CHAPTER 17: SUPPLEMENTARY PROBLEMS
ELECTROANALYTICAL TECHNIQUES

S17-1. How many amperes of current are required for 0.1000 mol of electrons to flow through a circuit in 1.000 h?

S17-2. Consider the electrolysis reactions

Cathode: $H_2O(l) + e^- \rightleftharpoons \frac{1}{2} H_2(g, 0.033 \text{ bar}) + OH^-(aq, 1.0 \text{ M})$

Anode: $Br^-(aq, 0.010 \text{ M}) \rightleftharpoons \frac{1}{2} Br_2(l) + e^-$

(a) Find the voltage needed to drive the net reaction with negligible current flow.

(b) Suppose the cell has a resistance of 4.3 Ω and a current of 52 mA is flowing. How much voltage is needed to overcome the cell resistance? This is the ohmic potential.

(c) Suppose that the anode reaction has an overpotential (activation energy) of 0.30 V and that the cathode overpotential is 0.08 V. What voltage is necessary to overcome these effects combined with those of parts a and b?

(d) Suppose that concentration polarization occurs. The concentration of OH^- at the cathode surface increases to 2.0 M and the concentration of Br^- at the anode surface decreases to 0.0020 M. What voltage is necessary to overcome these effects combined with those of parts b and c?

S17-3. Consider the cell below, whose resistance is 2.12 Ω.,

$Hg(l) | Hg_2Cl_2(s) | KCl(aq, \text{saturated}) || KCl(0.080 \text{ M}) | Cl_2(g, 0.10 \text{ bar}) | Pt(s)$

Suppose that there is no concentration polarization or overpotential.

(a) Write the spontaneous galvanic cell reaction.

(b) Calculate the voltage of the galvanic cell if it produces 25.0 mA.

(c) Ohmic potential opposes any electrochemical cell. It decreases the magnitude of the voltage output from a galvanic cell and increases the magnitude of the voltage that must be applied to an electrolysis cell. Calculate the voltage that must be applied to run the reaction above in reverse, as an electrolysis, at 25.0 mA.

(d) Calculate the electrolysis voltage for part c if concentration polarization changes the concentrations to $[Cl_2(g)]_s = 0.20$ bar and $[Cl^-]_s = 0.040$ M in the right half-cell.

(e) Overpotential also opposes any electrochemical cell. It decreases the magnitude of the voltage output from a galvanic cell and increases the magnitude of the voltage that must be applied to an electrolysis cell. Find the electrolysis voltage for part d if there is an overpotential of 0.15 V at the Pt electrode.

S17-4. A 0.531 4 g unknown containing lead tartrate, $Pb(O_2CCHOHCHOHCO_2)$ (FM 355.3), plus inert material was electrolyzed to produce 0.122 1 g of PbO_2 (FM 239.2). Was the PbO_2 deposited at the anode or at the cathode? Find the weight percent of lead tartrate in the unknown.

S17-5. An acidic solution is to be electrolyzed to reduce Fe^{2+} to Fe(*s*).

(a) Calculate the cathode potential (versus S.H.E.) needed to reduce the Fe^{2+} concentration to 0.10 μM if no concentration polarization occurs.

(b) What would be the potential versus saturated Ag | AgCl instead of S.H.E?

(c) Would the potential be more positive or more negative if concentration polarization occurred?

S17-6. What cathode potential (versus S.H.E.) is required to reduce 99.99% of Hg(II) from a solution containing 0.10 M Hg(II) in 1.0 M ammonia? Consider the reactions

$$Hg^{2+} + 4NH_3 \rightleftharpoons Hg(NH_3)_4^{2+} \qquad \beta_4 = 2 \times 10^{19}$$

$$Hg^{2+} + 2e^- \rightleftharpoons Hg(l) \qquad E^\circ = 0.852\ V$$

S17-7. Is it possible to remove 99% of a 1.0 μM FeY^{2-} impurity (by reduction to solid Fe) from a 10 mM CoY^{2-} solution at pH 4 without reducing any cobalt? Here, Y is EDTA and the total concentration of free EDTA is 10 mM.

S17-8. The experiment in Figure 17-8 required 4.11 mA for 834 s for complete reaction of a 3.00-mL aliquot of unknown cyclohexene solution.

(a) How many moles of electrons passed through the cell?

(b) How many moles of cyclohexene reacted?

(c) What was the molarity of cyclohexene in the unknown?

S17-9. Electrolytic reduction of $TiCl_4$ to Ti(*s*) in molten NaCl solvent is complicated by formation of soluble $TiCl_3$ and $TiCl_2$ intermediates. The average oxidation state of Ti in such a mixture is measured in two steps [C. E. Baumgartner, *Anal. Chem.* **1992**, *64*, 2001]:

1. Total Ti is determined by inductively coupled plasma atomic emission.
2. Reducing equivalents of Ti are determined by dissolving the solidified $NaCl/TiCl_4/TiCl_3/TiCl_2$ mixture in a solution containing 4.mM Fe^{3+} in 1 M KCl and 0.12 M HCl under N_2. Prior to adding unknown, the Fe^{3+} solution is exhaustively electrolyzed at +0.6 V (versus saturated Ag | AgCl) to be sure that Fe^{2+} and other reducing impurities are ozidized. Addition of the unknown reduces Fe^{3+} to Fe^{2+},

$$Ti^{3+} + Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+} \qquad Ti^{2+} + 2Fe^{3+} \rightarrow Ti^{4+} + 2Fe^{2+}$$

The resulting Fe^{2+} is coulometrically oxidized back to Fe^{3+} to measure the reducing equivalents in the unknown.

In step 1, 42.37 mg of unknown was found to contain 2.03 mg of total titanium. In step 2, 51.36 mg of unknown was dissolved in 100.0 mL of 4.00 mM Fe^{3+} solution. Controlled-potential coulometry required 9.27 C for complete oxidation of Fe^{2+} back to Fe^{3+}. Find the average oxidation number of Ti in the unknown.

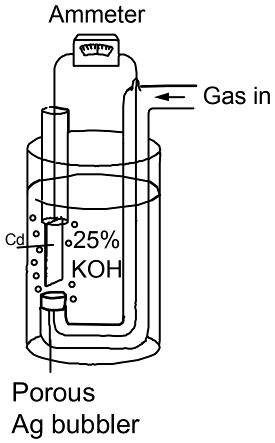
S17-10. A solution containing 0.402 49 g of $CoCl_2 \cdot xH_2O$ was exhaustively electrolyzed to deposit 0.099 37 g of metallic cobalt on a platinum cathode by the reaction $Co^{2+} + 2e^- \rightarrow Co(s)$. Calculate the number of moles of water per mole of cobalt in the reagent.

S17-11. Suppose that the following cell, producing a constant voltage of 1.02 V, is used to operate a light bulb with a resistance of 2.8 Ω.

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

How many hours are required for 5.0 g of Zn to be consumed?

S17-12. The galvanic cell pictured here can be used to measure the concentration of O_2 in gases. Oxygen is quantitatively reduced as it passes through the porous Ag bubbler, and Cd is oxidized to Cd^{2+} to complete the cell. Suppose that gas at 293 K and 1.00 bar is bubbled through the cell at a constant rate of 30.0 mL/min. How much current would be measured if the gas contains 1.00 ppt or 1.00 ppm (vol/vol) O_2?



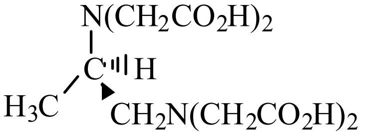
Anode reaction:

$$Cd(s) + 2OH^- \rightleftharpoons Cd(OH)_2(s) + 2e^-$$

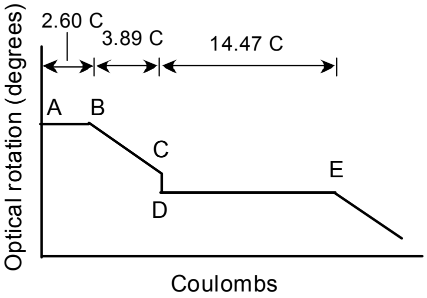
Cathode reaction:

$$\frac{1}{2}O_2(g) + H_2O + 2e^- \rightleftharpoons 2OH^-$$

S17-13. The ligand *R*-(—)-1,2-propylenediaminetetraacetic acid (PDTA) is an optically active relative of EDTA. [R. A. Gibbs and R. J. Palma, Sr., "Coulometric-Spectropolarimetric Titrations of Metal Ions with Chiral Ligands," *Anal. Chem.* **1976**, *48*, 1983.]


PDTA

The reaction of PDTA with a metal can be studied by observing changes in the optical rotation of the solution.



For the coulometric titration shown below, the initial solution contains PDTA and excess Hg^{2+}. Between points A and B, excess Hg^{2+} is reduced to Hg(*l*), which has no effect on the optical rotation. Between points B and C, $Hg(PDTA)^{2-}$ is reduced to Hg(*l*) plus $PDTA^{4-}$, which decreases the optical rotation. Excess $Hg(PDTA)^{2-}$ is still in solution at point C. When unknown Zn^{2+} solution is added, Zn^{2+} displaces Hg^{2+} from PDTA, changing the optical rotation from C to D. Then coulometric reduction of the liberated Hg^{2+} is continued beyond point D. At point E, the free Hg^{2+} is used up and $Hg(PDTA)^{2-}$ begins to be reduced, lowering the optical rotation once again. In a typical experiment, 2.000 mL of Zn^{2+} was added to the cell at point C. From the measured coulombs in the diagram, calculate $[Zn^{2+}]$ in the unknown.

S17-14. Consider the following cell, whose resistance is 3.50 Ω.

$Pt(s)|Fe^{2+}(0.10\ M), Fe^{3+}(0.10\ M), HClO_4(1\ M)||Ce^{3+}(0.050\ M), Ce^{4+}(0.10\ M), HClO_4(1\ M)|Pt(s)$

Suppose that there is no concentration polarization or overpotential.

(a) Calculate the voltage of the galvanic cell if it produces 30.0 mA.

(b) Calculate the voltage that must be applied to run the reaction in reverse, as an electrolysis, at 30.0 mA.

(c) Suppose that the galvanic cell in part (a) delivers 100 mA under the following conditions: $[Fe^{2+}]_s = 0.050$ M, $[Fe^{3+}]_s = 0.160$ M, $[Ce^{3+}]_s = 0.180$ M, $[Ce^{4+}]_s = 0.070$ M. Considering the ohmic potential and concentration polarization, calculate the cell voltage.

S17-15. Explain why controlled-potential electrolysis with a three-electrode cell is more selective (less prone to cause reactions of undesired species) than is a two-electrode cell with constant voltage between the two electrodes.

S17-16. Would you use an anodic or a cathodic depolarizer to prevent the potential of the working electrode from becoming too negative during reduction of Cu^{2+} to Cu(*s*)?

S17-17. A 1.00-L electrolysis cell initially containing 0.025 0 M Mn^{2+} and another metal ion, M^{3+}, is fitted with Mn and Pt electrodes. The reactions are

$$\mathrm{Mn}(s) \rightarrow \mathrm{Mn}^{2+} + 2e^-$$
$$\mathrm{M}^{3+} + 3e^- \rightarrow \mathrm{M}(s)$$

(a) Is the Mn electrode the anode or the cathode?

(b) A constant current of 2.60 A was passed through the cell for 18.0 min, causing 0.504 g of the metal M to plate out on the Pt electrode. What is the atomic mass of M?

(c) What will the concentration of Mn^{2+} in the cell be at the end of the experiment?

S17-18. Calculate the initial voltage that should be applied to electrolyze 0.010 M $Zn(OH)_4^{2-}$ in 0.10 M NaOH, using Ni electrodes. Assume that the current is 0.20 A, the anode current density is 100 A/m^2, the cell resistance is 0.35 Ω , and O_2 is evolved at 0.20 bar. The overpotential for O_2 evolution at a Ni surface at a current density of 100 A m^{-2} is 0.519 V. The reactions are

$$\text{Cathode:} \quad \mathrm{Zn(OH)_4^{2-}} + 2e^- \rightleftharpoons \mathrm{Zn}(s) + 4\mathrm{OH}^- \qquad E^\circ = -1.199\ \mathrm{V}$$
$$\text{Anode:} \quad \mathrm{H_2O} \rightleftharpoons \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{H}^+ + 2e^-$$

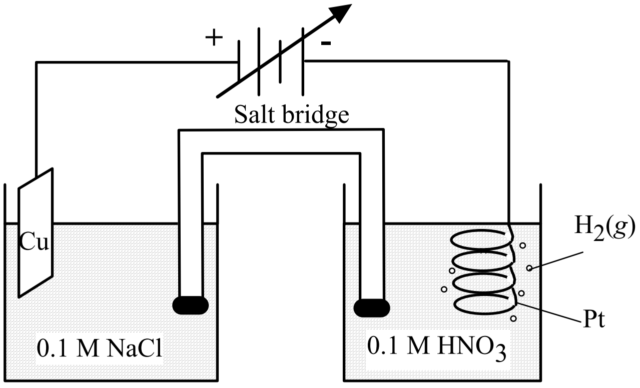
S17-19. Is it possible to remove 99% of a 1.0 μM CuY^{2-} impurity (by reduction to solid Cu) from a 10 mM CoY^{2-} solution at pH 4.0 without reducing any cobalt? Here, Y is EDTA and the total concentration of free EDTA is 10 mM.

