S13-1. Calculate $\alpha_Y^4-$ for EDTA at pH 6.62.

S13-2. (a) Find the conditional formation constant for Ca(EDTA)$^2-$ at pH 10.00.
(b) Find the concentration of free Ca$^{2+}$ in 0.050 M Na$_2$[Ca(EDTA)] at pH 10.00.

S13-3. A brainbuster! What is the quotient [MgY$^2-$]/[NaY$^3-$] in a solution prepared by mixing 0.100 M Na$_2$EDTA with an equal volume of 0.100 M Mg(NO$_3$)$_2$? Assume that the pH is high enough that there is a negligible amount of unbound EDTA. You can approach this problem by realizing that nearly all Mg$^{2+}$ will be bound to EDTA and nearly all Na$^+$ will be free.

S13-4. Consider the titration of 100.0 mL of 0.050 M EDTA at pH 10.00 with 0.100 M metal ion, $M^{n+}$.
(a) What is the equivalence volume, $V_e$, in milliliters?
(b) Calculate the concentration of total free EDTA at $V = \frac{1}{2} V_e$.
(c) What fraction ($\alpha_Y^4-$) of free EDTA is in the form Y$^4-$ at pH 10.00?
(d) The formation constant ($K_f$) is $10^{8.00}$. Calculate the value of the conditional formation constant $K'_f$ ($= \alpha_Y^4-K_f$).
(e) Calculate the concentration of free metal ion at $V = V_e$.
(f) What is the concentration of total free EDTA ion at $V = 1.100 V_e$?

S13-5. Calculate pFe$^{2+}$ at each of the following points in the titration of 25.00 mL of 0.020 M EDTA by 0.038 M Fe$^{2+}$ at pH 6.00: (a) 12.00 mL (b) $V_e$ (c) 14.00 mL

S13-6. Consider the titration of 50.0 mL of 0.011 M Y$^{3+}$ (Y = yttrium) with 0.022 M EDTA at pH 5.00. Calculate pY$^{3+}$ at the following volumes of added EDTA and sketch the titration curve:
(a) 0 mL (d) 24.0 mL (g) 25.1 mL
(b) 10.0 mL (e) 24.9 mL (h) 26.0 mL
(c) 20.0 mL (f) 25.0 mL (i) 30.0 mL

S13-7. Calculate pCd$^{2+}$ at each of the following points in the titration of 10.00 mL of 0.001 M Cd$^{2+}$ with 0.002 M EDTA at pH 12.00 in a solution whose NH$_3$ concentration is somehow fixed at 0.200 M:
(a) 0 mL (b) 1.00 mL (c) 4.90 mL (d) 5.00 mL (e) 5.10 mL (f) 6.00 mL

S13-8. Allosteric interactions. The molecule drawn below contains two large rings with oxygen atoms capable of binding metal atoms, one on each ring.
Calling the molecule L, we can represent the metal-binding reactions as

\[ \text{L} + \text{M} \rightleftharpoons \text{LM} \quad K_1 = \frac{[\text{LM}]}{[\text{L}][\text{M}]} \quad (A) \]

\[ \text{LM} + \text{M} \rightleftharpoons \text{LM}_2 \quad K_2 = \frac{[\text{LM}_2]}{[\text{LM}][\text{M}]} \quad (B) \]

If binding at one site influences binding at the other site, there is said to be an *allosteric interaction* between the sites. If binding at one site makes binding at the other site more favorable than it was in the absence of the first binding, there is said to be *positive cooperativity* between the sites. If binding at one site makes binding at the second site less favorable, there is *negative cooperativity* between the sites. If there is no interaction between sites, binding is said to be *noncooperative*. This means that a metal at one site has no effect on metal binding at the other site.

The binding of Hg(CF₃)₂ to the molecule above in benzene solution was found to have \( K_1 = 4.0 (\pm 0.1) \) \( K_2 \) [J. Rebek, Jr., T. Costello, L. Marshall, R. Wattley, R. C. Gadwood, and K. Onan, *J. Amer. Chem. Soc.* 1985, 107, 7481]. Show that \( K_1 = 4K_2 \) corresponds to noncooperative binding. *Hint:* If the two binding sites are represented as \( \text{□□} \) we can represent the equilibria as follows:

\[
\begin{array}{c}
\text{□□} \\
\xrightarrow{K_1} \\
\text{□□} + \\
\xrightleftharpoons{K_2} \\
\text{□□}
\end{array}
\]

where \( \text{□□} \) represents metal bound at one site. In noncooperative binding, the four populations \( \text{□□}, \text{□□}, \text{□□}, \text{□□} \) must be equal when the ligand is 50% saturated with metal.

**S13-9.** EDTA at pH 5 was titrated with standard Pb²⁺ using xylenol orange as indicator (Table 13-3). Which is the principal species of the indicator at pH 5? What color was observed before the equivalence point? after the equivalence point? What would be the color change if the titration were conducted at pH 8 instead of pH 5?
S13-10. A 25.00-mL sample containing Fe³⁺ was treated with 10.00 mL of 0.0367 M EDTA to complex all the Fe³⁺ and leave excess EDTA in solution. The excess EDTA was then back-titrated, requiring 2.37 mL of 0.0461 M Mg²⁺. What was the concentration of Fe³⁺ in the original solution?

S13-11. Express the hardness of water containing 3.2 mM Ca²⁺ + 1.1 mM Mg²⁺ in terms of mg CaCO₃/L. (FM CaCO₃ 100.09)

S13-12. Cyanide can be determined indirectly by EDTA titration. A known excess of Ni²⁺ is added to the cyanide to form tetracyanonickelate:

\[ 4\text{CN}^- + \text{Ni}^{2+} \rightarrow \text{Ni(CN)}_4^{2-} \]

When the excess Ni²⁺ is titrated with standard EDTA, Ni(CN)₄²⁻ does not react. In a cyanide analysis 12.7 mL of cyanide solution was treated with 25.0 mL of standard solution containing excess Ni²⁺ to form tetracyanonickelate. The excess Ni²⁺ required 10.1 mL of 0.0130 M EDTA for complete reaction. In a separate experiment, 39.3 mL of 0.0130 M EDTA was required to react with 30.0 mL of the standard Ni²⁺ solution. Calculate the molarity of CN⁻ in the 12.7-mL sample of unknown.

S13-13. A mixture of Mn²⁺, Mg²⁺, and Zn²⁺ was analyzed as follows: The 25.00-mL sample was treated with 0.25 g of NH₃OH⁺Cl⁻ (hydroxylammonium chloride, a reducing agent that maintains manganese in the +2 state), 10 mL of ammonia buffer (pH 10), and a few drops of eriochrome black T indicator and then diluted to 100 mL. It was warmed to 40°C and titrated with 39.98 mL of 0.04500 M EDTA to the blue end point. Then 2.5 g of NaF was added to displace Mg²⁺ from its EDTA complex. The liberated EDTA required 10.26 mL of standard 0.02065 M Mn²⁺ for complete titration. After this second end point was reached, 5 mL of 15 wt % aqueous KCN was added to displace Zn²⁺ from its EDTA complex. This time the liberated EDTA required 15.47 mL of standard 0.02065 M Mn²⁺. Calculate the number of milligrams of each metal (Mn²⁺, Zn²⁺, and Mg²⁺) in the 25.00-mL sample of unknown.

