

## CHAPTER 13

### FUNDAMENTALS OF ELECTROCHEMISTRY

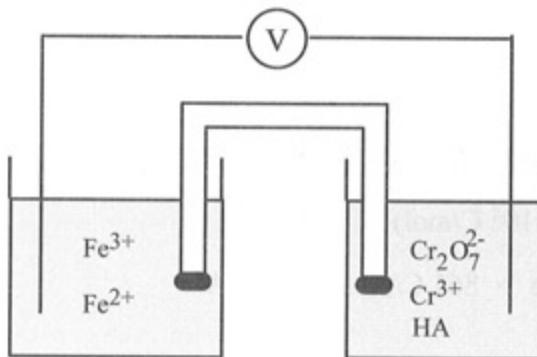
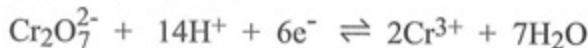
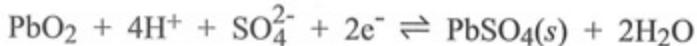
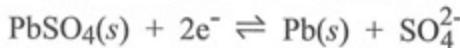
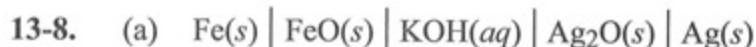
- 13-1.** Electric charge (coulombs) refers to the quantity of positive or negative particles. Current (amperes) is the quantity of charge moving past a point in a circuit each second. Electric potential (volts) measures the work that can be done by (or must be done to) each coulomb of charge as it moves from one point to another.
- 13-2.** (a)  $1/1.602\ 176\ 53 \times 10^{-19}\ \text{C/electron} = 6.241\ 509\ 48 \times 10^{18}\ \text{electrons/C}$
- (b)  $F = 96\ 485.338\ 3\ \text{C/mol}$
- 13-3.** (a)  $I = \text{coulombs/s. Every mol of O}_2 \text{ accepts 4 mol of e}^-.$   $16\ \text{mol O}_2/\text{day} = 64\ \text{mol e}^-/\text{day} = 7.41 \times 10^{-4}\ \text{mol e}^-/\text{s} = 71.5\ \text{C/s} = 71.5\ \text{A}$
- (b)  $I = \text{Power}/E = 500\ \text{W}/115\ \text{V} = 4.35\ \text{A}.$  The resting human uses 16 times as much current as the refrigerator.
- (c) Power =  $E \cdot I = (1.1\ \text{V})(71.5\ \text{A}) = 79\ \text{W}$
- 13-4.** (a)  $I = \frac{6.00\ \text{V}}{2.0 \times 10^3\ \text{W}} = 3.00\ \text{mA} = 3.00 \times 10^{-3}\ \text{C/s}$   
 $\left( \frac{3.00 \times 10^{-3}\ \text{C/s}}{9.649 \times 10^4\ \text{C/mol}} \right) (6.022 \times 10^{23}\ \text{e}^-/\text{mole}) = 1.87 \times 10^{16}\ \text{e}^-/\text{s}$
- (b)  $P = E \cdot I = (6.00\ \text{V})(3.00 \times 10^{-3}\ \text{A}) = 1.80 \times 10^{-2}\ \text{W}$   
 $\Rightarrow \frac{1.80 \times 10^{-2}\ \text{J/s}}{1.87 \times 10^{16}\ \text{e}^-/\text{s}} = 9.63 \times 10^{-19}\ \text{J/e}^-$
- (c)  $(1.87 \times 10^{16}\ \text{e}^-/\text{s})(1\ 800\ \text{s}) = 3.37 \times 10^{19}\ \text{electrons} = 5.60 \times 10^{-5}\ \text{mol}$
- (d)  $P = EI = E(E/R) = E^2/R \Rightarrow E = \sqrt{PR} = \sqrt{(100\ \text{W})(2.00 \times 10^3\ \text{W})} = 447\ \text{V}$
- 13-5.** (a)  $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$  ( $\text{I}_2$  is the oxidant)
- (b)  $2\text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$  ( $\text{S}_2\text{O}_3^{2-}$  is the reductant)
- (c)  $1.00\ \text{g S}_2\text{O}_3^{2-} / (112.13\ \text{g/mol}) = 8.92\ \text{mmol S}_2\text{O}_3^{2-} = 8.92\ \text{mmol e}^-$   
 $(8.92 \times 10^{-3}\ \text{mol})(9.649 \times 10^4\ \text{C/mol}) = 861\ \text{C}$
- (d) Current (A) = coulombs/s =  $861\ \text{C}/60\ \text{s} = 14.3\ \text{A}$

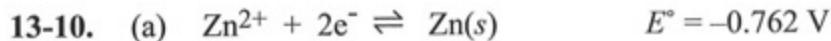
13-6.	(a)	Oxidation numbers of reactants:	N (in $\text{NH}_4^+$ )	-3	Cl (in $\text{ClO}_4^-$ )	+7	Al	0
		Oxidation numbers of products:	N (in $\text{N}_2$ )	0	Cl (in HCl)	-1	Al (in $\text{Al}_2\text{O}_3$ )	+3

$\text{NH}_4^+$  and Al are reducing agents and  $\text{ClO}_4^-$  is the oxidizing agent.

- (b) Formula mass of reactants =  $6(\text{FM } \text{NH}_4\text{ClO}_4) + 10(\text{FM Al}) = 974.75$   
Heat released per gram =  $9\ 334 \text{ kJ}/974.75 \text{ g} = 9.576 \text{ kJ/g}$

- 13-7. In a galvanic cell, two half-reactions are physically separated from each other. At the anode, oxidation generates electrons that can flow through the electric circuit to reach the cathode, where a reduction occurs. The favorable free energy change for the net reaction provides the driving force for electrons to flow through the circuit. There must be a connector (such as a salt bridge) between the two half-cells to allow ions to flow to maintain electroneutrality.





The Appendix lists standard reduction potentials for  $\text{Cl}_2(g)$  and  $\text{Cl}_2(aq)$ , but not for  $\text{Cl}_2(l)$ . Both listed potentials are close to 1.4 V, so the potential for  $\text{Cl}_2(l)$  is probably also close to 1.4 V. Electrons flow from the more negative electrode (Zn) through the circuit to the more positive electrode (C).

- (b) One mol of  $\text{Cl}_2$  requires 2 mol of  $\text{e}^-$ .

$$\text{Moles of Cl}_2 \text{ consumed in } 1.00 \text{ hr} = \frac{1}{2} (\text{mol of e}^-/\text{hr}) =$$

$$\left[ \frac{1}{2} \left( 1.00 \times 10^3 \frac{\text{C}}{\text{s}} \right) / (9.64 \times 10^4 \text{ C/mol}) \right] (3600 \text{ s/hr}) = 18.7 \text{ mol of Cl}_2 = 1.32 \text{ kg.}$$



(b)  $1 \text{ mA} = 1 \times 10^{-3} \frac{\text{C}}{\text{s}}$ .  $1 \text{ h} = 3600 \text{ s}$

$$1 \text{ mA}\cdot\text{h} = \left( 1 \times 10^{-3} \frac{\text{C}}{\text{s}} \right) (3600 \text{ s}) = 3.6 \text{ C}$$

(c)  $\frac{1 \text{ g LiCoO}_2}{97.87 \text{ g/mol}} = 1.02_{17} \times 10^{-2} \text{ mol LiCoO}_2$  which holds  $1.02_{17} \times 10^{-2} \text{ mol Li}^+$

$$\text{and } 1.02_{17} \times 10^{-2} \text{ mol e}^- \cdot (1.02_{17} \times 10^{-2} \text{ mol e}^-) \left( 9.649 \times 10^5 \frac{\text{C}}{\text{mol e}^-} \right) = 985.8 \text{ C}$$

$$\text{Charge capacity} = \left( 985.8 \frac{\text{C}}{\text{g LiCoO}_2} \right) \left( \frac{1 \text{ mA}\cdot\text{h}}{3.6 \text{ C}} \right) = 273.8 \frac{\text{mA}\cdot\text{h}}{\text{g LiCoO}_2}$$

(d) Fraction of Li available =  $\frac{140 \text{ mA}\cdot\text{h/g}}{273.8 \text{ mA}\cdot\text{h/g}} = 0.51$

- (e) Energy stored per unit mass = work that can be done / mass =  $E \cdot q / \text{mass}$

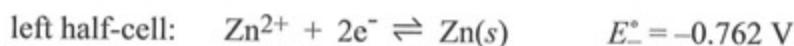
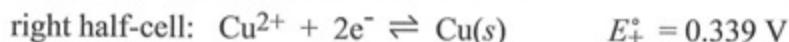
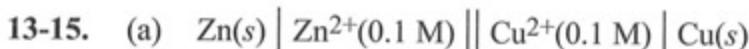
$$= (3.7 \text{ V}) \left( 140 \frac{\text{mA}\cdot\text{h}}{\text{g LiCoO}_2} \right) = (3.7 \text{ V}) \left( 0.140 \frac{\text{A}\cdot\text{h}}{\text{g LiCoO}_2} \right) = 0.52 \frac{\text{W}\cdot\text{h}}{\text{g LiCoO}_2}$$

- 13-12.**  $\text{Cl}_2$  is strongest because it has the most positive reduction potential.

- 13-13.** (a) Since it becomes harder to reduce  $\text{Fe(III)}$  to  $\text{Fe(II)}$  in the presence of  $\text{CN}^-$ ,  $\text{Fe(III)}$  is stabilized more than  $\text{Fe(II)}$ .

- (b) Since it becomes easier to reduce  $\text{Fe(III)}$  to  $\text{Fe(II)}$  in the presence of phenanthroline,  $\text{Fe(II)}$  is stabilized more than  $\text{Fe(III)}$ .

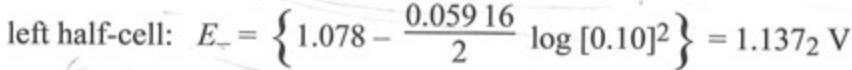
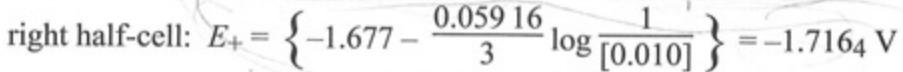
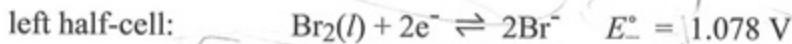
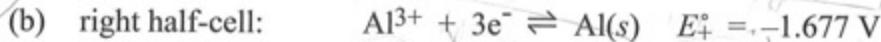
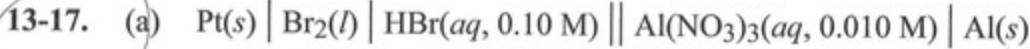
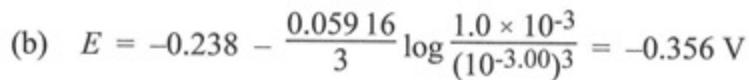
**13-14.**  $E^\circ$  applies when activities of reactants and products are unity.  $E$  applies to whatever activities exist. At equilibrium,  $E$  goes to zero.  $E^\circ$  is constant.



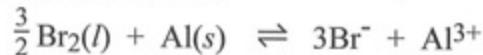
$$E = \left\{ 0.339 - \frac{0.05916}{2} \log \frac{1}{0.1} \right\} - \left\{ -0.762 - \frac{0.05916}{2} \log \frac{1}{0.1} \right\} = 1.101 \text{ V}$$

Since the voltage is positive, electrons are transferred from Zn to Cu. The net reaction is  $\text{Cu}^{2+} + \text{Zn}(s) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}$ .

- (b) Since  $\text{Cu}^{2+}$  ions are consumed in the right half-cell,  $\text{Zn}^{2+}$  ions must migrate from the left half-cell into the salt bridge to help balance charge. I hope you like  $\text{Zn}^{2+}$ , because that is what your body will take up.



$E = E_+ - E_- = -1.7164 - 1.1372 = -2.854 \text{ V}$ . The right electrode is more negative, so electrons flow from Al to Pt. Reduction occurs at the left-hand electrode. The spontaneous reaction is



- (c)  $14.3 \text{ mL of Br}_2 = 44.6 \text{ g} = 0.279 \text{ mol of Br}_2$ .  $12.0 \text{ g of Al} = 0.445 \text{ mol of Al}$ . The reaction requires  $3/2$  mol of  $\text{Br}_2$  for every mol of Al. The  $\text{Br}_2$  will be used up first.

- (d)  $0.231 \text{ mL of Br}_2 = 0.721 \text{ g of Br}_2 = 4.51 \times 10^{-3} \text{ mol Br}_2 = 9.02 \times 10^{-3} \text{ mol e}^- = 870 \text{ C}$ . Work =  $E \cdot q = (1.50)(870) = 1.31 \text{ kJ}$ .

$$(e) \quad I = \sqrt{P/R} = \sqrt{(1.00 \times 10^{-4})/(1.20 \times 10^3)} = 2.89 \times 10^{-4} \text{ A} \\ = 2.99 \times 10^{-9} \text{ mol e}^-/\text{s} = 9.97 \times 10^{-10} \text{ mol Al/s} = 2.69 \times 10^{-8} \text{ g/s}$$

- 13-18.** The activities of the solid reagents do not change until they are used up. The only aqueous species, OH<sup>-</sup>, is created at the cathode and consumed in equal amounts at the anode, so its concentration remains constant in the cell. Therefore, none of the activities change during the life cycle of the cell until something is used up.

**13-19.** (a) right half-cell:  $E_+ = \left\{ 0.222 - \frac{0.05916}{2} \log [Cl^-]^2 \right\} = 0.281_2 \text{ V}$   
 left half-cell:  $E_- = \left\{ -0.350 - \frac{0.05916}{2} \log [F^-]^2 \right\} = -0.290_8 \text{ V}$   
 $E = E_+ - E_- = 0.281_2 - (-0.290_8) = 0.572 \text{ V}$

- (b) Electrons flow from the left half-cell ( $E = -0.290_8 \text{ V}$ ) to the right half-cell ( $E = 0.281_2 \text{ V}$ ).

(c)  $[Pb^{2+}] = K_{sp} \text{ (for PbF}_2\text{)}/[F^-]^2 = (3.6 \times 10^{-8})/(0.10)^2 = 3.6 \times 10^{-6} \text{ M}$   
 $[Ag^+] = K_{sp} \text{ (for AgCl)}/[Cl^-] = (1.8 \times 10^{-10})/(0.10) = 1.8 \times 10^{-9} \text{ M}$   
 right half-cell:  $E_+ = \left\{ 0.799 - \frac{0.05916}{2} \log \frac{1}{[Ag^+]^2} \right\} = 0.281_2 \text{ V}$   
 left half-cell:  $E_- = \left\{ -0.126 - \frac{0.05916}{2} \log \frac{1}{[Pb^{2+}]} \right\} = -0.287_0 \text{ V}$   
 $E = E_+ - E_- = 0.281_2 - (-0.287_0) = 0.568 \text{ V}$

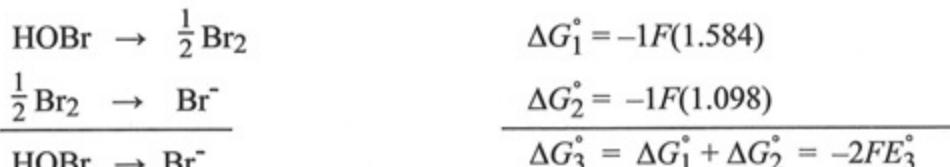
The agreement between the two calculations is reasonable.

- 13-20.** A hydrogen pressure of 727.2 Torr corresponds to  $(727.2 \text{ Torr})/(760 \text{ Torr/atm}) = 0.9568 \text{ atm}$ .  $(0.9568 \text{ atm})(1.01325 \text{ bar/atm}) = 0.9695 \text{ bar}$ .

$$0.7983 = E^\circ_{Ag^+|Ag} - 0.05916 \log \frac{[0.01000](0.914)}{(0.9695)^{1/2}[0.01000](0.898)}$$

$$\Rightarrow E^\circ_{Ag^+|Ag} = 0.7992 \text{ V}$$

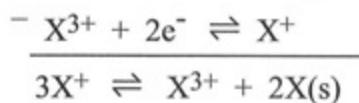
- 13-21.** Balanced reaction: HOBr + 2e<sup>-</sup> + H<sup>+</sup> ⇌ Br<sup>-</sup> + H<sub>2</sub>O



$$E_3^\circ = \frac{-1F(1.584) - 1F(1.098)}{-2F} = 1.341 \text{ V}$$

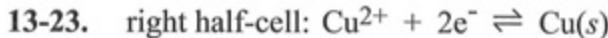


$$E_+^\circ = E_2^\circ$$

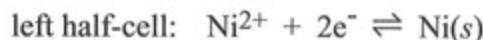


$$\begin{array}{c} E_-^\circ = E_1^\circ \\ \hline E_3^\circ = E_2^\circ - E_1^\circ \end{array}$$

If  $E_2^\circ > E_1^\circ$ , then  $E_3^\circ \geq 0$  and disproportionation is spontaneous.



$$E_+^\circ = 0.339 \text{ V}$$



$$E_-^\circ = -0.236 \text{ V}$$

The ionic strength of the right half-cell is 0.0090 M, and the ionic strength of the left half-cell is 0.0080 M. At  $\mu = 0.0090 \text{ M}$ ,  $\gamma_{Cu^{2+}} = 0.690$ .