S17-20. The electrolysis cell shown below was run at a constant current of 0.021 96 A. On one side, 49.22 mL of H_2 were produced (at 303 K and 0.996 bar); on the other side, Cu metal was oxidized to Cu^{2+}.

(a) How many moles of H_2 were produced?

(b) If 47.36 mL of EDTA were required to titrate the Cu^{2+} produced by the electrolysis, what was the molarity of the EDTA?

(c) For how many hours was the electrolysis run?



$Cu(s) \rightarrow \quad Cu^{2+} + 2e^-$ $\qquad$ $H_2O + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-$

S17-21. A mixture of trichloroacetate and dichloroacetate can be analyzed by selective reduction in a solution containing 2 M KCl, 2.5 M NH_3, and 1 M NH_4Cl. At a mercury cathode potential of –0.90 V (versus S.C.E.), only trichloroacetate is reduced:

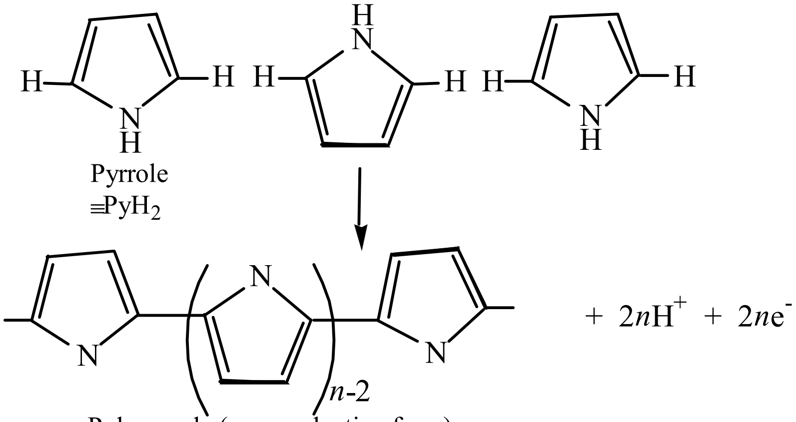
$$Cl_3CCO_2^- + H_2O + 2e^- \rightarrow Cl_2CHCO_2^- + OH^- + Cl^-$$

At a potential of –1.65 V, dichloroacetate reacts:

$$Cl_2CHCO_2^- + H_2O + 2e^- \rightarrow ClCH_2CO_2^- + OH^- + Cl^-$$

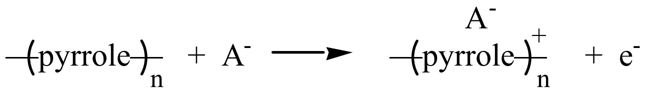
A hygroscopic mixture of trichloroacetic acid (FM 163.386) and dichloroacetic acid (FM 128.943) containing an unknown quantity of water weighed 0.721 g. Upon controlled potential electrolysis, 224 C passed at –0.90 V, and 758 C were required to complete the electrolysis at –1.65 V. Calculate the weight percent of each acid in the mixture.

S17-22. *A stoichiometry challenge*. Polypyrrole is an electrically conductive polymer synthesized by electrochemical oxidation of pyrrole. [R. K. Bunting, K. Swarat, D. Yan, and D. Finello, "Synthesis and Characterization of a Conducting Polymer," *J. Chem. Ed*. **1997**, *74*, 421.] If each pyrrole monomer loses just 2 electrons, the polymer is not conductive:

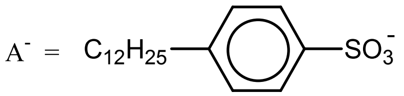


Polypyrrole (nonconductive form)

The polymer becomes conductive when it is oxidized further. For each electron lost (beyond 2 per monomer), an anion (A^-) must associate with the polymer for charge neutrality. The anion dodecylbenzenesulfonate, with a long hydrocarbon tail, is used to diminish the brittleness of the ionic polymer. There is typically one anion for every 2-3 pyrrole monomers.



$$-\!(\text{pyrrole})\!\!-_n + A^- \longrightarrow \overset{A^-}{-\!(\text{pyrrole})\!\!-_n^+} + e^-$$



Dodecylbenzenesulfonate anion

The net reaction to make conductive polypyrrole can be written

$$\underset{\text{Monomer}}{n\mathrm{PyH_2}} + A^- \rightarrow \underset{\substack{\text{Polymer}\\ \text{Formula mass =}\\ n(65.075) + 325.49}}{(\mathrm{Py})_n^+ A^-} + 2n\mathrm{H}^+ + \underset{\substack{\text{This many electrons}\\ \text{flow through the circuit}\\ \text{for every } n \text{ monomers}\\ \text{in the polymer}}}{(2n+1)e^-} \qquad \text{(A)}$$

In the formula mass of the polymer, 65.075 is the mass of a C_4H_3N pyrrole monomer unit and 325.49 is the mass of the anion. In a student synthesis, 13.5 mg of polymer were deposited on stainless steel foil immersed in 0.05 M pyrrole + 0.05 M sodium dodecylbenzenesulfonate after 154.4 min of electrolysis at 1.68 mA.

(a) Calculate how many coulombs and how many moles of electrons were liberated in Reaction A.

(b) Find the value of *n* in Reaction A.

S17-23. Polarographic data for the reduction of Al^{3+} in 0.2 M sodium acetate, pH 4.7, are given below. Construct a standard curve and determine the best straight line by the method of least squares. Calculate the standard deviation for the slope and the intercept. If an unknown solution gives $I_d = 0.904$ µA, calculate the concentration of Al^{3+} and estimate the uncertainty in concentration.

$[Al^{3+}]$ (mM)	I_d (corrected for residual current) (µA)	$[Al^{3+}]$ (mM)	I_d (corrected for residual current) (µA)
0.009 25	0.115	0.111	1.34
0.018 5	0.216	0.148	1.77
0.037 0	0.445	0.185	2.16
0.055 0	0.610	0.222	2.59
0.074 0	0.842	0.259	3.12

S17-24. The differential pulse polarogram of 3.00 mL of solution containing the antibiotic tetracycline in 0.1 M acetate, pH 4, gives a maximum current of 152 nA at a half-wave potential of –1.05 V (versus S.C.E.). When 0.500 mL containing 2.65 ppm of tetracycline was added, the current increased to 206 nA. Calculate the parts per million of tetracycline in the original solution.

S17-25. Chloroform can be used as an internal standard in the polarographic measurement of the pesticide DDT. A mixture containing 1.00 mM $CHCl_3$ and 1.00 mM DDT gave polarographic signals in the proportion

$$\frac{\text{Wave height of } CHCl_3}{\text{Wave height of DDT}} = 1.40$$

An unknown solution of DDT was treated with a tiny amount of pure $CHCl_3$ to give a concentration of 0.500 mM $CHCl_3$, without significantly changing the concentration of unknown. Now the relative signals are found to be

$$\frac{\text{Wave height of } CHCl_3}{\text{Wave height of DDT}} = 0.86$$

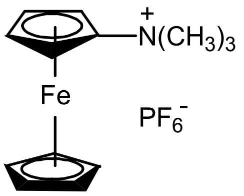
Find the concentration of DDT in the unknown.

S17-26. A mixture containing Tl^+, Cd^{2+}, and Zn^{2+} exhibited the following diffusion currents in two different experiments, A and B, run with the same electrolyte on different occasions:

		Concentration (mM)	I_d (μA)
Tl^+:	A	1.15	6.38
	B	1.21	6.11
Cd^{2+}:	A	1.02	6.48
	B	?	4.76
Zn^{2+}:	A	1.23	6.93
	B	?	8.54

Calculate the Cd^{2+} and Zn^{2+} concentrations in experiment B.

S17-27. Peak current (I_p) and scan rate (ν) are listed below for cyclic voltammetry of a water-soluble ferrocene derivative in 0.1 M NaCl , using a Nafion-coated Pt electrode [M. E. Gomez and A. E. Kaifer, *J. Chem. Ed.* **1992**, *69*, 502]. Nafion is a polymer with fixed negative charges and mobile, exchangeable counteranions. Its structure was shown in Problem 17-11. Prepare graphs of I_p vs. ν and I_p vs. $\sqrt{\nu}$ and state whether the ferrocene derivative is free in solution or confined to the electrode surface.



Scan rate (V/s)	Peak anodic current (μA)
0.050	0.73
0.100	1.32
0.150	1.89
0.200	2.22
0.250	2.89
0.300	3.39
0.350	3.87

S17-28. The half-wave potential ($E_{1/2}^{\text{comp}}$) for reduction of the metal-ligand complex (ML_p^+) is given by

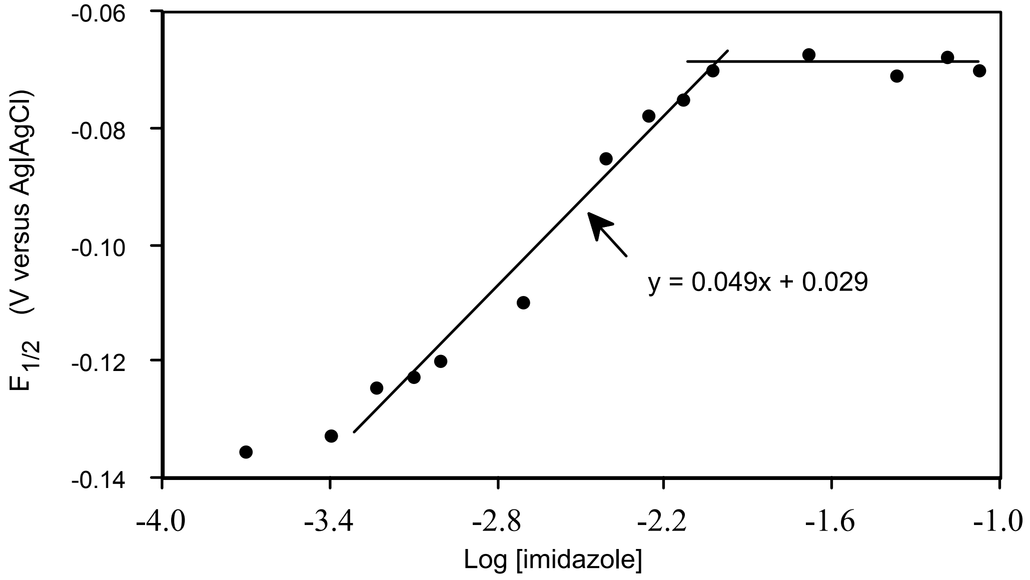
$$\text{ML}_\text{p}^+ + \text{e}^- \rightarrow \text{ML}_\text{q} + (p - q)\text{L}$$

$$E_{1/2} = E_{1/2}^{\text{free}} - 0.059 \log \frac{\beta_\text{p}^{\text{ox}}}{\beta_\text{q}^{\text{red}}} + 0.059(p - q)\log[\text{L}]$$

where potential for reduction in the absence of ligand, β is a formation constant, and [L] is the concentration of ligand.

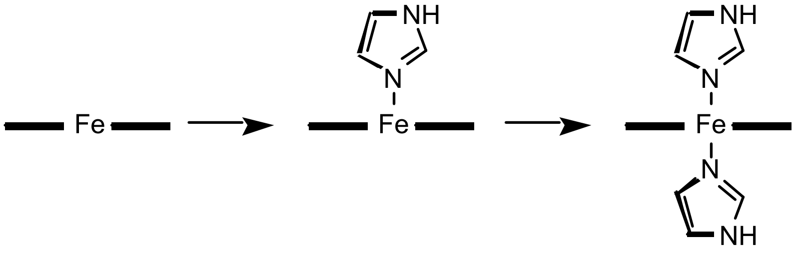
$$\beta_\text{p}^{\text{ox}} = \frac{[\text{ML}_\text{p}^+]}{[\text{M}^+][\text{L}]^\text{p}} \qquad\qquad \beta_\text{q}^{\text{red}} = \frac{[\text{ML}_\text{q}]}{[\text{M}][\text{L}]^\text{q}}$$

A graph of $E_{1/2}$ versus log[L] should have a slope of $0.059(p - q)$ and an intercept of $\{E_{1/2}^{\text{free}} - 0.059 \log (\beta_\text{p}^{\text{ox}}/\beta_\text{q}^{\text{red}})\}$. Experimental data for the reduction of an Fe^{3+} complex (M^+) to the Fe^{2+} complex (M) in the presence of the ligand imidazole (L) is shown



Dependence of half-wave potential (measured by cyclic voltammetry) on ligand concentration for reduction of Fe^{3+} complex to Fe^{2+} complex. [Data from D. K. Geiger. E. J. Pavlak and L. T. Kass, *J. Chem. Ed.* **1991**, *68*, 337. This article describes a student experiment for measuring binding constants.]

The species M is actually an iron-porphyrin complex (Problem S17-50) that can bind zero, one or two imidazole ligands in axial coordination positions:



M ML ML_2

(a) For the region $-3.4 < \log [L] < -2.1$, the slope in the graph is +0.049 V. Write a reduction reaction with appropriate numbers of ligands for reactants and products to describe the chemistry in this region. Given that $E_{1/2}^{\text{free}} = -0.18$ V, use the intercept (+0.029) of the line segment to estimate the value of $\log (\beta_p^{\text{ox}} / \beta_q^{\text{red}})$.

(b) For $\log [L] > -2.1$, the slope in the graph is zero. Write a reduction reaction with appropriate numbers of ligands for reactants and products to describe the chemistry in this region.