S13-14. Here is a procedure for the consecutive determination of Bi³⁺, Ti⁴⁺ and Al³⁺ in a mixture that might arise in the analysis of aluminum ore, clays or cements [M. A. El-Hamied Hafez, Talanta 1992, 39, 1189].

1. The solution is acidified to pH 1-2 with HNO₃, at which only Bi³⁺ has a large enough conditional formation constant to be titrated. The indicator semixylenol orange is added and the solution is titrated with standard EDTA until just reaching the end point color change from red (MIn) to yellow (In). This gives the Bi³⁺ content of the solution and
leaves Ti\(^{4+}\) and Al\(^{3+}\) uncomplexed.

(2) Then excess EDTA is added and the pH is raised to 5 with hexamine, which serves as a buffer and an auxiliary complexing ligand.

\[
\text{Hexamine } ((\text{CH}_2)_6\text{N}_4) \\
\text{(also called hexamethylenetetramine)} \\
pK_a \text{ for } (\text{CH}_2)_6\text{N}_4\text{H}^+ = 5.1
\]

The solution is boiled to complete the reaction with EDTA, cooled and titrated with Zn\(^{2+}\) until just reaching the end point color change from yellow (In) to red (MIn). Now the solution contains Bi(EDTA)\(^-\), Ti(EDTA) and Al(EDTA)\(^-\), with no excess EDTA.

(3) Excess H\(_2\)PO\(_4^\text{-}\) is added and the solution is boiled to displace Ti\(^{4+}\) from EDTA. Titration with standard Zn\(^{2+}\) until the end point color change is just reached gives the Ti\(^{4+}\) content.

(4) Finally, excess F\(^-\) is added and the solution is boiled to displace Al\(^{3+}\) from EDTA. Titration of the hot solution with standard Zn\(^{2+}\) until the end point color change is just reached gives the Al\(^{3+}\) content.

In step 1, 25.00 mL of unknown required 16.43 mL of 0.01044 M EDTA. Step 3 required 4.22 mL of 0.01276 M Zn\(^{2+}\) and step 4 consumed 25.92 mL of 0.01276 M Zn\(^{2+}\). Find the molarity of each cation in the original unknown. What color change is observed in steps (3) and (4)?


The spectrum on the next page shows changes that occur as metal M is titrated with ligand L.

\[
M + L \rightleftharpoons ML \\
K = \frac{[ML]}{[M][L]}
\]

Curve 0 is the spectrum of M and curves 1 through 5 result from additions of L. The species M and ML absorb in the region shown, but L has no absorbance. Both the initial solution and the titrant solution contain \(2.12 \times 10^{-4}\) M metal ion, so the total concentration of M plus ML remains constant throughout the experiment:
Spectrophotometric titration of species P (curve 0) with ligand X (curves 1-5).

Mass balance for M: \[ C_m = [M] + [ML] = 2.12 \times 10^{-4} \text{ M} \]

Mass balance for L: \[ C_l = [L] + [ML] \]

where \( C_l \) is the total ligand concentration after each addition. Substituting \([M] = C_m - [ML]\) and \([L] = C_l - [ML]\) into the equilibrium constant above, you can solve for \([ML]\):

\[
[ML] = \frac{1}{2} \left[ \left( C_m + C_l + \frac{1}{K} \right) - \sqrt{\left( C_m + C_l + \frac{1}{K} \right)^2 - 4C_mC_l} \right]
\]

Now we want to express the absorbance changes as a function of \( K \) and various known quantities. For a 1-cm-pathlength cell, you can show from Beer's law that the change of absorbance (\( \Delta A \)) at a given wavelength can be written \( \Delta A = \Delta \varepsilon [ML] \), where \( \Delta \varepsilon \) is the change in molar absorptivity between product and reactant (\( \Delta \varepsilon = \varepsilon_{ML} - \varepsilon_M \)).

Substituting in the expression for \([ML]\) above gives

\[
\Delta A = \frac{\Delta \varepsilon}{2} \left[ \left( C_m + C_l + \frac{1}{K} \right) - \sqrt{\left( C_m + C_l + \frac{1}{K} \right)^2 - 4C_mC_l} \right]
\]

*The least-squares problem:* The table below gives \( \Delta A \) as a function of \( C_l \).
Your job is to use a nonlinear least squares curve fitting procedure to find the best values of $\Delta \varepsilon$ and $K$ in the equation $\Delta A = f(C_l, \Delta \varepsilon, K)$ where $C_l$ is the independent variable ($x$), $\Delta A$ is the dependent variable ($y$), and the adjustable parameters are $\Delta \varepsilon$ and $K$. In the notation of the least squares program, $C_l$ is the variable $x[i]$, $\Delta \varepsilon$ is the constant $C[1]$ and $K$ is the constant $C[2]$.

To do the curve fitting, you can use the procedure "Nonlinear Least Squares Curve Fitting with Microsoft Excel Solver" described at the website for this book. To begin the least-squares procedure, we need estimates of $\Delta \varepsilon$ and $K$. For this purpose, let's pretend that curve 5 corresponds to complete conversion of M to ML. Therefore, $A_{ML} = \varepsilon_{ML}[ML] = 0.494 \approx \varepsilon_{ML} [2.12 \times 10^{-4} \text{ M}] \Rightarrow \varepsilon_{ML} \approx 2.33 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

From curve 0 we know $\varepsilon_M = A/[M] = 0.859/2.12 \times 10^{-4} = 4.05 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Therefore, $\Delta \varepsilon = \varepsilon_{ML} - \varepsilon_M \approx -1.72 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

To estimate $K$, suppose that the conversion of M to ML for curve 1 is in proportion to the absorbance change:

$$[ML] \approx \left(\frac{A_1 - A_0}{A_5 - A_0}\right) C_m \approx \left(\frac{0.745 - 0.859}{0.494 - 0.859}\right) (2.12 \times 10^{-4}) = 6.61 \times 10^{-4} \text{ M}$$

From the mass balance for metal, we estimate $[M] = C_m - [ML] \approx 1.46 \times 10^{-4} \text{ M}$. The mass balance for ligand gives $[L] = C_l - [ML] \approx 0.513 \times 10^{-3} - 6.61 \times 10^{-5} = 4.49 \times 10^{-4} \text{ M}$. Our estimate of the equilibrium constant is therefore

$$K = \frac{[ML]}{[M][L]} \approx \frac{6.61 \times 10^{-4}}{(1.46 \times 10^{-4})(4.49 \times 10^{-4})} = 1.0 \times 10^3$$

Happy hunting! The values produced by your least-squares program should be $\Delta \varepsilon = -1944 (\pm 25) \text{ M}^{-1} \text{ cm}^{-1}$ and $K = 829 (\pm 35)$. If you crave more, you can find spectrophotometric data for the sequence $M + L \rightarrow ML \rightarrow ML_2$ given by N. K. Kildahl, *J. Chem. Ed.* 1992, 69, 591.

Try deriving equations to fit these data with your least squares program and find the formation constants $K_1$ and $K_2$. 

