0.500\text{ mL}}{20.50\text{ mL}}} = \frac{8.02}{C_C \times \frac{0.500\text{ mL}}{21.00\text{ mL}} + 4.762}$$

$$0.0924C_C + 18.477 = 0.1956C_C$$

$$0.1032C_C = 18.477$$

$$C_C = 179\text{ ppm}$$

This is the concentration of ascorbic acid in the sample as analyzed; the mass of ascorbic acid in the original tablet is

$$\frac{179\text{ mg C}}{\text{L}} \times 0.1000\text{ L} \times \frac{0.9183\text{ g}}{0.5630\text{ g}} = 29.2\text{ mg C}$$

27. Figure SM11.8 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = -5.600 + (1.772\text{ ppb}^{-1}) \times C_{Sn^{4+}}$$

Substituting in the sample's limiting current gives the concentration of Sn^{4+} as 75.5 ppb as analyzed; the concentration of Sn^{4+} in the original sample, therefore, is

$$75.5\text{ ppb} \times \frac{1\text{ ppm}}{1000\text{ ppb}} \times \frac{30.00\text{ mL}}{0.500\text{ mL}} \times \frac{22.00\text{ mL}}{2.00\text{ mL}} = 49.8\text{ ppm}$$

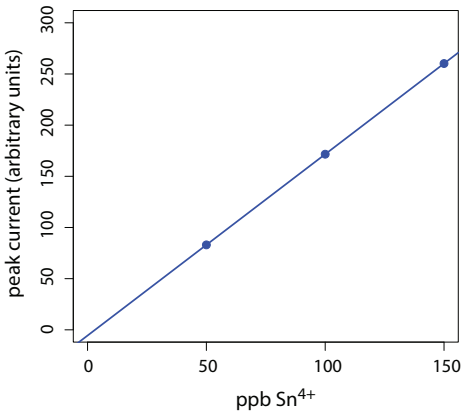

Figure SM11.8 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 27.

28. Figure SM11.9 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = -0.490 + (8.615\text{ mg}^{-1} \cdot 100\text{ mL}) \times C_{glucose}$$

Substituting in the sample's current gives the concentration of glucose as 2.796 mg/100 mL as analyzed; the concentration of glucose in the original sample, therefore, is

$$\frac{2.796\text{ mg}}{100\text{ mL}} \times \frac{10.00\text{ mL}}{2.00\text{ mL}} = \frac{14.0\text{ mg}}{100\text{ mL}}$$

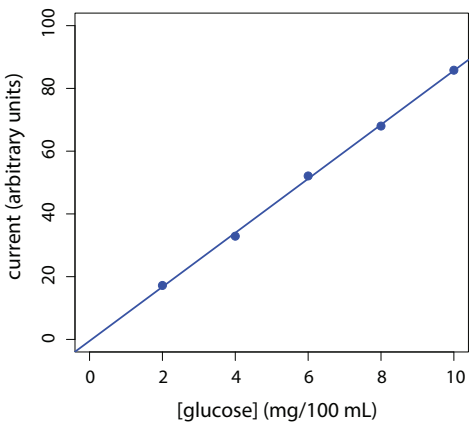

Figure SM11.9 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 28.

29. First, using the equation $i = kC$, we convert the peak currents and concentrations for each analyte at each potential into values of k, which we gather together in the following table (units: μg^{-1} mL)

analyte	k at –0.385 V	k at –0.455 V	k at –0.557 V
Pb^{2+}	26.1	2.9	0
Tl^{+}	3.9	11.75	1.6
In^{3+}	0	0	57.25

Because In^{3+} does not contribute to the current when the potential is –0.385 V or –0.455 V, we can use the sample's currents at these potentials to determine the concentration of Pb^{2+} and of Tl^{+} by solving the following pair of simultaneous equations

$$60.6 = (26.1\ \mu g^{-1}\ mL)\, C_{Pb^{2+}} + (3.9\ \mu g^{-1}\ mL)\, C_{Tl^{+}}$$

$$28.8 = (2.9\ \mu g^{-1}\ mL)\, C_{Pb^{2+}} + (11.75\ \mu g^{-1}\ mL)\, C_{Tl^{+}}$$