At  $\mu = 0.0080 \text{ M}$ ,  $\gamma_{Ni^{2+}} = 0.705$ .

$$\begin{aligned} E_+ &= E_+^\circ - \frac{0.05916}{2} \log \frac{1}{[Cu^{2+}] \gamma_{Cu^{2+}}} \\ &= 0.339 - \frac{0.05916}{2} \log \frac{1}{(0.0030)(0.690)} = 0.2596 \text{ V} \\ E_- &= E_-^\circ - \frac{0.05916}{2} \log \frac{1}{[Ni^{2+}] \gamma_{Ni^{2+}}} \\ &= -0.236 - \frac{0.05916}{2} \log \frac{1}{(0.0020)(0.705)} = -0.3203 \text{ V} \end{aligned}$$

$$E = E_+ - E_- = 0.580 \text{ V}$$

Electrons flow from Ni ( $E = -0.3203 \text{ V}$ ) to Cu ( $E = 0.2596 \text{ V}$ ).

13-24. (a)  $E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{(+257 \times 10^3 \text{ J/mol})}{(2)(9.6485 \times 10^4 \text{ C/mol})} = 1.33 \text{ V}$

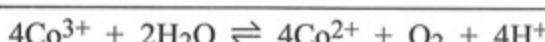
(b)  $K = 10^{nE^\circ/0.05916} = 1 \times 10^{45}$



$$E_+^\circ = 1.92 \text{ V}$$

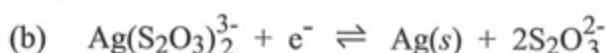


$$E_-^\circ = 1.229 \text{ V}$$

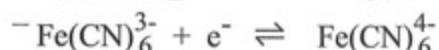


$$E^\circ = 0.691 \text{ V}$$

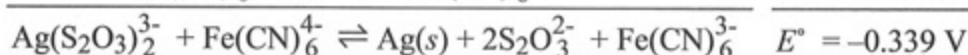
$$\Delta G^\circ = -4FE^\circ = -2.7 \times 10^5 \text{ J} \quad K = 10^{4E^\circ/0.05916} = 10^{47}$$



$$E_+^\circ = 0.017 \text{ V}$$

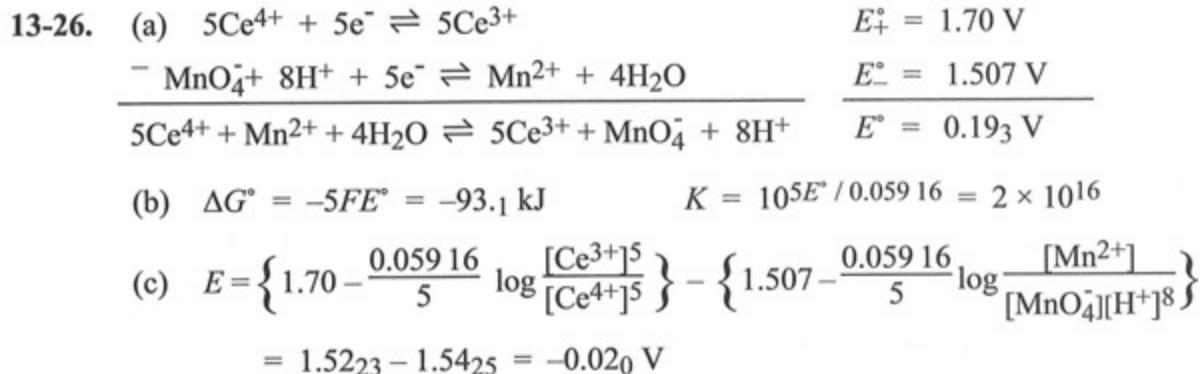


$$E_-^\circ = 0.356 \text{ V}$$

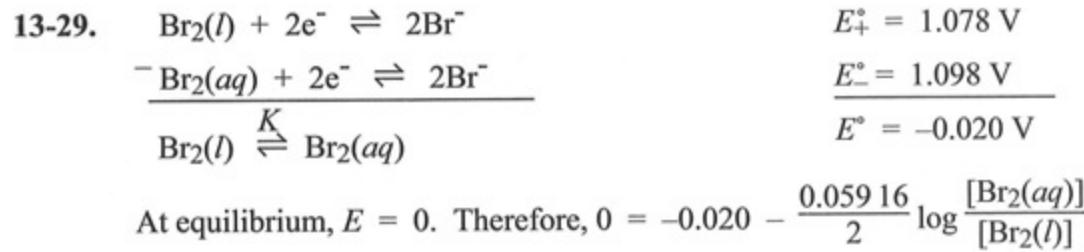
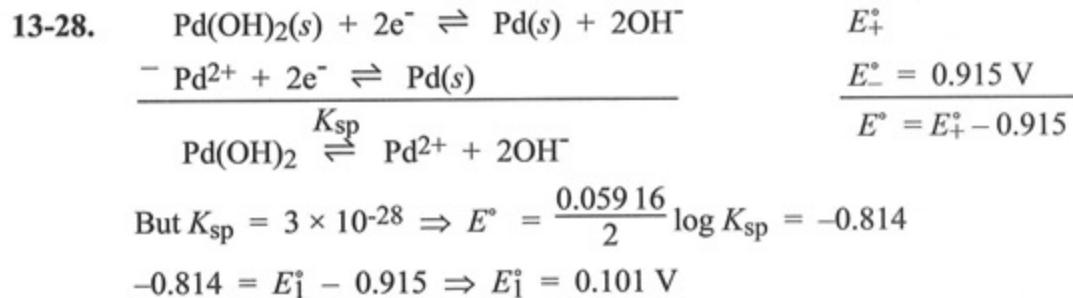
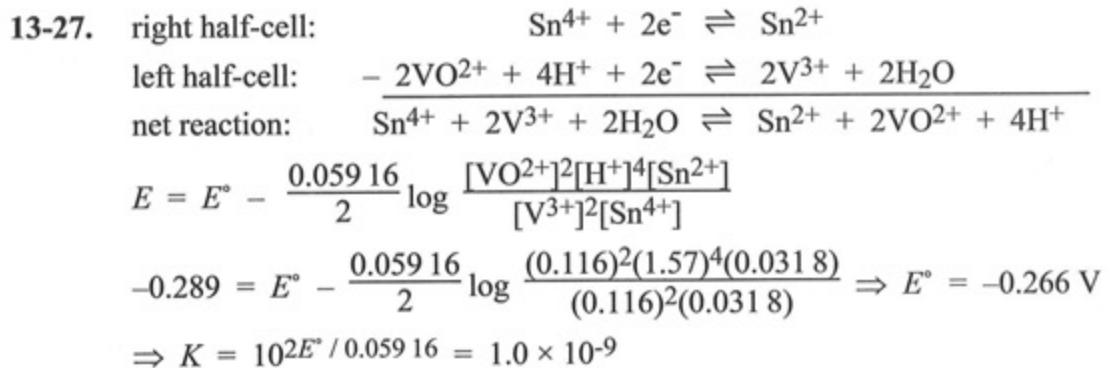
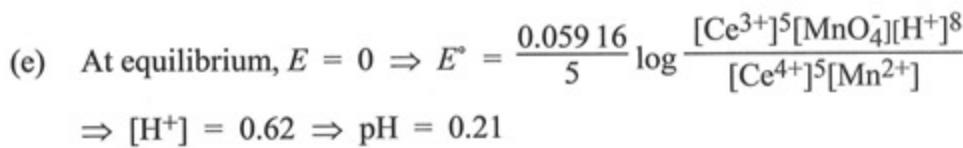


$$\Delta G^\circ = -1FE^\circ = 32.7 \text{ kJ}$$

$$K = 10^{1E^\circ/0.05916} = 1.9 \times 10^{-6}$$

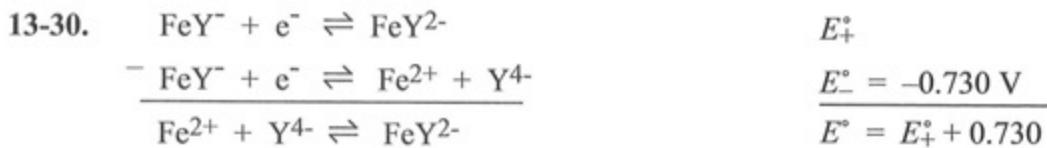


(d)  $\Delta G = -5FE = +10 \text{ kJ}$



$$\Rightarrow K = \frac{[\text{Br}_2(aq)]}{[\text{Br}_2(l)]} = 0.21_1 \text{ M.}$$

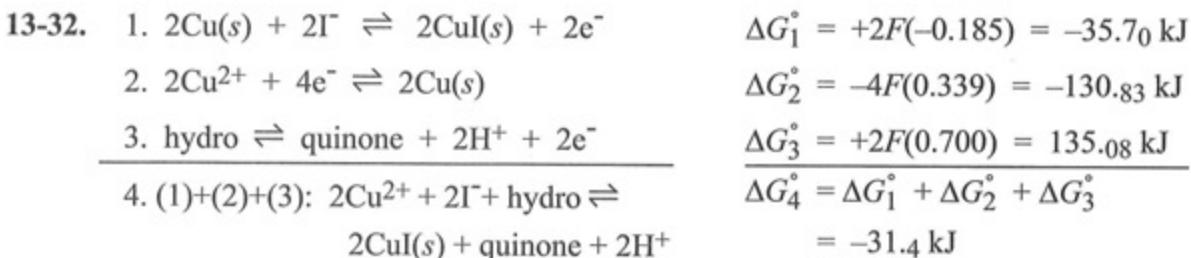
That is, the solubility of  $\text{Br}_2$  in water is  $0.21_1 \text{ M} = 34 \text{ g/L}$ .



But  $E^\circ = 0.05916 \log [K_f \text{ (for } \text{FeY}^{2-})] = 0.846 \text{ V} \Rightarrow E_+^\circ = E^\circ - E_-^\circ = 0.116 \text{ V.}$

13-31.  $E^\circ(T) = E^\circ + \frac{dE^\circ}{dT} \Delta T$

$$E^\circ(50^\circ \text{ C}) = -1.677 \text{ V} + (0.533 \times 10^{-3} \text{ V/K})(25 \text{ K}) = -1.664 \text{ V}$$



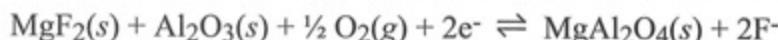
Since  $2\text{e}^-$  are transferred in the net reaction,  $E_4^\circ = \frac{-\Delta G_4^\circ}{2F} = +0.163 \text{ V}$

$$K = 10^{2(0.163)/0.05916} = 3.2 \times 10^5.$$

13-33. (a)  $E(\text{right}) = E^\circ(\text{right}) - \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}}^2(\text{right})}{P_{\text{O}_2}^{1/2}(\text{right})}$

$$E(\text{left}) = E^\circ(\text{left}) - \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}}^2(\text{left})}{P_{\text{O}_2}^{1/2}(\text{left})}$$

Net reaction: reverse left half-reaction and add it to right half-reaction:



Nernst equation for net reaction:

$$E(\text{right}) - E(\text{left}) = E^\circ(\text{right}) - E^\circ(\text{left}) - \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}}^2(\text{right})}{P_{\text{O}_2}^{1/2}(\text{right})} + \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}}^2(\text{left})}{P_{\text{O}_2}^{1/2}(\text{left})}$$

The activities of  $F^-$  are the same on both sides and the activities of  $O_2$  are also the same on both sides, so the  $\ln$  terms cancel, leaving  $E(\text{cell}) = E^\circ(\text{right}) - E^\circ(\text{left}) = E^\circ(\text{cell})$ .

- (b)  $\Delta G^\circ = -nFE^\circ = -(2)(9.648 \times 10^4 \text{ C/mol})(0.1529 \text{ J/C}) = -29.51 \text{ kJ/mol}$ , where we made use of the fact that a volt is equivalent to one joule/coulomb.

$$(c) \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

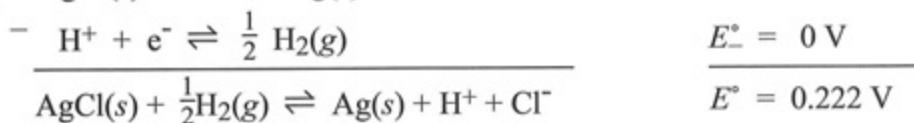
$$\begin{aligned} -nFE^\circ &= \Delta H^\circ - T\Delta S^\circ = -nF(0.1223 + 3.06 \times 10^{-5} T) \\ &= -nF(0.1223 \text{ V}) - nF(3.06 \times 10^{-5} T) \\ &= \underbrace{-nF(0.1223 \text{ V})}_{\Delta H^\circ} - \underbrace{T\{nF(3.06 \times 10^{-5} \text{ V/K})\}}_{\Delta S^\circ} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ &= -nF(0.1223 \text{ V}) = -(2)(9.648 \times 10^4 \text{ C/mol})(0.1223 \text{ J/C}) \\ &= -23.60 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= nF(3.06 \times 10^{-5} \text{ V/K}) \\ &= (2)(9.648 \times 10^4 \text{ C/mol})(3.06 \times 10^{-5} \text{ V/K}) \\ &= 5.90 \text{ C}\cdot\text{V}/(\text{K}\cdot\text{mol}) = 5.90 \text{ J}/(\text{K}\cdot\text{mol}), \text{ where we made use of the conversion coulomb}\cdot\text{volt} = \text{joule}. \end{aligned}$$

- 13-34.** In the right half-cell, the reaction  $Hg^{2+} + Y^{4-} \rightleftharpoons HgY^{2-}$  is at equilibrium, even though the net cell reaction  $Hg^{2+} + H_2 \rightleftharpoons Hg(l) + 2H^+$  is not at equilibrium.

- 13-35.** (a)  $\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^- \quad E_+^\circ = 0.222 \text{ V}$



$$E = 0.222 - 0.05916 \log \frac{[\text{H}^+][\text{Cl}^-]}{\sqrt{P_{\text{H}_2}}}$$

$$(b) 0.485 = 0.222 - 0.05916 \log \frac{(10^{-3.60})[\text{Cl}^-]}{\sqrt{1.00}} \Rightarrow [\text{Cl}^-] = 0.143 \text{ M}$$

- 13-36.** (a) Left: quinone +  $2H^+ + 2e^- \rightleftharpoons$  hydroquinone  $E_-^\circ = 0.700 \text{ V}$



$$E(\text{left}) = 0.700 - \frac{0.05916}{2} \log \frac{[\text{hydroquinone}]}{[\text{quinone}][\text{H}^+]^2}$$

$$E(\text{right}) = 0.268 - \frac{0.05916}{2} \log [\text{Cl}^-]^2$$

$$(b) E(\text{cell}) = E(\text{right}) - E(\text{left})$$

$$= \left\{ 0.268 - \frac{0.05916}{2} \log [\text{Cl}^-]^2 \right\} - \left\{ 0.700 - \frac{0.05916}{2} \log \frac{[\text{hydroquinone}]}{[\text{quinone}][\text{H}^+]^2} \right\}$$

$$E(\text{cell}) = -0.432 - \frac{0.05916}{2} \log \frac{[\text{quinone}][\text{H}^+]^2[\text{Cl}^-]^2}{[\text{hydroquinone}]}$$

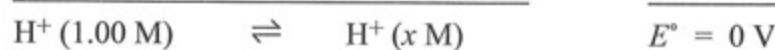
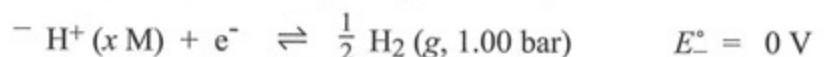
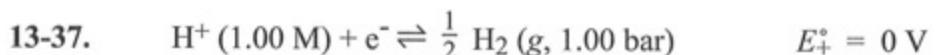
Setting  $[\text{Cl}^-] = 0.50 \text{ M}$  and noting  $[\text{quinone}] = [\text{hydroquinone}]$ , we find

$$E(\text{cell}) = -0.432 - 0.05916 \log (0.50) - 0.05916 \log [\text{H}^+]$$

$$E(\text{cell}) = -0.414 + 0.05916 \text{ pH} \quad (\text{A} = -0.414, \text{B} = 0.05916 \text{ V per pH unit})$$

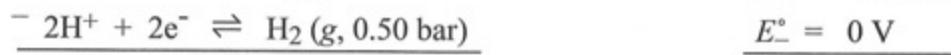
(c)  $E(\text{cell}) = -0.414 + 0.05916 (4.50) = -0.148$