<table>
<thead>
<tr>
<th>Curve</th>
<th>$C_l$ (M)</th>
<th>Absorbance at 525 nm</th>
<th>$\Delta A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.859</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>$0.515 \times 10^{-3}$</td>
<td>0.745</td>
<td>-0.114</td>
</tr>
<tr>
<td>2</td>
<td>$1.03 \times 10^{-3}$</td>
<td>0.676</td>
<td>-0.183</td>
</tr>
<tr>
<td>3</td>
<td>$2.06 \times 10^{-3}$</td>
<td>0.609</td>
<td>-0.250</td>
</tr>
<tr>
<td>4</td>
<td>$4.11 \times 10^{-3}$</td>
<td>0.544</td>
<td>-0.315</td>
</tr>
<tr>
<td>5</td>
<td>$9.23 \times 10^{-3}$</td>
<td>0.494</td>
<td>-0.365</td>
</tr>
</tbody>
</table>
S13-16. Aliquots of a single metal ion solution were titrated with EDTA and two different indicators. Results of replicate measurements are shown below. Do the two indicators give equivalent results at the 95% confidence level?

- Pyrocatechol violet: 2.034, 2.048, 2.000, 2.055, 2.018, 2.022 mM
- Xylenol orange: 2.044, 2.053, 2.061, 2.030, 2.049 mM

S13-17. An EDTA titration was used to monitor periodically a metal ion concentration in an industrial process stream. Long experience with the method showed that the mean value was 0.1664 M with a standard deviation of 0.0028 M.

(a) What percentage of measurements is expected in the range 0.1700 to 0.1750 M?
(b) What percentage is expected to exceed 0.1750 M?
(c) To monitor the process, you plan to withdraw a sample of the stream and conduct four replicate analyses. Explain how you would set the warning and action lines if you were drawing a control chart for this process.

S13-18. (a) A method involving ultrafiltration has been proposed for removing metal cations from industrial waste. In ultrafiltration, a solution containing large and small molecules is forced under pressure to flow through a semipermeable membrane whose pores are large enough for small molecules to pass, but not large enough for large molecules to pass. To sequester metal ions, a water-soluble polymer containing many carboxyl (–CO₂H) groups is added to the waste. The carboxyl groups can bind cations. When the liquid is concentrated by ultrafiltration, small molecules and solvent pass through the membrane, but the polymer containing undesirable cations is retained.

Draw a sketch of this process and explain how it can be used to concentrate metals from a waste stream.

(b) The effect of pH on the ultrafiltration of two cations is shown on the next page. Explain the shapes of these curves. Which metal has a higher formation constant for binding to the polymer?
Effect of pH on retention of metal ion during ultrafiltration of waste stream containing added metal-binding polymer.

S14-1. (a) Identify the oxidizing and reducing agents among the reactants below and write a balanced half-reaction for each.

\[ 2S_2O_4^{2-} + TeO_3^{2-} + 2OH^- \rightleftharpoons 4SO_3^{2-} + Te(s) + H_2O \]

Dithionite    Tellurite    Sulfite

(b) How many coulombs of charge are passed from reductant to oxidant when 1.00 g of Te is deposited?

(c) If Te is created at a rate of 1.00 g/h, how much current is flowing?

S14-2. Draw a picture of each of the following cells, showing the location of each chemical species. For each cell, write an oxidation for the left half-cell and a reduction for the right half-cell.

(a) \( Au(s) | Fe(CN)_6^{4-} (aq) , Fe(CN)_6^{3-} (aq) || Ag(CN)_2^- (aq) , KCN(aq) | Ag(s) \)

(b) \( Pt(s) | Hg(l) | Hg_2Cl_2(s) | KCl(aq) || ZnCl_2(aq) | Zn(s) \)

S14-3. Find the theoretical electrical storage capacity of cells that make use of the following chemical reactions. Express your answer in ampere \cdot hours per kilogram of reactants, where 1 A\cdot h provides 1 A for 1 h. Thus if consumption of 0.5 kg of reactants produces 3 A\cdot h, the storage capacity would be 3 A\cdot h/0.5 kg = 6 A\cdot h/kg. Which cell produces the most electricity per kilogram, and which the least?

(a) Lead-acid battery: \( Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \)

(FM of reactants = 207.2 + 239.2 + 2 \times 98.079 = 642.6.)

(b) Carbon-zinc dry cell: \( Zn + 2NH_4Cl + 2MnO_2 \rightarrow ZnCl_2(NH_3)_2 + 2MnO(OH) \)

(FM of reactants = 346.25.)

(c) Nickel-cadmium cell: \( 2Ni(OH)_2 + Cd(OH)_2 \rightarrow NiO(OH) + Cd + 2H_2O \)

(FM of reactants = 331.84.)

(d) Sulfur-aluminum battery: \( 2Al + 3S + 3KOH + 3H_2O \rightarrow 2Al(OH)_3 + 3KHS \)

(FM of reactants = 372.525.)

(e) Hydrogen-oxygen fuel cell: \( 2H_2 + O_2 \rightarrow 2H_2O \) (FM of reactants = 36.031)

S14-4. Which will be the strongest reducing agent under standard conditions (all activities = 1): Se, \( Sn^{4+}, Cr^{2+}, Mg^{2+} \), or \( Fe(CN)_6^{4-} \)?

S14-5. Use Le Châtelier's principle and half-reactions from Appendix H to find which of the following become stronger reducing agents when the solution becomes more basic. Which are unchanged, and which become weaker?

\[
\begin{align*}
\text{Cl}_2 & \quad \text{Al} & \quad \text{H}_2\text{S} & \quad \text{MnO}_4^{2-} & \quad \text{S}_2\text{O}_3^{2-} \\
\text{Chlorine} & \quad \text{Aluminum} & \quad \text{Hydrogen sulfide} & \quad \text{Manganate} & \quad \text{Thiosulfate}
\end{align*}
\]
S14-6. Consider the cell

Pt(s) | H₂(g, 0.100 bar) | H⁺(aq, pH = 2.54) || Cl⁻(aq, 0.200 M) | Hg₂Cl₂(s) | Hg(l) | Pt(s)

(a) Write a reduction reaction and Nernst equation for each half-cell

For the Hg₂Cl₂ half-reaction, \( E^\circ = 0.268 \) V.

(b) Find \( E \) for the net cell reaction and state whether reduction will occur at the left- or right-hand electrodes.

S14-7. Consider a circuit in which the left half-cell was prepared by dipping a Pt wire in a beaker containing an equimolar mixture of Cr²⁺ and Cr³⁺. The right half-cell contained a Tl rod immersed in 1.00 M TiClO₄.

(a) Use line notation to describe this cell. (b) Calculate the cell voltage.

(c) Write the spontaneous net cell reaction.

(d) When the two electrodes are connected by a salt bridge and a wire, which terminal (Pt or Tl) will be the anode?

S14-8. Write a balanced chemical equation (in acid solution) for the reaction represented by the question mark below. Calculate \( E^\circ \) for the reaction.

\[
\begin{align*}
\text{NO}_3^- &\rightarrow \text{NO}_2(g) & \text{HNO}_2 &\rightarrow \text{NO} \\
0.773 & & 1.108 &\
0.955 & & &
\end{align*}
\]

S14-9. Calculate \( E^\circ \), \( \Delta G^\circ \), and \( K \) for each of the following reactions.

(a) Cu(s) + Cu²⁺ ⇌ 2Cu⁺ (b) 2F₂(g) + H₂O ⇌ F₂O(g) + 2H⁺ + 2F⁻

S14-10. A solution contains 0.010 M IO₅⁻, 0.010 M I⁻, 1.00 × 10⁻⁴ M I₃⁻, and pH 6.00 buffer.