S17-29. Ammonia can be titrated with hypobromite, but the reaction is somewhat slow:

$$2NH_3 + 3OBr^- \rightleftharpoons N_2 + 3Br^- + 3H_2O$$

The titration can be performed with a rotating Pt electrode held at +0.20 V (versus S.C.E.) to monitor the concentration of OBr^-:

$$\text{Cathode:} \quad OBr^- + 2H^+ + 2e^- \rightleftharpoons Br^- + H_2O$$

The current would be near zero before the equivalence point if the OBr^- were consumed quickly in the titration. However, the sluggish titration reaction does not consume all the OBr^- after each addition, and some current is observed. The increasing current beyond the equivalence point can be extrapolated back to the residual current to find the endpoint. A solution containing 30.0 mL of 4.43×10^{-5} M NH_4Cl was titrated with NaOBr in 0.2 M $NaHCO_3$, with the following results:

OBr^- (mL)	I	OBr^- (mL)	I	OBr^- (mL)	I	OBr^- (mL)	I
0.000	0.03	0.400	3.74	0.700	1.63	0.780	6.84
0.100	1.42	0.500	3.79	0.720	2.89	0.800	8.08
0.200	2.61	0.600	3.20	0.740	4.17	0.820	9.36
0.300	3.26	0.650	2.09	0.760	5.53	0.840	10.75

Prepare a graph of current versus volume of OBr^-, and find the molarity of the NaOBr solution.

S17-30. Karl Fischer reagent containing I_2, SO_2, base and alcohol may be delivered from a buret, instead of generating the I_2 coulometrically. The reagent may be standardized by titration with H_2O dissolved in methanol. A 25.00-mL aliquot of Karl Fischer reagent reacted with 34.61 mL of methanol to which was added 4.163 mg of H_2O per mL. When pure "dry" methanol was titrated, 25.00 mL of methanol reacted with 3.18 mL of the same Karl Fischer reagent. A suspension of 1.000 g of a hydrated crystalline salt in 25.00 mL of methanol consumed a total of 38.12 mL of Karl Fischer reagent. Calculate the weight percent of water in the crystal.

S17-31. Hydrogen peroxide is found in concentrations of 10^{-8} to 10^{-4} M in water droplets in the troposphere — the lower 10 to 17 km of the atmosphere, where there is substantial vertical mixing (below the stratosphere, which is the next 30 to 40 km of the atmosphere). Oxidation of H_2O_2 with a rotating Pt electrode at +0.4 V (versus S.C.E.) gave the following calibration data. [J. Lagrange and P. Lagrange, *Fresenius J. Anal. Chem.* **1991**, *339*, 452.]

$[H_2O_2]$, M	Diffusion current (nA) (± standard deviation)
1.00×10^{-4}	6 995 ±112
5.00×10^{-5}	3 510 ±74
1.00×10^{-5}	698 ±11
5.00×10^{-6}	345 ±18
1.00×10^{-6}	64.4 ±3.9
5.00×10^{-7}	32.4 ±1.8
1.00×10^{-7}	6.88 ±0.64
5.00×10^{-8}	3.17 ±0.32
2.00×10^{-8}	1.03 ±0.20

(a) Prepare a graph of log(current) versus $\log[H_2O_2]$ to show that the response is linear over four orders of magnitude.

(b) From a graph of current versus $[H_2O_2]$ (not log(current) versus $\log[H_2O_2]$), find the slope and intercept and their uncertainties by the method of least squares.

(c) Find $[H_2O_2]$ (and its uncertainty) for an unknown whose diffusion current is 300 ± 15 nA.

S17-32. **Weighted least squares.** The previous problem gave an example in which the uncertainties associated with different data points is different. We now show how to compute the least squares best straight line when errors in x_i are negligible, but each value of y_i has a standard deviation s_i. These are found by measuring y several times for each value of x. We associate a weighting factor, w_i, with each value of y_i:

$$\text{Weighting factor} = w_i = \frac{1}{s_i^2}$$

The smaller the standard deviation of y_i, the greater will be the weighting factor for y_i. That is, we weight the more certain values of y greater than the less certain values of y when we compute the least squares straight line. Using the weighting factor $w_i = 1/s_i^2$, the parameters for the straight line are

$$\text{Denominator} = D = (\Sigma w_i)(\Sigma w_i x_i^2) - (\Sigma w_i x_i)^2$$

$$\text{Slope} = m = \frac{(\Sigma w_i)(\Sigma w_i x_i y_i) - (\Sigma w_i x_i)(\Sigma w_i y_i)}{D}$$

$$\text{Intercept} = b = \frac{(\Sigma w_i y_i)(\Sigma w_i x_i^2) - (\Sigma w_i x_i)(\Sigma w_i x_i y_i)}{D}$$

$$\text{Variance of } y = s_y^2 = \frac{(\Sigma w_i)d_i^2}{n-2}$$

(where $d_i = y_i - mx_i - b$ and there are n data points)

$$\text{Variance of slope} = s_m^2 = \frac{(\Sigma w_i)s_y^2}{D}$$

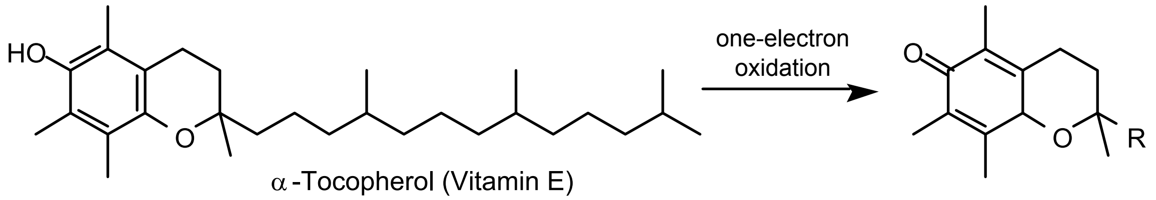
$$\text{Variance of intercept} = s_b^2 = \frac{(\Sigma w_i x_i^2)s_y^2}{D}$$

Prepare a spreadsheet that uses the data in the previous problem to find the slope and intercept (and their uncertainties) for a graph of current versus [H_2O_2]. Compare your parameters to those found by the unweighted treatment in the previous problem.

S17-33. **A spreadsheet for fitting the equation $y = A + Bx + Cx^2$.** At the end of this problem is a spreadsheet that you can copy onto your computer to fit quadratic equations and to estimate the uncertainties in the parameters A, B and C. [The *formulas* in this spreadsheet come from R. T. O'Neill and D. C. Flaspohler (*J. Chem. Ed.* **1990**, *67*, 40), which provides a general recipe for fitting equations of the form $y = A{*}f(x, z, w....) + B{*}g(x, z, w....) + C{*}h(x, z, w....) + ...$, where A, B, C ... are constants and f, g, h are functions of the variables x, z, w....] In column A, N is the number of data points and T is the number of terms to be fit. Since we are looking for three coefficients (A, B, and C), $T = 3$. The data are entered in columns B and C and their weights (discussed in the previous problem) are in column D. If weights are unknown, set all weights to unity. The parameters A, B, and C are found in cells A15, A17 and A19 and their estimated uncertainties are in cells D15, D17 and D19. The other quantities in the table are used in the computations, but are not part of the final answer.

α-Tocopherol (Vitamin E) is a lipid-soluble anti-oxidant that can be oxidized at 0.67 V (versus S. C. E.) at a glassy carbon electrode in 0.12 M H_2SO_4 in a 1:1 ethanol:benzene mixture.

(Note: In recipes calling for the carcinogen, benzene, try substituting toluene.)



Calibration data for voltammetry of standard solutions is given below.

[α-Tocopherol] (μg/mL)	Peak current (μA)	[α-Tocopherol] (μg/mL)	Peak current (μA)
13.0	18.2	62.1	82.4
26.1	36.0	91.0	115.3
37.9	52.7	118.6	148.4
50.5	68.3	169.2	200.0

(a) Copy the spreadsheet onto your computer to find the values of *A*, *B* and *C* for the equation

$$\text{Current} = A + B[\alpha\text{-tocopherol}] + C[\alpha\text{-tocopherol}]^2$$

(b) Prepare a graph of the calibration data, showing the curve computed in part a.

(c) Calculate the concentration (and uncertainty) of α-tocopherol in an unknown that gave a peak current of 170 ±1 μA. For the uncertainty, compute the concentrations corresponding to 170 + 1 = 171 μA and to 170 – 1 = 169 μA.

Spreadsheet for fitting the equation $y = A + Bx + Cx^2$

	A	B	C	D	E	F	G	H
1	N (points)=	x	y	weight=w	w*y*y	w*y	w*y*x	w*y*x*x
2	8	13.0	18.2	1	3.31E+02	1.82E+01	2.37E+02	3.08E+03
3	T (terms)=	26.1	36.0	1	1.30E+03	3.60E+01	9.40E+02	2.45E+04
4	3	37.9	52.7	1	2.78E+03	5.27E+01	2.00E+03	7.57E+04
5		50.5	68.3	1	4.66E+03	6.83E+01	3.45E+03	1.74E+05
6		62.1	82.4	1	6.79E+03	8.24E+01	5.12E+03	3.18E+05
7		91.0	115.3	1	1.33E+04	1.15E+02	1.05E+04	9.55E+05
8		118.6	148.4	1	2.20E+04	1.48E+02	1.76E+04	2.09E+06
9		169.2	200.0	1	4.00E+04	2.00E+02	3.38E+04	5.73E+06
10								
11		Column sums:		8	91175.83	721.3	73672.26	9363164.19
12	Denominator		Standard deviationof y =					
13	6.31E+12			0.9191				
14	A =		Standard deviation (A) =				Q' =	
15	0.966634			0.955			102742.6354	
16	B =		Standard deviation (B) =				Q =	
17	1.385127			0.0267			91171.60663	
18	C =		Standard deviation (C) =				V =	
19	-0.001236			0.0001			0.844674477	
20	Formulas:							
21	A13 = (F11*(J11*L11-K11*K11)+G11*(J11*K11-I11*L11)+H11*(I11*K11-J11*J11))/A13							
22	A15 = (F11*(J11*L11-K11*K11)+G11*(J11*K11-I11*L11)+H11*(I11*K11-J11*J11))/A13							
23	A17 = (F11*(J11*K11-I11*L11)+G11*(D11*L11-J11*J11)+H11*(I11*J11-D11*K11))/A13							
24	A19 = (F11*(I11*K11-J11*J11)+G11*(I11*J11-D11*K11)+H11*(D11*J11-I11*I11))/A13							
25	D15 = Sqrt(G19*(J11*L11-K11*K11)/A13)							
26	D17 = Sqrt(G19*(D11*L11-J11*J11)/A13)							
27	D19 = Sqrt(G19*(D11*J11-I11*I11)/A13)							
28	G15 = A15*(A15*D11+A17*I11+A19*J11)+A17*(A15*I11+A17*J11+A19*K11)							
29	G17 = G15+A19*(A15*J11+A17*K11+A19*L11)							
30	G19 = (E11-G17)/(A2-A4)							

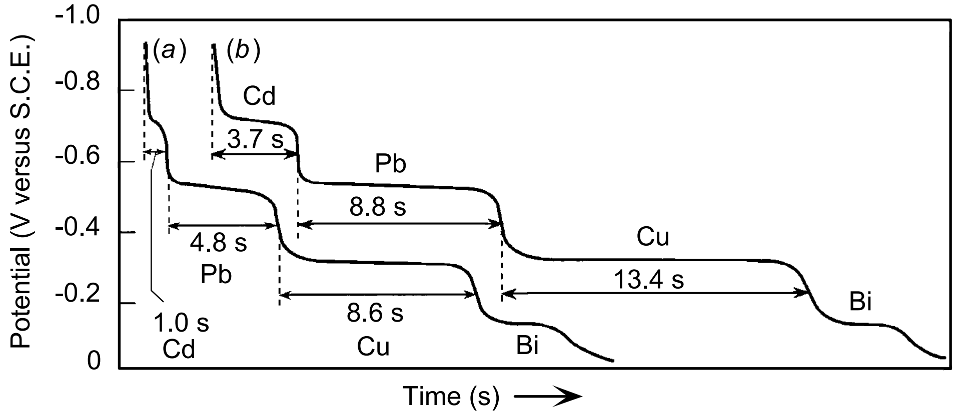
	I	J	K	L
1	w*x	w*x*x	w*x^3	w*x^4
2	1.30E+01	1.69E+02	2.20E+03	2.86E+04
3	2.61E+01	6.81E+02	1.78E+04	4.64E+05
4	3.79E+01	1.44E+03	5.44E+04	2.06E+06
5	5.05E+01	2.55E+03	1.29E+05	6.50E+06
6	6.21E+01	3.86E+03	2.39E+05	1.49E+07
7	9.10E+01	8.28E+03	7.54E+05	6.86E+07
8	1.19E+02	1.41E+04	1.67E+06	1.98E+08
9	1.69E+02	2.86E+04	4.84E+06	8.20E+08
10				
11	568.4	59668.88	7708446.95	1.11E+09

S17-34. Potentiometric stripping analysis. In a typical procedure, a glassy carbon working electrode is coated with a film of liquid mercury by reduction of Hg^{2+} for a few minutes. The electrode is then washed with water and transferred to analyte containing ~1 mg of Hg^{2+} per liter. After purging the solution with N_2 and leaving it under a blanket of N_2, a controlled potential is applied for a fixed time to reduce some of the analyte into the mercury film. The potentiostat is then *disconnected* from the electrodes and replaced by a potentiometer. The voltage between the working and reference electrodes is then recorded as a function of time. [For a student experiment in potentiometric stripping analysis, see C. W. K. Chow, D. E. Davey, M. R. Haskard, D. E. Mulcahy, and T. C. W. Yeow, *J. Chem. Ed.* **1994**, *71*, 997.]