Multiplying the second equation by 26.1/2.9 and subtracting it from the first equation leaves us with

$$-198.6 = -(101.85\ \mu g^{-1}\ mL)\, C_{Tl^{+}}$$

$$C_{Tl^{+}} = 1.95\ \mu g/mL \approx 2.0\ \mu g/mL$$

Substituting back into the first of the simultaneous equations a concentration for Tl^{+} of 1.95 μg/mL gives the concentration of Pb^{2+} as

$$C_{Pb^{2+}} = \frac{60.6 - (3.9\ \mu g^{-1}\ mL)(1.95\ \mu g/mL)}{26.1\ \mu g^{-1}\ mL} = 2.03\ \mu g/mL$$

$$C_{Pb^{2+}} \approx 2.0\ \mu g/mL$$

At a potential of –0.557 V, the current is

$$54.1 = (57.25\ \mu g^{-1}\ mL)\, C_{In^{3+}} + (1.6\ \mu g^{-1}\ mL)\, C_{Tl^{+}}$$

Substituting in the concentration of Tl^{+} and solving for the concentration of In^{3+} gives

$$C_{In^{3+}} = \frac{54.1 - (1.6\ \mu g^{-1}\ mL)(1.95\ \mu g/mL)}{57.25\ \mu g^{-1}\ mL} = 0.89\ \mu g/mL$$

30. Figure SM11.10 shows how the method's sensitivity changes as a function of pH. Superimposed on the *x*-axis is a ladder diagram for NH_4^+. The sudden drop in sensitivity above a pH of 8.3 corresponds to the conversion of NH_4^+ to NH_3; however, the increase in the sensitivity from a pH of 6.2 to a pH of 8.3 must be a function of the enzyme's properties as the concentration of NH_4^+ is the same over this range of pH values.

31. (a) The following relationships exist between the eight measurements (A – H) and the seven groups (I – VII) into which the trace metals are divided

(A) ASV-labile metals after filtration: I + II + III

(B) total metals after filtration: I + II + III + IV + V + VI + VII

(C) ASV-labile metals after ion-exchange: II + III

(D) total metals after ion-exchange: II + III + VI + VII

(E) ASV-labile metals after UV: I + II + III + IV + VI

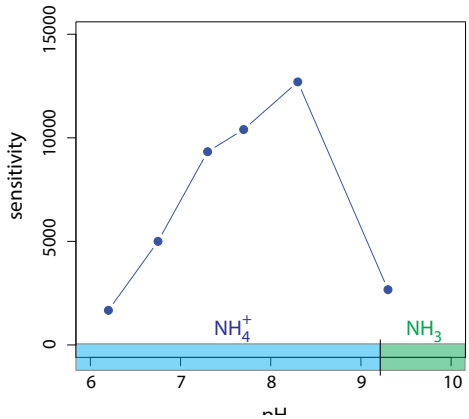

Figure SM11.10 The sensitivity of an amperometric biosensor for NH_4^+ over the pH range 6.2 to 9.3. Superimposed on the x-axis is a ladder diagram for NH_4^+, which shows its weak acid form in **blue** and its weak base form in **green**.

(F) total metals after UV: I + II + III + IV + V + VI + VII

(G) ASV-labile metals after ion-exchange and UV: III

(H) total metals after ion-exchange and UV: III + VII

Using these eight measurements, the following set of equations define each metal ion's total concentration, C_{tot}, and the concentration of the metal ion in each of the seven groups

