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_2EDTA 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 0 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 26 M EDTA by 0.038 55 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 1 M Y^{3+} (Y = yttrium) with 0.022 2 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) 25.0mL   (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 00 M Cd^{2+} with 0.002 00 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.
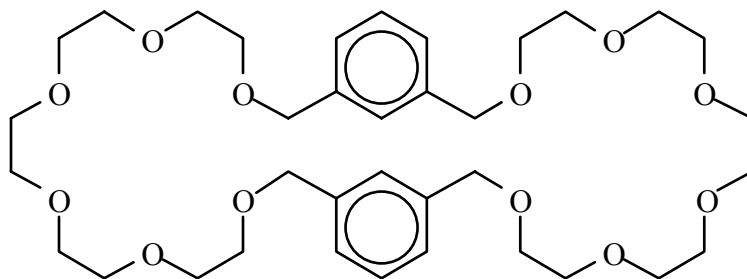
Calling the molecule L, we can represent the metal-binding reactions as

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

$$LM + M \rightleftharpoons LM_2 \qquad K_2 = \frac{[LM_2]}{[LM][M]} \qquad (B)$$
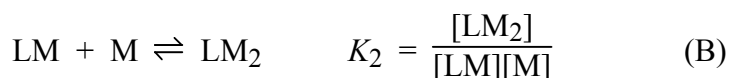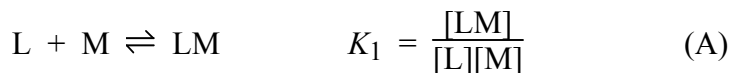
If binding at one site influences binding at the other site, there is said to be an *allosteric interaction* between the sites. If binding at one site makes binding at the other site more favorable than it was in the absence of the first binding, there is said to be *positive cooperativity* between the sites. If binding at one site makes biding 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 $Hg(CF_3)_2$ 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 we can represent the equilibria as follows:
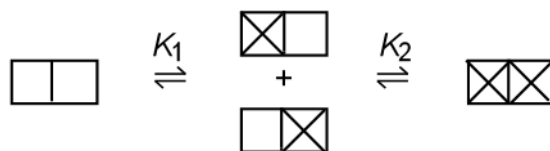
where represents metal bound at one site. In noncooperative binding, the four populations , , , and must be equal when the ligand is 50% saturated with metal.

S13-9. EDTA at pH 5 was titrated with standard Pb^{2+} 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 Fe^{3+} was treated with 10.00 mL of 0.036 7 M EDTA to complex all the Fe^{3+} and leave excess EDTA in solution. The excess EDTA was then back-titrated, requiring 2.37 mL of 0.046 1 M Mg^{2+}. What was the concentration of Fe^{3+} in the original solution?

S13-11. Express the hardness of water containing 3.2 mM Ca^{2+} + 1.1 mM Mg^{2+} in terms of mg $CaCO_3$/L. (FM $CaCO_3$ 100.09)

S13-12. Cyanide can be determined indirectly by EDTA titration. A known excess of Ni^{2+} is added to the cyanide to form tetracyanonickelate:

$$4CN^- + Ni^{2+} \rightarrow Ni(CN)_4^{2-}$$
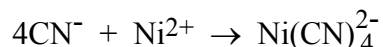
When the excess Ni^{2+} is titrated with standard EDTA, $Ni(CN)_4^{2-}$ does not react. In a cyanide analysis 12.7 mL of cyanide solution was treated with 25.0 mL of standard solution containing excess Ni^{2+} to form tetracyanonickelate. The excess Ni^{2+} required 10.1 mL of 0.013 0 M EDTA for complete reaction. In a separate experiment, 39.3 mL of 0.013 0 M EDTA was required to react with 30.0 mL of the standard Ni^{2+} solution. Calculate the molarity of CN^- in the 12.7-mL sample of unknown.

S13-13. A mixture of Mn^{2+}, Mg^{2+}, and Zn^{2+} was analyzed as follows: The 25.00-mL sample was treated with 0.25 g of $NH_3OH^+Cl^-$ (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 0.045 00 M EDTA to the blue end point. Then 2.5 g of NaF was added to displace Mg^{2+} from its EDTA complex. The liberated EDTA required 10.26 mL of standard 0.020 65 M Mn^{2+} for complete titration. After this second end point was reached, 5 mL of 15 wt % aqueous KCN was added to displace Zn^{2+} from its EDTA complex. This time the liberated EDTA required 15.47 mL of standard 0.020 65 M Mn^{2+}. Calculate the number of milligrams of each metal (Mn^{2+}, Zn^{2+}, and Mg^{2+}) in the 25.00-mL sample of unknown.

S13-14. Here is a procedure for the consecutive determination of Bi^{3+}, Ti^{4+} and Al^{3+} 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 HNO_3, at which only Bi^{3+} 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 Bi^{3+} 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.
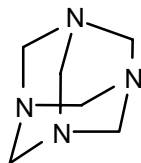
Hexamine $((CH_2)_6N_4)$
(also called hexamethylenetetramine)
pK_a for $(CH_2)_6N_4H^+ = 5.1$

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 $H_2PO_4^-$ 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 0.010 44 M EDTA. Step 3 required 4.22 mL of 0.012 76 M Zn^{2+} and step 4 consumed 25.92 mL of 0.012 76 M Zn^{2+}. Find the molarity of each cation in the original unknown. What color change is observed in steps (3) and (4)?