When the potentiostat is disconnected, analyte such as Pb^{2+} that was reduced to Pb and dissolved in the mercury film is oxidized by Hg^{2+} from the solution:

$$\text{Pb(in Hg)} + Hg^{2+} \rightarrow Pb^{2+} + \text{Hg}(l)$$

The amalgamated Pb is being titrated by Hg^{2+} from the solution and the potential of the working electrode remains close to $E_{1/2}$ for Pb(in Hg)|Pb^{2+}. When Pb is used up, the electrode potential suddenly becomes more positive. The time between disconnecting the potentiostat and the sudden potential change is proportional to the concentration of Pb^{2+} in the unknown.



Potentiometric stripping curves from a sample containing Cd^{2+}, Pb^{2+}, Cu^{2+} and Bi^{3+} *(a)* before and *(b)* after addition of 0.5 μg/L of Cd^{2+}, Pb^{2+}, and Cu^{2+}. There was no dilution caused by the standard addition. The sample contained 0.5 M NaCl, 0.05 M HCl, and 1 mg of Hg^{2+}/L.
[From L. D. Jagner, *Anal.. Chem.* **1978**, *50*, 1924.]

Trace a of the figure above shows potentiometric stripping of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Bi^{3+}. After 128 min of reduction at –0.95 V (versus S. C. E.), the potentiostat was disconnected and the voltage between the working and reference electrodes was measured as the reduced analytes reacted with Hg^{2+}. For 1.0 s, the potential remained near –0.72 V while the following reaction occurred:

$$\text{Cd(in Hg)} + Hg^{2+} \rightarrow Cd^{2+} + \text{Hg}(l)$$

Then the voltage suddenly changed to –0.52 V for 4.8 s while Pb was oxidized. This was followed by 8.6 s at –0.31 V as Cu was oxidized to Cu^{2+} and ~4 s at –0.14 V as Bi was oxidized to Bi^{3+}.

In trace b of the figure above, standard additions of 0.5 µg/L of Cd^{2+}, Pb^{2+}, and Cu^{2+} were made to the solution from trace a (with negligible dilution). Find the concentration of Pb^{2+} in the original unknown.

S17-35. From the data for the standard addition shown in the previous problem, find the concentration of Cu^{2+} in the unknown.

S17-36. In a standard addition experiment similar to the one in Problem S17-34, the following signals were observed for Pb^{2+}:

unknown: 4.5 s
unknown + 0.50 µg/L Pb^{2+}: 8.6 s
unknown + 1.00 µg/L Pb^{2+}: 12.9 s

Dilution of the unknown by the standards was negligible. Prepare a standard addition graph to find the concentration of Pb^{2+} in the unknown.

S17-37. Based on the standard addition in Problem S17-34, find the concentration of Cd^{2+} in the unknown.

S17-38. In a standard addition experiment similar to the one in Problem S17-34, the following signals were observed for Cu^{2+}. Dilution of the unknown by the standards was negligible. Prepare a standard addition graph to find the concentration of Cu^{2+} in the unknown.

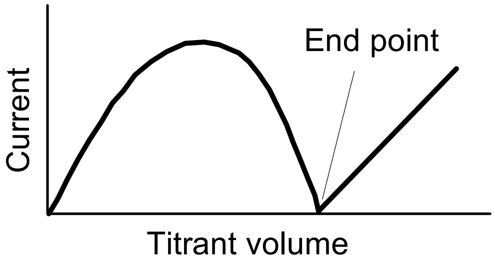
Unknown: 8.6 s
Unknown + 0.50 µg/L Cu^{2+}: 12.5 s
Unknown + 1.00 µg/L Cu^{2+}: 16.6 s

S17-39. **Biamperometric Titrations.** The procedure employing two polarizable electrodes for amperometric detection of an end point is called a *biamperometric titration*. Figure a below illustrates the shape of the curve obtained for the biamperometric titration of I_2 with $S_2O_3^{2-}$. The titration reaction is

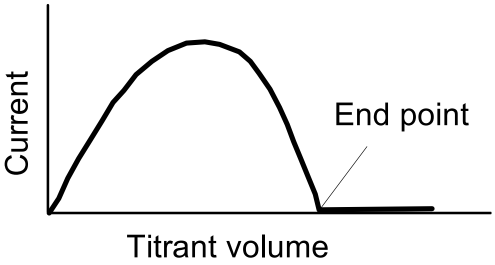
$$\underset{\text{Thiosulfate}}{2S_2O_3^{2-}} + I_2{}^{-} \rightarrow 2I^- + \underset{\text{Tetrathionate}}{S_4O_6^{2-}} \qquad (1)$$

The $I_2 \mid I^-$ couple reacts reversibly at a Pt electrode, but the $S_2O_3^{2-} \mid S_4O_6^{2-}$ couple does not. That is, the reaction $I_2 + 2e^- \rightleftharpoons 2I^-$ occurs readily at the Pt surface, but the reaction $S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$ does not.

(a)



(b)



Now consider what happens when $S_2O_3^{2-}$ is added to I_2. At first, no I^- is present and only residual current is observed. As the reaction proceeds, I^- is created and current is conducted between the two polarizable electrodes by means of the following reactions:

cathode: $I_2 + 2e^- \rightarrow 2I^-$
anode: $2I^- \rightarrow I_2 + 2e^-$

The current reaches a maximum near the middle of the titration, when both I_2 and I^- are present. The current then decreases as more I_2 is consumed by Reaction 1. Beyond the end point, no I_2 is present and only residual current flows. The end point of a biamperometric titration is sometimes called a *dead stop* end point.

A schematic biamperometric titration curve for the addition of Ce^{4+} to Fe^{2+} is shown in Figure b above. The titration is $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$ and both couples ($Ce^{4+} \mid Ce^{3+}$ and $Fe^{3+} \mid Fe^{2+}$) react reversibly at the Pt electrodes. Explain the shape of the titration curve.

S17-40. (a) Br_2 can be generated for quantitative analysis by addition of standard BrO_3^- to excess Br^- in acidic solution:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3H_2O + 3Br_2$$

Consider the *biamperometric* titration (defined in the previous problem) of H_3AsO_3 with Br_2:

$$Br_2 + H_3AsO_3 + H_2O \rightarrow 2Br^- + H_3AsO_4 + 2H^+$$

A solution containing H_3AsO_3 and Br^- is titrated with standard BrO_3^-.

Given that the $H_3AsO_4 \mid H_3AsO_3$ couple does not react at a Pt electrode, predict the shape of a graph of current versus volume of titrant.

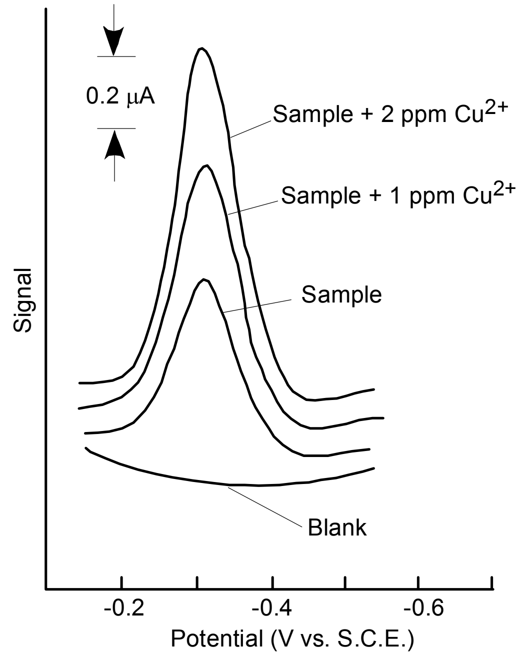
(b) Sketch a graph of voltage versus volume of I_2 added for a *bipotentiometric* titration of H_3AsO_3 with I_2.

S17-41. The analysis of Ni^{2+} at the nanogram level is possible with differential pulse polarography, which gives derivative-peak-shaped signals very much like square wave polarography. Addition of dimethylglyoxime to an ammonium citrate buffer enhances the response by a factor of 15.

Ni^{2+} (ppb)	Peak current (μA)	Ni^{2+} (ppb)	Peak current (μA)
19.1	0.095	114	0.500
38.2	0.173	132	0.581
57.2	0.258	151	0.650
76.1	0.346	170	0.721
95.0	0.429		

Construct a standard curve and predict how much current is expected if 54.0 μL of solution containing 10.0 ppm Ni^{2+} is added to 5.00 mL of buffer.

S17-42. A large quantity of Fe^{3+} interferes with the polarographic analysis of Cu^{2+} because Fe^{3+} is reduced at less negative potentials than is Cu^{2+} in most supporting electrolytes. Interference is eliminated by addition of hydroxylamine (NH_2OH), which reduces Fe^{3+}, but not Cu^{2+}. The figure shows the differential pulse polarogram of Cu^{2+} in the presence of 1 000 ppm of Fe^{3+} with saturated $NH_3OH^+Cl^-$ as supporting electrolyte. Each sample was made up to the *same final volume*. Averaging responses for the two standard additions, find $[Cu^{2+}]$ in the sample solution.



Differential pulse polarograms.

Modulation amplitude: 25 mV.
Drop interval: 1 s.
Scan rate: 2 mV/s.

Each scan is offset (displaced vertically) from the previous one. When you measure the peak heights relative to the blank, subtract the vertical displacement at the left edge of the scan.

[EG&G Princeton Applied Research Corp., Application Note 151.]

S17-43. To see how polarography is used in measuring equilibrium constants, consider a solution containing the ions M^{3+} and M^{2+}. The potential for reduction of M^{3+} is

$$E = E^\circ - 0.059\,16 \log \frac{[M^{2+}]}{[M^{3+}]}$$

Suppose that a ligand that binds only to M^{3+} is added to the solution. The potential needed for reduction of M^{3+} will change, because the quotient $[M^{2+}]/[M^{3+}]$ changes. The potential can be predicted if we know the formation constant of the metal-ligand complex. Alternatively, measuring the reduction potential tells us the formation constant. In polarography, the half-wave potential is sensitive to equilibria involving analyte.

For the reduction of a complex ion to yield an amalgam plus free ligand

$$ML_p^{n-pb} + ne^- + Hg \rightleftharpoons M(\text{in Hg}) + pL^{-b} \qquad (A)$$

$E_{1/2}$ is related to $E_{1/2}$ for the free metal ion in a noncomplexing medium by the following equation.

$$E_{1/2} = E_{1/2}(\text{for free } M^{n+}) - \frac{0.059\,16}{n} \log \beta_p - \frac{0.059\,16p}{n} \log [L^{-b}] \qquad (B)$$

where β_p is the equilibrium constant for the reaction $M^{n+} + pL^{-b} = ML_p^{n-pb}$. A graph of $E_{1/2}$ versus $\log[L^{-b}]$ has a slope of $-0.059\,16p/n$ and a y-intercept of $[E_{1/2}$ (for free M^{n+}) $- (0.059\,16/n)\log \beta_p]$.

Polarographic data for the reaction

$$HPbO_2^- + H_2O + 2e^- + Hg \rightleftharpoons Pb(\textit{in Hg}) + 3OH^-$$

are given below.

$E_{1/2}$ (V versus S.C.E)	$[OH^-]$ (M, free OH^-)
–0.603	0.011
–0.649	0.038
–0.666	0.060
–0.681	0.099
–0.708	0.201
–0.734	0.448
–0.747	0.702
–0.755	1.09

The species $HPbO_2^-$ can be treated as $Pb(OH)_3^-$ by virtue of the equilibrium

$$Pb(OH)_3^- \rightleftharpoons HPbO_2^- + H_2O$$

Use the preceding data to show that $p = 3$ in Equation A, and find the value of β_3 for $Pb(OH)_3^-$. The value of $E_{1/2}$(for free Pb^{2+}) in Equation B is –0.41 V. This is the half-wave potential for the reaction $Pb^{2+} + 2e^- \rightleftharpoons Pb(\mathit{in\ Hg})$ in 1 M HNO_3.

S17-44. Sketch the shape of a bipotentiometric titration curve (E versus volume added) for the addition of Ce^{4+} to Fe^{2+}. Both the $Ce^{4+}|Ce^{3+}$ and $Fe^{3+}|Fe^{2+}$ couples react reversibly at Pt electrodes.

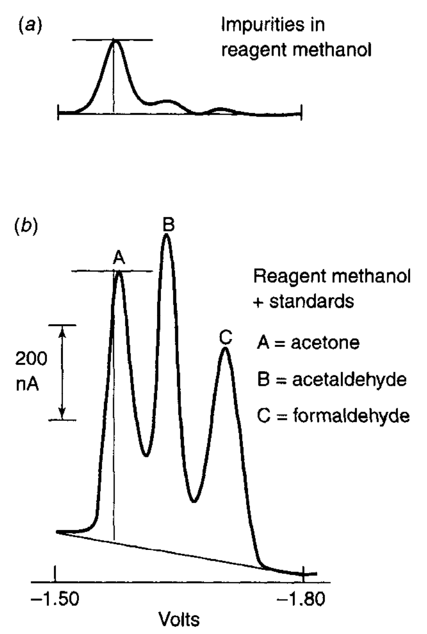
S17-45. Draw graphs showing the voltage ramps used in sampled current and square wave polarography. Label the axes and key operating parameters.