$C_{tot} = (B + F)/2$

$I = A - C$

$II = C - G$

$III = G$

$IV = E - A - D + C + H - G$

$V = C_{tot} - E - H + G$

$VI = D - C - H + G$

$VII = H - G$

(b) For Cd^{2+}, we have

$C_{tot} = (0.28 + 0.28)/2 = 0.28$ ppb

$I = 0.24 - 0.21 = 0.03$ ppb

$II = 0.21 - 0.00 = 0.21$ ppb

$III = 0.00$ ppb

$IV = 0.26 - 0.24 - 0.26 + 0.21 + 0.02 - 0.00 = -0.01$ ppb

$V = 0.28 - 0.26 - 0.02 + 0.00 = 0$ ppb

$VI = 0.26 - 0.21 - 0.02 + 0.00 = 0.03$ ppb

$VII = 0.02 - 0.00 = 0.02$ ppb

and for Pb^{2+}, we have

$C_{tot} = (0.50 + 0.50)/2 = 0.50$ ppb

$I = 0.39 - 0.33 = 0.06$ ppb

$II = 0.33 - 0.00 = 0.33$ ppb

$III = 0.00$ ppb

$IV = 0.37 - 0.39 - 0.43 + 0.33 + 0.12 - 0.00 = 0.00$ ppb

$V = 0.50 - 0.37 - 0.12 + 0.00 = 0.01$ ppb

$VI = 0.43 - 0.33 - 0.12 + 0.00 = -0.02$ ppb

$VII = 0.12 - 0.00 = 0.12$ ppb

and for Cu^{2+}, we have

$C_{tot} = (0.40 + 0.43)/2 = 0.415$ ppb

$I = 0.26 - 0.17 = 0.09$ ppb

Be sure to convince yourself that these equations are correct. For example

$$A = I + II + III$$

and

$$C = II + III$$

which makes

$$A - C = I + II + III - II - III = I$$

$$\text{II} = 0.17 - 0.00 = 0.17 \text{ ppb}$$

$$\text{III} = 0.00 \text{ ppb}$$

$$\text{IV} = 0.33 - 0.26 - 0.24 + 0.17 + 0.10 - 0.00 = 0.10 \text{ ppb}$$

$$\text{V} = 0.415 - 0.33 - 0.10 + 0.00 = -0.015 \text{ ppb}$$

$$\text{VI} = 0.24 - 0.17 - 0.10 + 0.00 = -0.03 \text{ ppb}$$

$$\text{VII} = 0.10 - 0.00 = 0.10 \text{ ppb}$$

Several of the concentrations have negative values, which, of course, is not possible; these values, which range from –0.03 to –0.01 suggest that concentrations of ±0.03 are the result of random error in the measurement process.

Based on our results, it appears that Cd^{2+} is present primarily as strong, labile organic complexes or labile metals absorbed on organic solids (Group II); that Pb^{2+} is present primarily as free metal ions and weak, labile organic and inorganic complexes (Group I), as strong, labile organic complexes or labile metals absorbed on organic solids (Group II), and as strong nonlabile inorganic complexes or as non-labile metals absorbed on inorganic solids (Group VII); and that Cu^{2+} is present primarily as free metal ions and weak, labile organic and inorganic complexes (Group I), as strong, labile organic complexes or labile metals absorbed on organic solids (Group II), as weaker nonlabile organic complexes (Group IV), and as strong nonlabile inorganic complexes or as nonlabile metals absorbed on inorganic solids (Group VII).

32. Letting C_{Cu} represent the concentration of copper in seawater, we have the following two equations for the sample and the standard addition

$$26.1 = k\left\{C_{Cu} \times \frac{20.00 \text{ mL}}{25.00 \text{ mL}}\right\}$$

$$38.4 = k\left\{C_{Cu} \times \frac{20.00 \text{ mL}}{25.00 \text{ mL}} + (5.00\ \mu\text{M}) \times \frac{0.10 \text{ mL}}{25.00 \text{ mL}}\right\}$$

Solving both equations for k and setting them equal to each other

$$\frac{26.1}{C_{Cu} \times \frac{20.00 \text{ mL}}{25.00 \text{ mL}}} = \frac{38.4}{C_{Cu} \times \frac{20.00 \text{ mL}}{25.00 \text{ mL}} + 0.0200\ \mu\text{M}}$$

$$20.88 C_{Cu} + 0.522\ \mu\text{M} = 30.72 C_{Cu}$$

$$9.84 C_{Cu} = 0.522\ \mu\text{M}$$

gives the concentration of copper as 0.0530 μM. The concentration of Cu^{2+} in mg/L, therefore, is

$$\frac{0.053 \times 10^{-6} \text{ mol}}{\text{L}} \times \frac{63.546 \text{ g}}{\text{mol}} \times \frac{10^{6}\ \mu\text{g}}{\text{g}} = 3.37\ \mu\text{g/L}$$

33. Letting C_{thio} represent the concentration of the thioamide drug in the sample of urine, we have the following two equations for the sample and the standard addition

$$0.562 = k\left\{C_{thio} \times \frac{2.00\ mL}{4.00\ mL}\right\}$$

$$0.837 = k\left\{C_{thio} \times \frac{2.00\ mL}{4.10\ mL} + (5.00\ \mu M) \times \frac{0.10\ mL}{4.10\ mL}\right\}$$

Solving both equations for k and setting them equal to each other

$$\frac{0.562}{C_{thio} \times \frac{2.00\ mL}{4.00\ mL}} = \frac{0.837}{C_{thio} \times \frac{2.00\ mL}{4.10\ mL} + 0.1220\ \mu M}$$

$$0.2741 C_{thio} + 0.06856\ \mu M = 0.4185 C_{thio}$$

$$0.1444 C_{thio} = 0.06856\ \mu M$$

gives the drug's concentration as 0.47 μM.