Since  $E < 0$ , electrons flow from right to left ( $\text{Hg} \rightarrow \text{Pt}$ ) through the meter.



$$E = 0.490 = 0 - 0.05916 \log [\text{H}^+] \Rightarrow [\text{H}^+] = 5.2 \times 10^{-9} \text{ M}$$

$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} = \frac{(0.050)(K_w/[\text{H}^+])}{0.10} = 9.6 \times 10^{-7}$$



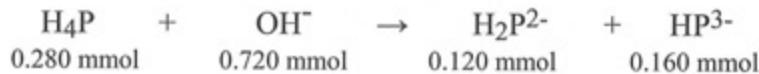
$$E = -0.266 - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2} [\text{M}^{2+}]}$$

$[\text{H}^+]$  in the left half-cell is found by considering the titration of 28.0 mL of the tetraprotic pyrophosphoric acid (abbreviated  $\text{H}_4\text{P}$ ) with 72.0 mL of KOH.

$$28.0 \text{ mL of } 0.0100 \text{ M H}_4\text{P} = 0.280 \text{ mmol}$$

$$72.0 \text{ mL of } 0.0100 \text{ M KOH} = 0.720 \text{ mmol}$$

First, 0.280 mmol  $\text{OH}^-$  consumes 0.280 mmol of  $\text{H}_4\text{P}$ , giving 0.280 mmol of  $\text{H}_3\text{P}^-$  and  $(0.720 - 0.280) = 0.440$  mmol of  $\text{OH}^-$ . Then 0.280 mmol  $\text{OH}^-$  consumes 0.280 mmol of  $\text{H}_3\text{P}^-$ , giving 0.280 mmol of  $\text{H}_2\text{P}^{2-}$  and  $(0.440 - 0.280) = 0.160$  mmol of  $\text{OH}^-$ . Finally, 0.160 mmol of  $\text{OH}^-$  reacts with 0.280 mmol of  $\text{H}_2\text{P}^{2-}$  to create 0.160 mmol of  $\text{HP}^{3-}$ , leaving 0.120 mmol of unreacted  $\text{H}_2\text{P}^{2-}$ .



$$\text{pH} = \text{p}K_3 + \log \frac{[\text{HP}^{3-}]}{[\text{H}_2\text{P}^{2-}]} = 6.70 + \log \frac{0.160}{0.120} = 6.82 \Rightarrow [\text{H}^+] = 1.50 \times 10^{-7} \text{ M}$$

Putting the known values of  $[H^+]$  and  $P_{H_2}$  into the Nernst equation gives

$$\begin{aligned} -0.246 &= -0.266 - \frac{0.05916}{2} \log \frac{[H^+]^2}{P_{H_2} [M^{2+}]} \\ &= -0.266 - \frac{0.05916}{2} \log \frac{[1.50 \times 10^{-7}]^2}{0.50 [M^{2+}]} \Rightarrow [M^{2+}] = 2.13 \times 10^{-13} M \end{aligned}$$

In the right half-cell we have the equilibrium

	$M^{2+}$	$+ FEDTA$	$\rightleftharpoons$	$MY^{2-}$
initial mmol/mL	$\frac{0.280}{100}$	$\frac{0.720}{100}$	—	—
final mmol/mL	small	$\frac{0.440}{100}$		$\frac{0.280}{100}$

$$K_f = \frac{[MY^{2-}]}{[M^{2+}] \alpha_{Y^{2-}} FEDTA} = \frac{0.280/100}{(2.13 \times 10^{-13})(0.0042)(0.440/100)} = 7.1 \times 10^{14}$$

- 13-39. right half-cell:  $Pb^{2+}(\text{right}) + 2e^- \rightleftharpoons Pb(s)$   $E_+^\circ = -0.126 V$   
 left half-cell:  $\frac{-Pb^{2+}(\text{left}) + 2e^- \rightleftharpoons Pb(s)}{Pb^{2+}(\text{right}) \rightleftharpoons Pb^{2+}(\text{left})}$   $E_-^\circ = -0.126 V$   
 $E^\circ = 0$

Nernst equation for net cell reaction:

$$-0.0018 = -\frac{0.05916}{2} \log \frac{[Pb^{2+}(\text{left})]}{[Pb^{2+}(\text{right})]} \Rightarrow \frac{[Pb^{2+}(\text{left})]}{[Pb^{2+}(\text{right})]} = 1.15$$

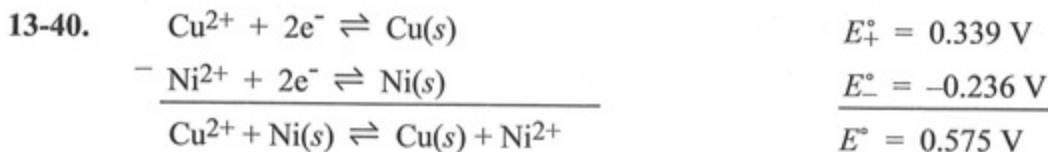
For each half-cell, we can write  $[CO_3^{2-}] = K_{sp}$  (for  $PbCO_3$ ) /  $[Pb^{2+}]$

$$\frac{[CO_3^{2-}(\text{left})]}{[CO_3^{2-}(\text{right})]} = \frac{K_{sp} \text{ (for } PbCO_3\text{)}/[Pb^{2+}(\text{left})]}{K_{sp} \text{ (for } PbCO_3\text{)}/[Pb^{2+}(\text{right})]} = \frac{1}{1.15} = 0.87$$

In each compartment the  $Ca^{2+}$  concentration is equal to the total concentration of all carbonate species (since  $PbCO_3$  is much less soluble than  $CaCO_3$ ). Let the fraction of all carbonate species in the form  $CO_3^{2-}$  be  $\alpha_{CO_3^{2-}}$

(i.e.,  $[CO_3^{2-}] = \alpha_{CO_3^{2-}} [\text{total carbonate}]$ ). We can say that  $[Ca^{2+}] = [\text{total carbonate}] = [CO_3^{2-}] / \alpha_{CO_3^{2-}}$ . The value of  $\alpha_{CO_3^{2-}}$  is the same in both compartments, since the pH is the same. Now we can write

$$\begin{aligned} \frac{K_{sp}(\text{calcite})}{K_{sp}(\text{aragonite})} &= \frac{[Ca^{2+}(\text{left})][CO_3^{2-}(\text{left})]}{[Ca^{2+}(\text{right})][CO_3^{2-}(\text{right})]} = \frac{[CO_3^{2-}(\text{left})]^2 / \alpha_{CO_3^{2-}}}{[CO_3^{2-}(\text{right})]^2 / \alpha_{CO_3^{2-}}} \\ &= (0.87)^2 = 0.76. \end{aligned}$$



The ionic strength of the right half-cell is 0.10 M and  $\gamma_{\text{Cu}^{2+}} = 0.405$ .

The ionic strength of the left half-cell is 0.010 M and  $\gamma_{\text{Ni}^{2+}} = 0.675$ .

$$0.512 = 0.575 - \frac{0.059\ 16}{2} \log \frac{(0.002\ 5)(0.675)}{[\text{Cu}^{2+}](0.405)} \Rightarrow [\text{Cu}^{2+}] = 3.09 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = [\text{Cu}^{2+}] \gamma_{\text{Cu}^{2+}} [\text{IO}_3^-]^2 \gamma_{\text{IO}_3^-}^2 = (3.09 \times 10^{-5})(0.405)(0.10)^2(0.775)^2 = 7.5 \times 10^{-8}$$

- 13-41.**  $E^\circ'$  is the effective reduction potential for a half-reaction at pH 7, instead of pH 0. Since living systems tend to have a pH much closer to 7 than to 0,  $E^\circ'$  provides a better indication of redox behavior in an organism.

**13-42.** (a)  $E = 0.731 - \frac{0.059\ 16}{2} \log \frac{P_{\text{C}_2\text{H}_4}}{P_{\text{C}_2\text{H}_2} [\text{H}^+]^2}$

(b)  $E = \underbrace{0.731 + 0.059\ 16 \log [\text{H}^+]}_{\text{This is } E^\circ \text{ when pH = 7}} - \frac{0.059\ 16}{2} \log \frac{P_{\text{C}_2\text{H}_4}}{P_{\text{C}_2\text{H}_2}}$

(c)  $E^\circ' = 0.731 + 0.059\ 16 \log (10^{-7.00}) = 0.317 \text{ V}$

**13-43.**  $E = E^\circ - \frac{0.059\ 16}{2} \log \frac{[\text{HCN}]^2}{P_{(\text{CN})_2} [\text{H}^+]^2}$

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

$$E = 0.373 - \frac{0.059\ 16}{2} \log \frac{[\text{H}^+]^2 F_{\text{HCN}}^2}{([\text{H}^+] + K_a)^2 P_{(\text{CN})_2} [\text{H}^+]^2}$$

$$E = 0.373 + \underbrace{0.059\ 16 \log ([\text{H}^+] + K_a)}_{\text{This is } E^\circ \text{ when pH = 7}} - \frac{0.059\ 16}{2} \log \frac{F_{\text{HCN}}^2}{P_{(\text{CN})_2}}.$$

Inserting  $K_a = 6.2 \times 10^{-10}$  for HCN and  $[\text{H}^+] = 10^{-7.00}$  gives

$$E^\circ' = 0.373 + 0.059\ 16 \log (10^{-7.00} + 6.2 \times 10^{-10}) = -0.041 \text{ V}.$$



$$E = 0.204 - \frac{0.05916}{2} \log \frac{[\text{HCO}_2\text{H}]^2}{[\text{H}_2\text{C}_2\text{O}_4][\text{H}^+]^2}$$

$$\text{But } [\text{HCO}_2\text{H}] = \frac{[\text{H}^+] F_{\text{HCO}_2\text{H}}}{[\text{H}^+] + K_a} \text{ and } [\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}^+]^2 F_{\text{H}_2\text{C}_2\text{O}_4}}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2}.$$

Putting these expressions into the Nernst equation gives

$$E = 0.204 - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2 F_{\text{HCO}_2\text{H}}^2 ([\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2)}{([\text{H}^+] + K_a)^2 [\text{H}^+]^2 F_{\text{H}_2\text{C}_2\text{O}_4} [\text{H}^+]^2}$$

$$E = 0.204 - \underbrace{\frac{0.05916}{2} \log \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2}{([\text{H}^+] + K_a)^2 [\text{H}^+]^2}}_{\text{This is } E^\circ \text{ when pH = 7}} - \frac{0.05916}{2} \log \frac{F_{\text{HCO}_2\text{H}}^2}{F_{\text{H}_2\text{C}_2\text{O}_4}}.$$

Putting in  $[\text{H}^+] = 10^{-7.00} \text{ M}$ ,  $K_a = 1.80 \times 10^{-4}$ ,  $K_1 = 5.62 \times 10^{-2}$ , and  $K_2 = 5.42 \times 10^{-5}$  gives  $E^\circ = -0.268 \text{ V}$ .



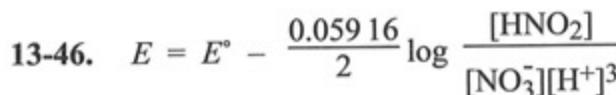
$$\text{But } [\text{HOx}] = \frac{[\text{H}^+] F_{\text{HOx}}}{[\text{H}^+] + K_a} \text{ and } [\text{H}_2\text{Red}^-] = \frac{[\text{H}^+]^2 F_{\text{H}_2\text{Red}^-}}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2}.$$

Putting these values into the Nernst equation gives

$$E = E^\circ - 0.05916 \log \frac{[\text{H}^+]^2 F_{\text{H}_2\text{Red}^-} ([\text{H}^+] + K_a)}{[\text{H}^+] F_{\text{HOx}} ([\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2)}$$

$$E = E^\circ - \underbrace{0.05916 \log \frac{[\text{H}^+] ([\text{H}^+] + K_a)}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2}}_{E^\circ} - 0.05916 \log \frac{F_{\text{H}_2\text{Red}^-}}{F_{\text{HOx}}}.$$

Since  $E^\circ = 0.062 \text{ V}$ , we find  $E^\circ = -0.036 \text{ V}$ .

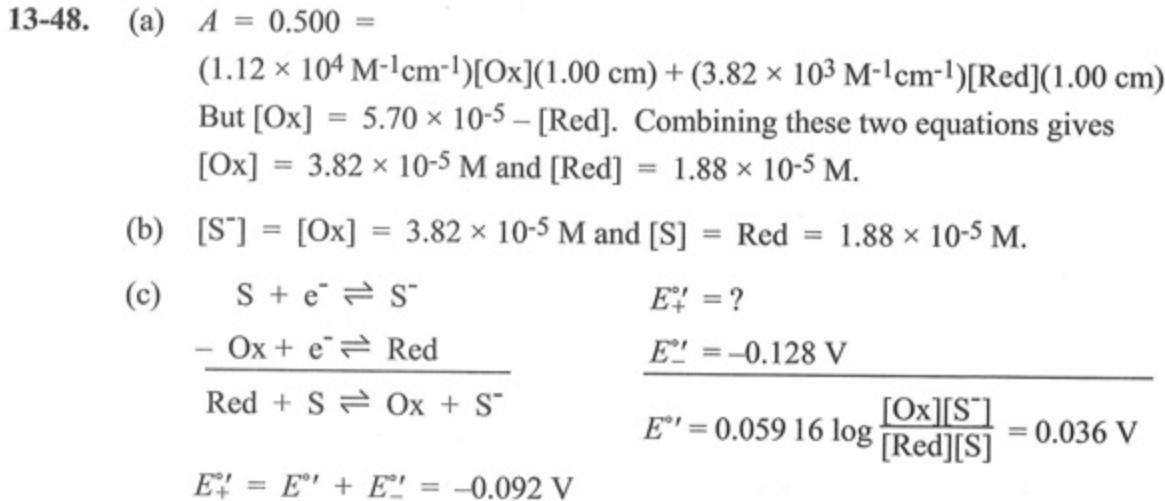
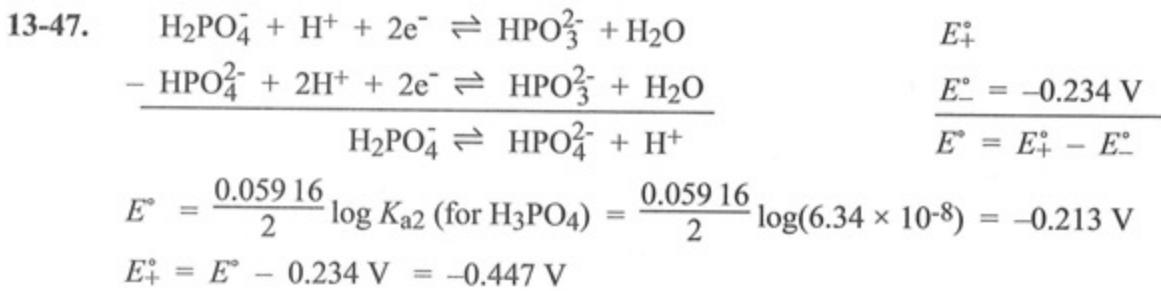


$$\text{But } [\text{HNO}_2] = \frac{[\text{H}^+] F_{\text{HNO}_2}}{[\text{H}^+] + K_a} \text{ and } [\text{NO}_3^-] = F_{\text{NO}_3^-}.$$

Putting these values into the Nernst equation gives

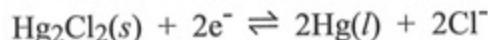
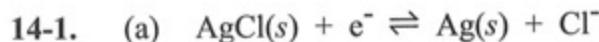
$$E = E^\circ - \underbrace{\frac{0.05916}{2} \log \frac{1}{([\text{H}^+] + K_a)[\text{H}^+]^2}}_{E^\circ} - \frac{0.05916}{2} \log \frac{F_{\text{HNO}_2}}{F_{\text{NO}_3^-}}$$

$$E^{\circ'} = 0.433 = 0.940 - \frac{0.05916}{2} \log \frac{1}{(10^{-7} + K_a)(10^{-7})^2} \Rightarrow K_a = 7.2 \times 10^{-4}.$$



## CHAPTER 14

### ELECTRODES AND POTENTIOMETRY



$$(b) E = E_+ - E_- = 0.241 - 0.197 = 0.044 \text{ V}$$

- 14-2.** (a) 0.326 V (b) 0.086 V (c) 0.019 V (d) -0.021 V (e) 0.021 V

**14-3.**  $E = E_+ - E_-$

$$E = \left\{ 0.771 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - (0.241) = 0.684 \text{ V}$$

**14-4.**  $E = E^\circ - 0.05916 \log \mathcal{A}_{\text{Cl}^-}$

$$0.280 = 0.268 - 0.05916 \log \mathcal{A}_{\text{Cl}^-} \Rightarrow \mathcal{A}_{\text{Cl}^-} = 0.627$$

- 14-5.** For the saturated Ag-AgCl electrode, we can write:  $E = E^\circ - 0.05916 \log \mathcal{A}_{\text{Cl}^-}$ . Putting in  $E = 0.197$  and  $E^\circ = 0.222 \text{ V}$  gives  $\mathcal{A}_{\text{Cl}^-} = 2.65$ . For the S.C.E., we can write:  $E = E^\circ - 0.05916 \log \mathcal{A}_{\text{Cl}^-} = 0.268 \text{ V} - 0.05916 \log 2.65 = 0.243 \text{ V}$ .