S13-15. A Spectrophotometric Metal-Ligand Binding Problem Using Nonlinear Least-Squares Curve Fitting

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

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

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 2.12×10^{-4} M metal ion, so the total concentration of M plus ML remains constant throughout the experiment:
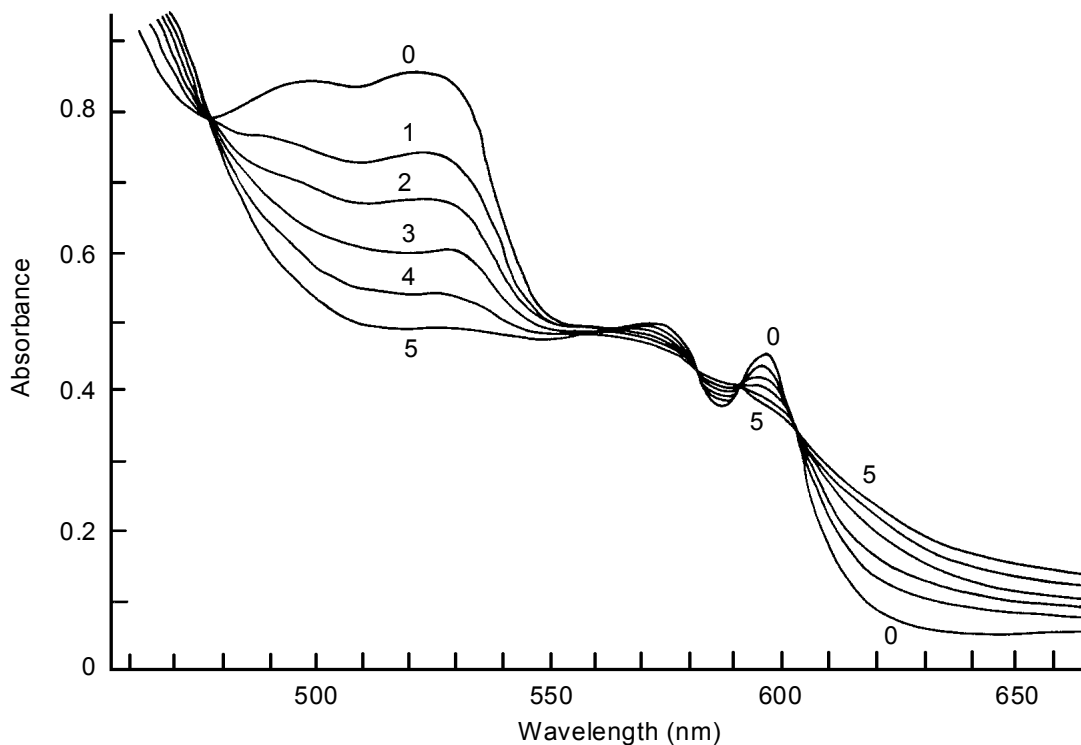
Spectrophotometric titration of species P (curve 0) with ligand X (curves 1-5).
[From J. R. Long and R.S. Drago, *J. Chem. Ed.* **1982**, *59*, 1037.]

Mass balance for M: $C_m = [M] + [ML] = 2.12 \times 10^{-4}$ 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 (ΔA) 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 ΔA as a function of C_l.

Curve	C_1 (M)	Absorbance at 525 nm	ΔA
0	0	0.859	—
1	0.515×10^{-3}	0.745	−0.114
2	1.03×10^{-3}	0.676	−0.183
3	2.06×10^{-3}	0.609	−0.250
4	4.11×10^{-3}	0.544	−0.315
5	9.23×10^{-3}	0.494	−0.365

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 $\Delta A = f(C_1, \Delta\varepsilon, K)$ *where C_1 is the independent variable (x), ΔA is the dependent variable (y), and the adjustable parameters are $\Delta\varepsilon$ and K. In the notation of the least squares program, C_1 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, $A_{ML} = \varepsilon_{ML}[ML]$

$$0.494 \approx \varepsilon_{ML}[2.12 \times 10^{-4} \text{ M}] \Rightarrow \varepsilon_{ML} \approx 2.33 \times 10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}$$

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

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 $[M] = C_m - [ML] \approx 1.46 \times 10^{-4}$ M. The mass balance for ligand gives $[L] = C_1 - [ML] \approx 0.513 \times 10^{-3} - 6.61 \times 10^{-5} = 4.49 \times 10^{-4}$ 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 $\Delta\varepsilon = -1\,944$ (± 25) M$^{-1}\cdot$cm^{-1} and $K = 829$ (± 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.

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 0.166 4 M with a standard deviation of 0.002 8 M.

(a) What percentage of measurements is expected in the range 0.170 0 to 0.175 0 M?

(b) What percentage is expected to exceed 0.175 0 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 ($-CO_2H$) 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?
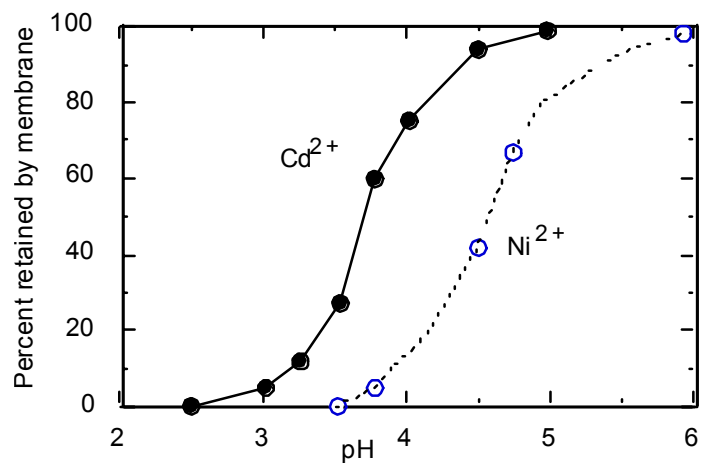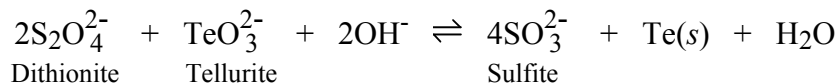
Effect of pH on retention of metal ion during ultrafiltration of waste stream containing added metal-binding polymer.