34. Figure SM11.11 shows the calibration data and calibration curve, the equation for which is

$$i = 15.52\ nA + (4.47 \times 10^8\ nA/M)\, C_{V(V)}$$

For a standard addition, the concentration of V(V) is the absolute value of the x-intercept; thus,

$$\frac{0 - 15.52\ nA}{4.47 \times 10^8\ nA/M} = -3.5 \times 10^{-8}$$

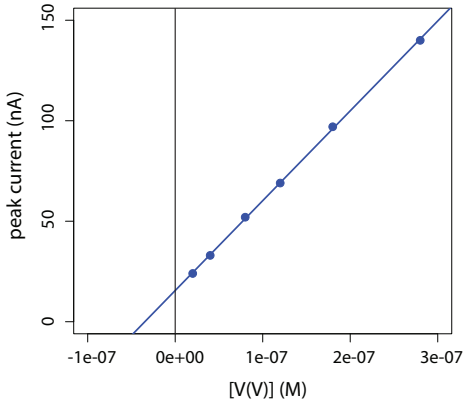

Figure SM11.11 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 34.

35. A positive potential corresponds to a negative free energy; thus, the more positive the potential, the more thermodynamically favorable the reaction. In this case, because Cu^{2+} forms a strong complex with EDTA, CuY^{2-}, we expect that $E^{\circ}_{CuY^{2-}/Cu} < E^{\circ}_{Cu^{2+}/Cu} = +0.342\ V$.

36. Lead forms several stable hydroxy-complexes, such as $Pb(OH)_3^-$, that shift the reduction potential toward more negative values.

37. To show that the reduction of Pb^{2+} is reversible, we plot the potential on the y-axis versus $\log\{i/(i_l - i)\}$ on the x-axis, which should result in a straight-line with a slope of $-0.05916/n$ and a y-intercept of $E_{1/2}$. Figure SM11.12 shows the resulting data and regression line, the equation for which is

$$E = -0.390 - 0.02948 \log \frac{i}{i_l - i}$$

From the slope, we find that

$$-0.02948 = \frac{-0.05916}{n}$$

$$n = 2.01 \approx 2$$

which makes sense for the reduction of Pb^{2+}; thus, the straight-line and the slope suggest that the reduction of Pb^{2+} is reversible.

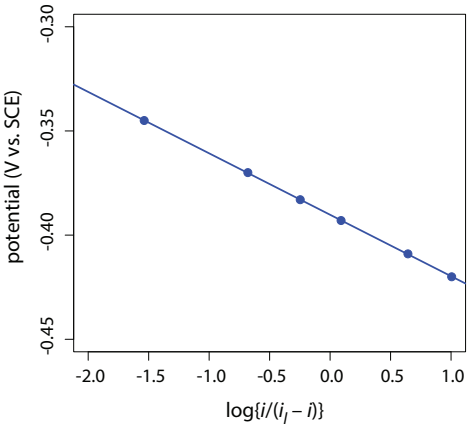

Figure SM11.12 Data (**blue** dots) and regression line (**blue** line) for Problem 37, which confirms that the reduction of Pb^{2+} is reversible.

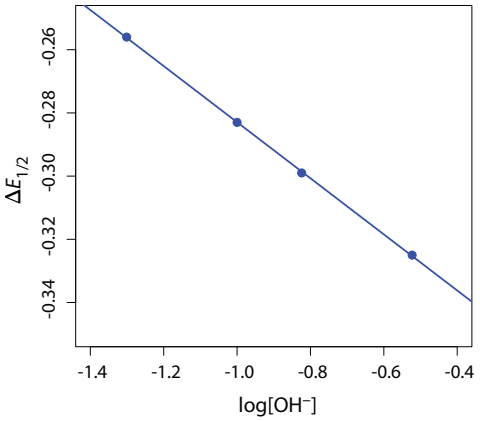

Figure SM11.13 Data (**blue** dots) and regression line (**blue** line) for Problem 37 used to determine the stoichiometry and the formation constant for a complex between Pb^{2+} and OH^-.