- 14-6.** (a)  $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(s) \quad E^\circ = 0.339 \text{ V}$

$$(b) E_+ = 0.339 - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]} = 0.309 \text{ V}$$

$$(c) E = E_+ - E_- = 0.309 - 0.241 = 0.068 \text{ V}$$

- 14-7.** A silver electrode serves as an indicator for  $\text{Ag}^+$  by virtue of the equilibrium  $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(s)$  that occurs at its surface. If the solution is saturated with silver halide, then  $[\text{Ag}^+]$  is affected by changes in halide concentration. Therefore, the electrode is also an indicator for halide.

- 14-8.**  $V_e = 20.0 \text{ mL}$ .  $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(s) \Rightarrow E_+ = 0.799 - 0.05916 \log \frac{1}{[\text{Ag}^+]}$

$$0.1 \text{ mL}: \quad [\text{Ag}^+] = \underbrace{\left( \frac{19.9}{20.0} \right)}_{\substack{\text{Fraction} \\ \text{remaining concentration}}} \underbrace{(0.0500 \text{ M})}_{\substack{\text{Original} \\ \text{concentration}}} \underbrace{\left( \frac{10.0}{10.1} \right)}_{\substack{\text{Dilution} \\ \text{factor}}} = 0.0493 \text{ M}$$

$\overbrace{\phantom{0.0493}}^{\text{Fraction}}$      $\overbrace{\phantom{0.0493}}^{\text{Original}}$      $\overbrace{\phantom{0.0493}}^{\text{Dilution}}$   
                        remaining concentration      factor

$$E = E_+ - E_- = \left\{ 0.799 - 0.05916 \log \frac{1}{0.0493} \right\} - 0.241 = 0.481 \text{ V}$$

30.0 mL: This is 10.0 mL past  $V_e \Rightarrow [Br^-] = \left(\frac{10.0}{40.0}\right)(0.025\ 0\ M) = 0.00625\ M$

$$[Ag^+] = K_{sp}/[Br^-] = (5.0 \times 10^{-13})/0.00625 = 8.0 \times 10^{-11}\ M$$

$$E = E_+ - E_- = \left\{ 0.799 - 0.05916 \log \frac{1}{8.0 \times 10^{-11}} \right\} - 0.241 = -0.039\ V.$$

- 14-9.** The reaction in the right half-cell is  $Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$

$$E = E_+ - E_-$$

$$-0.027 = 0.852 - \frac{0.05916}{2} \log \frac{1}{[Hg^{2+}]} - (0.241)$$

$$\Rightarrow [Hg^{2+}] = 2.7 \times 10^{-22}\ M.$$

The cell contains 5.00 mmol EDTA (in all forms) and 1.00 mmol Hg(II) in 100 mL. 1.00 mmol EDTA reacts with 1.00 mmol Hg(II), leaving 4.00 mmol EDTA.

$$K_f = \frac{[HgY^{2-}]}{[Hg^{2+}][Y^{4-}]} = \frac{[HgY^{2-}]}{[Hg^{2+}]\alpha_{Y4-}[EDTA]}$$

$$K_f = \frac{(1.00\ mmol/100\ mL)}{(2.7 \times 10^{-22})(0.30)(4.00\ mmol/100\ mL)} = 3.1 \times 10^{21}$$

- 14-10.** (a)  $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$E^\circ = 0.771\ V$$

$$(b) E = E_+ - E_-$$

$$-0.126 = 0.771 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.241 \Rightarrow \frac{[Fe^{2+}]}{[Fe^{3+}]} = 1.2 \times 10^{11}$$

$$(c) \frac{K_f(FeEDTA^-)}{K_f(FeEDTA^{2-})} = \frac{[FeEDTA^-]}{[Fe^{3+}][EDTA^{4-}]} \div \frac{[FeEDTA^{2-}]}{[Fe^{2+}][EDTA^{4-}]}$$

$$= \frac{[FeEDTA^-]}{[FeEDTA^{2-}]} \cdot \frac{[Fe^{2+}]}{[Fe^{3+}]} = \left( \frac{1.00 \times 10^{-3}}{2.00 \times 10^{-3}} \right) (1.2 \times 10^{11}) = 6 \times 10^{10}$$

- 14-11.**  $E = E_+ - E_- = -0.429 - 0.05916 \log \frac{[CN^-]^2}{[Cu(CN)_2^-]} - 0.197$

Putting in  $E = -0.440\ V$  and  $[Cu(CN)_2^-] = 1.00\ mM$  gives  $[CN^-] = 0.847\ mM$ .

$$pH = pK_a(HCN) + \log \frac{[CN^-]}{[HCN]} = 9.21 + \log \frac{8.47 \times 10^{-4}}{1.00 \times 10^{-3} - 8.47 \times 10^{-4}} = 9.954$$

Now we use the pH to see how much HA reacted with KOH:

HA	+	$OH^-$	$\rightarrow$	$A^-$	+	$H_2O$
initial mmol		10.0		$x$		—
final mmol		$10.0 - x$		—		$x$

$$\text{pH} = \text{p}K_a(\text{HA}) + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$9.954 = 9.50 + \log \frac{x}{10.0 - x} \Rightarrow x = 7.40 \text{ mmol of OH}^-$$

$$[\text{KOH}] = \frac{7.40 \text{ mmol}}{25.0 \text{ mL}} = 0.296 \text{ M}$$

- 14-12.** Junction potential arises because different ions diffuse at different rates across a liquid junction, leading to a separation of charge. The resulting electric field retards fast-moving ions and accelerates the slow-moving ions until a steady-state junction potential is reached. This limits the accuracy of a potentiometric measurement, because we do not know what part of a measured cell voltage is due to the process of interest and what is due to the junction potential. The cell in Figure 13-4 has no junction potential because there are no liquid junctions.
- 14-13.**  $\text{H}^+$  has greater mobility than  $\text{K}^+$ . The  $\text{HCl} \mid \text{KCl}$  junction will be negative because  $\text{H}^+$  diffuses into the  $\text{KCl}$  region faster than  $\text{K}^+$  diffuses into the  $\text{HCl}$  region.  $\text{K}^+$  has a greater mobility than  $\text{Na}^+$ , so this junction has the opposite sign. The  $\text{HCl} \mid \text{KCl}$  voltage is larger, because the difference in mobility between  $\text{H}^+$  and  $\text{K}^+$  is greater than the difference in mobility between  $\text{K}^+$  and  $\text{Na}^+$ .
- 14-14.** Relative mobilities:
- |                               |                                  |
|-------------------------------|----------------------------------|
| $\text{K}^+ \rightarrow 7.62$ | $\text{NO}_3^- \rightarrow 7.40$ |
| $5.19 \leftarrow \text{Na}^+$ | $7.91 \leftarrow \text{Cl}^-$    |
- Both the cation and anion diffusion cause negative charge to build up on the left.
- 14-15.** Velocity = mobility  $\times$  field =  $(36.30 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})) \times (7800 \text{ V/m}) = 2.83 \times 10^{-3} \text{ m s}^{-1}$  for  $\text{H}^+$  and  $(7.40 \times 10^{-8})(7800) = 5.77 \times 10^{-4} \text{ m s}^{-1}$  for  $\text{NO}_3^-$ . To cover 0.120 m will require  $(0.120 \text{ m})/(2.83 \times 10^{-3} \text{ m s}^{-1}) = 42.4 \text{ s}$  for  $\text{H}^+$  and  $(0.120)/(5.77 \times 10^{-4}) = 208 \text{ s}$  for  $\text{NO}_3^-$ .
- 14-16.** (a)  $E^\circ = 0.799 \text{ V} \Rightarrow K = 10^{0.799/0.05916} = 3.20 \times 10^{13}$
- (b)  $K' = 10^{0.801/0.05916} = 3.46 \times 10^{13}$ .  $K'/K = 1.08$ . The increase is 8%.
- (c)  $K = 10^{0.100/0.05916} = 49.0$ .  $K' = 10^{0.102/0.05916} = 53.0$   
 $K'/K = 1.08$ . The change is still 8%.

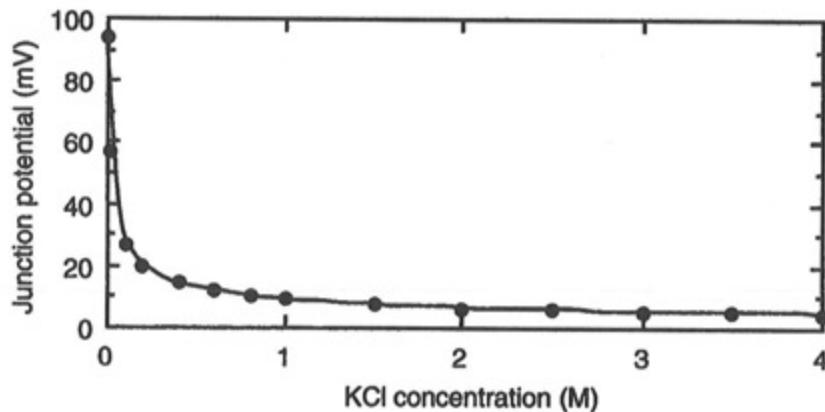
- 14-17.** Both half-cell reactions are the same ( $\text{AgCl} + \text{e}^- \rightleftharpoons \text{Ag} + \text{Cl}^-$ ) and the concentration of  $\text{Cl}^-$  is the same on both sides. In principle, the voltage of the cell would be 0 if there were no junction potential. The measured voltage can be attributed to the junction potential. In practice, if both sides contained 0.1 M HCl (or 0.1 M KCl), the two electrodes would probably produce a small voltage because no two real cells are identical. This voltage can be measured and subtracted from the voltage measured with the HCl | KCl junction.

- 14-18.** (a) In phase  $\alpha$ , we have 0.1 M  $\text{H}^+$  ( $u = 36.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ) and 0.1 M  $\text{Cl}^-$  ( $u = 7.91 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ). In phase  $\beta$ , we have 0.1 M  $\text{K}^+$  ( $u = 7.62 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ) and 0.1 M  $\text{Cl}^-$  ( $u = 7.91 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ).

Substituting into the Henderson equation gives

$$E_j = \frac{(36.3 \times 10^{-8})(0 - 0.1) + (7.62 \times 10^{-8})(0.1 - 0) - (7.91 \times 10^{-8})(0.1 - 0.1)}{(36.3 \times 10^{-8})(0 - 0.1) + (7.62 \times 10^{-8})(0.1 - 0) + (7.91 \times 10^{-8})(0.1 - 0.1)} \times \\ 0.05916 \log \frac{(36.3 \times 10^{-8})(0.1) + (7.91 \times 10^{-8})(0.1)}{(7.62 \times 10^{-8})(0.1) + (7.91 \times 10^{-8})(0.1)} = 26.9 \text{ mV}$$

(b)



(c)

[HCl]	y M HCl   1mM KCl	y M HCl   4 M KCl
$10^{-4} \text{ M}$	9.1 mV	4.6 mV
$10^{-3} \text{ M}$	26.9 mV	3.6 mV
$10^{-2} \text{ M}$	57.3 mV	3.0 mV
$10^{-1} \text{ M}$	93.6 mV	4.7 mV

- 14-19.** Ideally, the electrode should be calibrated at  $37^\circ$  using two buffers bracketing the pH of the blood. It would be reasonable to use the MOPS and HEPES buffers in Table 14-3 that are recommended for use with physiologic fluids. The pH of these standards at  $37^\circ\text{C}$  is 6.695 and 7.370. The standards should be

thermostatted to 37° during calibration, and the blood should also be at 37° during the measurement.

- 14-20.** Uncertainty in pH of standard buffers, junction potential, junction potential drift, sodium or acid errors at extreme pH values, equilibration time, hydration of glass, temperature of measurement and calibration, and cleaning of electrode
- 14-21.** The error measured in the graph is -0.33 pH units. The electrode will indicate  $11.00 - 0.33 = 10.67$ .
- 14-22.** Saturated potassium hydrogen tartrate and 0.05 *m* potassium hydrogen phthalate
- 14-23.** If the alkaline solution has a high concentration of Na<sup>+</sup> (as in NaOH), the Na<sup>+</sup> cation competes with H<sup>+</sup> for cation exchange sites on the glass surface. The glass responds as if H<sup>+</sup> were present, and the apparent pH is lower than the actual pH.
- 14-24.** The junction potential changes from -6.4 mV to -0.2 mV. A change of  $6.4 - 0.2 = +6.2$  mV appears to be a pH change of  $+6.2/59.16 = +0.10$  pH units.
- 14-25.** (a)  $(4.63)(59.16 \text{ mV}) = 274 \text{ mV}$ . The factor 59.16 mV is the value of  $(RT \ln 10)/F$  at 298.15 K.  
 (b) At 310.15 K (37°C),  $(RT \ln 10)/F$   
 $= (8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(310.15 \text{ K})(\ln 10)/(96485 \text{ C mol}^{-1}) = 61.54 \text{ mV}$   
 $(4.63)(61.54 \text{ mV}) = 285 \text{ mV}$ .
- 14-26.** pH of 0.025 *m* KH<sub>2</sub>PO<sub>4</sub>/0.025 *m* Na<sub>2</sub>HPO<sub>4</sub> at 20°C = 6.881  
 pH of 0.05 *m* potassium hydrogen phthalate at 20°C = 4.002  

$$\frac{E_{\text{Unknown}} - E_{\text{S1}}}{\text{pH}_{\text{Unknown}} - \text{pH}_{\text{S1}}} = \frac{E_{\text{S2}} - E_{\text{S1}}}{\text{pH}_{\text{S2}} - \text{pH}_{\text{S1}}}$$
  

$$\frac{E_{\text{Unknown}} - (-18.3 \text{ mV})}{\text{pH}_{\text{Unknown}} - 6.881} = \frac{(+146.3 \text{ mV}) - (-18.3 \text{ mV})}{4.002 - 6.881} = -57.17_3 \text{ mV/pH unit}$$
  

$$\text{pH}_{\text{Unknown}} = \frac{E_{\text{Unknown}} - (-18.3 \text{ mV})}{-57.17_3 \text{ mV/pH unit}} + 6.881 = 5.686$$
  
 Observed slope =  $-57.17_3 \text{ mV/pH unit}$   
 Theoretical slope =  $-\frac{RT \ln 10}{F}$   
 $= -\frac{[8.31447 \text{ V}\cdot\text{C}/(\text{mol}\cdot\text{K})][293.15 \text{ K}] \ln 10}{9.64853 \times 10^4 \text{ C/mol}} = -0.05817 \text{ V}$

$$\beta = \frac{\text{observed slope}}{\text{theoretical slope}} = \frac{-57.173 \text{ mV}}{-58.17 \text{ mV}} = 0.983$$

- 14-27.** (a) There is negligible change in the concentrations of the buffer species when we mix the acid  $\text{H}_2\text{PO}_4^-$  with its conjugate base,  $\text{HPO}_4^{2-}$ . The ionic strength of  $0.0250 \text{ m } \text{KH}_2\text{PO}_4$  (a 1:1 electrolyte) is  $0.0250 \text{ m}$ . The ionic strength of  $0.0250 \text{ m } \text{Na}_2\text{HPO}_4$  (a 2:1 electrolyte) is  $0.0750 \text{ m}$ . The total ionic strength is  $0.100 \text{ m}$ .

$$(b) K_2 = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{HPO}_4^{2-}] \gamma_{\text{HPO}_4^{2-}}}{[\text{H}_2\text{PO}_4^-] \gamma_{\text{H}_2\text{PO}_4^-}}$$

But  $K_2 = 10^{-7.198}$  and  $[\text{H}^+] \gamma_{\text{H}^+} = 10^{-\text{pH}} = 10^{-6.865}$

$$\text{Therefore, } \frac{\gamma_{\text{HPO}_4^{2-}}}{\gamma_{\text{H}_2\text{PO}_4^-}} = \frac{K_2 [\text{H}_2\text{PO}_4^-]}{[\text{H}^+] \gamma_{\text{H}^+} [\text{HPO}_4^{2-}]} = \frac{10^{-7.198}[0.0250]}{10^{-6.865}[0.0250]} = 0.4645$$

(We can use molality or any other units for concentrations because they cancel in the numerator and denominator.)