[Data from K. E. Geckeler and K. Volchek, "Removal of Hazardous Substances from Water using Ultrafiltration in Conjunction with Soluble Polymers," *Environ. Sci. Tech*. **1996**, *30*, 725.]
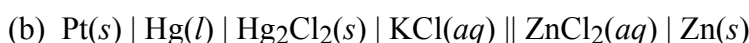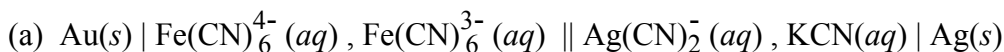
S14-1. (a) Identify the oxidizing and reducing agents among the reactants below and write a balanced half-reaction for each.
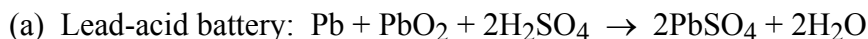
$$2S_2O_4^{2-} \ + \ TeO_3^{2-} \ + \ 2OH^- \ \rightleftharpoons \ 4SO_3^{2-} \ + \ Te(s) \ + \ H_2O$$

Dithionite   Tellurite   Sulfite

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

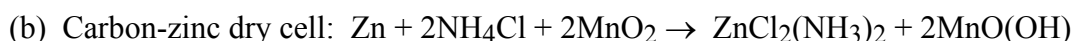   (c) If Te is created at a rate of 1.00 g/h, how much current is flowing?

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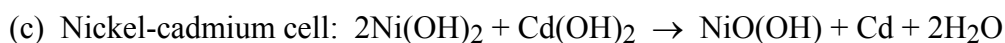
     (a) $Au(s) \,|\, Fe(CN)_6^{4-} \,(aq)\,, Fe(CN)_6^{3-} \,(aq) \,\|\, Ag(CN)_2^- \,(aq)\,, KCN(aq) \,|\, Ag(s)$

     (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 · hours per kilogram of reactants, where 1 A·h provides 1 A for 1 h. Thus if consumption of 0.5 kg of reactants produces 3 A·h, the storage capacity would be 3 A·h/0.5 kg = 6 A·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)
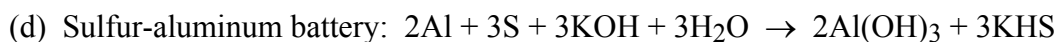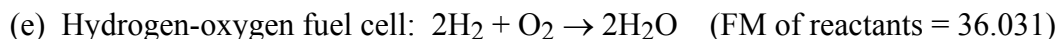
S14-4. Which will be the strongest reducing agent under standard conditions (all activities = 1): Se, Sn^{4+}, Cr^{2+}, Mg^{2+}, or $Fe(CN)_6^{4-}$?

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?

Cl_2	Al	H_2S	MnO_4^{2-}	$S_2O_3^{2-}$
Chlorine	Aluminum	Hydrogen sulfide	Manganate	Thiosulate

S14-6. Consider the cell

   $Pt(s) \mid H_2(g, 0.100 \text{ bar}) \mid H^+(aq, pH = 2.54) \parallel Cl^-(aq, 0.200 \text{ M}) \mid Hg_2Cl_2(s) \mid Hg(l) \mid Pt(s)$
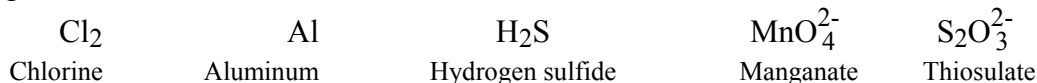
   (a) Write a reduction reaction and Nernst equation for each half-cell
       For the Hg_2Cl_2 half-reaction, $E° = 0.268$ V.

   (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
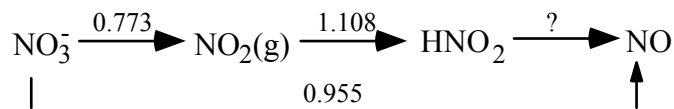   containing an equimolar mixture of Cr^{2+} and Cr^{3+}. The right half-cell contained a Tl rod
   immersed in 1.00 M $TlClO_4$.

   (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
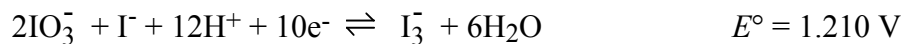   (Pt or Tl) will be the anode?

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

$$NO_3^- \xrightarrow{0.773} NO_2(g) \xrightarrow{1.108} HNO_2 \xrightarrow{?} NO$$
$$NO_3^- \xrightarrow{\hspace{2cm} 0.955 \hspace{2cm}} NO$$

S14-9. Calculate $E°$, $\Delta G°$, and K for each of the following reactions.
   (a) $Cu(s) + Cu^{2+} \rightleftharpoons 2Cu^+$ (b) $2F_2(g) + H_2O \rightleftharpoons F_2O(g) + 2H^+ + 2F^-$

S14-10. A solution contains 0.010 0 M IO_3^-, 0.010 0 M I^-, 1.00×10^{-4} M I_3^-, and pH 6.00 buffer.

   Consider the reactions

$$2IO_3^- + I^- + 12H^+ + 10e^- \rightleftharpoons I_3^- + 6H_2O \qquad\qquad E° = 1.210 \text{ V}$$
$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad\qquad E° = 0.535 \text{ V}$$

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

   (b) Calculate $\Delta G°$ and K for the reaction.

   (c) Calculate E for the conditions given above.

   (d) Calculate ΔG for the conditions given above.

   (e) At what pH would the concentrations of IO_3^-, I^-, and I_3^- listed above be in equilibrium
       at 298 K?