Consider the reactions

\[
\begin{align*}
2\text{IO}_5^- + \text{I}^- + 12\text{H}^+ + 10e^- &\rightleftharpoons \text{I}_3^- + 6\text{H}_2\text{O} & E^\circ &= 1.210 \text{ V} \\
\text{I}_3^- + 2e^- &\rightleftharpoons 3\text{I}^- & E^\circ &= 0.535 \text{ V}
\end{align*}
\]

(a) Write a balanced net reaction that can occur in this solution.

(b) Calculate \( \Delta G^\circ \) and \( K \) for the reaction.

(c) Calculate \( E \) for the conditions given above.

(d) Calculate \( \Delta G \) for the conditions given above.

(e) At what pH would the concentrations of IO₅⁻, I⁻, and I₃⁻ listed above be in equilibrium at 298 K?
S14-11. From the half-reactions below, calculate the solubility product of Mg(OH)$_2$.

\[
\begin{align*}
\text{Mg}^{2+} + 2e^- & \rightleftharpoons \text{Mg(s)} \quad E^* = -2.360 \text{ V} \\
\text{Mg(OH)}_2(s) + 2e^- & \rightleftharpoons \text{Mg(s)} + 2\text{OH}^- \quad E^* = -2.690 \text{ V}
\end{align*}
\]

S14-12. The standard free energy of vaporization of Cl$_2$(aq) is $\Delta G^\circ = -6.9 \text{ kJ/mol}$ at 298 K. Given that $E^*$ for the reaction Cl$_2$(g) + 2e$^- \rightleftharpoons$ 2Cl$^-$ is 1.360 V, find $E^*$ for the reaction Cl$_2$(aq) + 2e$^- \rightleftharpoons$ 2Cl$^-$.

S14-13. Consider the cell S.H.E. $|\text{Ag(S}_2\text{O}_3\text{)}_2^{3-}(\text{aq},0.010 \text{ M}), \text{S}_2\text{O}_3^{2-}(\text{aq},0.050 \text{ M})|\text{Ag(s)}$

(a) Using the half-reaction Ag(S$_2$O$_3$)$_2^{3-} + e^- \rightleftharpoons \text{Ag(s)} + 2\text{S}_2\text{O}_3^{2-}$, calculate the cell voltage ($E$, not $E^*$).

(b) Alternatively, the cell could have been described with the half-reaction Ag$^+$ + e$^- \rightleftharpoons \text{Ag(s)}$

Using the cell voltage from part a, calculate [Ag$^+$] in the right half-cell.

(c) Use the answer to part b to find the formation constant for the reaction

\[
\text{Ag}^+ + 2\text{S}_2\text{O}_3^{3-} \rightleftharpoons \text{Ag(S}_2\text{O}_3\text{)}_2^{3-} \quad \text{Thiosulfate}
\]

S14-14. The following cell has a voltage of 1.018 V. Find $K_a$ for formic acid, HCO$_2$H.

Pt(s) $|\text{UO}_2^{2+}(0.050 \text{ M}), \text{U}^4+(0.050 \text{ M}), \text{HCO}_2\text{H}(0.10 \text{ M}), \text{HCO}_2\text{Na}(0.30 \text{ M})$ $|| \text{Fe}^{3+}(0.050 \text{ M}), \text{Fe}^{2+}(0.025 \text{ M})|\text{Pt(s)}$

S14-15. For the following cell, the half-reactions can be written

Right half-cell: \quad \text{Pb}^{2+}(\text{right}) + 2e^- \rightleftharpoons \text{Pb(s)}

Left half-cell: \quad \text{Pb}^{2+}(\text{left}) + 2e^- \rightleftharpoons \text{Pb(s)}

(a) Given that $K_{sp}$ for Pb(HPO$_4$)$_2(s)$ is $2.0 \times 10^{-10}$, find [HPO$_4^{2-}$] in the left half-cell.

(b) If the measured cell voltage is 0.097 V, calculate $K_{sp}$ for PbF$_2(s)$. 
S14-16. The monstrous cell below was set up. Then 50.0 mL of 0.044 M Na₂EDTA was added to the right-hand compartment and 50.0 mL of 0.070 M NaOH was added to the left-hand compartment. The cell voltage leveled off at +0.418 V. Find the formation constant for CuY²⁻ (where Y = EDTA).

\[ \text{Pb(HPO}_4\text{)}(s) \quad \text{Pb} \\
\text{Sb}_2\text{O}_3 \quad \text{Sb} \\
\text{Solution prepared from} \quad 25.0 \text{ mL of 0.124 M Na}_2\text{PO}_4 \quad \text{Prepared by mixing} \quad 25.0 \text{ mL of 0.124 M Pb(NO}_3\text{)}_2 \]
\[ \text{and 25.0 mL of 0.248 M HClO}_4 \quad \text{and 25.0 mL of 0.248 M KF} \]

S14-17. Evaluate \( E'' \) for the half-reaction \( \text{CO}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O} \).

S14-18. Evaluate \( E'' \) for the half-reaction \( \text{CO}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCO}_2\text{H(aq)} \).

S14-19. The standard reduction potential of anthraquinone-2,6-disulfonate is 0.229 V.
Anthraquinone-2,6-disulfonate

The reduced product is a diprotic acid with $pK_1 = 8.10$ and $pK_2 = 10.52$. Calculate $E^\circ$ (pH = 7) for anthraquinone-2,6-disulfonate.

**S14-20. How do we know that mercury(I) is a dimer?** Techniques including X-ray crystallography, spectroscopy, and magnetic measurements demonstrate that mercury(I) is almost always found as the dimer, Hg$_2^{2+}$. Here is a student electrochemical measurement that allows you to distinguish monomeric Hg$^+$ from Hg$_2^{2+}$. [D. Bhattacharya and D. G. Peters, "Use of Electrochemical Concentration Cells to Demonstrate the Dimeric Nature of Mercury(I) in Aqueous Media," *J. Chem. Ed.* 1995, 72, 64.] A concentration cell is one in which the only difference between the two half-cells is the concentration of a reacting species. The following concentration cell was used for all measurements:

$$\text{Hg | Hg(I)(C}_L\text{) || Hg(I)(C}_R\text{) | Hg}$$

where Hg(I) is present at a concentration $C_L$ in the left half-cell and at a concentration $C_R$ in the right half-cell. Stock solution A was prepared from 2.8 g of mercury(I) nitrate monohydrate, which is either HgNO$_3 \cdot $H$_2$O (FM 280.61) if Hg(I) is monatomic, or Hg$_2$(NO$_3$)$_2 \cdot $2H$_2$O (FM 561.22) if Hg(I) is diatomic. The salt was dissolved in 100.0 mL of 0.16 M HNO$_3$ containing a few drops of liquid Hg to prevent oxidation of Hg(I). Solution B was 1.6 M HNO$_3$. Five concentration cells in the following table were set up and their voltage was measured.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Left half-cell</th>
<th>Right half-cell</th>
<th>Voltage (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>solution A</td>
<td>solution A</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10.0 mL A + 17.4 mL B diluted to 100.0 mL</td>
<td>solution A</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>10.0 mL of cell 2 solution + 17.4 mL B diluted to 100.0 mL</td>
<td>solution A</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>10.0 mL of cell 3 solution + 17.4 mL B diluted to 100.0 mL</td>
<td>solution A</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>10.0 mL of cell 4 solution + 17.4 mL B diluted to 100.0 mL</td>
<td>solution A</td>
<td>119</td>
</tr>
</tbody>
</table>
(a) Write the two half-reactions for the concentration cell and write the Nernst equation for the complete cell if Hg(I) is monatomic (i.e., Hg\(^+\)).