- (c) To get a pH of 7.000, we need to increase the concentration of base ( $\text{HPO}_4^{2-}$ ) and decrease the concentration of acid ( $\text{H}_2\text{PO}_4^-$ ). To maintain a constant ionic strength, we must decrease  $\text{KH}_2\text{PO}_4$  three times as much as we increase  $\text{Na}_2\text{HPO}_4$ , because  $\text{Na}_2\text{HPO}_4$  contributes three times as much as  $\text{KH}_2\text{PO}_4$  to the ionic strength. So let's increase  $\text{Na}_2\text{HPO}_4$  by  $x$  and decrease  $\text{KH}_2\text{PO}_4$  by  $3x$ .

$$K_2 = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{HPO}_4^{2-}] \gamma_{\text{HPO}_4^{2-}}}{[\text{H}_2\text{PO}_4^-] \gamma_{\text{H}_2\text{PO}_4^-}}$$

$$\Rightarrow 10^{-7.198} = \frac{10^{-7.000}[0.0250 + x]}{[0.0250 - 3x]} (0.4645) \Rightarrow x = 0.0018 \text{ m.}$$

The new concentrations should be  $\text{Na}_2\text{HPO}_4 = 0.0268 \text{ m}$  and  $\text{KH}_2\text{PO}_4 = 0.0196 \text{ m}$ .

- 14-28.** Analyte ions equilibrate with ion-exchange sites at the outer surface of the ion-selective membrane. Diffusion of analyte ions out of the membrane creates a slight charge imbalance (an electric potential difference) across the interface between the membrane and the analyte solution. Changes in analyte ion concentration in the solution change the potential difference across the outer boundary of the ion-selective membrane.

A compound electrode contains a second chemically active membrane outside the ion-selective membrane. The second membrane may be semipermeable and only allow the species of interest to pass through. Alternatively, the second membrane may contain a substance (such as an enzyme) that reacts with analyte to generate the species to which the ion-selective membrane responds.

- 14-29.** The selectivity coefficient  $K_{A,X}^{\text{Pot}}$  tells us the relative response of an ion-selective electrode to the ion of interest (A) and an interfering ion (X). The smaller  $K_{A,X}^{\text{Pot}}$ , the more selective is the electrode (smaller response to the interfering ion).
- 14-30.** A mobile molecule dissolved in the membrane liquid phase binds tightly to the ion of interest and weakly to interfering ions.
- 14-31.** A metal ion buffer maintains the desired (small) concentration of metal ion from a large reservoir of metal complex (ML) and free ligand (L). If you just tried to dissolve  $10^{-8}$  M metal ion in most solutions or containers, the metal would probably bind to the container wall or to an impurity in the solution and be lost.
- 14-32.** Electrodes respond to *activity*. If the ionic strength is constant, the activity coefficient of analyte will be constant in all standards and unknowns. In this case, the calibration curve can be written directly in terms of concentration.
- 14-33.** (a)  $-0.230 = \text{constant} - 0.05916 \log (1.00 \times 10^{-3}) \Rightarrow \text{constant} = -0.407 \text{ V}$   
 (b)  $-0.300 = -0.407 - 0.05916 \log x \Rightarrow x = 1.55 \times 10^{-2} \text{ M}$   
 (c)  $-0.230 = \text{constant} - 0.05916 \log (1.00 \times 10^{-3})$   
 $\underline{-0.300 = \text{constant} - 0.05916 \log x}$   
 subtract:  $0.070 = -0.05916 \log \frac{1.00 \times 10^{-3}}{x} \Rightarrow x = 1.52 \times 10^{-2} \text{ M}$
- 14-34.**  $E_1 = \text{constant} + \frac{0.05916}{2} \log [1.00 \times 10^{-4}]$   
 $E_2 = \text{constant} + \frac{0.05916}{2} \log [1.00 \times 10^{-3}]$   
 $\Delta E = E_2 - E_1 = \frac{0.05916}{2} \log \frac{1.00 \times 10^{-3}}{1.00 \times 10^{-4}} = +0.0296 \text{ V}$
- 14-35.**  $[F^-]_{\text{Providence}} = 1.00 \text{ mg F}^-/\text{L} = 5.26 \times 10^{-5} \text{ M}$   
 $E_{\text{Providence}} = \text{constant} - 0.05916 \log [5.26 \times 10^{-5}]$   
 $E_{\text{Foxboro}} = \text{constant} - 0.05916 \log [F^-]_{\text{Foxboro}}$

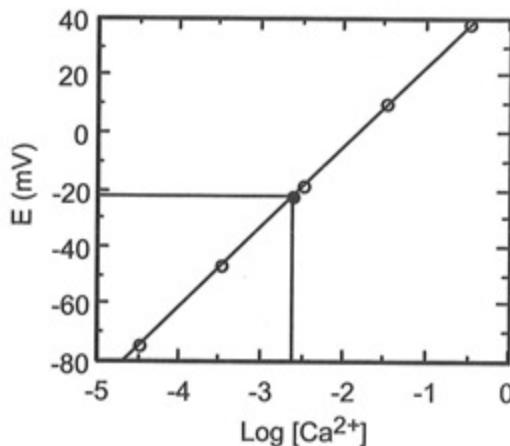
$$\begin{aligned}\Delta E &= E_{\text{Foxboro}} - E_{\text{Providence}} = 0.0400 \text{ V} \\ &= -0.05916 \log \frac{[\text{F}^-]_{\text{Foxboro}}}{5.26 \times 10^{-5}} \Rightarrow [\text{F}^-]_{\text{Foxboro}} = 1.11 \times 10^{-5} \text{ M} = 0.211 \text{ mg/L}\end{aligned}$$

- 14-36.**  $\text{K}^+$  has the largest selectivity coefficient of Group 1 ions and therefore interferes the most.  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  are the worst of the Group 2 ions. Since  $\log K_{\text{Li}^+, \text{K}^+}^{\text{Pot}} \approx -2$ , there must be 100 times more  $\text{K}^+$  than  $\text{Li}^+$  to give equal response.

**14-37.**  $\frac{[\text{ML}]}{[\text{M}][\text{L}]} = 4.0 \times 10^8 = \frac{0.030 \text{ M}}{[\text{M}](0.020 \text{ M})} \Rightarrow [\text{M}] = 3.8 \times 10^{-9} \text{ M}$

- 14-38.** (a) The least squares parameters are

$$E = 51.10 (\pm 0.24) + 28.14 (\pm 0.085) \log [\text{Ca}^{2+}] \quad (s_y = 0.27)$$



- (b) The slope is  $0.02814 \text{ V} = \beta(0.05916 \text{ V})/2 \Rightarrow \beta = 0.951$ .  
(c) If we use Equation 4-27 in a spreadsheet, we find  $\log [\text{Ca}^{2+}] = -2.615_3 (\pm 0.007_2)$  using  $s_y = 0.3$  and  $k = 4$ .

From Table 3-1, we can write that if  $F = 10^x$ ,  $e_F/F = (\ln 10)e_x$ .

In this problem,  $F = [\text{Ca}^{2+}] = 10^{-2.615_3 (\pm 0.007_2)}$

$$e_F/F = (\ln 10)(0.007_2) = 0.016_6$$

$$e_F = (0.016_6)F = 4.0 \times 10^{-5} \Rightarrow F = 2.43 (\pm 0.04) \times 10^{-3} \text{ M.}$$

- 14-39.** At pH 7.2 the effect of  $\text{H}^+$  will be negligible because  $[\text{H}^+] \ll [\text{Li}^+]$ :

$$-0.333 \text{ V} = \text{constant} + 0.05916 \log [3.44 \times 10^{-4}] \Rightarrow \text{constant} = -0.128 \text{ V.}$$

At pH 1.1 ( $[\text{H}^+] = 0.079 \text{ M}$ ), we must include interference by  $\text{H}^+$ :

$$E = -0.128 + 0.05916 \log [3.44 \times 10^{-4} + (4 \times 10^{-4})(0.079)] = -0.331 \text{ V.}$$

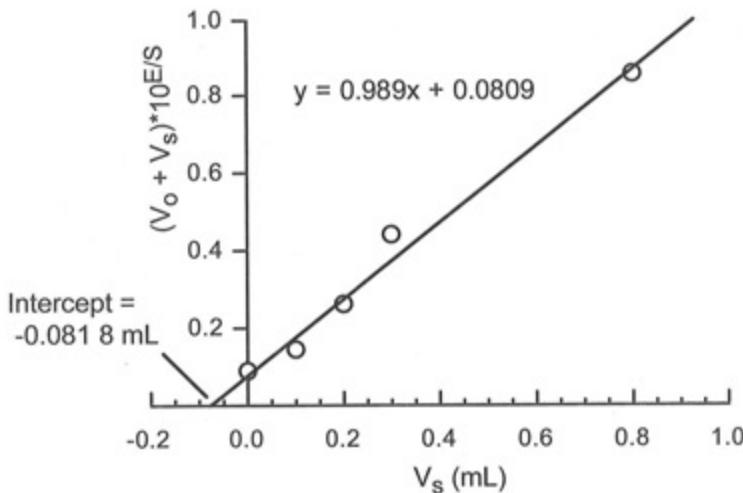
- 14-40.** The function to plot on the  $y$ -axis is  $(V_0 + V_s) 10^{E/S}$ , where  $S = -(\beta RT \ln 10)/nF$ .

(The minus sign comes from the equation for the response of the electrode, which has a minus sign in front of the log term.) Putting in  $\beta = 0.933$ ,  $R = 8.3145$  J/(mol·K),  $F = 96\,485$  C/mol,  $T = 303.15$  K, and  $n = 2$  gives  $S = -0.028\,06$  J/C = 0.028 06 V. (You can get the relation of J/C = V from the equation  $\Delta G = -nFE$ , in which the units are J = (mol)(C/mol)(V).)

$V_s$ (mL)	$E$ (V)	$y$
0	0.079 0	0.084 1
0.100	0.072 4	0.144 9
0.200	0.065 3	0.259 9
0.300	0.058 8	0.443 8
0.800	0.050 9	0.856 5

The graph has a slope of  $m = 0.989$  and an intercept of  $b = 0.080\,9$ , giving an  $x$ -intercept of  $-b/m = -0.081\,8$  mL. The concentration of original unknown is

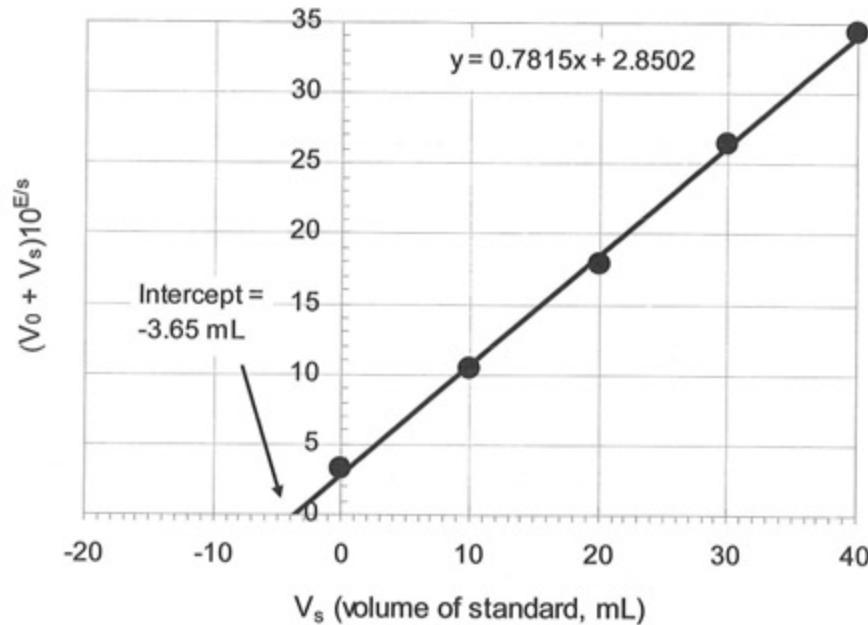
$$c_X = -\frac{(x\text{-intercept}) c_S}{V_0} = -\frac{(-0.081\,8 \text{ mL})(0.020\,0 \text{ M})}{55.0 \text{ mL}} = 3.0 \times 10^{-5} \text{ M.}$$



- 14-41. (a)** The following spreadsheet and graph are shown. The  $x$ -intercept is at  $-3.65$  mL with a standard deviation in cell B26 of  $s = 0.484$  mL. The intercept gives us the concentration of ammonia nitrogen in the volume  $V_0 = 101.0$  mL:

$$\begin{aligned} x\text{-intercept} &= -3.65 \text{ mL} = -\frac{V_0 c_X}{c_S} \\ \Rightarrow c_X &= \frac{(x\text{-intercept}) c_S}{V_0} = \frac{(3.65 \text{ mL})(10.0 \text{ ppm})}{101.0 \text{ mL}} = 0.3614 \text{ ppm} \end{aligned}$$

	A	B	C	D	E	F	G	H
1	Standard Addition: Ammonia in Seawater							
2								
3	$V_0 =$	101 mL						
4	$c_s =$	10 ppm						
5	$s =$	0.0566 V						
6								
7	x			y				
8	Added standard (mL)	$E = \text{cell}$ voltage (V)	$V_0 + V_s$ (mL)	$(V_0 + V_s)10^{E/s}$ (mL)				
9								
10	0.00	-0.0844	101.0	3.26				
11	10.00	-0.0581	111.0	10.44				
12	20.00	-0.0469	121.0	17.95				
13	30.00	-0.0394	131.0	26.37				
14	40.00	-0.0347	141.0	34.37				
15								
16	LINEST output:				Highlight cells B17:D19			
17	m	0.7815	2.8502	b	Type '=LINEST(D10:D14,A10:A14,TRUE,TRUE)			
18	$s_m$	0.0137	0.3364	$s_b$	Press CTRL+SHIFT+ENTER (on PC)			
19	$R^2$	0.9991	0.4343	$s_y$	Press COMMAND+RETURN (on Mac)			
20								
21	$x\text{-intercept} = -b/m =$	-3.647 mL			To find 95% confidence interval			
22	n =	5	B22 = COUNT(A10:A14)		we need Student's t for			
23	Mean y =	18.479	B23 = AVERAGE(D10:D14)		3 degrees of freedom			
24	$\sum(x_i - \text{mean } x)^2 =$	1000	B24 = DEVSQ(A10:A14)		TINV(0.05,3) = 3.182446			
25	Std deviation of				t*s =	1.541109		
26	x-intercept =	0.484 mL						
27	B26 = (C19/ABS(B17))*SQRT((1/B22) + B23^2/(B17^2*B24))							



The concentration of ammonia nitrogen in the original 100.0 mL of seawater, which had been diluted from 100.0 to 101.0 mL, is  $\frac{101.0 \text{ mL}}{100.0 \text{ mL}} (0.3614 \text{ ppm}) = 0.365 \text{ ppm}$ . The 95% confidence interval is equal to Student's  $t$  times the standard deviation:

$$95\% \text{ confidence interval} = \pm t \cdot s = \pm (3.18)(0.484 \text{ mL}) = \pm 1.54 \text{ mL}$$

where  $t$  is for 95% confidence and  $5 - 2 = 3$  degrees of freedom because there are 5 data points on the standard addition curve. You can find  $t$  in the table of Student's  $t$  or you can compute it with the statement “=TINV(0.05,3)” in cell G24 in the spreadsheet. The confidence interval of  $\pm 1.54 \text{ mL}$  corresponds to a relative uncertainty of  $100 \times \frac{1.54 \text{ mL}}{3.65 \text{ mL}} = 42\%$ .

The absolute uncertainty is  $(0.042)(0.365 \text{ ppm}) = 0.15 \text{ ppm}$ . The concentration of ammonia nitrogen in the seawater can be expressed as  $0.36 \pm 0.15 \text{ ppm}$ .

- (b) Added standards should increase analytical signal by a factor of 1.5 to 3. In this experiment, analytical signal is  $(V_0 + V_S)10^{E/S} = 3.26 \text{ mL}$  for unknown and  $34.37 \text{ mL}$  for final standard. The final signal is 10 times as great as the initial signal, which is  $\sim 3$  times more than the recommended limit.

- 14-42.** For the first line of data, with  $A = \text{Na}^+$  and  $X = \text{Mg}^{2+}$

$$\begin{aligned}\log K_{A,X}^{\text{Pot}} &= \frac{z_A F(E_X - E_A)}{RT \ln 10} + \log \left( \frac{\mathcal{A}_A}{\mathcal{A}_X^{z_A/z_X}} \right) \\ &= \frac{(+1)(96\,485 \text{ C/mol})(-0.385 \text{ V})}{(8.3145 \text{ V}\cdot\text{C}/[\text{mol}\cdot\text{K}])(294.65 \text{ K}) \ln 10} + \log \left( \frac{10^{-3}}{(10^{-3})^{1/2}} \right) = -8.09.\end{aligned}$$

For the second line of data,  $\log K_{A,X}^{\text{Pot}} = -8.15$ .