S17-46. An unknown gave a polarographic signal of 10.0 μA. When 1.00 mL of 0.050 0 M standard was added to 100.0 mL of unknown, the signal increased to 14.0 μA. Find the concentration of the original unknown.

S17-47. The following diffusion currents were measured at –0.6 V for $CuSO_4$ in 2 M NH_4Cl / 2M NH_3. Use the method of least squares to estimate the molarity and uncertainty in molarity of an unknown solution giving I_d = 15.6 μA.

$[Cu^{2+}]$ (mM)	I_d (μA)	$[Cu^{2+}]$ (mM)	I_d (μA)
0.039 3	0.256	0.990	6.37
0.078 0	0.520	1.97	13.00
0.158 5	1.058	3.83	25.0
0.489	3.06	8.43	55.8

S17-48. A polarogram of reagent-grade methanol is shown here, along with that of a standard made by adding an additional 0.001 00 wt % acetone, 0.001 00 wt % acetaldehyde, and 0.001 00 wt % formaldehyde to reagent-grade methanol. Estimate the weight percent of acetone in reagent-grade methanol.



Differential pulse polarogram of reagent grade methanol and methanol containing added standards

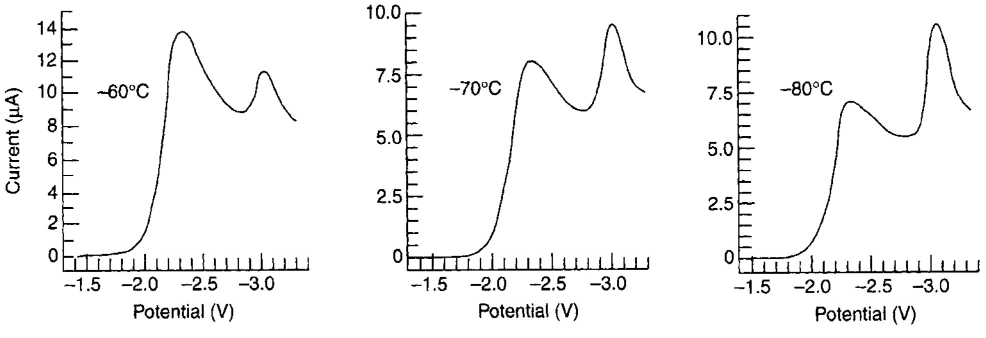
[D. B. Palladino, *Am. Lab.* August 1992, p. 56].

Solutions were prepared by diluting 25 mL of methanol (or methanol plus standards) up to 100 mL with water containing buffer and hydrazine sulfate. The latter reacts with carbonyl compounds to form hydrazones, which are the electroactive species in this analysis.

$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + \underset{\text{Hydrazine}}{H_2N\text{-}NH_2} \rightarrow \underset{\text{Acetone hydrazone}}{(CH_3)_2C{=}N\text{-}NH_2} \xrightarrow{2e^- + 2H^+} (CH_3)_2CH\text{-}NH\text{-}NH_2$$

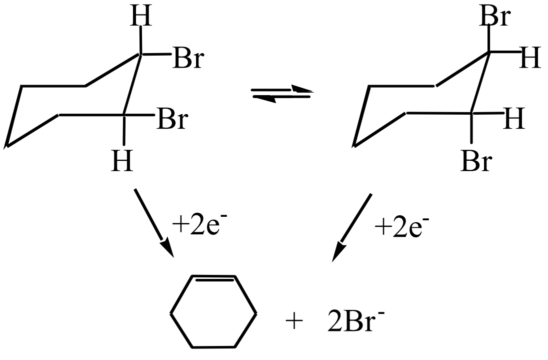
The current-voltage relation when the copper electrode is immersed in the Fe^{3+} solution is the same as the sum of curves a and b. Sketch this curve and estimate the *mixed potential* at which the current is 0. This is the potential at which the reaction $Fe^{3+} + Cu(s) \rightleftharpoons Fe^{2+} + Cu^{+}$ comes to equilibrium.

S17-49. The cyclic voltammograms shown here are due to the irreversible reduction of *trans*-1,2-dibromocyclohexane. At room temperature, just one peak is seen (not shown). At low temperatures, two peaks are seen. At –60°C, the relative size of the peak near –3.1 V increases if the scan rate is increased.

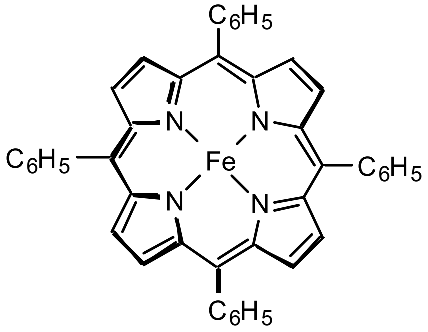


Voltammograms of 2.0 mM *trans*-1,2-dibromocyclohexane at a frozen mercury-drop electrode in butyronitrile with 0.10 M $(n\text{-}C_4H_9)_4NClO_4$ electrolyte. Scan rate = 1.00 V/s. (D.H. Evans, K.M. O'Connell, R.A. Petersen, and M.J. Kelly, *J. Chem. Ed.* **1983**, *60*, 290.)

Use the following scheme to explain these observations.



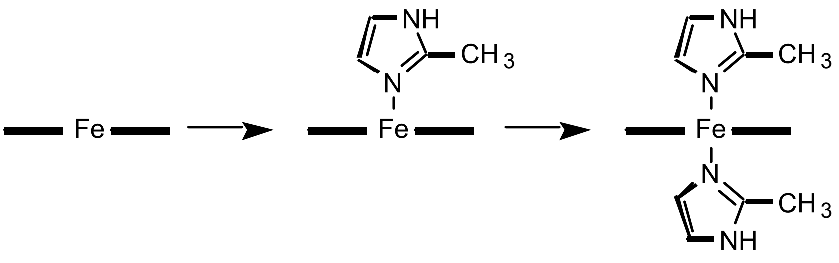
S17-50. Tetraphenylporphyrin^{2-} binds a metal ion at the center of a planar ring containing four nitrogen ligands.



(*meso*-tetraphenylporphyrinato)iron(II)

PFe

When the Fe^{3+} complex, PFe^+, is reduced at a glassy carbon electrode in dimethylformamide solvent containing tetraethylammonium perchlorate electrolyte, reduction waves are observed at –0.18 ($Fe^{3+} \rightarrow Fe^{2+}$) and –1.02 V ($Fe^{2+} \rightarrow Fe^{+}$) versus Ag | AgCl. When a 10 mM concentration of 2-methylimidazole is added to 1 mM PFe^+, the waves shift to –0.14 and –1.11. [V. D. K. Geiger, E. J. Pavlak, and L. T. Kass, *J. Chem. Ed.* **1991**, *68*, 337.] 2-Methylimidazole can bind to one or both axial sites of the complex.



PFe PFeL (side view) $PFeL_2$

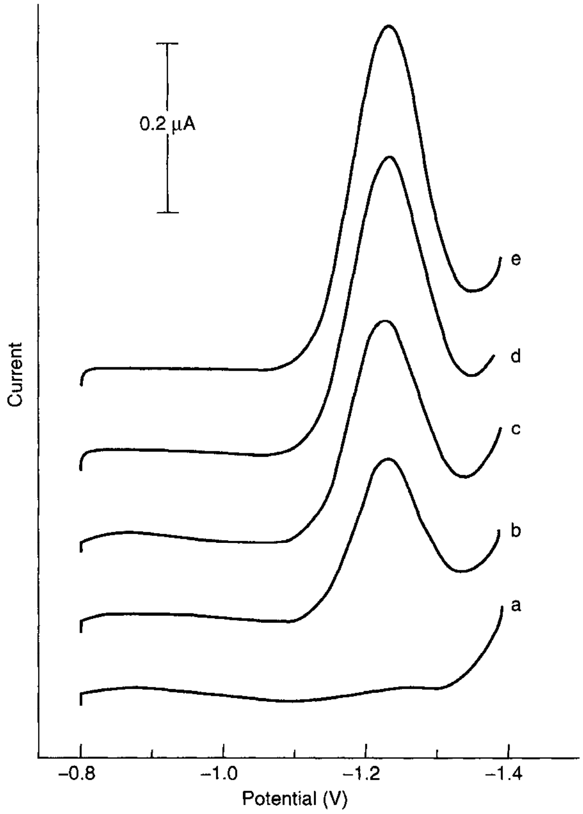
From these shifts, decide which oxidation state (Fe^{3+}, Fe^{2+}, or Fe^{+}) is most stabilized by the ligand. That is, which oxidation state has the greatest binding constant for 2-methylimidazole?

S17-51. Why is a dropping-mercury electrode preferred for cathodic reactions in amperometry, whereas a rotating platinum disk electrode is preferred for anodic reactions?

S17-52. Cr(VI) in soil at a hazardous waste site was analyzed in the field by first dissolving the soil by microwave digestion in ultrapure HNO_3. For anodic stripping voltammetry, 10-100 μL of sample or standard was injected in 10 mL of supporting electrolyte plus 50 mM diethylenetriaminepentaacetic acid chelating agent. In the following results, curve a is a reagent blank. Curve b is unknown solution. Curves c-e show successive additions of 0.25 ppb Cr(VI).

(a) Find the concentration of Cr(VI) in the unknown solution. Then multiply your result by 2.00×10^5 (based on dilutions during sample preparation) to find the concentration of Cr(VI) in the original soil.

(b) Use Equation 5-17 to find the uncertainty in Cr(VI) in the original soil.



Anodic stripping voltammograms of Cr(VI) from contaminated soil from K. B. Olsen, J. Wang, R. Setladji, and J. Lu, *Environ. Sci. Tech.* **1994**, 28, 2074.

CHAPTER 18: SUPPLEMENTARY PROBLEMS
FUNDAMENTALS OF SPECTROPHOTOMETRY

S18-1. Calculate the frequency (in hertz), wavenumber (in cm^{-1}) and energy (in joules per photon and kJ per mole of photons) of (a) ultraviolet light with a wavelength of 250 nm and (b) infrared light with a wavelength of 10 μm.

S18-2. A 15.0-mg sample of a compound with a molecular mass of 384.63 was dissolved in a 5-mL volumetric flask. A 1.00-mL aliquot was withdrawn, placed in a 10-mL volumetric flask, and diluted to the mark.

(a) Find the concentration of sample in the 5-mL flask.

(b) Find the concentration in the 10-mL flask.

(c) The 10-mL sample was placed in a 0.500-cm cuvet and gave an absorbance of 0.634 at 495 nm. Find the molar absorptivity (ε_{495}, with units of $\text{M}^{-1}\cdot\text{cm}^{-1}$) at this wavelength.

S18-3. A 0.267 g quantity of a compound with a molecular mass of 337.69 was dissolved in 100.0 mL of ethanol. Then 2.000 mL was withdrawn and diluted to 100.0 mL. The spectrum of this solution exhibited a maximum absorbance of 0.728 at 438 nm in a 2.000 cm cell. Find the molar absorptivity of the compound.

S18-4. During an assay of the thiamine (vitamin B_1) content of a pharmaceutical preparation, the percent transmittance scale was accidentally read, instead of the absorbance scale of the spectrophotometer. One sample gave a reading of 82.2% *T*, and a second sample gave a reading of 50.7% *T* at a wavelength of maximum absorbance. What is the ratio of concentrations of thiamine in the two samples?

S18-5. (a) A 3.73×10^{-5} M solution of Compound A from a spectrophotometric analysis has a maximum absorbance of 0.494 at 401 nm in a 1.000-cm cell, while a reagent blank from the same analysis has an absorbance of 0.053 at 401 nm. Find the molar absorptivity of Compound A.

(b) A 5.00 mL aliquot of unknown solution containing Compound A was mixed with color forming reagents and diluted to a final volume of 250.0 mL to give an absorbance of 0.777 at 401 nm in a 1.000-cm cell. The reagent blank had an absorbance of 0.053. Find the concentration of Compound A in the unknown solution.

S18-6. Spectrophotometric analysis of phosphate can be performed by the following procedure:

Standard	A. KH_2PO_4 (FM 136.09): 81.37 mg dissolved in 500.0 mL of water
solutions	B. $Na_2MoO_4 \cdot 2H_2O$ (sodium molybdate): 1.25 g in 50 mL of 5 M H_2SO_4
	C. $H_3NNH_3^{2+}\ SO_4^{2-}$ (hydrazine sulfate) : 0.15 g in 100 mL of H_2O

Procedure Place the sample (either an unknown or the standard phosphate solution, A) in a 5-mL volumetric flask, and add 0.500 mL of B plus 0.200 mL of C. Dilute to almost 5 mL with water, and heat at 100˚C for 10 minutes to form a blue product ($H_3PO_4(MoO_3)_{12}$, 12-molybdophosphoric acid). Cool the flask to room temperature, dilute to the mark with water, mix well, and measure the absorbance at 830 nm in a 1.00-cm cell.

(a) When 0.140 mL of solution A was analyzed, an absorbance of 0.829 was recorded. A blank carried through the same procedure gave an absorbance of 0.017. Find the molar absorptivity of blue product.

(b) A solution of the phosphate-containing iron-storage protein ferritin was analyzed by this procedure. The unknown contained 1.35 mg of ferritin, which was digested in a total volume of 1.00 mL to release phosphate from the protein. Then 0.300 mL of this solution was analyzed by the procedure above and found to give an absorbance of 0.836. A blank carried through this procedure gave an absorbance of 0.038. Find the weight percent of phosphorus in the ferritin.