(b) Write the two half-reactions for the concentration cell and write the Nernst equation for the complete cell if Hg(I) is diatomic (i.e., Hg\(^{2+}\)).

(c) Prepare a graph of \(E\) versus \(\log(C_L/C_R)\) showing the lines predicted by your answers to (a) and (b).

(d) Calculate the quotient \(C_L/C_R\) for cells 1-5. Does your answer depend on whether Hg(I) is monatomic or diatomic?

(e) Plot the experimental points on the graph in (c). Is Hg(I) monatomic or diatomic?

(f) What is the purpose of solution B in the left half-cell?

(g) We cheated a little. If the starting material were Hg\(^{2+}\), we would have obtained the same experimental results. Suggest any analytical experiments that could tell you the oxidation number of Hg in the starting material.
S15-1. Convert the potentials listed below. The Ag|AgCl and calomel reference electrodes are saturated with KCl.

(a) \(-0.222\) vs S.H.E. = ? vs Ag|AgCl  
(b) \(0.523\) vs Ag|AgCl = ? vs S.H.E.  
(c) \(-0.523\) vs S.C.E. = ? vs Ag|AgCl 
(d) \(0.035\) vs Ag|AgCl = ? vs S.C.E.  
(e) \(-0.035\) vs calomel = ? vs Ag|AgCl 

S15-2. What is the cell voltage when saturated calomel and Pt electrodes are dipped into a solution containing 0.002 17 M Br2 (aq) and 0.234 M Br\(^-\)?

S15-3. A 50.0 mL solution of 0.100 M NaSCN was titrated with 0.200 M AgNO\(_3\) in the cell:

S.C.E.||titration solution|Ag(s)

Find the cell voltage for these volumes of titrant: 0.1, 10.0, 25.0 and 30.0 mL.

S15-4. The right-hand compartment of the cell below was titrated with ligand while monitoring the cell voltage:Ag(s) | Ag\(^+\) (aq, 0.100 M, 25.0 mL)||Ag\(^+\) (aq, 0.100 M, 75.0 mL)|Ag(s)

With 1.52 M ammonia titrant, the end point was observed at 9.8 mL, while 1.72 M ethylenediamine (Section 13-1) gave an end point of 5.0 mL. In both cases, the measured cell voltage was near \(-0.15\) V at the end point. [H. Meyer, \textit{J. Chem. Ed.} \textbf{1992}, \textit{69}, 499; D. C. Luehrs, \textit{J. Chem. Ed.} \textbf{1995}, \textit{72}, 668.]

(a) Write the half-reactions, net reaction and Nernst equation for the cell.
(b) Write the stoichiometry of the observed reactions with the titrants.
(c) From the observed voltage, find the concentration of uncomplexed Ag\(^+\) at the end points.

S15-5. The titration solution in the cell below had a total volume of 50.0 mL and contained 0.100 M Mg\(^{2+}\) and 1.00 \(\times\) 10\(^{-5}\) M Zn(EDTA)\(^{2-}\) at a pH of 10.00

S.C.E.||Zn(s)|titration solution

What will be the cell voltage when 10.0 mL of 0.100 M EDTA has been added?  
(\textit{Hint}: See Exercise 15-B.)

S15-6. Which side of the liquid junction 0.1 M HCl | 0.1 M LiBr will be negative?

S15-7. How many seconds will it take for (a) \(\text{OH}^-\) and (b) \(\text{F}^-\) to migrate a distance of 1.00 cm in a field of 1.00 kV/m?
S15-8. (a) Write an expression analogous to Equation 15-8 to describe the response of a La$^{3+}$-selective electrode to La$^{3+}$ ion.

(b) If $\beta \approx 1.00$, by how many mV will the potential change when the electrode is removed from $1.00 \times 10^{-4}$ M LaClO$_4$ and placed in $1.00 \times 10^{-3}$ M LaClO$_4$?

(c) By how many millivolts will the potential of the electrode change if the electrode is removed from $2.36 \times 10^{-4}$ M LaClO$_4$ and placed in $4.44 \times 10^{-3}$ M LaClO$_4$?

(d) The electrode potential is +100 mV in $1.00 \times 10^{-4}$ M LaClO$_4$ and the selectivity coefficient $k_{La^{3+},Fe^{3+}}$ is $\frac{1}{1200}$. What will be the potential when 0.010 M Fe$^{3+}$ is added?

S15-9. A metal ion buffer was prepared from 0.050 M ML and 0.50 M L, where ML is a metal-ligand complex and L is free ligand. $M + L \rightleftharpoons ML \quad K_f = 3.6 \times 10^{10}$

Calculate the concentration of free metal ion, M, in this buffer.

S15-10. A calcium ion-selective electrode obeys Equation 15-8, in which $\beta = 0.970$ and $n_{Ca^{2+}} = 2$. The selectivity coefficients for several ions are listed.

<table>
<thead>
<tr>
<th>Interfering ion, Y</th>
<th>$k_{Ca^{2+},Y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>0.040</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>0.021</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.081</td>
</tr>
</tbody>
</table>

In $1.00 \times 10^{-3}$ M Ca$^{2+}$, the reading was +300.0 mV. What would be the voltage if the solution had the same calcium concentration plus [Mg$^{2+}$] = $1.00 \times 10^{-3}$ M, [Ba$^{2+}$] = $1.00 \times 10^{-3}$ M, and [Zn$^{2+}$] = $5.00 \times 10^{-4}$ M? (Use concentrations instead of activities to answer this question.) If they are present at equal concentrations, which ion interferes the most with the Ca$^{2+}$ electrode?

S15-11. An ion-selective electrode used to measure the cation M$^{2+}$ obeys the equation

$$E = \text{constant} + \frac{0.0571}{2} \log \left\{ [M^{2+}] + 0.020 \, [Fe^{2+}] \right\}$$

When the electrode was immersed in 100.0 mL of unknown containing M$^{2+}$ in 0.020 M Fe(NO$_3$)$_2$, the reading was 194.6 mV (versus S.C.E.). When 1.00 mL of 0.0307 M M$^{2+}$ (in 0.0.020 M Fe(NO$_3$)$_2$) was added to the unknown, the reading increased to 200.7 mV. Find the concentration of M$^{2+}$ in the original unknown.

S15-12. A magnesium ion buffer was made by mixing 10.0 mL of 1.00 mM MgSO$_4$, 10.0 mL of 1.30 mM EDTA, and 5.00 mL of buffer, pH 10.00. What is the concentration of free metal ion in this solution? Answer the same question for MnSO$_4$ used instead of MgSO$_4$. 
S15-13. I can't take all this activity! A pH electrode was immersed in solutions containing 0.0100 M HClO₄ and variable concentrations of NaClO₄. After correcting for variation of junction potential with ionic strength (µ), the results below were obtained. Calculate the activity coefficient of H⁺ as a function of ionic strength and make a graph of your results. Include a point for µ = 0 on your graph.