The first and second lines should give the same selectivity coefficient. The difference is experimental error.

For the third line of data, with  $A = \text{Na}^+$  and  $X = \text{K}^+$ :

$$\log K_{A,X}^{\text{Pot}} = \frac{(+1)(96\,485 \text{ C/mol})(-0.285 \text{ V})}{(8.3145 \text{ V}\cdot\text{C}/[\text{mol}\cdot\text{K}])(294.65 \text{ K}) \ln 10} + \log \left( \frac{10^{-3}}{(10^{-3})^{1/1}} \right) = -4.87.$$

For the fourth line of data,  $\log K_{A,X}^{\text{Pot}} = -4.87$ .

- 14-43.** For  $\text{Na}^+$ : error in  $\mathcal{A}_{\text{H}^+}(\%) = \frac{(10^{-8.6})^{1/1}(10^{-2.0})}{(10^{-8.0})^{1/1}} \times 100 = 0.25\%$

$$\text{For } \text{Ca}^{2+}: \text{error in } \mathcal{A}_{\text{H}^+}(\%) = \frac{(10^{-7.8})^{2/1}(10^{-2.0})}{(10^{-8.0})^{2/1}} \times 100 = 2.5\%$$

$$14-44. \quad E = \text{constant} + \frac{\beta(0.05916)}{2} \log ([\text{Ca}^{2+}] + K_{\text{Ca}^{2+}, \text{Mg}^{2+}}^{\text{Pot}} [\text{Mg}^{2+}])$$

A                      B

For the first two solutions we can write

$$-52.6 \text{ mV} = A + B \log (1.00 \times 10^{-6}) = A - 6B$$

$$+16.1 \text{ mV} = A + B \log (2.43 \times 10^{-4}) = A - 3.614B.$$

Subtraction gives  $68.7 \text{ mV} = 2.386B \Rightarrow B = 28.80 \text{ mV}$ .

Putting this value of B back into the first equation gives  $A = 120.2 \text{ mV}$ .

The third set of data now gives the selectivity coefficient:

$$-38.0 \text{ mV} = 120.2 + 28.80 \log [10^{-6} + K_{\text{Ca}^{2+}, \text{Mg}^{2+}}^{\text{Pot}} (3.68 \times 10^{-3})]$$

$$\Rightarrow K_{\text{Ca}^{2+}, \text{Mg}^{2+}}^{\text{Pot}} = 6.0 \times 10^{-4}$$

$$E = 120.2 + 28.80 \log ([\text{Ca}^{2+}] + 6.0 \times 10^{-4} [\text{Mg}^{2+}]).$$

- 14-45. There is a large excess of EDTA in the buffer. We expect essentially all lead to be in the form  $\text{PbY}^{2-}$  (where Y = EDTA).

$$[\text{PbY}^{2-}] = \frac{1.0}{101.0} (0.10 \text{ M}) = 9.9 \times 10^{-4} \text{ M}$$

$$\text{Total EDTA} = \frac{100.0}{101.0} (0.050 \text{ M}) = 0.0495 \text{ M}$$

$$\text{Free EDTA} = 0.0495 \text{ M} - 9.9 \times 10^{-4} \text{ M} = 0.0485 \text{ M}$$

EDTA bound  
to  $\text{Pb}^{2+}$



$$K_f' = \frac{[\text{PbY}^{2-}]}{[\text{Pb}^{2+}][\text{EDTA}]}$$

$$\Rightarrow [\text{Pb}^{2+}] = \frac{[\text{PbY}^{2-}]}{K_f'[\text{EDTA}]} = \frac{9.9 \times 10^{-4}}{(1.46 \times 10^{10})(0.0485)} = 1.4 \times 10^{-12} \text{ M}$$

- 14-46.  $[\text{Hg}^{2+}]$  in the buffers is computed from equilibrium constants for the solubility of  $\text{HgX}_2$  and formation of complex ions such as  $\text{HgX}_3^-$ . Since the data for  $\text{HgCl}_2$  are not in line with the data for  $\text{Hg}(\text{NO}_3)_2$  and  $\text{HgBr}_2$ , equilibrium constants used for the  $\text{HgCl}_2$  system could be in error. Whenever we make a buffer by mixing *calculated* quantities of reagents, we are at the mercy of the quality of tabulated equilibrium constants.

14-47. (a) slope = 29.58 mV =  $\frac{E_2 - E_1}{\log \mathcal{A}_2 - \log \mathcal{A}_1} = \frac{(-25.90) - 2.06}{\log \mathcal{A}_2 - (-3.000)}$

$$\Rightarrow \mathcal{A}_2 = 1.13 \times 10^{-4}$$



$$\text{But } \mathcal{A}_{\text{Ca}^{2+}} = 1.13 \times 10^{-4} = (5.00 \times 10^{-4} - x)(0.405)$$

$\gamma$  from Table 7-1

$$\Rightarrow x = 2.2 \times 10^{-4} \text{ M}$$

$$K_f = \frac{[\text{CaA}^-]\gamma_{\text{CaA}^-}}{[\text{Ca}^{2+}]\gamma_{\text{Ca}^{2+}}[\text{A}^{3-}]\gamma_{\text{A}^{3-}}}$$

$$K_f = \frac{(2.20 \times 10^{-4})(0.79)}{(1.13 \times 10^{-4})[(0.998)(5 \times 10^{-4} - 2.20 \times 10^{-4})](0.115)}$$

$$K_f = 4.8 \times 10^4$$

- 14-48. Analyte adsorbed on the surface of the gate changes the electric potential of the gate. This, in turn, changes the current between the source and drain. The potential that must be applied by the external circuit to restore the current to its initial value is a measure of the change in gate potential. Following the Nernst equation, there is close to a 59 mV change in gate potential for each factor-of-10 change in activity of univalent analyte at 25°C. The key to ion-specific response is to have a chemical on the gate that selectively binds one analyte.

## CHAPTER 15

### REDOX TITRATIONS

- 15-1.**
- (a)  $\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}$
  - (b)  $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} E^\circ = 0.767 \text{ V}$   
 $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+} E^\circ = 1.70 \text{ V}$
  - (c)  $E = \left\{ 0.767 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - \left\{ 0.241 \right\} \quad (\text{A})$   
 $E = \left\{ 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - \left\{ 0.241 \right\} \quad (\text{B})$
  - (d) 10.0 mL: Use Eq. (A) with  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 40.0/10.0$ , since  $V_e = 50.0 \text{ mL} \Rightarrow E = 0.490 \text{ V}$ .  
25.0 mL:  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 25.0/25.0 \Rightarrow E = 0.526 \text{ V}$   
49.0 mL:  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 1.0/49.0 \Rightarrow E = 0.626 \text{ V}$   
50.0 mL: This is  $V_e$ , where  $[\text{Ce}^{3+}] = [\text{Fe}^{3+}]$  and  $[\text{Ce}^{4+}] = [\text{Fe}^{2+}]$ . Eq. 15-11 gives  $E_+ = 1.23 \text{ V}$  and  $E = 0.99 \text{ V}$ .  
51.0 mL: Use Eq. (B) with  $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 50.0/1.0 \Rightarrow E = 1.36 \text{ V}$ .  
60.0 mL:  $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 50.0/10.0 \Rightarrow E = 1.42 \text{ V}$   
100.0 mL:  $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 50.0/50.0 \Rightarrow E = 1.46 \text{ V}$
- 15-2.**
- (a)  $\text{Ce}^{4+} + \text{Cu}^+ \rightarrow \text{Ce}^{3+} + \text{Cu}^{2+}$
  - (b)  $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+} \quad E^\circ = 1.70 \text{ V}$   
 $\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+ \quad E^\circ = 0.161 \text{ V}$
  - (c)  $E = \left\{ 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - \left\{ 0.197 \right\} \quad (\text{A})$   
 $E = \left\{ 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \right\} - \left\{ (0.197) \right\} \quad (\text{B})$
  - (d) 1.00 mL: Use Eq. (A) with  $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 1.00/24.0$ , since  $V_e = 25.0 \text{ mL} \Rightarrow E = 1.58 \text{ V}$ .  
12.5 mL:  $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 12.5/12.5 \Rightarrow E = 1.50 \text{ V}$   
24.5 mL:  $[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 24.5/0.5 \Rightarrow E = 1.40 \text{ V}$   
25.0 mL:  $E_+ = 1.70 - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$   
 $E_+ = 0.161 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]}$   


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$$2E_+ = 1.861 - 0.05916 \log \frac{[\text{Ce}^{3+}][\text{Cu}^+]}{[\text{Ce}^{4+}][\text{Cu}^{2+}]}$$

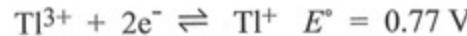
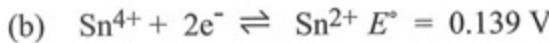
At the equivalence point,  $[Ce^{3+}] = [Cu^{2+}]$  and  $[Ce^{4+}] = [Cu^+]$ .  
Therefore, the log term above is zero and  $E_+ = 1.86_1/2 = 0.930$  V.

$$E = 0.930 - 0.197 = 0.733 \text{ V}$$

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

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

50.0 mL:  $[Cu^+]/[Cu^{2+}] = 25.0/25.0 \Rightarrow E = -0.036$  V



$$(c) E = \left\{ 0.139 - \frac{0.05916}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]} \right\} - \{0.241\} \quad (\text{A})$$

$$E = \left\{ 0.77 - \frac{0.05916}{2} \log \frac{[Tl^+]}{[Tl^{3+}]} \right\} - \{0.241\} \quad (\text{B})$$

(d) 1.00 mL: Use Eq. (A) with  $[Sn^{2+}]/[Sn^{4+}] = 4.00/1.00$ , since  $V_e = 5.00$  mL  $\Rightarrow E = -0.120$  V.

2.50 mL:  $[Sn^{2+}]/[Sn^{4+}] = 2.50/2.50 \Rightarrow E = -0.102$  V

4.90 mL:  $[Sn^{2+}]/[Sn^{4+}] = 0.10/4.90 \Rightarrow E = -0.052$  V

$$\underline{5.00 \text{ mL}: E_+ = 0.139 - \frac{0.05916}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}}$$

$$\underline{E_+ = 0.77 - \frac{0.05916}{2} \log \frac{[Tl^+]}{[Tl^{3+}]}}$$

$$\underline{2E_+ = 0.909 - \frac{0.05916}{2} \log \frac{[Sn^{2+}][Tl^+]}{[Sn^{4+}][Tl^{3+}]}}$$

At the equivalence point,  $[Sn^{4+}] = [Tl^+]$  and  $[Sn^{2+}] = [Tl^{3+}]$ .

Therefore, the log term above is zero and  $E_+ = 0.909/2 = 0.454$  V.

$$E = 0.454 - 0.241 = 0.21 \text{ V}$$

5.10 mL: Use Eq. (B) with  $[Tl^+]/[Tl^{3+}] = 5.00/0.10 \Rightarrow E = 0.48$  V

10.0 mL: Use Eq. (B) with  $[Tl^+]/[Tl^{3+}] = 5.00/5.00 \Rightarrow E = 0.53$  V



(b) The equivalence volume is 10.0 mL.

At 5.0 mL, half of the  $Fe^{3+}$  is titrated and the ratio  $[Fe^{2+}]/[Fe^{3+}]$  is 5.0/5.0:



$$E = E_+ - E_- = \left\{ 0.767 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \right\} - \{0.197\}$$

$$= \left\{ 0.767 - 0.05916 \log \frac{5.0}{5.0} \right\} - \{ 0.197 \} = 0.570$$

10.0 mL is the equivalence point. We multiply the ascorbic acid Nernst equation by 2 and add it to the iron Nernst equation:

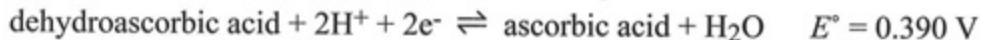
$$\begin{aligned} E_+ &= 0.767 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \\ 2E_+ &= 2 \left( 0.390 - \frac{0.05916}{2} \log \frac{\text{ascorbic acid}}{\text{dehydro}[\text{H}^+]^2} \right) \\ 3E_+ &= 1.547 - 0.05916 \log \frac{[\text{Fe}^{2+}][\text{ascorbic acid}]}{[\text{Fe}^{3+}][\text{dehydro}][\text{H}^+]^2} \end{aligned}$$

At the equivalence point, the stoichiometry of the titration reaction tells us that  $[\text{Fe}^{2+}] = 2[\text{dehydroascorbic acid}]$  and  $[\text{Fe}^{3+}] = 2[\text{ascorbic acid}]$ . Inserting these equalities into the log term just shown gives

$$\begin{aligned} 3E_+ &= 1.547 - 0.05916 \log \frac{2[\text{dehydro}][\text{ascorbic acid}]}{2[\text{ascorbic acid}][\text{dehydro}][\text{H}^+]^2} \\ 3E_+ &= 1.547 - 0.05916 \log \frac{1}{[\text{H}^+]^2} \end{aligned}$$

Using  $[\text{H}^+] = 10^{-0.30}$  gives  $E_+ = 0.504 \text{ V}$  and  $E = 0.504 - 0.197 = 0.307 \text{ V}$ .

At 15.0 mL, the ratio  $[\text{dehydro}]/[\text{ascorbic acid}]$  is 10.0/5.0:



$$\begin{aligned} E &= E_+ - E_- = \left\{ 0.390 - \frac{0.05916}{2} \log \frac{\text{ascorbic acid}}{\text{dehydro}[\text{H}^+]^2} \right\} - \{ 0.197 \} \\ &= \left\{ 0.390 - \frac{0.05916}{2} \log \frac{[5.0]}{[10.0][10^{-0.30}]^2} \right\} - \{ 0.197 \} = 0.184 \text{ V} \end{aligned}$$

- 15-5. (a) Titration reaction:  $\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightarrow \text{Sn}^{4+} + 2\text{Fe}^{2+} \quad V_e = 25.0 \text{ mL}$



$$(c) E = \left\{ 0.732 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - \{ 0.241 \} \quad (\text{A})$$

$$E = \left\{ 0.139 - \frac{0.05916}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} \right\} - \{ 0.241 \} \quad (\text{B})$$

- (d) Representative calculations:

$$\underline{1.0 \text{ mL}}: E_+ = 0.139 - \frac{0.05916}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$\text{initial mol Sn}^{2+} = (25.0 \text{ mL})(0.0500 \frac{\text{mmol}}{\text{mL}}) = 1.25 \text{ mmol}$$

$$\text{mol Fe}^{3+} \text{ added} = (1.0 \text{ mL})(0.100 \frac{\text{mmol}}{\text{mL}}) = 0.10 \text{ mmol}$$

$$[\text{Sn}^{4+}] = \frac{\frac{1}{2}(0.10 \text{ mmol})}{26.0 \text{ mL}} = 1.92 \times 10^{-3} \text{ M}$$

$$[\text{Sn}^{2+}] = \frac{1.25 - \frac{1}{2}(0.10) \text{ mmol}}{26.0 \text{ mL}} = 4.62 \times 10^{-2} \text{ M}$$

$$E_+ = 0.139 - \frac{0.05916}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$E_+ = 0.139 - \frac{0.05916}{2} \log \frac{4.62 \times 10^{-2}}{1.92 \times 10^{-3}} = 0.098 \text{ V}$$

$$E = E_+ - E_- = 0.098 - 0.241 = -0.143 \text{ V}$$

25.0 mL: At the equivalence point, we add the two indicator electrode Nernst equations. To make the factor in front of the log term the same in both equations, we can multiply the  $\text{Sn}^{4+} | \text{Sn}^{2+}$  equation by 2:

$$E_+ = 0.139 - \frac{0.05916}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$2E_+ = 0.278 - 0.05916 \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$E_+ = 0.732 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

Now add the last two equations to get

$$3E_+ = 1.010 - 0.05916 \log \left( \frac{[\text{Sn}^{2+}][\text{Fe}^{2+}]}{[\text{Sn}^{4+}][\text{Fe}^{3+}]} \right)$$

But at the equivalence point,  $2[\text{Sn}^{4+}] = [\text{Fe}^{2+}]$  and  $2[\text{Sn}^{2+}] = [\text{Fe}^{3+}]$ .

Substituting these identities into the log term gives

$$3E_+ = 1.010 - 0.05916 \log \left( \frac{[\text{Sn}^{2+}]2[\text{Sn}^{4+}]}{[\text{Sn}^{4+}]2[\text{Sn}^{2+}]} \right)$$

So the log quotient in the log term is 1 and the logarithm is 0. Therefore,  $E_+ = 1.010/3 = 0.337 \text{ V}$  and  $E = E_+ - E_- = 0.337 - 0.241 = 0.096 \text{ V}$ .