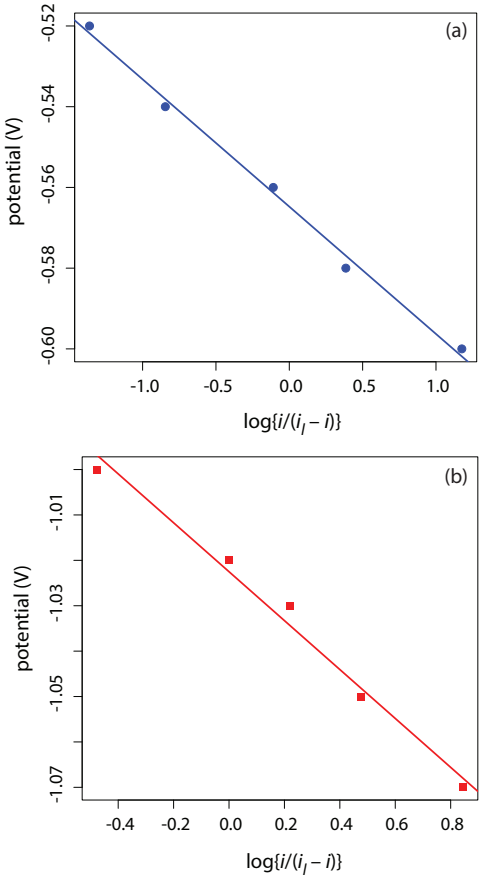

Figure SM11.14 Data and regression line for Problem 38: (a) reduction of Cd^{2+} and (b) reduction of Ni^{2+}.

The value of $E_{1/2}$ for the reduction of Pb^{2+} is equal to the *y*-intercept of the data in Figure SM11.12, or –0.390 V. To characterize the lead-hydroxy complex's stoichiometry and formation constant, we plot $\Delta E_{1/2}$ on the *y*-axis, where

$$\Delta E_{1/2} = (E_{1/2})_{\text{complex}} - (E_{1/2})_{\text{no complex}} = (E_{1/2})_{\text{complex}} + 0.390 \text{ V}$$

and log[OH^-] on the *x*-axis. Figure SM11.13 shows the resulting plot and regression line, the equation for which is

$$\Delta E_{1/2} = -0.3717 - 0.08878 \log [OH^-]$$

Using the slope, we find that for the complex $Pb(OH)_p^{2-p}$

$$-0.08878 = -\frac{0.05916p}{n} = -\frac{0.05916p}{2}$$

the value of *p* is 3.0; thus, the complex is $Pb(OH)_3^-$. Using the *y*-intercept, we find that the complex's overall formation constant

$$-0.3717 = -\frac{0.05916}{n} \log \beta_3 = -\frac{0.05916}{2} \log \beta_3$$

is 3.68×10^{12}.

38. To evaluate each metal ion for its reversibility, we plot its potential on the *y*-axis versus $\log\{i/(i_l - i)\}$ on the *x*-axis, which should result in a straight-line with a slope of $-0.05916/n$ and a *y*-intercept of $E_{1/2}$. Figure SM11.14a shows the results for Cd^{2+} and Figure SM11.14b shows the results for Ni^{2+}. For Cd^{2+}, a regression analysis of the data yields on equation of

$$E = -0.565 - 0.0315 \log \frac{i}{i_l - i}$$

From the slope, we find that

$$-0.0315 = \frac{-0.05916}{n}$$

$$n = 1.9 \approx 2$$

A two-electron reduction for Cd^{2+} is consistent with a reversible reduction reaction of

$$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(Hg)$$

where Cd(Hg) represents the formation of an amalgam of cadmium and mercury. For Ni^+, a regression analysis of the data yields on equation of

$$E = -1.02 - 0.0539 \log \frac{i}{i_l - i}$$

From the slope, we find that

$$-0.0539 = \frac{-0.05916}{n}$$

$$n = 1.1$$

A one-electron reduction for Ni^{2+} is not consistent with its reduction reaction of

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(Hg)$$

Presumably there is a slow rate of electron transfer that prevents the reduction from displaying electrochemical reversibility.

39. To evaluate electrochemical reversibility for cyclic voltammetry we examine values for ΔE_p, where $\Delta E_p = E_{p,a} - E_{p,c}$. For an electrochemically reversible reaction, ΔE_p is independent of scan rate and equal to $0.05916/n$. For *p*-phenyldiamine, ΔE_p varies from 0.044 V at a scan rate of 2 mV/s to 0.117 V at a scan rate of 100 mV/s, all of which exceed the theoretical value of $0.05916/2 = 0.02953$ V; thus, the reaction is not electrochemically reversible. For each scan rate, the ratio of the cathodic peak current and the anodic peak currents are approximately 1.00, which means the reaction must be chemically reversible; thus, the lack of electrochemical reversibility presumably results from slow kinetics and not from a chemical reaction.