S14-11. From the half-reactions below, calculate the solubility product of $Mg(OH)_2$.

$$Mg^{2+} + 2e^- \rightleftharpoons Mg(s) \qquad\qquad\qquad E° = -2.360 \text{ V}$$
$$Mg(OH)_2(s) + 2e^- \rightleftharpoons Mg(s) + 2OH^- \qquad E° = -2.690 \text{ V}$$
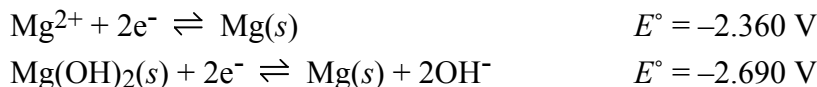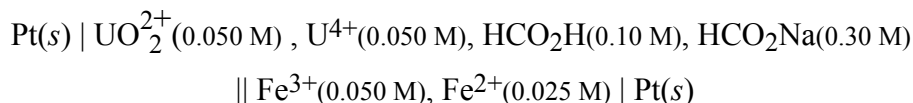
S14-12. The standard free energy of vaporization of $Cl_2(aq)$ is $\Delta G° = -6.9$ kJ/mol at 298 K. Given that $E°$ for the reaction $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ is 1.360 V, find $E°$ for the reaction $Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$.

S14-13. Consider the cell S.H.E. $\|$ $Ag(S_2O_3)_2^{3-}(aq,0.010 \text{ M})$, $S_2O_3^{2-}(aq,0.050 \text{ M})$ $|$ $Ag(s)$

(a) Using the half-reaction $Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$, calculate the cell voltage (E, not $E°$).

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

$$Ag^+ + 2S_2O_3^{2-} \overset{K_f}{\rightleftharpoons} Ag(S_2O_3)_2^{3-}$$
$$\text{Thiosulfate}$$
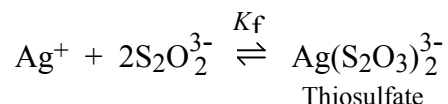
S14-14. The following cell has a voltage of 1.018 V. Find K_a for formic acid, HCO_2H.

$$Pt(s) \,|\, UO_2^{2+}(0.050 \text{ M}) , \, U^{4+}(0.050 \text{ M}), \, HCO_2H(0.10 \text{ M}), \, HCO_2Na(0.30 \text{ M})$$
$$\|\, Fe^{3+}(0.050 \text{ M}), \, Fe^{2+}(0.025 \text{ M}) \,|\, Pt(s)$$

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

Right half-cell: $Pb^{2+}(right) + 2e^- \rightleftharpoons Pb(s)$
Left half-cell: $Pb^{2+}(left) + 2e^- \rightleftharpoons Pb(s)$
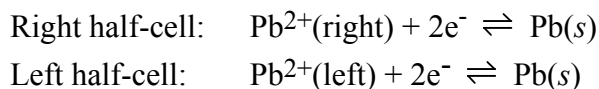
(a) Given that K_{sp} for $Pb(HPO_4)(s)$ is 2.0×10^{-10}, find $[HPO_4^{2-}]$ in the left half-cell.

(b) If the measured cell voltage is 0.097 V, calculate K_{sp} for $PbF_2(s)$.

Pb(HPO$_4$)(s)

Precipitated PbF$_2$ (s)

Solution prepared from
25.0 mL of 0.124 M Na$_3$PO$_4$
and 25.0 mL of 0.248 M HClO$_4$

Prepared by mixing
25.0 mL of 0.124 M Pb(NO$_3$)$_2$
and 25.0 mL of 0.248 M KF
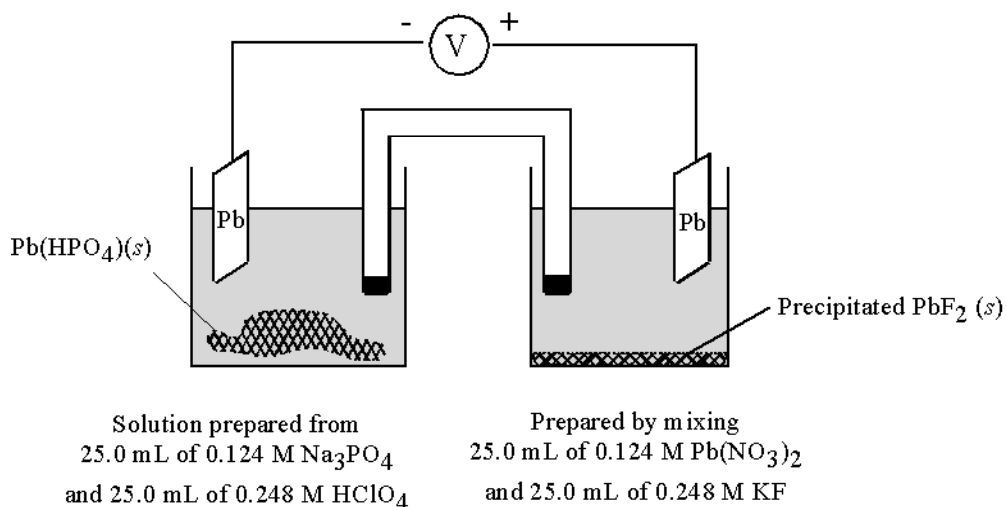
S14-16. The monstrous cell below was set up. Then 50.0 mL of 0.044 4 M Na$_2$EDTA was added to the right-hand compartment and 50.0 mL of 0.070 0 M NaOH was added to the left-hand compartment. The cell voltage leveled off at +0.418 V. Find the formation constant for CuY^{2-} (where Y = EDTA).