26.0 mL:  $E_+ = 0.732 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$

There is 1.0 mL of  $\text{Fe}^{3+}$  beyond the equivalence point.

$$[\text{Fe}^{3+}] = \frac{(1.0 \text{ mL})(0.100 \text{ M})}{51.0 \text{ mL}} = 1.96 \times 10^{-3} \text{ M}$$

The first 25.0 mL of  $\text{Fe}^{3+}$  were converted to  $\text{Fe}^{2+}$ , so

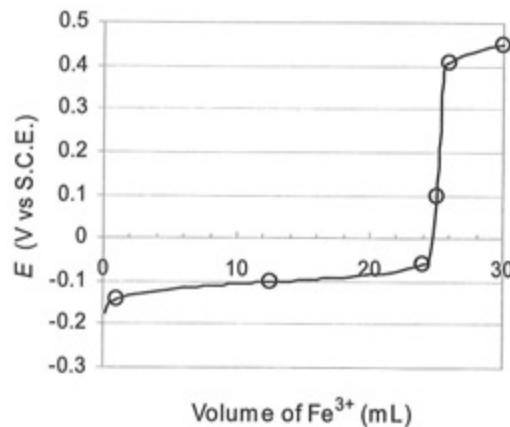
$$[\text{Fe}^{2+}] = \frac{(25.0 \text{ mL})(0.100 \text{ M})}{51.0 \text{ mL}} = 4.90 \times 10^{-2} \text{ M}$$

$$E_+ = 0.732 - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E_+ = 0.732 - 0.05916 \log \frac{4.90 \times 10^{-2}}{1.96 \times 10^{-3}} = 0.649 \text{ V}$$

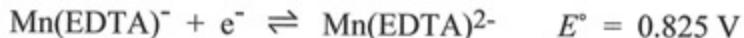
$$E = E_+ - E_- = 0.649 - 0.241 = 0.408 \text{ V}$$

mL	$E$ (V)	mL	$E$ (V)	mL	$E$ (V)
1.0	-0.143	24.0	-0.061	26.0	0.408
12.5	-0.102	25.0	0.096	30.0	0.450



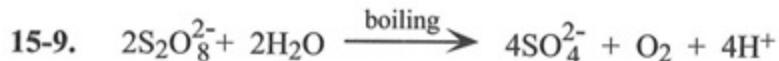
- 15-6.** Diphenylamine sulfonic acid: colorless  $\rightarrow$  red-violet  
 Diphenylbenzidine sulfonic acid: colorless  $\rightarrow$  violet  
*tris* (2,2'-bipyridine) iron: red  $\rightarrow$  pale blue  
 Ferroin: red  $\rightarrow$  pale blue

- 15-7.** The reduction potentials are



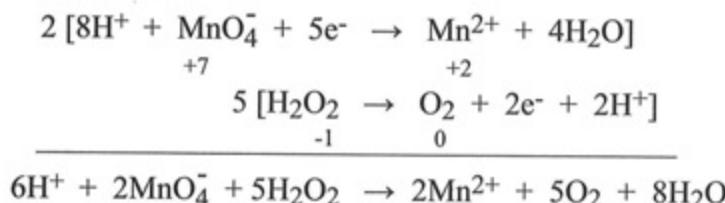
The end point will be between 0.139 and 0.825 V. Tris(2,2'-bipyridine) iron has too high a reduction potential (1.120 V) to be useful for this titration.

- 15-8.** Preoxidation and prerduction refer to adjusting the oxidation state of analyte to a suitable value for a titration. The preoxidation or prerduction agent must be destroyed so it does not interfere with the titration by reacting with titrant.

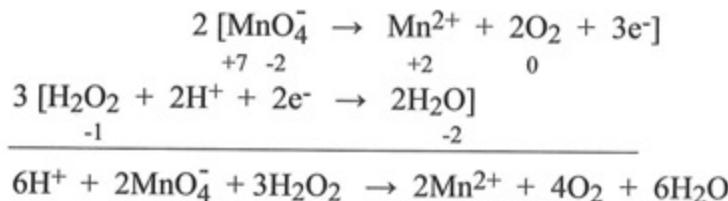


- 15-10.** A Jones reductor is a column packed with zinc granules coated with zinc amalgam. Prereduction is accomplished by passing analyte solution through the column.
- 15-11.** Cr<sup>3+</sup> and TiO<sup>2+</sup> would interfere if they were reduced to Cr<sup>2+</sup> and Ti<sup>3+</sup>. In the Jones reductor, Zn is a strong enough reductant to react with Cr<sup>3+</sup> and TiO<sup>2+</sup>.
- $$E^\circ = -0.764 \text{ for the } \text{Zn}^{2+}|\text{Zn} \text{ couple}$$
- $$E^\circ = -0.42 \text{ for the } \text{Cr}^{3+}|\text{Cr}^{2+} \text{ couple}$$
- $$E^\circ = 0.1 \text{ for the } \text{TiO}^{2+}|\text{Ti}^{3+} \text{ couple}$$
- In the Walden reductor, Ag is not strong enough to reduce Cr<sup>3+</sup> and TiO<sup>2+</sup>:
- $$E^\circ = 0.222 \text{ for the } \text{AgCl}|\text{Ag couple}$$
- 15-12.** A weighed amount of the solid mixture is added to a solution containing excess standard Fe<sup>2+</sup> plus phosphoric acid. Each mol of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidizes 2 mol of Fe<sup>2+</sup> to Fe<sup>3+</sup>. Excess Fe<sup>2+</sup> is then titrated with standard KMnO<sub>4</sub> to find out how much Fe<sup>2+</sup> was consumed by the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The phosphoric acid masks the yellow color of Fe<sup>3+</sup>, making the end point easier to see.
- 15-13.** (a)  $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- (b)  $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2(s) + 2\text{H}_2\text{O}$
- (c)  $\text{MnO}_4^- + \text{e}^- \rightleftharpoons \text{MnO}_4^{2-}$
- 15-14.**  $3\text{MnO}_4^- + 5\text{Mo}^{3+} + 4\text{H}^+ \rightarrow 3\text{Mn}^{2+} + 5\text{MoO}_2^{2+} + 2\text{H}_2\text{O}$   
 $(16.43 - 0.04) = 16.39 \text{ mL of } 0.010\ 33 \text{ M KMnO}_4 = 0.169\ 3 \text{ mmol of MnO}_4^-$ ,  
which will react with  $(5/3)(0.169\ 3) = 0.282\ 2 \text{ mmol of Mo}^{3+}$ .  
 $[\text{Mo}^{3+}] = 0.282\ 2 \text{ mmol}/25.00 \text{ mL} = 0.011\ 29 \text{ M} (= \text{original } [\text{MoO}_4^{2-}])$ .
- 15-15.**  $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$   
 $(27.66 - 0.04) = 27.62 \text{ mL of } 0.021\ 23 \text{ M KMnO}_4 = 0.586\ 37 \text{ mmol of MnO}_4^-$ ,  
which reacts with  $(5/2)(0.586\ 37) = 1.465\ 9 \text{ mmol of H}_2\text{O}_2$ , which came from  
25.00 mL of diluted solution  $\Rightarrow [\text{H}_2\text{O}_2] = 1.465\ 9 \text{ mmol}/25.00 \text{ mL} =$   
0.058 64 M in the dilute solution. The original solution was ten times more  
concentrated = 0.586 4 M.

**15-16.** (a) Scheme 1:



Scheme 2:



(b)  $\frac{1.023 \text{ g NaBO}_3 \cdot 4\text{H}_2\text{O}}{153.86 \text{ g/mol}} = 6.649 \text{ mmol NaBO}_3$

One tenth of this quantity was titrated = 0.6649 mmol NaBO<sub>3</sub>, producing 0.6649 mmol H<sub>2</sub>O<sub>2</sub> by the reaction BO<sub>3</sub><sup>-</sup> + 2H<sub>2</sub>O → H<sub>2</sub>O<sub>2</sub> + H<sub>2</sub>BO<sub>3</sub><sup>-</sup>.

In Scheme 1, 2MnO<sub>4</sub><sup>-</sup> react with 5H<sub>2</sub>O<sub>2</sub>

$$\Rightarrow 0.6649 \text{ mmol H}_2\text{O}_2 \text{ requires } \frac{2}{5}(0.6649) = 0.2660 \text{ mmol MnO}_4^-$$

$$\frac{0.2660 \text{ mmol MnO}_4^-}{0.01046 \text{ mmol KMnO}_4/\text{ml}} = 25.43 \text{ mL KMnO}_4 \text{ required}$$

In Scheme 2, 2MnO<sub>4</sub><sup>-</sup> react with 3H<sub>2</sub>O<sub>2</sub>

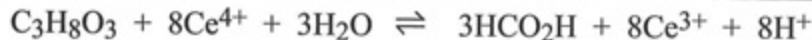
$$\Rightarrow 0.6649 \text{ mmol H}_2\text{O}_2 \text{ requires } \frac{2}{3}(0.6649) = 0.4433 \text{ mmol MnO}_4^-$$

$$\frac{0.4433 \text{ mmol MnO}_4^-}{0.01046 \text{ mmol KMnO}_4/\text{ml}} = 42.38 \text{ mL KMnO}_4 \text{ required}$$

**15-17.** 2MnO<sub>4</sub><sup>-</sup> + 5H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 6H<sup>+</sup> → 2Mn<sup>2+</sup> + 10CO<sub>2</sub> + 8H<sub>2</sub>O

18.04 mL of 0.006363 M KMnO<sub>4</sub> = 0.1148 mmol of MnO<sub>4</sub><sup>-</sup>, which reacts with (5/2)(0.1148) = 0.2870 mmol of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, which came from (2/3)(0.2870) = 0.1913 mmol of La<sup>3+</sup>. [La<sup>3+</sup>] = 0.1913 mmol/50.00 mL = 3.826 mM.

**15-18.** C<sub>3</sub>H<sub>8</sub>O<sub>3</sub> + 3H<sub>2</sub>O ⇌ 3HCO<sub>2</sub>H + 8e<sup>-</sup> + 8H<sup>+</sup>  
 glycerol formic acid  
 (average oxidation (oxidation  
 number of C = -2/3) number of C = +2)



One mole of glycerol requires eight moles of Ce<sup>4+</sup>.

$$50.0 \text{ mL of } 0.0837 \text{ M Ce}^{4+} = 4.185 \text{ mmol}$$

$$12.11 \text{ mL of } 0.0448 \text{ M Fe}^{2+} = 0.543 \text{ mmol}$$

$$\text{Ce}^{4+} \text{ reacting with glycerol} = 3.642 \text{ mmol}$$

$$\text{glycerol} = (1/8)(3.642) = 0.4552 \text{ mmol} = 41.9 \text{ mg} \Rightarrow \text{original solution} =$$

$$41.9 \text{ wt\% glycerol}$$

**15-19.** 50.00 mL of 0.1186 M Ce<sup>4+</sup> = 5.930 mmol Ce<sup>4+</sup>

$$31.13 \text{ mL of } 0.04289 \text{ M Fe}^{2+} = \underline{1.335 \text{ mmol Fe}^{2+}}$$

$$4.595 \text{ mmol Ce}^{4+} \text{ consumed by NO}_2^-$$

Since two moles of Ce<sup>4+</sup> react with one mole of NO<sub>2</sub><sup>-</sup>, there must have been

$$1/2(4.595) = 2.298 \text{ mmol of NaNO}_2 = 0.1585 \text{ g in 25.0 mL. In 500.0 mL,}$$

$$\text{there would be } \left(\frac{500.0}{25.0}\right)(0.1585) = 3.170 \text{ g} = 78.67\% \text{ of the 4.030 g sample.}$$

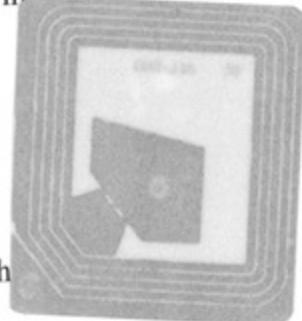
- 15-20.** Step 2 gives the total Cr content of the crystal, since each Cr<sup>x+</sup> ion in any oxidation state is oxidized and reacts with 3Fe<sup>2+</sup>.

$$\text{Step 2: } \frac{(0.703 \text{ mL})(2.786 \text{ mM})}{0.1566 \text{ g of crystal}} = \frac{12.51 \mu\text{mol Fe}^{2+}}{\text{g of crystal}}$$

$$\frac{\frac{1}{3}(12.51) \mu\text{mol Cr}}{\text{g of crystal}} = \frac{4.169 \mu\text{mol Cr}}{\text{g of crystal}}$$

Step 1 tells us how much Cr<sup>x+</sup> is oxidized above the +3 state. Each with  $(x - 3)$  Fe<sup>2+</sup>.

$$\text{Step 1: } \frac{(0.498 \text{ mL})(2.786 \text{ mM})}{0.4375 \text{ g of crystal}} = \frac{3.171 \mu\text{mol Fe}^{2+}}{\text{g of crystal}}$$



Since one gram of crystal contains 4.169 μmol of Cr that reacts with 3.171 μmol of Fe<sup>2+</sup>, the average oxidation state of Cr is  $3 + \frac{3.171}{4.169} = +3.761$ .

Total Cr (from Step 2) = 4.169 μmol Cr per gram = 217 μg per gram of crystal.

- 15-21.** (a) Theoretical molarity =  $(3.214 \text{ g/L})/(158.034 \text{ g/mol}) = 0.020337 \text{ M}$ .

(b) 25.00 mL of 0.020337 M KMnO<sub>4</sub> = 0.50843 mmol. But two moles of MnO<sub>4</sub><sup>-</sup>

react with five moles of H<sub>3</sub>AsO<sub>3</sub>, which comes from  $\frac{5}{4}$  moles of As<sub>4</sub>O<sub>6</sub>.

The moles of As<sub>4</sub>O<sub>6</sub> needed to react with 0.50843 mmol of MnO<sub>4</sub><sup>-</sup> =

$$(1/2)(5/4)(0.50843) = 0.31777 \text{ mmol} = 0.12574 \text{ g of As}_4\text{O}_6.$$

$$(c) \frac{0.5084_3 \text{ mmol KMnO}_4}{0.1257_4 \text{ g As}_2\text{O}_3} = \frac{x \text{ mmol KMnO}_4}{0.1468 \text{ g As}_4\text{O}_6} \Rightarrow x = 0.5936_1 \text{ mmol}$$

$$\text{KMnO}_4 \text{ in } (29.98 - 0.03) = 29.95 \text{ mL} \Rightarrow [\text{KMnO}_4] = 0.01982 \text{ M.}$$

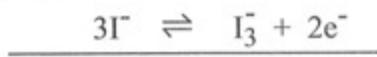
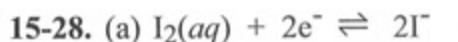
- 15-22.**  $\text{I}^-$  reacts with  $\text{I}_2$  to give  $\text{I}_3^-$ . This reaction increases the solubility of  $\text{I}_2$  and decreases its volatility.
- 15-23.** Standard triiodide can be prepared from a weighed amount of  $\text{KIO}_3$  with acid plus excess iodide. Alternatively, triiodide solution can be standardized by reaction with standard  $\text{S}_2\text{O}_3^{2-}$  prepared from anhydrous  $\text{Na}_2\text{S}_2\text{O}_3$ .
- 15-24.** Starch is not added until just before the end point in iodometry, so it does not irreversibly bind to  $\text{I}_2$  which is present during the whole titration.
- 15-25.** (a) 50.00 mL contains exactly 1/10 of the  $\text{KIO}_3 = 0.1022 \text{ g} = 0.4775_7 \text{ mmol KIO}_3$ . Each mol of iodate makes 3 mol of triiodide, so  $\text{I}_3^- = 3(0.4775_7) = 1.432_7 \text{ mmol}$ .
- (b) Two moles of thiosulfate react with one mole of  $\text{I}_3^-$ . Therefore, there must have been  $2(1.432_7) = 2.865_4 \text{ mmol}$  of thiosulfate in 37.66 mL, so the concentration is  $(2.865_4 \text{ mmol})/(37.66 \text{ mL}) = 0.07608_7 \text{ M}$ .
- (c) 50.00 mL of  $\text{KIO}_3$  make  $1.432_7 \text{ mmol I}_3^-$ . The unreacted  $\text{I}_3^-$  requires 14.22 mL of sodium thiosulfate =  $(14.22 \text{ mL})(0.07608_7 \text{ M}) = 1.082_0 \text{ mmol}$ , which reacts with  $\frac{1}{2}(1.082_0 \text{ mmol}) = 0.541_0 \text{ mmol I}_3^-$ . The ascorbic acid must have consumed the difference =  $1.432_7 - 0.541_0 = 0.891_7 \text{ mmol I}_3^-$ . Each mole of ascorbic acid consumes one mole of  $\text{I}_3^-$ , so mol ascorbic acid =  $0.891_7 \text{ mmol}$ , which has a mass of  $(0.891_7 \times 10^{-3} \text{ mol})(176.13 \text{ g/mol}) = 0.157_1 \text{ g}$ . Ascorbic acid in the unknown =  $100 \times (0.157_1 \text{ g})/(1.223 \text{ g}) = 12.8 \text{ wt\%}$ .
- (d) Starch should not be added until just before the end point because  $\text{I}_3^-$  is present throughout the titration and will irreversibly bind to starch if the starch is added too early.
- 15-26.**  $2\text{Cu}^{2+} + 5\text{I}^- \rightarrow 2\text{CuI}(s) + \text{I}_3^-$        $\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$   
 23.33 mL of 0.04668 M  $\text{Na}_2\text{S}_2\text{O}_3 = 1.089_0 \text{ mmol S}_2\text{O}_3^{2-} = 0.5445 \text{ mmol I}_3^-$ , which came from  $1.089_0 \text{ mmol Cu}^{2+} = 69.20 \text{ mg Cu}$ . This much Cu comes from