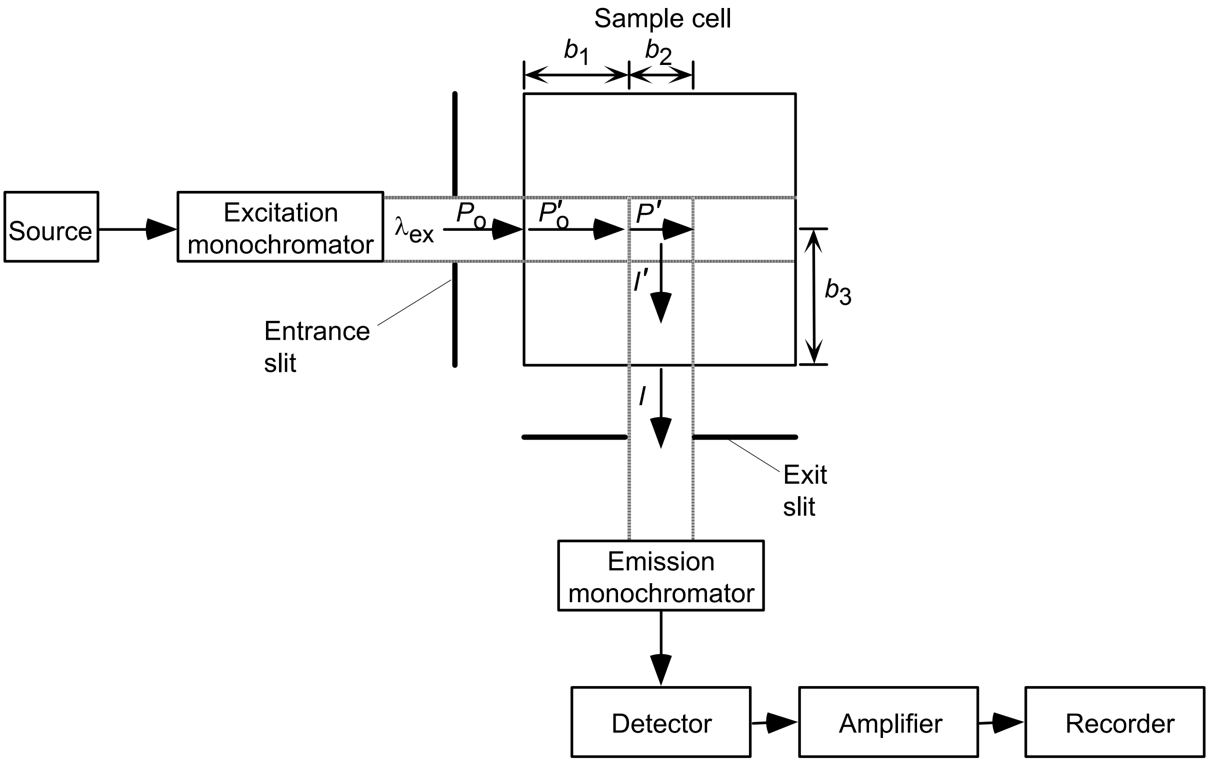
S18-7. *Dependence of fluorescence intensity on concentration*. [For a laboratory experiment on this topic, see S. A. Tucker, V. L. Amszi, and W. E. Acree, Jr., *J. Chem. Ed.* **1992**, *69*, A8.] To derive a relation between the incident irradiance and emission intensity, consider the sample cell on the next page. We expect emission intensity to be proportional to the irradiance absorbed by the sample. That is, a certain proportion of the absorbed radiation will appear as emission under a given set of conditions (solvent, temperature, etc.). The exit slit in the figure is set to observe emission from a region whose width is b_2.

Let the incident irradiance (W/m^2, also called *intensity*) striking the cell be called P_0. Some of this is absorbed by the sample over the pathlength b_1 in the figure, so the irradiance striking the central region of the cell is

$$\text{irradiance striking central region} = P_0' = P_0 \cdot 10^{-\varepsilon_{ex} b_1 c} \qquad \text{(A)}$$

where ε_{ex} is the molar absorptivity at the wavelength λ_{ex}. The irradiance of the beam when it has traveled the additional distance b_2 is

$$P' = P_0' \cdot 10^{-\varepsilon_{ex} b_2 c} \qquad \text{(B)}$$



The emission intensity I is proportional to the irradiance absorbed in the central region of the cell:

$$\text{emission intensity} = I' = k'(P'_0 - P') \qquad \text{(C)}$$

where k' is a constant of proportionality dependent on the emitting molecule and the conditions. Not all the radiation emitted from the center of the cell in the direction of the exit slit is observed. Some is absorbed by the solution between the center and the edge of the cell. The emission intensity I emerging from the cell is given by Beer's law:

$$I = I' - 10^{-\varepsilon_{em} b_3 c} \qquad \text{(D)}$$

where ε_{em} is the molar absorptivity at the emission wavelength and b_3 is the distance from the center to the side of the cell.

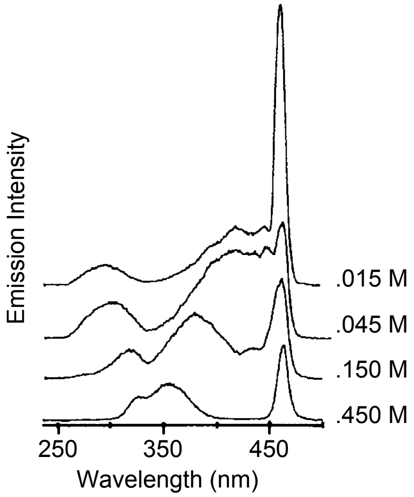
Combining Equations C and D gives an expression for emission intensity:

$$I = k'(\mathrm{P}'_0 - P')10^{-\varepsilon_{em} b_3 c} \qquad \text{(E)}$$

Substituting values of P'_0 and P' from Equations A and B, we obtain a relation between the incident irradiance and the emission intensity:

$$\begin{aligned} I &= k'(P_0 \cdot 10^{-\varepsilon_{ex} b_1 c} - P_0 \cdot 10^{-\varepsilon_{ex} b_1 c} - 10^{-\varepsilon_{ex} b_2 c})\, 10^{-\varepsilon_{em} b_3 c} \\ &= k'P_0 \cdot \underbrace{10^{-\varepsilon_{ex} b_1 c}}_{\substack{\text{Loss of intensity}\\ \text{in region 1}}} - \underbrace{(1 - 10^{-\varepsilon_{ex} b_2 c})}_{\substack{\text{Emission is}\\ \text{proportional to}\\ \text{absorption of light}\\ \text{in region 2}}} - \underbrace{10^{-\varepsilon_{em} b_3 c}}_{\substack{\text{Loss of intensity}\\ \text{in region 3}}} \qquad \text{(F)} \end{aligned}$$

Equation F allows us to calculate emission intensity as a function of solute concentration. At low concentration, emission increases with increasing concentration of analyte, because absorption is small and emission is proportional to emitter concentration. At high concentration, emission actually decreases, because absorption increases more rapidly than the emission. We say the emission is *quenched* (decreased) by self-absorption. At high concentration, even the *shape* of the emission spectrum can change, because absorption and emission both depend on wavelength. The figure below illustrates these effects.



Concentration dependence of fluorescence intensity of biacetyl in CCl_4 with $\lambda_{ex} = 422$ nm and $\lambda_{em} = 464$ nm.

[From G. Henderson, *J. Chem. Ed.* **1977**, *54*, 57.]

When the absorbance terms (the exponents) in Equation F are small, the equation can be greatly simplified. The result is

$$I = kP_0c \qquad \text{(G)}$$

where $k = k'\varepsilon_{ex}b_2 \ln 10$. That is, when the absorbance is small, the emission intensity is directly proportional to the sample concentration (c) and to the incident irradiance (P_0). For most analytical applications, Equation G is obeyed and emission intensity is proportional to concentration.

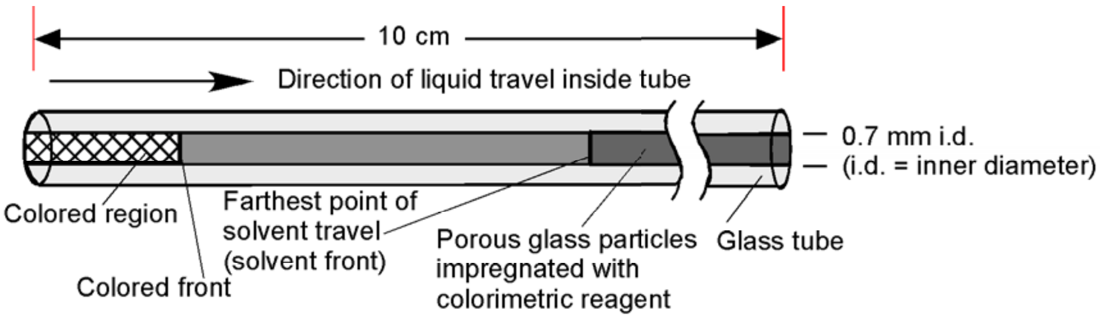
Finally, the problem! Consider a fluorescence experiment in which the cell is arranged so that b_1 and b_3 are negligible and, therefore, self-absorption can be neglected. To a first approximation, emission intensity is proportional to solute concentration. At what absorbance ($= \varepsilon_{ex}b_2c$) will emission be 5% below the value expected if emission is proportional to concentration?

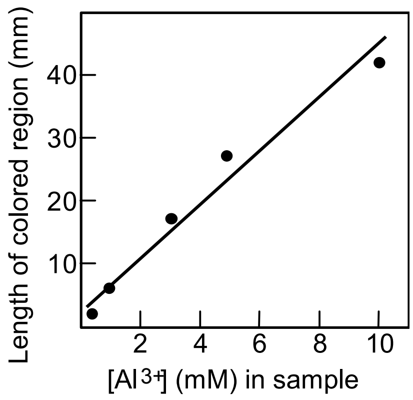
S18-8. How can the sample cell in the previous problem be positioned to minimize the self-absorption expressed in the terms $10^{-\varepsilon_{ex} b_1 c}$ and $10^{-\varepsilon_{ex} b_3 c}$ in Equation F?

S18-9. Consider a fluorescence experiment in using the cell in Problem S18-7 in which ε_{ex} = 1 530 M^{-1} cm^{-1}, ε_{em} = 495 M^{-1} cm-1 , b_1 = 0.400 cm, b_2 = 0.200 cm, and b_3 = 0.500 cm in Equation F. Use a spreadsheet to make a graph of relative fluorescence intensity versus concentration for the following concentrations of solute: 1.00×10^{-7}, 1.00×10^{-6}, 1.00×10^{-5}, 1.00×10^{-4}, 1.00×10^{-3}, and 1.00×10^{-2} M.

S18-10. Consider the fluorescence experiment in Problem S18-7 in which ε_{ex} = 2 120 $M^{-1} \cdot cm^{-1}$, ε_{em} = 810 $M^{-1} \cdot cm^{-1}$, b_1 = 0.300 cm, b_2 = 0.400 cm, and b_3 = 0.500 cm. Make a graph of relative fluorescence intensity versus concentration for the following concentrations of solute: 1.00×10^{-7}, 1.00×10^{-6}, 1.00×10^{-5}, 1.00×10^{-4}, 1.00×10^{-3}, and 1.00×10^{-2} M.

S18-11. *Disposable tube detectors for water analysis.* The capillary tube shown in the figure is filled with particles of porous glass impregnated with a colorimetric reagent that reacts with a desired analyte. For example, to measure Al^{3+} in a wastewater stream, the glass contains the reagent Alizarin Red S, which forms a red complex with Al^{3+}. When the tube is dipped into water, liquid is taken up by capillary action. The liquid moves from left to right in the diagram, and the front of color formation lags behind the front of liquid travel. If a fixed volume of liquid is passed through the tube, *the length of the colored region is proportional to the concentration of* Al^{3+} *in the water*. Explain why this is so. (Similar sensors are used to detect hazardous gases such as phosphine, PH_3, in air.)

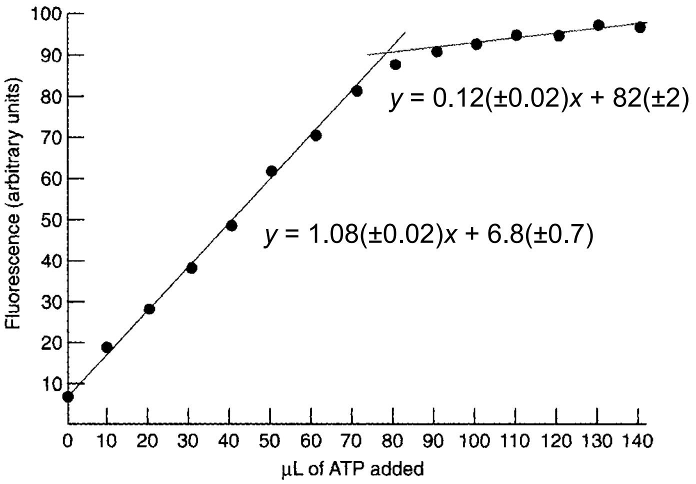




Calibration graph for Al^{3+} using tube containing Alizarin Red S.

[Data from I. Kuselman, B. I. Kuyavskaya, and O. Lev, *Anal. Chim. Acta* **1992**, *256*, 65.]