100.0 mL of 0.015 2 M
nitrilotriacetic acid
(a neutral compound, of course)

100.0 mL of solution containing
1.37 mM Cu(EDTA)$^{2-}$ and
23.8 mM Ca(NO$_3$)$_2$
buffered to pH 9.76
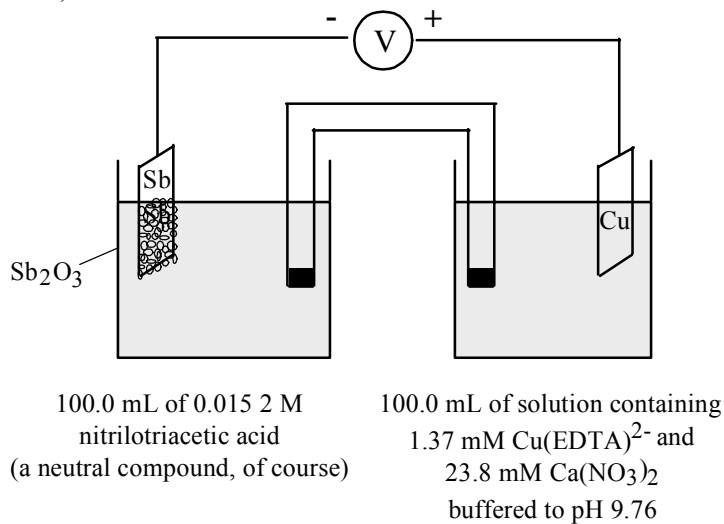
S14-17. Evaluate $E°'$ for the half-reaction $CO_2(g) + 2H^+ + 2e^- \rightleftharpoons CO(g) + H_2O$.
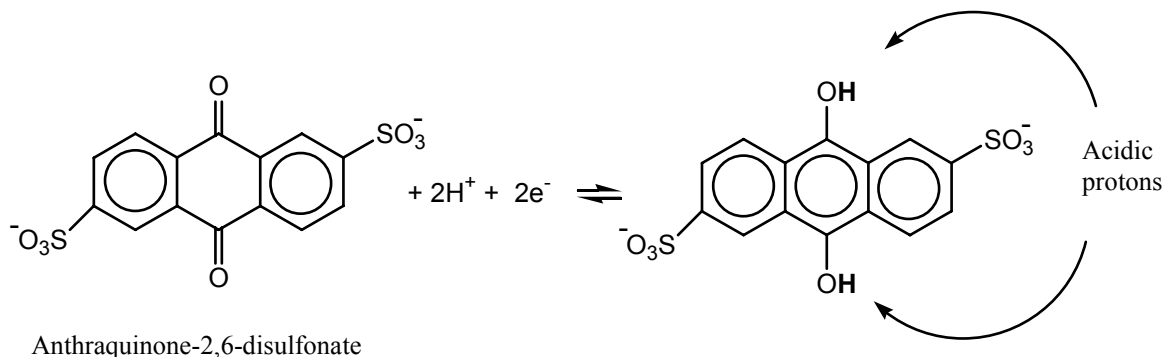
S14-18. Evaluate $E°'$ for the half-reaction $CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H(aq)$.

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 $E°'$ (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:

$$Hg \mid Hg(I)(C_L) \parallel Hg(I)(C_R) \mid Hg$$
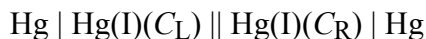
where Hg(I) is present at a concentration C_L in the left half-cell and at a concentration C_R in the right half-cell. Stock solution A was prepared from 2.8 g of mercury(I) nitrate monohydrate, which is either $HgNO_3 \cdot H_2O$ (FM 280.61) if Hg(I) is monatomic, or $Hg_2(NO_3)_2 \cdot 2H_2O$ (FM 561.22) 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.

Cell	Left half-cell	Right half-cell	Voltage (mV)
1	solution A	solution A	0
2	10.0 mL A + 17.4 mL B diluted to 100.0 mL	solution A	29
3	10.0 mL of cell 2 solution + 17.4 mL B diluted to 100.0 mL	solution A	62
4	10.0 mL of cell 3 solution + 17.4 mL B diluted to 100.0 mL	solution A	90
5	10.0 mL of cell 4 solution + 17.4 mL B diluted to 100.0 mL	solution A	119

(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^{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

(d) 0.035 vs Ag|AgCl = ? vs S.C.E.

(b) 0.523 vs Ag|AgCl = ? vs S.H.E.

(e) −0.035 vs calomel = ? vs Ag|AgCl

(c) −0.523 vs S.C.E. = ? 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 Br_2 (*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:

$$S.C.E. \| \text{titration solution} | Ag(s)$$
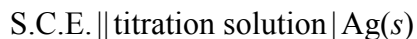
Find the cell voltage for these volumes of titrant: 0.1, 10.0, 25.0 and 30.0 mL.

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, *J. Chem. Ed.* **1992**, *69*, 499; D. C. Luehrs, *J. Chem. Ed.* **1995**, *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 1.00×10^{-5} M $Zn(EDTA)^{2-}$ at a pH of 10.00

$$S.C.E. \| Zn(s) | \text{titration solution}$$

What will be the cell voltage when 10.0 mL of 0.100 M EDTA has been added?
(*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) OH^- and (b) 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 1.00×10^{-4} M $LaClO_4$ and placed in 1.00×10^{-3} M $LaClO_4$?

(c) By how many millivolts will the potential of the electrode change if the electrode is removed from 2.36×10^{-4} M $LaClO_4$ and placed in 4.44×10^{-3} M $LaClO_4$?

(d) The electrode potential is +100 mV in 1.00×10^{-4} M $LaClO_4$ and the selectivity coefficient $k_{La^{3+},Fe^{3+}}$ is $\frac{1}{1\,200}$. 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. $M + L \rightleftharpoons ML$ $K_f = 3.6 \times 10^{10}$

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.