<table>
<thead>
<tr>
<th>µ (M)</th>
<th>pH</th>
<th>µ (M)</th>
<th>pH</th>
<th>µ (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>2.13</td>
<td>1.20</td>
<td>2.05</td>
<td>2.00</td>
<td>1.86</td>
</tr>
<tr>
<td>0.30</td>
<td>2.16</td>
<td>1.50</td>
<td>1.99</td>
<td>2.40</td>
<td>1.76</td>
</tr>
<tr>
<td>0.50</td>
<td>2.16</td>
<td>1.60</td>
<td>1.96</td>
<td>2.50</td>
<td>1.73</td>
</tr>
<tr>
<td>1.00</td>
<td>2.09</td>
<td>1.80</td>
<td>1.92</td>
<td>3.00</td>
<td>1.59</td>
</tr>
</tbody>
</table>


S15-14. *Standard addition.* A perchlorate ion-selective electrode immersed in 50.0 mL of unknown ClO₄⁻ solution gave a potential of 358.7 mV versus S.C.E. When 1.00 mL of 0.050 M NaClO₄ was added, the potential changed to 346.1 mV. Assuming that the electrode has a Nernstian response (β = 1.00), find the concentration of ClO₄⁻ in the unknown.

S15-15. Cyanide ion was measured indirectly with a solid-state ion-selective electrode containing a silver sulfide membrane. Assuming that the electrode response is Nernstian and that the ionic strength of all solutions is constant, we can write the electrode response as

\[ E = \text{constant} + 0.05916 \log[\text{Ag}^+] \]

To an unknown cyanide solution was added Ag(CN)₂⁻ such that [Ag(CN)₂⁻] = 1.0 × 10⁻⁵ M in the final solution. This complex ion behaves as a silver ion buffer in the presence of CN⁻:

\[ \text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag(CN)}_2^- \]

\[ K = \beta_2 = \frac{[\text{Ag(CN)}_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{19.85} \]

(a) Suppose that the unknown contained 8.0 × 10⁻⁶ M CN⁻ and the potential was found to be +206.3 mV. Then a *standard addition* of CN⁻ was made to bring the CN⁻ concentration to 12.0 × 10⁻⁶ M. What will be the new potential?

(b) Now consider a real experiment in which 50.0 mL of unknown gave a potential of 134.8 mV before a standard addition of CN⁻ was made. After adding 1.00 mL of 2.50 × 10⁻⁴ M KCN, the potential dropped to 118.6 mV. What was the concentration of CN⁻ in the 50.0-mL sample? For this part, we do not know the value of the constant in the equation for \( E \). That is, you cannot use the value of the constant derived from part (a) of this question.
S15-16. The following standard addition table assumes that an electrode has a Nernstian response to analyte:

Standard addition table: 10 mL of standard added to 100 mL of sample.
(To obtain sample concentration, multiply standard concentration by $Q$.)

<table>
<thead>
<tr>
<th>$\Delta E$ mV</th>
<th>$Q$</th>
<th>$\Delta E$ mV</th>
<th>$Q$</th>
<th>$\Delta E$ mV</th>
<th>$Q$</th>
<th>$\Delta E$ mV</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>8</td>
<td>0.199</td>
<td>16</td>
<td>0.095 2</td>
<td>24</td>
<td>0.055 6</td>
</tr>
<tr>
<td>1</td>
<td>0.696</td>
<td>9</td>
<td>0.178</td>
<td>17</td>
<td>0.088 4</td>
<td>25</td>
<td>0.052 3</td>
</tr>
<tr>
<td>2</td>
<td>0.529</td>
<td>10</td>
<td>0.160</td>
<td>18</td>
<td>0.082 2</td>
<td>26</td>
<td>0.049 4</td>
</tr>
<tr>
<td>3</td>
<td>0.423</td>
<td>11</td>
<td>0.145</td>
<td>19</td>
<td>0.076 7</td>
<td>27</td>
<td>0.046 6</td>
</tr>
<tr>
<td>4</td>
<td>0.351</td>
<td>12</td>
<td>0.133</td>
<td>20</td>
<td>0.071 6</td>
<td>28</td>
<td>0.044 0</td>
</tr>
<tr>
<td>5</td>
<td>0.297</td>
<td>13</td>
<td>0.121</td>
<td>21</td>
<td>0.067 1</td>
<td>29</td>
<td>0.041 6</td>
</tr>
<tr>
<td>6</td>
<td>0.257</td>
<td>14</td>
<td>0.112</td>
<td>22</td>
<td>0.062 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.225</td>
<td>15</td>
<td>0.103 0</td>
<td>23</td>
<td>0.059 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As an example, suppose chloride ion is measured with an ion-selective electrode and a reference electrode. The electrodes are placed in 100.0 mL of sample, and a reading of 228.0 mV is obtained. Then 10.0 mL of standard containing 100.0 ppm of Cl$^-$ is added, and a new reading of 210.0 mV is observed. Because $|\Delta E| = 18.0$ mV, $Q = 0.082 2$ in the preceding table. Therefore, the original concentration of Cl$^-$ was $(0.082 2)(100$ ppm$) = 8.22$ ppm.

(a) What molarity of Cl$^-$ is 8.22 ppm? Assume that the density of unknown is 1.00 g/mL.

(b) Use the original concentration of 8.22 ppm and the original potential of 228.0 mV to show that the second potential should be 210.0 mV if the electrode response obeys the equation $E = \text{constant} - 0.059 16 \log[\text{Cl}^-]$.

(c) How would you change the table to use it for Ca$^{2+}$ instead of Cl$^-$?

S15-17. (a) Derive the value of 0.696 for the second value of $Q$ in the standard addition table of the previous problem.

(b) On the basis of your derivation, create a spreadsheet that computes $Q$ as a function of $\Delta E$ and reproduce the table in the previous problem.

S15-18. Fourteen ion-selective electrodes were used to measure Ca$^{2+}$ in the same solution with the following results: [Ca$^{2+}$] = 1.24, 1.13, 1.20, 1.20, 1.30, 1.12, 1.27, 1.19, 1.27, 1.22, 1.23, 1.23, 1.25, 1.24 mM [M. Umemoto, W. Tani, K. Kuwa, and Y. Ujihira, "Measuring Calcium in Plasma," Anal. Chem. 1994, 66, 352A.]. Find the 95% confidence interval for the mean. If the actual concentration is known to be 1.19 mM, are the results of the ion-selective electrode within experimental error of the known value at the 95% confidence level?
S15-19. Calibration data for a $F^-$ electrode in pure KF solutions is given in the table. Convert each concentration from $10^{-1}$ to $10^{-7}$ M into an activity and make a graph of $E$ versus $\log A_{F^-}$. Decide which points lie on a straight line and find the least-squares slope of the line. Find the value of $\beta$ in the equation $E = \text{constant} - \beta(0.05916) \log(A_{F^-})$.