S18-12. *Fluorescence titration.* The coenzyme $NADP^+$ can be assayed by a titration in which it is converted to the fluorescent product NADPH by the action of adenosine triphosphate (ATP) plus several enzymes. A hypothetical titration curve is shown here. In this titration, the fluorescence intensity is plotted versus microliters of added ATP. The first eight points lie on one line, and the points from 90 to 140 μL lie on a second line. The uncertainties in slope and intercept of these lines are one standard deviation, as determined by the method of least squares. The end point of the titration lies at the intersection of the two lines. Using the equations for the two lines, *determine the volume of ATP (in microliters) at the equivalence point.* Also, use the standard deviations of the slopes and intercepts to *estimate the standard deviation of the volume of ATP at the equivalence point.* Express your answer (μL ± standard deviation) with an appropriate number of significant figures.



CHAPTER 19: SUPPLEMENTARY PROBLEMS
APPLICATIONS OF SPECTROPHOTOMETRY

S19-1. Consider compounds X and Y in the example in Section 19-1 labeled "Analysis of a Mixture Using Equations 19-6." A mixture of X and Y in a 0.100-cm cell had an absorbance of 0.282 at 272 nm and 0.303 at 327 nm. Find the concentrations of X and Y in the mixture.

S19-2. Spectrophotometric data for three compounds is given below. A solution containing X, Y, and Z in a 1.000-cm cuvet had absorbances of 0.846 at 246 nm, 0.400 at 298 nm, and 0.555 at 360 nm. Modify the spreadsheet in Figure 19-5 to handle 3 simultaneous equations and find the concentrations of X, Y, and Z in the mixture.

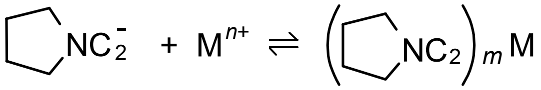
	ε (M^{-1} cm^{-1})		
λ (nm)	X	Y	Z
246	12 200	3 210	290
298	4 140	6 550	990
360	3 000	2 780	8 080

S19-3. Use the table from the previous problem to answer this question. A solution containing X, Y and Z in a *2.000-cm* cuvet had absorbances of 0.666 at 246 nm, 0.498 at 298 nm and 0.360 at 360 nm. Using a spreadsheet for three simultaneous linear equations, find the concentrations of X, Y and Z in the mixture.

S19-4. Compound P, which absorbs light at 517 nm, was titrated with X, which does not absorb at this wavelength. The product, PX, also absorbs at 517 nm. A series of solutions containing a fixed concentration of P (0.001 00 M) was prepared with variable concentrations of X. The absorbance of each solution was measured in a 1.000-cm cell, and the concentration of free X was determined by an independent method. The results are shown below. Prepare a Scatchard plot to find the equilibrium constant and $\Delta\varepsilon$ for the reaction $X + P \rightleftharpoons PX$.

[X] M	Absorbance	[X] M	Absorbance
0.0	0.213	0.0509	0.493
0.005 09	0.243	0.0650	0.563
0.008 52	0.263	0.0779	0.633
0.0173	0.313	0.0932	0.703
0.0295	0.383	0.1062	0.763
0.0387	0.433		

S19-5. Solutions of metal ions and the ligand ammonium 1-pyrrolidinecarbodithioate were prepared in aqueous solution and the resulting complexes were extracted into chloroform. Spectrophotometric results for Zn^{2+} and Ga^{3+} are given below. The reference solution for each measurement was a reagent blank prepared with ligand but no metal ion. From the absorption data, find the ligand:metal stoichiometry in the complexes.



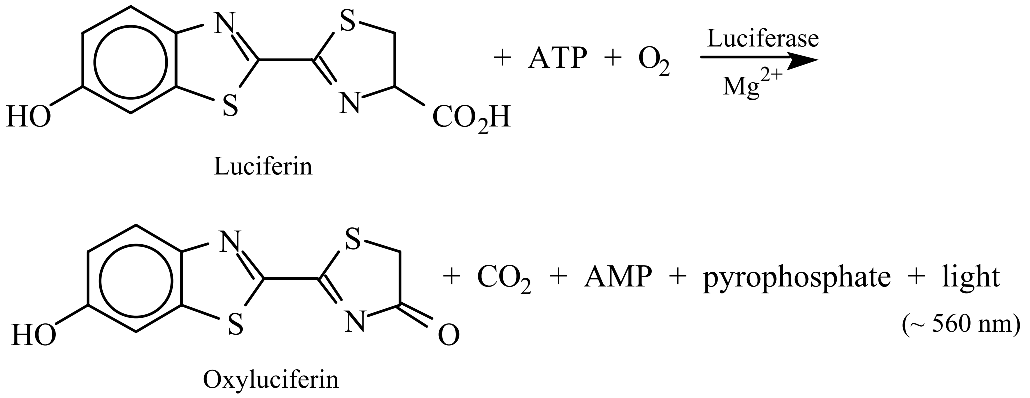
1-pyrrolidinecarbodithioate

Mole fraction of metal ion	Zn^{2+} Relative absorbance at 315 nm at pH 5.20	Ga^{3+} Relative absorbance at 308 nm at pH 2.30
0.05	0.145	0.204
0.10	0.298	0.406
0.15	0.440	0.594
0.20	0.589	0.750
0.25	0.720	0.778
0.30	0.818	0.759
0.33	0.836	—
0.40	0.795	0.665
0.50	0.689	0.551
0.60	0.548	0.442
0.70	0.403	0.321
0.80	0.274	0.204
0.90	0.143	0.088

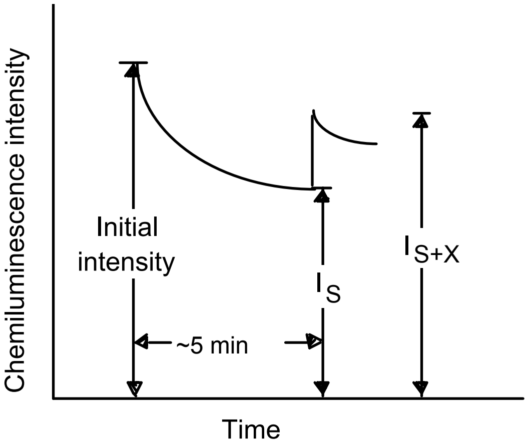
Data from W. Likussar and D. F. Boltz, *Anal. Chem.* **1971**, *43*, 1273.

S19-6. In a time-resolved fluorescence immunoassay, a solution was irradiated at 340 nm and Eu^{3+} emission was observed at 613 nm. What is the energy difference (kJ/mol) between these two wavelengths? This difference is converted to heat in the solution.

S19-7. A sensitive assay for ATP is based on its participation in the light-producing reaction of the firefly. The reaction catalyzed by the enzyme luciferase is



When the reactants are mixed, the solution gives off light. The light intensity decays slowly due to product inhibition of the reaction. Otherwise, the light would have a steady intensity because *the rate at which reactants are consumed is negligible*. That is, ATP and luciferin maintain their original concentrations throughout the few minutes that the reaction might be monitored. Some typical experimental results are shown below.



Let the initial concentration of ATP in the reaction be [S]. Suppose that additional ATP is added, increasing the concentration in the reaction to [S] + [X]. The kinetic description of the reaction predicts that the increase in light intensity after the addition will be given by

$$\frac{I_{\mathrm{S}}}{I_{\mathrm{S+X}}} = \frac{1}{[\mathrm{S}]+[\mathrm{X}]}\left(\frac{K[\mathrm{S}]}{K+[\mathrm{S}]}\right) + \frac{[\mathrm{S}]}{K+[\mathrm{S}]}$$

where K is constant.

(a) Suppose that [S] = 250 μM and after 5 minutes I_{S} = 58.7 arbitrary intensity units. Then a standard addition of [X] = 200 μM is made, and $I_{\mathrm{S+X}}$ is found to be 74.5 units. Use these data to find the value of K in the equation above.

(b) When the intensity had decayed to 63.5 units, an unknown aliquot of ATP was added to the reaction, and the intensity increased to 74.6 units. How much was the increase in concentration caused by the unknown aliquot?

[Problem from J. J. Lemasters and C. R. Hackenbrock, *Methods of Enzymology*, **1978**, *57*, 36. A student experiment using luciferase for the assay of ATP or reduced nicotine adenine dinucleotide (NADH) is described by T. C. Selig, K. A. Drozda, and J. A. Evans, *J. Chem. Ed.*, **1984**, *61*, 918.]

S19-8. *Solving simultaneous linear equations by Cramer's rule.* The equations

$$\begin{array}{rcl} 3x \quad - y & = & 5 \\ \underbrace{-2x + 10y}_{\text{Coefficients}} & = & \underbrace{6}_{\text{Constants}} \end{array}$$

may be broken into a matrix of coefficients and a "vector" of constants:

$$\begin{array}{c}\text{coefficient}\\ \text{matrix}\end{array} = \begin{bmatrix} 3 & -1 \\ -2 & 10 \end{bmatrix} \qquad\qquad \begin{array}{c}\text{constant}\\ \text{vector}\end{array} = \begin{bmatrix} 5 \\ 6 \end{bmatrix}$$

The determinant of the coefficient matrix is

$$D = \begin{vmatrix} 3 & -1 \\ -2 & 10 \end{vmatrix} = 3 \cdot 10 - (-1) \cdot (-2) = 28$$

and the solutions are given by Equations 19-6 in which the constant vector is used to replace either the first or second column of the coefficient matrix in the numerator:

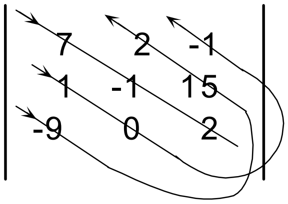
$$x = \begin{vmatrix} 5 & -1 \\ 6 & 10 \end{vmatrix} /D = [5 \cdot 10 - (-1) \cdot (6)]/28 = 2$$

$$y = \begin{vmatrix} 3 & 5 \\ -2 & 6 \end{vmatrix} /D = [3 \cdot 6 - (5) \cdot (-2)]/28 = 1$$

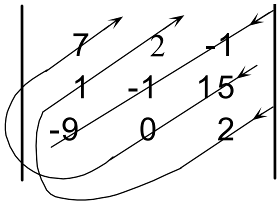
The procedure for using determinants to solve simultaneous equations is called *Cramer's rule*. For three simultaneous equations, Cramer's rule looks like this:

$$\begin{array}{rrrcr} 7x & + 2y & -z & = & 15 \\ x & -y & +15z & = & 112 \\ -9x & & +2z & = & -22 \end{array}$$

The 3×3 determinant of coefficients is evaluated in a pitchfork pattern:



positive terms:
(7)(–1)(2), (1)(0)(–1), (–9)(15)(2)



negative terms:
(–1)(–1)(–9), (2)(1)(2), (7)(0)(15)

$$\mathrm{D} = \begin{vmatrix} 7 & 2 & -1 \\ 1 & -1 & 15 \\ -9 & 0 & 2 \end{vmatrix} =$$

$$(7)(-1)(2) + (1)(0)(-1) + (-9)(15)(2) - (-1)(-1)(-9) - (2)(1)(2) - (7)(0)(15) = -279$$

To solve three simultaneous equations, we replace the first, second, or third column in the coefficient matrix by the constant vector:

$$x = \frac{\begin{vmatrix} 15 & 2 & -1 \\ 112 & -1 & 15 \\ -22 & 0 & 2 \end{vmatrix}}{D} = \frac{-1\,116}{-279} = 4 \qquad y = \frac{\begin{vmatrix} 7 & 15 & -1 \\ 1 & 112 & 15 \\ -9 & -22 & 2 \end{vmatrix}}{D} = \frac{837}{-279} = -3$$

$$z = \frac{\begin{vmatrix} 7 & 2 & 15 \\ 1 & -1 & 112 \\ -9 & 0 & -22 \end{vmatrix}}{D} = \frac{-1\,953}{-279} = 7$$

(a) Rows 3 through 10 of the spreadsheet below are for solving two simultaneous equations. The coefficient matrix is in columns A and B. The constant vector is in column C and the solution is in column D. The denominator is evaluated in cell A7. Set up a spreadsheet like this and use it to reproduce the example beneath Equations 19-6. You can use this spreadsheet for any 2×2 problem.

(b) Rows 13 through 28 of the spreadsheet solve three simultaneous equations. The coefficient matrix is in columns A, B, and C. The constant vector is in column D and the solution is in column E. The denominator is evaluated in cell A19. Set up a spreadsheet like this to reproduce the 3×3 example above.