Interfering ion, Y	$k_{Ca^{2+},Y}$
Mg^{2+}	0.040
Ba^{2+}	0.021
Zn^{2+}	0.081

In 1.00×10^{-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

$$E = \text{constant} + \frac{0.057\,1}{2} \log \{[M^{2+}] + 0.020\,0\,[Fe^{2+}]\}$$

When the electrode was immersed in 100.0 mL of unknown containing M^{2+} in 0.020 0 M $Fe(NO_3)_2$, the reading was 194.6 mV (versus S.C.E.). When 1.00 mL of 0.030 7 M M^{2+} (in 0.0.020 0 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 0.010 0 M
$HClO_4$ and variable concentrations of $NaClO_4$. 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 $\mu = 0$ on your graph.

μ (M)	pH	μ (M)	pH	μ (M)	pH
0.10	2.13	1.20	2.05	2.00	1.86
0.30	2.16	1.50	1.99	2.40	1.76
0.50	2.16	1.60	1.96	2.50	1.73
1.00	2.09	1.80	1.92	3.00	1.59

Data from L. Pezza, M. Molina, M. de Moraes, C. B. Melios, and J. O. Tognolli, *Talanta* **1996**, *43*, 1689.

S15-14. *Standard addition*. A perchlorate ion-selective electrode immersed in 50.0 mL of unknown
ClO_4^- solution gave a potential of 358.7 mV versus S.C.E. When 1.00 mL of 0.050 M $NaClO_4$
was added, the potential changed to 346.1 mV. Assuming that the electrode has a Nernstian
response ($\beta = 1.00$), find the concentration of ClO_4^- 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 = $ constant +
$0.059\,16 \log[Ag^+]$. To an unknown cyanide solution was added $Ag(CN)_2^-$ such that
$[Ag(CN)_2^-] = 1.0 \times 10^{-5}$ M in the final solution. This complex ion behaves as a silver ion
buffer in the presence of CN^-:

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

(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.)

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

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

$E = \text{constant} - 0.059\,16 \log[Cl^-]$

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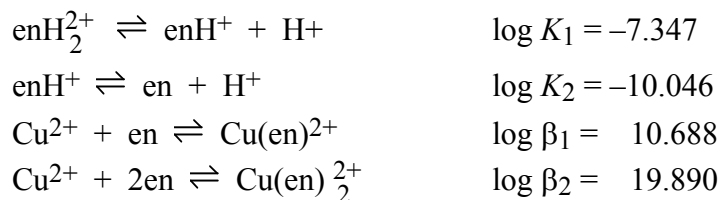
(b) On the basis of your derivation, create a spreadsheet that computes Q as a function of ΔE and reproduce the table in the previous problem.

S15-18. Fourteen ion-selective electrodes were used to measure Ca^{2+} in the same solution with the following results:[25] $[Ca^{2+}] = 1.24, 1.13, 1.20, 1.20, 1.30, 1.12, 1.27, 1.19, 1.27, 1.22, 1.23,$ 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 $\log \mathcal{A}_{F^-}$. Decide which points lie on a straight line and find the least-squares slope of the line. Find the value of β in the equation $E = \text{constant} - \beta(0.059\ 16) \log(\mathcal{A}_{F^-})$.

| [KF] (M)	E (mV)	[KF] (M)	E (mV)
1.00	0.0	1.00×10^{-4}	217.4
1.00×10^{-1}	52.2	1.00×10^{-5}	276.1
1.00×10^{-2}	106.1	1.00×10^{-6}	323.0
1.00×10^{-3}	161.7	1.00×10^{-7}	340.0

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 0.001 00 M $Cu(NO_3)_2$, 0.015 0 M ethylenediamine ($H_2NCH_2CH_2NH_2$, 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:

$$enH_2^{2+} \rightleftharpoons enH^+ + H^+ \qquad\qquad \log K_1 = -7.347$$

$$enH^+ \rightleftharpoons en + H^+ \qquad\qquad \log K_2 = -10.046$$

$$Cu^{2+} + en \rightleftharpoons Cu(en)^{2+} \qquad\qquad \log \beta_1 = 10.688$$

$$Cu^{2+} + 2en \rightleftharpoons Cu(en)_2^{2+} \qquad\qquad \log \beta_2 = 19.890$$

(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^{2+}, as well.)

(b) There are six unknown concentrations in this system: $[enH_2^{2+}]$, $[enH^+]$, $[en]$, $[Cu^{2+}]$, $[Cu(en)^{2+}]$, 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 0.020 0 M In^+ by 0.050 0 M Cu^{2+} 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 Cu^{2+}: 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 0.025 0 M Fe^{3+} by 0.050 0 M Cu^+ to give Fe^{2+} and Cu^{2+},
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
0.010 0 M V^{2+} is titrated with 0.010 0 M Ce^{4+} in 1 M $HClO_4$: 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 Mo^{3+}. The filtrate required 22.11 mL of 0.012 34 M $KMnO_4$ to reach the
purple end point.
$$MnO_4^- \ + \ Mo^{3+} \rightarrow Mn^{2+} \ + \ MoO_2^{2+}$$
A blank required 0.07 mL. Find the molarity of molybdate in the unknown.

S16-5. A 25.00-mL sample containing La^{3+} 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 0.004 321 M
$KMnO_4$. Calculate the molarity of La^{3+} in the unknown.

S16-6. An aqueous glycerol solution weighing 153.2 mg was treated with 50.0 mL of 0.089 9 M Ce^{4+}
in 4 M $HClO_4$ at 60°C for 15 minutes to oxidize the glycerol to formic acid:

$$CH_2 - CH - CH_2$$
$$\;\;|\quad\;\;|\quad\;\;|$$
$$\;\;OH\;\;\;OH\;\;OH$$

Glycerol
FM 92.095

HCO_2H
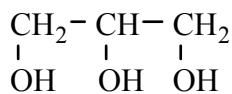
Formic acid

The excess Ce^{4+} required 10.05 mL of 0.043 7 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:


Nitrosobenzene
FM 107.112

Nitrobenzene
FM 123.111

Aniline
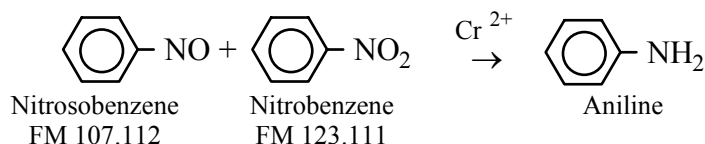
The titration required 21.57 mL of 0.050 00 M Cr^{2+} to reach a potentiometric end point. Find the weight percent of nitrosobenzene in the mixture.