<table>
<thead>
<tr>
<th>[KF] (M)</th>
<th>$E$ (mV)</th>
<th>[KF] (M)</th>
<th>$E$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.0</td>
<td>$1.00 \times 10^{-4}$</td>
<td>217.4</td>
</tr>
<tr>
<td>$1.00 \times 10^{-1}$</td>
<td>52.2</td>
<td>$1.00 \times 10^{-5}$</td>
<td>276.1</td>
</tr>
<tr>
<td>$1.00 \times 10^{-2}$</td>
<td>106.1</td>
<td>$1.00 \times 10^{-6}$</td>
<td>323.0</td>
</tr>
<tr>
<td>$1.00 \times 10^{-3}$</td>
<td>161.7</td>
<td>$1.00 \times 10^{-7}$</td>
<td>340.0</td>
</tr>
</tbody>
</table>

S15-20. Cu$^{2+}$ buffers were prepared for the range $pCu^{2+} = 3$ to 19 for calibration of a Cu$^{2+}$ ion-selective electrode at a constant ionic strength of $\mu = 0.6$ M [R. De Marco, "Response of Copper(II) Ion-Selective Electrodes in Seawater," *Anal. Chem.* 1994, 66, 3202]. Buffers were prepared by mixing 0.00100 M Cu(NO$_3$)$_2$, 0.0150 M ethylenediamine (H$_2$NCH$_2$CH$_2$NH$_2$, abbreviated en), and adjusting the pH to selected values with HNO$_3$. The value of pH fixes the value of $pCu^{2+}$. The following equilibrium constants apply at $\mu = 0.6$ M:

\[
\begin{align*}
enH_2^2+ & \rightleftharpoons \text{enH}^+ + \text{H}^+ & \log K_1 &= -7.347 \\
enH^+ & \rightleftharpoons \text{en} + \text{H}^+ & \log K_2 &= -10.046 \\
Cu^{2+} + \text{en} & \rightleftharpoons \text{Cu(en)}^{2+} & \log \beta_1 &= 10.688 \\
Cu^{2+} + 2\text{en} & \rightleftharpoons \text{Cu(en)}^{2+}_2 & \log \beta_2 &= 19.890
\end{align*}
\]

(a) Write an equation for the fraction of free en (i.e., en not bound to Cu$^{2+}$) in the form enH$^+$ at a given pH. (Once you've figured this out, it should be trivial to write equations for the fractions in the forms en and enH$^+_2$, as well.)

(b) There are six unknown concentrations in this system: [enH$^+_2$], [enH$^+$], [en], [Cu$^{2+}$], [Cu(en)$^{2+}$], and [Cu(en)$_2$$^{2+}$] (because the pH is known). Four of the six equations needed to define the system are the preceding equilibrium equations. Write the other two necessary equations.
S16-1. Consider the titration of 50.0 mL of 0.0200 M In⁺ by 0.0500 M Cu²⁺ using Pt and saturated calomel electrodes to find the end point.
(a) Write a balanced titration reaction.
(b) Write two different half-reactions for the indicator electrode.
(c) Write two different Nernst equations for the net cell reaction.
(d) Calculate \( E \) at the following volumes of Cu²⁺: 1.00, 20.0, 39.0, 40.0, 41.0, and 80.0 mL. Sketch the titration curve.

S16-2. Consider the titration of 50.0 mL of 0.0250 M Fe³⁺ by 0.0500 M Cu⁺ to give Fe²⁺ and Cu²⁺, using Pt and saturated Ag | AgCl electrodes to find the end point.
(a) Write a balanced titration reaction.
(b) Write two different half-reactions for the indicator electrode.
(c) Write two different Nernst equations for the net cell reaction.
(d) Calculate \( E \) at the following volumes of Cu⁺: 1.0, 12.5, 24.5, 25.0, 25.5, and 30.0 mL. Sketch the titration curve.

S16-3. Vanadium(II) undergoes three stepwise oxidation reactions: \( V^{2+} \rightarrow V^{3+} \rightarrow VO^{2+} \rightarrow VO_2^+ \)
Calculate the potential (versus S.C.E.) at each of the following volumes when 10.0 mL of 0.0100 M \( V^{2+} \) is titrated with 0.0100 M Ce⁴⁺ in 1 M HClO₄: 5.0, 15.0, 25.0, and 35.0 mL. Sketch the titration curve.

S16-4. When 50.00 mL of unknown was passed through a Jones reductor, molybdate ion (\( MoO_4^{2-} \)) was converted to Mo³⁺. The filtrate required 22.11 mL of 0.01234 M KMnO₄ to reach the purple end point.
\[
\text{MnO}_4^- + \text{Mo}^{3+} \rightarrow \text{Mn}^{2+} + \text{MoO}_2^{2+}
\]
A blank required 0.07 mL. Find the molarity of molybdate in the unknown.

S16-5. A 25.00-mL sample containing La³⁺ was treated with sodium oxalate to precipitate \( La_2(C_2O_4)_3 \), which was washed, dissolved in acid, and titrated with 12.34 mL of 0.004321 M KMnO₄. Calculate the molarity of La³⁺ in the unknown.

S16-6. An aqueous glycerol solution weighing 153.2 mg was treated with 50.0 mL of 0.0899 M Ce⁴⁺ in 4 M HClO₄ at 60°C for 15 minutes to oxidize the glycerol to formic acid:
The excess Ce\(^{4+}\) required 10.05 mL of 0.0437 M Fe\(^{2+}\) to reach a ferroin end point. What is the weight percent of glycerol in the unknown?

**S16-7.** A mixture of nitrobenzene and nitrosobenzene weighing 24.43 mg was titrated with Cr\(^{2+}\) to give aniline:

\[
\begin{align*}
\text{NO} + \text{NO}_2 & \rightarrow \text{NH}_2
\end{align*}
\]

Nitrosobenzene (FM 107.112) and Nitrobenzene (FM 123.111) to give Aniline.

The titration required 21.57 mL of 0.0500 M Cr\(^{2+}\) to reach a potentiometric end point. Find the weight percent of nitrosobenzene in the mixture.

**S16-8.** A solution containing Be and several other metals was treated with excess EDTA to mask the other metals. Then excess acetoacetanilide was added at 50°C at pH 7.5 to precipitate beryllium ion:

\[
\text{Be}^{2+} + 2 \text{O} \text{C} \text{O} \text{NHC}_6\text{H}_5 \rightarrow \text{Be} \text{O} \text{O} \text{NHC}_6\text{H}_5
\]

The precipitate was dissolved in 6 M HCl and treated with 50.0 mL of solution containing 0.1392 g of KBrO\(_3\) (FM 167.00) plus 0.5 g of KBr. Bromine produced by these reagents reacts with acetoacetanilide as follows:

\[
\text{O} \text{O} \text{NHC}_6\text{H}_5 + \text{Br}_2 \rightarrow \text{O} \text{O} \text{NH} \text{O} \text{Br} + \text{HBr}
\]

After five minutes, the excess Br\(_2\) was destroyed by adding 2 g of KI (FM 166.00). The I\(_2\) released by the Br\(_2\) required 19.18 mL of 0.05000 M Na\(_2\)S\(_2\)O\(_3\). Calculate the number of milligrams of Be in the original solution.

**S16-9.** As in Problem 16-30, a sample of Bi\(_2\)Sr\(_2\)(Ca\(_{0.8}\)Y\(_{0.2}\))Cu\(_2\)O\(_x\) (FM 770.14 + 15.9994\(x\)) was analyzed to find the oxidation states of Bi and Cu. In Experiment A, a sample of Bi\(_2\)Sr\(_2\)(Ca\(_{0.8}\)Y\(_{0.2}\))Cu\(_2\)O\(_x\) weighing 110.6 mg was dissolved in 50.0 mL of 1 M HCl containing 2.000 mM CuCl. After reaction with the superconductor, coulometry detected 0.0522 mmol of
unreacted Cu\(^{+}\) in the solution. In Experiment B, 143.9 mg of superconductor was dissolved in 50.0 mL of 1 M HCl containing 1.000 mM FeCl\(_{2}\) \(\cdot\) 4H\(_2\)O. After reaction with the superconductor, coulometry detected 0.0213 mmol of unreacted Fe\(^{2+}\). Find the average oxidation numbers of Bi and Cu in the superconductor, and the oxygen stoichiometry coefficient, \(x\).