	A	B	C	D	E
1	Spreadsheets for solving 2 or 3 simultaneous equations by Cramer's rule				
2			Constant	Solution	
3	Coefficient matrix (2x2)		vector	vector	
4	3	-1	5	2	
5	-2	10	6	1	
6	Denominator = determinant of coefficient matrix =				
7	28				
8	A7 = A4*B5-B4*A5				
9	D4 = (C4*B5-C5*B4)/A7				
10	D5 = (A4*C5-C4*A5)/A7				
11					
12				Constant	Solution
13	Coefficient matrix (3x3)			vector	vector
14	7	2	-1	15	4
15	1	-1	15	112	-3
16	-9	0	2	-22	7
17					
18	Denominator = determinant of coefficient matrix				
19	-279				
20					
21	A19 = A14*B15*C16+A15*B16*C14+B14*C15*A16-C14*B15*A16				
22		-B14*A15*C16-C15*B16*A14			
23	E14 = (D14*B15*C16+D15*B16*C14+B14*C15*D16-C14*B15*D16				
24		-B14*D15*C16-C15*B16*D14)/A19			
25	E15 = (A14*D15*C16+A15*D16*C14+D14*C15*A16-C14*D15*A16				
26		-D14*A15*C16-C15*D16*A14)/A19			
27	E16 = (A14*B15*D16+A15*B16*D14+B14*D15*A16-D14*B15*A16				
28		-B14*A15*D16-D15*B16*A14)/A19			

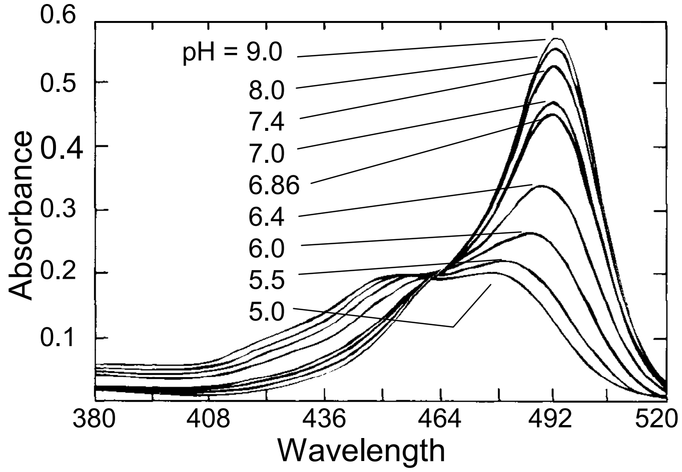
S19-9. *Solving simultaneous linear equations by Cramer's rule.*

Spectroscopic data for the indicators thymol blue (TB), semithymol blue (STB), and methylthymol blue (MTB) are shown in the table. A solution of TB, STB, and MTB in a 1.000-cm cuvet had absorbances of 0.412 at 455 nm, 0.350 at 485 nm, and 0.632 at 545 nm. Use Cramer's rule from the previous problem to find the concentrations of TB, STB, and MTB in the mixture by means of a 3x3 determinant.

	ε (M^{-1} cm^{-1})		
λ (nm)	TB	STB	MTB
455	4 800	11 100	18 900
485	7 350	11 200	11 800
545	36 400	13 900	4 450

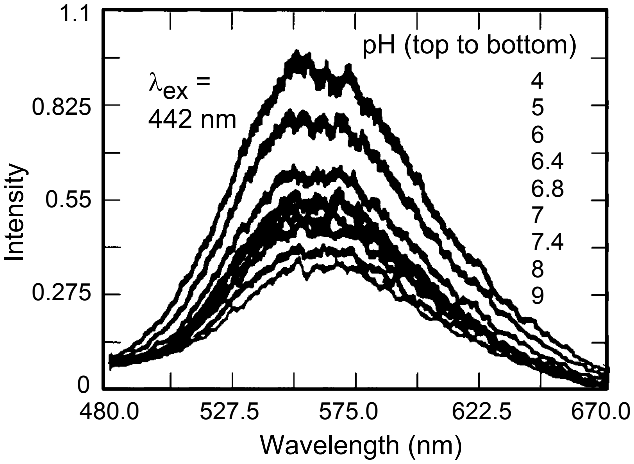
Data from S. Kiciak, H. Gontarz, and E. Krzyżanowska, "Monitoring the Synthesis of Semimethylthymol Blue and Methylthymol Blue,"*Talanta* **1995**, *42*, 1245.

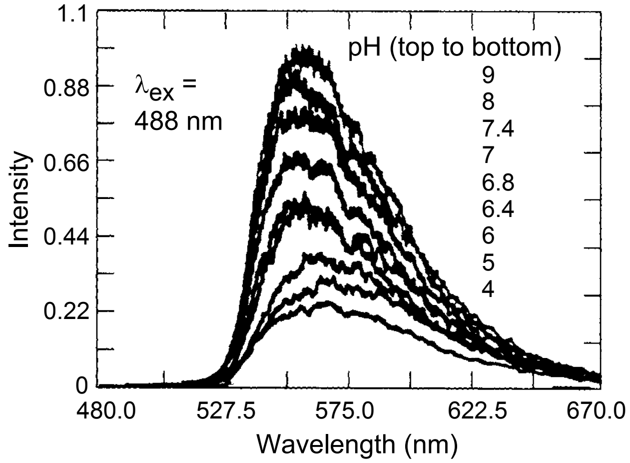
S19-10. This problem describes how the fiber-optic pH sensor at the beginning of Chapter 10 works. The tip of the optical fiber has a highly fluorescent chromophore, fluorescein, incorporated into a polymer. The absorption spectrum of the fluorescein chromophore has an isosbestic point at 461 nm. At shorter wavelengths, the absorbance decreases as pH increases. At longer wavelengths, the absorbance increases as pH increases.



Absorption spectrum of *N*-fluoresceinylacrylamide monomer as a function of pH. [From W. Tan, S.-Y. Shi, S. Smith, D. Birnbaum and R. Kopelman, *Science* **1992**, *258*, 778.]

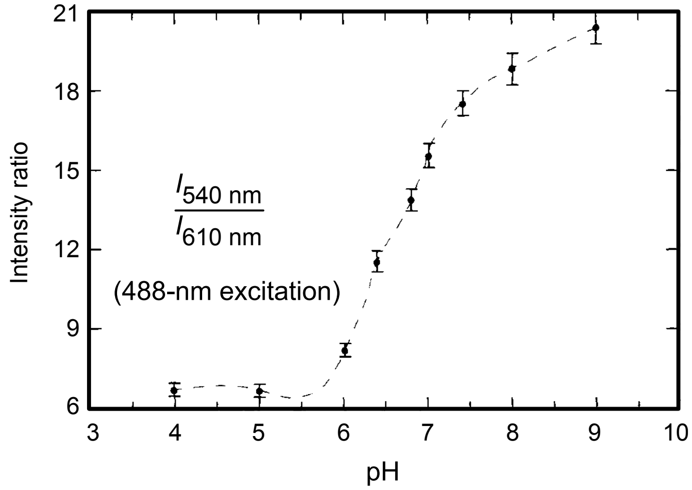
(a) Fluorescence emission spectra of the polymer at the tip of the sensor are shown here. When the excitation wavelength is 442 nm, fluorescence intensity decreases with increasing pH. When the excitation wavelength is 488 nm, fluorescence intensity increases with increasing pH. Explain why.





Fluorescence intensity from polymer tip of the fiber optic sensor shown at the beginning of Chapter 10. [From W. Tan, S.-Y. Shi, S. Smith, D. Birnbaum and R. Kopelman, *Science* **1992**, *258*, 778.]

(b) The following graph shows the ratio of fluorescence intensities at two wavelengths, with excitation at 488 nm. (Ratios are used because they are fairly constant from experiment to experiment, whereas absolute intensity at one wavelength is difficult to reproduce.) Explain the shape of this curve and explain how the optical fiber can be used to measure pH.



Calibration graph showing relation of fluorescence intensity ratio to pH
[From W. Tan, S.-Y. Shi, S. Smith, D. Birnbaum and R. Kopelman, *Science* **1992**, *258*, 778.]

S19-11. A sensor for gaseous O_2 based on Ru(II) luminescence quenching was constructed with a Ru compound incorporated into a thin-film silica gel. The film is illuminated with 400–500 nm light from a light-emitting diode. Luminescence at wavelengths ≥570 nm is measured by a photodiode. When gas passes over the film, O_2 from the gas diffuses into the film and decreases the luminescence. The concentration of O_2 in the film is proportional to the concentration of O_2 in the gas phase. Data from two different thin films are shown in the table. Film 1 is quite porous and film 2 is denser and less porous.

Volume % O_2 in gas	Photodiode response (V) to film 1	Photodiode response (V) to film 2
0.0	7.60	8.42
10.0	4.61	6.63
20.0	3.33	5.30
40.0	2.18	3.57
60.0	1.52	2.54
80.0	1.22	1.87
100.0	0.95	1.43

Data from C. McDonagh, B. D. MacCraith and A. K. McEvoy, "Tailoring of Sol–Gel Films for Optical Sensing of O_2," *Anal. Chem.* **1998**, *70*, 45.

(a) For each film, prepare a graph of I_o/I_Q versus O_2 volume percent. I_o is the photoluminescence intensity in the absence of quencher (O_2) and I_Q is the intensity in the presence of quencher. I_o/I_Q is equal the quotient of detector response in the absence and presence of quencher.

(b) What is the theoretical behavior of the graphs in part (a) based on the Stern-Volmer equation?

(c) Try fitting each data set with a straight line and see if the prediction in part (b) is true. Suggest an explanation for what you observe.

CHAPTER 20: SUPPLEMENTARY PROBLEMS
SPECTROPHOTOMETERS

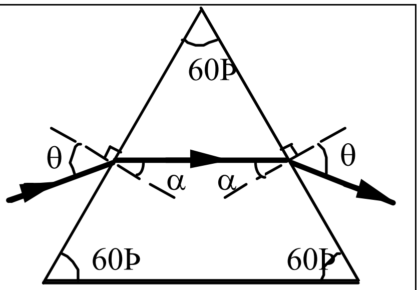
S20-1. (a) Find the critical value of θ_i in Figure 20-18 beyond which there is total internal reflection in an As_2Se_3-based infrared optical fiber whose core refractive index is 2.7 and whose cladding refractive index is 2.0.

(b) Referring to Problem 21-18, calculate the quotient power out/power in for a 0.50-m-long fiber with a loss of 0.012 dB/m.

S20-2. Light passes from quartz (medium 1) to carbon disulfide (medium 2) in Figure 20-17 at (a) $\theta_1 = 30^\circ$ or (b) $\theta_1 = 0^\circ$. Find the angle θ_2 in each case.

S20-3. (a) For the 60° prism below, use Snell's law to show that light traveling through the prism parallel to the base enters and exits at the same angle, θ.

(b) The index of refraction of the prism is 1.500 and the index of refraction of air is 1.000.

Find the angle θ in the diagram.	

S20-4. What is the ratio of power per unit area (the exitance, W/m^2) radiating from a blackbody at 900 K compared to one at 300K? Calculate the exitance at 900 K.

S20-5. A long iron cylinder with a diameter of 0.64 cm is heated yellow hot (1 100°C) and then allowed to begin cooling. The density of iron is 7.86 g/cm^3 and the heat capacity at this temperature is 0.606 J/(g·K).

(a) Consider a 1-cm length of the cylinder far from either end. Calculate the rate of cooling of this 1-cm section by blackbody radiation (ignoring the surface area at the ends of the cylinder). For this calculation, compute the blackbody exitance from the iron at a temperature of 1 100°C. Subtract from this the exitance of the surroundings into the iron. You can approximate the surroundings as a blackbody at a temperature of 300 K. The blanket of atmosphere behaves essentially as a blackbody because it is so thick.

(b) Calculate the rate of cooling for a thinner cylinder with a 0.064 cm diameter at 1 100°C.

S20-6. Consider a reflection grating operating with an incident angle of 20° in Figure 20-6.

(a) How many lines per centimeter should be etched in the grating if the first-order diffraction angle for 400 nm (visible) light is to be 10°?

(b) Answer the same question for 1 000 cm^{-1} (infrared) light.

S20-7. (a) What resolution is required for a diffraction grating to resolve adjacent lines in the spectrum of calcium ions at wavelengths of 443.495 and 443.567 nm? What is the difference between these two spectral lines in wavenumbers (cm^{-1}) and frequency (Hz)?

(b) With a resolution of 10^4, how close in nm is the closest line to 443.495 nm that can barely be resolved?

(c) Calculate the second order ($n = 2$) resolution of a 6.00-cm-long grating ruled at 212 lines/mm.

(d) Find the angular dispersion ($\Delta\phi$) between light rays with wavelengths of 443.495 and 443.567 nm for second order diffraction ($n = 2$) and 20th order diffraction from a grating with 200 lines/mm and $\phi = 10.0°$.

S20-8. The true absorbance of a sample is 1.26, but 0.4 % stray light reaches the detector. Find the apparent transmittance and apparent absorbance of the sample.

S20-9. The interferometer mirror of a Fourier transform infrared spectrophotometer travels ±2 cm.

(a) How many centimeters is the maximum retardation, Δ?

(b) What is the approximate resolution (cm^{-1}) of the instrument?

(c) At what retardation interval, δ, must the interferogram be sampled (converted to digital form) to cover a spectral range of 0–4 000 cm^{-1}?

S20-10. A spectrum has a signal-to-noise ratio of 3/1. How many spectra must be averaged to increase the signal-to-noise ratio to 9/1?

S20-11. A shipboard flow injection analytical procedure for measuring Fe^{2+} in sea water is based on chemiluminescence from the dye brilliant sulfoflavin in the presence of Fe^{2+} and H_2O_2. Data from a series of standard additions is shown below. Use all 12 points to construct a standard addition graph and find [Fe^{2+}] in the unknown.

Sample	Detector signal		
Unknown	12.0	12.0	11.0
Unknown + 5.25 nM Fe^{2+}	27.2	26.5	26.5
Unknown + 7.88 nM Fe^{2+}	39.9	41.7	39.1
Unknown + 10.5 nM Fe^{2+}	53.9	56.2	55.3

V. A. Elrod, K. S. Johnson and K. H. Coale, *Anal. Chem.* **1991**, *63*, 893