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:
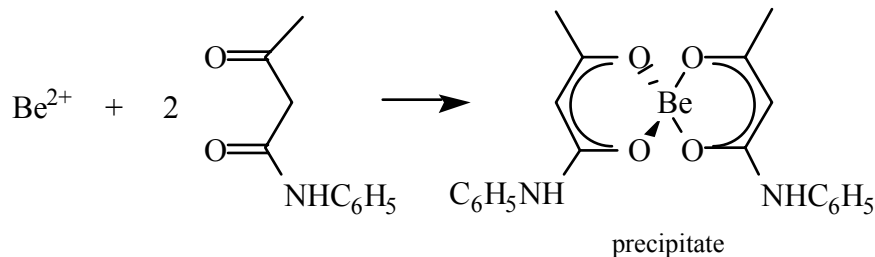
precipitate

The precipitate was dissolved in 6 M HCl and treated with 50.0 mL of solution containing 0.139 2 g of $KBrO_3$ (FM 167.00) plus 0.5 g of KBr. Bromine produced by these reagents reacts with acetoacetanilide as follows:
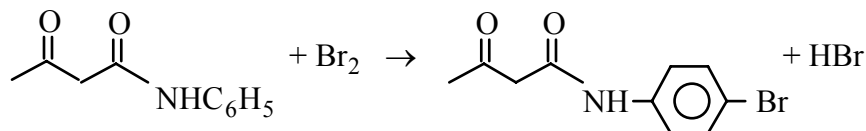

After five minutes, the excess Br_2 was destroyed by adding 2 g of KI (FM 166.00). The I_2 released by the Br_2 required 19.18 mL of 0.050 00 M $Na_2S_2O_3$. Calculate the number of milligrams of Be in the original solution.

S16-9. As in Problem 16-30, a sample of $Bi_2Sr_2(Ca_{0.8}Y_{0.2})Cu_2O_x$ (FM 770.14 + 15.999 4x) was analyzed to find the oxidation states of Bi and Cu. In Experiment A, a sample of $Bi_2Sr_2(Ca_{0.8}Y_{0.2})Cu_2O_x$ 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 0.052 2 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 $FeCl_2 \cdot 4H_2O$. 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]:
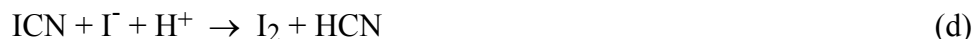
1. Bi^{3+} is precipitated by $Cr(SCN)_6^{3-}$: $Bi^{3+} + Cr(SCN)_6^{3-} \rightarrow Bi[Cr(SCN)_6](s)$ (a)
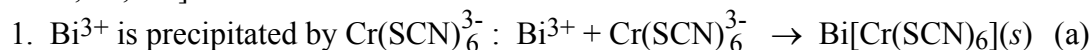
2. The precipitate is filtered, washed, and treated with bicarbonate to release $Cr(SCN)_6^{3-}$:

$$Bi[Cr(SCN)_6] + HCO_3^- + H_2O \rightarrow (BiO)_2CO_3(s) + Cr(SCN)_6^{3-} + H^+ \quad (b)$$
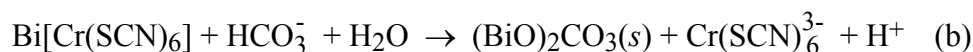
3. I_2 is added to the filtrate after removal of the $(BiO)_2CO_3(s)$:

$$Cr(SCN)_6^{3-} + I_2 + H_2O \rightarrow SO_4^{2-} + ICN + I^- + H^+ + Cr^{3+} \qquad (c)$$

4. Upon acidification to pH 2.5, HCN is created:
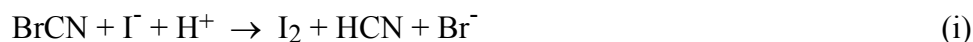
$$ICN + I^- + H^+ \rightarrow I_2 + HCN \qquad (d)$$

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:

$$Br_2 + I^- + H_2O \rightarrow IO_3^- + H^+ + Br^- \qquad (e)$$
$$Br_2 + HCN \rightarrow BrCN + H^+ + Br^- \qquad (f)$$

6. Excess Br_2 is destroyed with formic acid:

$$Br_2 + HCO_2H \rightarrow Br^- + CO_2 + H^+ \qquad (g)$$

7. Addition of excess I^- produces I_2:

$$IO_3^- + I^- + H^+ \rightarrow I_2 + H_2O \qquad (h)$$
$$BrCN + I^- + H^+ \rightarrow I_2 + HCN + Br^- \qquad (i)$$