**S16-10.** A sensitive titration of Bi\(^{3+}\) is based on the following sequence [G.A. Parker, *J. Chem. Ed.* 1980, 57, 721]:

1. Bi\(^{3+}\) is precipitated by Cr(SCN)\(_6\)^\(-3\) : 
   \[ \text{Bi}^{3+} + \text{Cr(SCN)}^6^- \rightarrow \text{Bi}[\text{Cr(SCN)}6](s) \] (a)
2. The precipitate is filtered, washed, and treated with bicarbonate to release Cr(SCN)\(_6\)^\(-3\):
   \[ \text{Bi}[\text{Cr(SCN)}6] + \text{HCO}_3^- + \text{H}_2\text{O} \rightarrow (\text{BiO})_2\text{CO}_3(s) + \text{Cr(SCN)}^6^- + \text{H}^+ \] (b)
3. I\(_2\) is added to the filtrate after removal of the (BiO)\(_2\)CO\(_3\)(s):
   \[ \text{Cr(SCN)}^6^- + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{ICN} + \text{I}^- + \text{H}^+ + \text{Cr}^{3+} \] (c)
4. Upon acidification to pH 2.5, HCN is created:
   \[ \text{ICN} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{HCN} \] (d)
5. The I\(_2\) in this mixture is removed by extraction with chloroform. Excess bromine water is then added to the aqueous phase to convert iodide to iodate and HCN to BrCN:
   \[ \text{Br}_2 + \text{I}^- + \text{H}_2\text{O} \rightarrow \text{IO}_3^- + \text{H}^+ + \text{Br}^- \] (e)
   \[ \text{Br}_2 + \text{HCN} \rightarrow \text{BrCN} + \text{H}^+ + \text{Br}^- \] (f)
6. Excess Br\(_2\) is destroyed with formic acid:
   \[ \text{Br}_2 + \text{HCO}_2\text{H} \rightarrow \text{Br}^- + \text{CO}_2 + \text{H}^+ \] (g)
7. Addition of excess I\(^-\) produces I\(_2\):
   \[ \text{IO}_3^- + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O} \] (h)
   \[ \text{BrCN} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{HCN} + \text{Br}^- \] (i)
8. Finally, the iodine is titrated with a standard solution of sodium thiosulfate.

Show that 228 mol of thiosulfate will be required for each mole of Bi\(^{3+}\) that is analyzed.

**S16-11.** *Analysis of Organic Compounds with Periodic Acid.* Periodic acid is a powerful oxidizing agent that exists under different conditions as paraperiodic acid (H\(_5\)IO\(_6\)), metaperiodic acid (HIO\(_4\)), and various deprotonated forms of the acids. Sodium metaperiodate (NaIO\(_4\)) is usually used to prepare a solution that is standardized by addition to excess KI in bicarbonate solution at pH 8-9:

\[ \text{IO}_4^- + 3\text{I}^- + \text{H}_2\text{O} \rightleftharpoons \text{IO}_3^- + \text{I}_3^- + 2\text{OH}^- \] (A)
The $I_3^-$ released is titrated with thiosulfate to complete the standardization. (In acidic solution, Reaction A goes further: $\text{H}_5\text{IO}_6 + 11\text{I}^- + 7\text{H}^+ \rightleftharpoons 4\text{I}_3^- + 6\text{H}_2\text{O}$.)

Periodate is especially useful for the analysis of organic compounds (such as carbohydrates) containing hydroxyl, carbonyl or amino groups adjacent to each other. In this oxidation, known as the Malaprade reaction, the carbon-carbon bond between the two functional groups is broken and the following changes occur:
1. A hydroxyl group is oxidized to an aldehyde or a ketone.
2. A carbonyl group is oxidized to a carboxylic acid.
3. An amine is converted to an aldehyde plus ammonia (or a substituted amine if the original compound was a secondary amine).

When there are three or more adjacent functional groups, oxidation begins near one end of the molecule.

The reactions are performed at room temperature for about one hour with a known excess of periodate. At higher temperatures, further nonspecific oxidations occur. Solvents such as methanol, ethanol, dioxane, or acetic acid may be added to the aqueous solution to increase the solubility of the organic reactant. After the reaction is complete, the unreacted periodate is analyzed by using Reaction A, followed by thiosulfate titration of the liberated $I_3^-$. Some examples of the Malaprade reactions follow:

(1) $\text{CH}_3\text{CH}\{\text{CHCH}_3 + \text{IO}_4^- \rightarrow \text{CH}_3\text{CH} + \text{HCCCH}_3 + \text{IO}_3^- + \text{H}_2\text{O}$
2,3-Dihydroxybutane

(2) $\text{CH}_2\{\text{CHCH}_2 + \text{IO}_4^- \rightarrow \text{CH}_2 + \text{HCCH}_2 + \text{IO}_3^- + \text{H}_2\text{O}$
Glycerol

(3) $\text{CH}_2\{\text{CHCO}_2 + \text{IO}_4^- \rightarrow \text{CH}_2 + \text{CHCO}_2 + \text{NH}_4^+ + \text{IO}_3^-$
Serine

Finally, here is your problem. Write a balanced equation for the reaction of periodate ($\text{IO}_4^-$) with:
**S16-12.** An enzyme involved in the catalysis of redox reactions has an oxidized form and a reduced form differing by two electrons. The oxidized form of this enzyme was mixed at pH 7 with the oxidized form of a redox indicator whose two forms differ by one electron. The mixture was protected by an inert atmosphere and partially reduced with sodium dithionite. The equilibrium composition of the mixture was determined by spectroscopic analysis:

- enzyme(oxidized) $4.2 \times 10^{-5}$ M
- indicator(oxidized) $3.9 \times 10^{-5}$ M
- enzyme(reduced) $1.8 \times 10^{-5}$ M
- indicator(reduced) $5.5 \times 10^{-5}$ M

Given that $E^\circ = -0.187$ V for the indicator, find $E^\circ$ for the enzyme.

**S16-13.** This problem uses Beer's law. Aqueous solutions of radioactive materials develop micromolar concentrations of H$_2$O$_2$ as a result of nuclear irradiation of H$_2$O. The following procedure was developed to measure aqueous H$_2$O$_2$ with a detection limit near 0.3 µM [N. V. Klassen, D. Marchington, and H. C. E. McGowan, "H$_2$O$_2$ Determination by the I$_3^-$ Method and by KMnO$_4$ Titration," *Anal. Chem.* 1994, 66, 2921.]. To 500.0 mL of unknown H$_2$O$_2$ solution are carefully added 20 mL of 18 M H$_2$SO$_4$ with stirring. After cooling to room temperature, the solution is titrated with standard 0.02 m (molal) KMnO$_4$ until pink color persists. Titrant is delivered from a dropper with a fine tip and the quantity of titrant is measured gravimetrically by weighing the delivery bottle plus the dropper before and after the titration. Excess KMnO$_4$ in the titrated solution is measured spectrophotometrically at the end of the experiment. In one experiment, 0.933 g of 0.020 46 m KMnO$_4$ (FM 158.03) was added to produce pink color and the absorbance of the titrated solution at 525 nm was 0.018 in a 1.000-cm cuvet. The molar absorptivity of KMnO$_4$ at the 525 nm is $2.45 \times 10^3$ M$^{-1}$ cm$^{-1}$. Assuming that the final titration volume was 500.9 mL, find the molarity of H$_2$O$_2$ in the unknown. After you see how the numbers work out in this example, suggest experimental modifications that will increase the sensitivity (lower the detection limit) of the procedure.