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_5IO_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:

$$IO_4^- + 3I^- + H_2O \rightleftharpoons IO_3^- + I_3^- + 2OH^- \qquad (A)$$
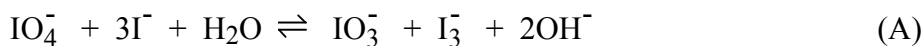
The I_3^- released is titrated with thiosulfate to complete the standardization. (In acidic solution, Reaction A goes further: $H_5IO_6 + 11I^- + 7H^+ \rightleftharpoons 4I_3^- + 6H_2O$.)
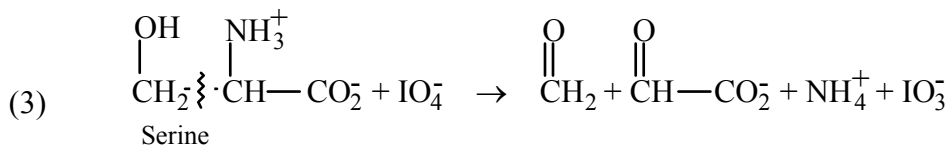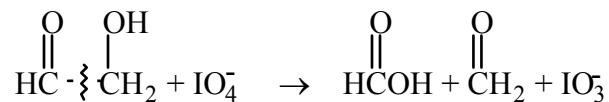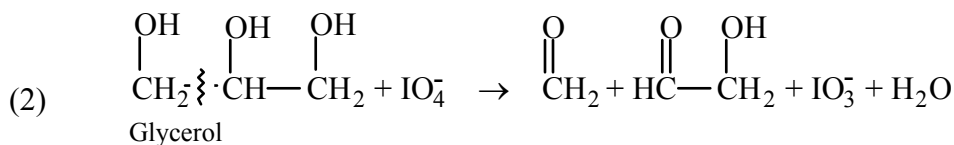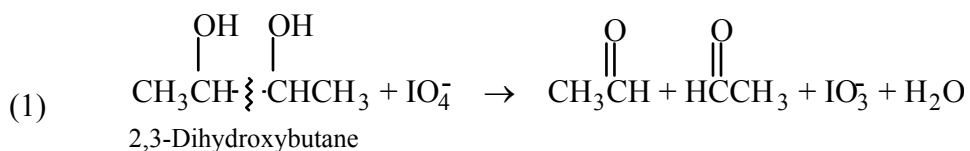
Periodate is especially useful for the analysis of organic compounds (such as carbohydrates) containing hydroxyl, carbonyl or amino groups adjacent to each other. In this oxidation, known as the *Malaprade reaction*, the carbon-carbon bond between the two functional groups is broken and the following 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).
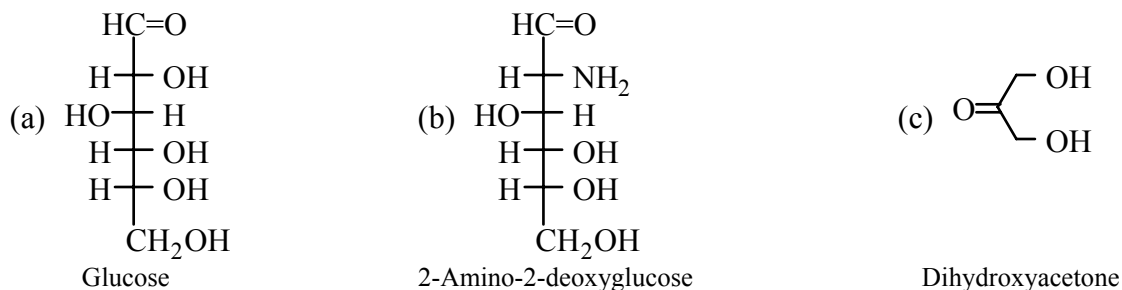
When there are three or more adjacent functional groups, oxidation begins near one end of the molecule.

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)
$$\underset{\text{2,3-Dihydroxybutane}}{CH_3\overset{OH}{\overset{|}{CH}} \{\cdot \overset{OH}{\overset{|}{CH}}CH_3} + IO_4^- \rightarrow CH_3\overset{O}{\overset{||}{CH}} + H\overset{O}{\overset{||}{C}}CH_3 + IO_3^- + H_2O$$

(2)
$$\underset{\text{Glycerol}}{\overset{OH}{\overset{|}{CH_2}} \{\cdot \overset{OH}{\overset{|}{CH}} - \overset{OH}{\overset{|}{CH_2}}} + IO_4^- \rightarrow \overset{O}{\overset{||}{CH_2}} + H\overset{O}{\overset{||}{C}} - \overset{OH}{\overset{|}{CH_2}} + IO_3^- + H_2O$$

$$H\overset{O}{\overset{||}{C}} \cdot \{ \overset{OH}{\overset{|}{CH_2}} + IO_4^- \rightarrow H\overset{O}{\overset{||}{C}}OH + \overset{O}{\overset{||}{CH_2}} + IO_3^-$$

(3)
$$\underset{\text{Serine}}{\overset{OH}{\overset{|}{CH_2}} \{\cdot \overset{NH_3^+}{\overset{|}{CH}} - CO_2^-} + IO_4^- \rightarrow \overset{O}{\overset{||}{CH_2}} + \overset{O}{\overset{||}{CH}} - CO_2^- + NH_4^+ + IO_3^-$$

Finally, here is your problem. Write a balanced equation for the reaction of periodate (IO_4^-) with:

HC=O

H — OH
(a) HO — H
H — OH
H — OH
CH₂OH
Glucose

HC=O

H — NH₂
(b) HO — H
H — OH
H — OH
CH₂OH
2-Amino-2-deoxyglucose

(c) O=⟨ — OH / — OH
Dihydroxyacetone

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

Given that $E°' = -0.187$ V for the indicator, find $E°'$ for the enzyme.

S16-13. This problem uses Beer's law. Aqueous solutions of radioactive materials develop micromolar concentrations of H_2O_2 as a result of nuclear irradiation of H_2O. The following procedure was developed to measure aqueous H_2O_2 with a detection limit near 0.3 µM [N. V. Klassen, D. Marchington, and H. C. E. McGowan, "H_2O_2 Determination by the I_3^- Method and by $KMnO_4$ Titration," *Anal. Chem.* **1994**, *66*, 2921.]. To 500.0 mL of unknown H_2O_2 solution are carefully added 20 mL of 18 M H_2SO_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 2.45×10^3 M^{-1} cm^{-1}. Assuming that the final titration volume was 500.9 mL, find the molarity of H_2O_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.