1/5 of the original solid, which therefore contained  $346.0 \text{ mg Cu} = 11.43 \text{ wt\%}$ . There is a great deal of  $\text{I}_3^-$  present at the start of the titration, so starch should not be added until just before the end point.



$$25.00 \text{ mL of } 0.01044 \text{ M } \text{I}_3^- = 0.2610_0 \text{ mmol } \text{I}_3^-$$

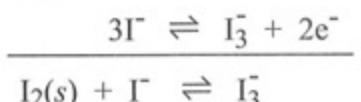
14.44 mL of 0.009336 M  $\text{Na}_2\text{S}_2\text{O}_3 = 0.1348_1 \text{ mmol Na}_2\text{S}_2\text{O}_3$ , which would have reacted with 0.067406 mmol  $\text{I}_3^-$ . Therefore, the quantity of  $\text{I}_3^-$  that reacted with  $\text{H}_2\text{S}$  was  $0.2610_0 - 0.067406 = 0.19359 \text{ mmol}$ . Since 1 mol of  $\text{I}_3^-$  reacts with 1 mol of  $\text{H}_2\text{S}$ , the  $\text{H}_2\text{S}$  concentration was  $0.19359 \text{ mmol}/25.00 \text{ mL} = 0.007744 \text{ M}$ .  $\text{I}_3^-$  is present at the start of the titration, so starch should not be added until just before the end point.



$$K = 10^{2(0.085)/0.05916} = 7 \times 10^2$$

$$E^\circ = 0.620 \text{ V}$$

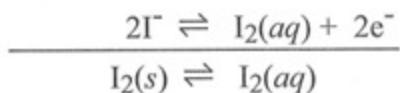
$$\frac{E^\circ = -0.535 \text{ V}}{E^\circ = 0.085 \text{ V}}$$



$$K = 10^{2(-0.000)/0.05916} = 1.0$$

$$E^\circ = 0.535 \text{ V}$$

$$\frac{E^\circ = -0.535 \text{ V}}{E^\circ = 0.000 \text{ V}}$$



$$K = [\text{I}_2(aq)] = 10^{2(-0.085)/0.05916} = 1.3 \times 10^{-3} \text{ M} = 0.34 \text{ g of I}_2/\text{L}$$

$$E^\circ = 0.535 \text{ V}$$

$$\frac{E^\circ = -0.620 \text{ V}}{E^\circ = -0.085 \text{ V}}$$

- 15-29.** Each mole of  $\text{NH}_3$  liberated in the Kjeldahl digestion reacts with 1 mole of  $\text{H}^+$  in the standard  $\text{H}_2\text{SO}_4$  solution. Six moles of  $\text{H}^+$  left (3 moles of  $\text{H}_2\text{SO}_4$ ) after reaction with  $\text{NH}_3$  will react with 1 mole of iodate by Reaction 15-18 to release 3 moles of  $\text{I}_3^-$ . Two moles of thiosulfate react with 1 mole of  $\text{I}_3^-$  in Reaction 15-19. Therefore each mole of thiosulfate corresponds to  $\frac{1}{2}$  mol of residual  $\text{H}_2\text{SO}_4$ .

$$\text{mol NH}_3 = 2(\text{initial mol H}_2\text{SO}_4 - \text{final mol H}_2\text{SO}_4)$$

$$\text{mol NH}_3 = 2 \left( \text{initial mol H}_2\text{SO}_4 - \frac{1}{2} \times \text{mol thiosulfate} \right)$$

- 15-30.** (a)  $\text{IO}_3^- + 8\text{I}^- + 6\text{H}^+ \rightleftharpoons 3\text{I}_3^- + 3\text{H}_2\text{O}$ . The stock solution contained  $\{0.804 \text{ g KIO}_3 (\text{FM } 214.00) + 5 \text{ g KI (\text{FM } 166.00)}\} / 100 \text{ mL}$ , which translates into  $0.03758 \text{ M KIO}_3$  plus  $0.30 \text{ M KI}$ , giving a mole ratio  $\text{KI/KIO}_3 = 18$ , which is a good excess of the 8:1 ratio required in the reaction.  $5.00 \text{ mL}$  of the stock solution contain  $0.1879_2 \text{ mmol KIO}_3$  plus  $1.5 \text{ mmol KI}$ .  $1.0 \text{ mL}$  of  $6.0 \text{ M H}_2\text{SO}_4$  contains  $6 \text{ mmol H}_2\text{SO}_4$ , which is a large excess for the reaction. Neither KI nor  $\text{H}_2\text{SO}_4$  needs to be measured accurately.



- (c)  $0.1879_2 \text{ mmol KIO}_3$  delivered to the wine generates  $3 \times 0.1879_2 = 0.5637_6 \text{ mmol I}_3^-$ . The excess, unreacted  $\text{I}_3^-$  required  $12.86 \text{ mL}$  of  $0.04818 \text{ M Na}_2\text{S}_2\text{O}_3 = 0.61959 \text{ mmol Na}_2\text{S}_2\text{O}_3$ . Each mole of unreacted  $\text{I}_3^-$  requires 2 moles of  $\text{Na}_2\text{S}_2\text{O}_3$ , so there must have been  $(0.61959)/2 = 0.3098 \text{ mmol I}_3^-$  left over from the reaction with sulfite. Therefore, the  $\text{I}_3^-$  that reacted with sulfite was  $(0.5637_6 - 0.3098) = 0.2540 \text{ mmol I}_3^-$ . One mole of  $\text{I}_3^-$  reacts with 1 mole of sulfite, so there must have been  $0.2540 \text{ mmol SO}_3^{2-}$  in  $50.0 \text{ mL}$  of wine.  $[\text{SO}_3^{2-}] = 0.2540 \text{ mmol}/50.0 \text{ mL} = 5.079 \times 10^{-3} \text{ M}$ . With a formula mass of 80.06 for sulfite, the sulfite content is  $406.6 \text{ mg/L}$ .

$$(d) s_{\text{spooled}} = \sqrt{\frac{2.2^2(3-1) + 2.1^2(3-1)}{3+3-2}} = 2.15$$

$$t_{\text{calculated}} = \frac{|277.7 - 273.2|}{2.15} \sqrt{\frac{3 \cdot 3}{3+3}} = 2.56$$

$t_{\text{table}} = 2.776$  for 95% confidence and  $3+3-2 = 4$  degrees of freedom

$t_{\text{calculated}} < t_{\text{table}}$ , so the difference is not significant at 95% confidence level.

- 15-31.**  $25.00 \text{ mL}$  of  $0.02000 \text{ M KBrO}_3 = 0.5000 \text{ mmol of BrO}_3^-$ , which generates  $1.500 \text{ mmol of Br}_2$ . One mole of excess  $\text{Br}_2$  generates one mole of  $\text{I}_2$  (from  $\text{I}^-$ ) and one mole of  $\text{I}_2$  consumes 2 moles of  $\text{S}_2\text{O}_3^{2-}$ . Since  $\text{mmol of S}_2\text{O}_3^{2-} = (8.83)(0.05113) = 0.4515 \text{ mmol}$ ,  $\text{I}_2 = 0.2257 \text{ mmol}$  and  $\text{Br}_2$  consumed by reaction with 8-hydroxyquinoline =  $1.500 - 0.2257 = 1.274 \text{ mmol}$ . But one mole of

8-hydroxyquinoline consumes 2 moles of Br<sub>2</sub>, so 8-hydroxyquinoline = 0.6371 mmol and Al<sup>3+</sup> = 0.6371/3 = 0.2124 mmol = 5.730 mg.

- 15-32.** (a) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> contains 1 Cu<sup>3+</sup> and 2 Cu<sup>2+</sup>. YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub> contains no Cu<sup>3+</sup> and 3 Cu<sup>2+</sup>. The moles of Cu<sup>3+</sup> in the formula YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-z</sub> are therefore 1 - 2z. The moles of superconductor in 1 g of superconductor are [1 g]/[(666.246 - 15.9994 z)g/mol]. The difference between experiments B and A is 5.68 - 4.55 = 1.13 mmol S<sub>2</sub>O<sub>3</sub><sup>2-</sup>/g of superconductor. Since 1 mol of thiosulfate is equivalent to 1 mol of Cu<sup>3+</sup>, there are 1.13 mmol Cu<sup>3+</sup>/g of superconductor.

$$\frac{\text{mol Cu}^{3+}}{\text{mol superconductor}} = 1 - 2z = \frac{1.13 \cdot 10^{-3} \text{ mol Cu}^{3+}}{\left( \frac{1 \text{ g superconductor}}{(666.246 - 15.9994 z) \text{ g/mol}} \right)}$$

Solving this equation gives z = 0.125. The formula is YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.875</sub>.

$$(b) 1 - 2z = \frac{[5.68(\pm 0.05) - 4.55(\pm 0.10)] \cdot 10^{-3}}{\left( \frac{1}{666.246 - 15.9994 z} \right)}$$

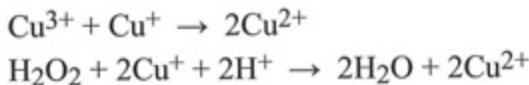
$$1 - 2z = \frac{1.13 (\pm 0.112) \cdot 10^{-3}}{\left( \frac{1}{666.246 - 15.9994 z} \right)}$$

$$1 - 2z = 0.75286 (\pm 0.07449) - 0.018079 (\pm 0.001789) z$$

$$0.247124 (\pm 0.074488) = 1.98192 (\pm 0.00179) z$$

$$z = 0.125 \pm 0.038. \quad \text{The formula is YBa}_2\text{Cu}_3\text{O}_{6.875} \pm 0.038.$$

- 15-33.** A superconductor containing unknown quantities of Cu(I), Cu(II), Cu(III), and peroxide (O<sub>2</sub><sup>2-</sup>) is dissolved in a known excess of Cu(I) in oxygen-free HCl solution. Possible reactions are



Unreacted Cu(I) is then measured by coulometry to find out how much Cu(I) was consumed by the dissolving superconductor. The amount of Cu(I) consumed is equal to the moles of Cu<sup>3+</sup> plus 2 times the moles of O<sub>2</sub><sup>2-</sup> in the superconductor.

The coulometry is done under Ar to prevent oxidation of Cu(I) by O<sub>2</sub> from the air. If the superconductor contained Cu(I) (but no Cu(III) or peroxide), then the amount of Cu(I) found by coulometry would be greater than the known amount used in the original solution.

- 15-34.** (a) Initial  $\text{Fe}^{2+}$  in 5.000 mL =  $(5.000 \text{ mL})(0.100 \text{ M}) = 0.500 \text{ mmol}$ .  
 $\text{K}_2\text{Cr}_2\text{O}_7$  required for titration of unreacted  $\text{Fe}^{2+}$   
 $= (3.228 \text{ mL})(0.01593 \text{ M } \text{K}_2\text{Cr}_2\text{O}_7) = 0.05142 \text{ mmol}$ .  
 But 1 mmol  $\text{K}_2\text{Cr}_2\text{O}_7$  reacts with 6 mmol  $\text{Fe}^{2+}$  by the reaction  
 $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 2\text{K}^+ + 14\text{H}_2\text{O}$ .  
 Therefore,  $\text{Fe}^{2+}$  left after reaction with  $\text{Li}_{1+y}\text{CoO}_2$   
 $= (0.05142 \text{ mmol})(6 \text{ mmol } \text{Fe}^{2+}/\text{mmol } \text{K}_2\text{Cr}_2\text{O}_7) = 0.3085 \text{ mmol}$ .  
 $\text{Fe}^{2+}$  consumed by  $\text{Co}^{3+} = (0.5000 - 0.3085) = 0.1915 \text{ mmol}$ .  
 1 mol  $\text{Fe}^{2+}$  is consumed by 1 mol  $\text{Co}^{3+}$ , so  $\text{Co}^{3+}$  in 25.00 mg solid sample = 0.1915 mmol.
- (b) Co in 25.00 mg solid =  $(0.564 \text{ g Co/g solid})(25.00 \text{ g solid}) = 14.10 \text{ mg}$   
 Co in 25.00 mg solid =  $(14.10 \text{ mg})/(58.933 \text{ g/mol}) = 0.2393 \text{ mmol}$   
 From (a), we know that  $\text{Co}^{3+} = 0.1915 \text{ mmol}$ , so  
 $\text{Co}^{2+} = 0.2393 - 0.1915 = 0.0478 \text{ mmol}$ .  
 $\text{Co oxidation state} = \frac{(0.0478 \text{ mmol})(2+) + (0.1915 \text{ mmol})(3+)}{0.2392 \text{ mmol}} = 2.80$
- (c) If Co has an average oxidation number of +2.80 and O has an oxidation number of -2, Li must contribute a charge of  $4 - 2.80 = 1.20$ . Therefore, the formula is  $\text{Li}_{1.20}\text{CoO}_2$  and  $y = 0.20$ .
- (d) Theoretical weight percent for metals in  $\text{Li}_{1.20}\text{CoO}_2$ :  
 Formula mass =  $1.20(6.941) + 1(58.933) + 2(15.9994) = 99.261$   
 $\text{wt\% Li} = 100 \times 1.20(6.941)/99.261 = 8.39\%$   
 $\text{wt\% Co} = 100 \times 58.933/99.261 = 59.37\%$   
 $\frac{\text{wt\% Li}}{\text{wt\% Co}} = 0.1413$   
 The observed quotient  $\text{wt\% Li}/\text{wt\% Co}$  is  $0.1388 \pm 0.0006$ , which is not exactly equal to the quotient computed from the oxidation number. The difference represents experimental error between the two methods used find the stoichiometry.
- 15-35.** Denote the average oxidation number of Bi as  $3 + b$  and the average oxidation number of Cu as  $2 + c$ .
- $$\text{Bi}_2^{3+b}\text{Sr}_2^{2+}\text{Ca}^{2+}\text{Cu}_2^{2+c}\text{O}_x$$
- Positive charge =  $6 + 2b + 4 + 2 + 4 + 2c = 16 + 2b + 2c$   
 The charge must be balanced by  $\text{O}^{2-} \Rightarrow x = 8 + b + c$ .  
 The formula mass of the superconductor is  $760.37 + 15.9994(8 + b + c)$ .

One gram contains  $1/[760.37 + 15.9994(8 + b + c)]$  moles.

(a) Experiment A: Initial  $\text{Cu}^+ = 0.2000 \text{ mmol}$ ; final  $\text{Cu}^+ = 0.1085 \text{ mmol}$ .

Therefore, 102.3 mg of superconductor consumed 0.0915 mmol  $\text{Cu}^+$ .

$2 \times \text{mmol Bi}^{5+} + \text{mmol Cu}^{3+}$  in 102.3 mg of superconductor = 0.0915.

Experiment B: Initial  $\text{Fe}^{2+} = 0.1000 \text{ mmol}$ ; final  $\text{Fe}^{2+} = 0.0577$

mmol. Therefore, 94.6 mg of superconductor consumed 0.0423 mmol  $\text{Fe}^{2+}$ .

$2 \times \text{mmol Bi}^{5+}$  in 94.6 mg of superconductor = 0.0423.

Normalizing to 1 gram of superconductor gives

Expt A:  $2(\text{mmol Bi}^{5+}) + \text{mmol Cu}^{3+}$  in 1 g of superconductor = 0.89443

Expt B:  $2(\text{mmol Bi}^{5+})$  in 1 g of superconductor = 0.44715

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

Therefore, we can rewrite the two previous equations as

$$\text{mmol Bi}^{4+} + \text{mmol Cu}^{3+} \text{ in 1 g of superconductor} = 0.89443 \quad (1)$$

$$\text{mmol Bi}^{4+} \text{ in 1 g of superconductor} = 0.44715 \quad (2)$$

Subtracting (2) from (1) gives

$$\text{mmol Cu}^{3+} \text{ in 1 g of superconductor} = 0.44728 \quad (3)$$

Equations (2) and (3) tell us that the stoichiometric relationship in the formula of the superconductor is  $b/c = 0.44715/0.44728 = 0.9997$ .

Since 1 g of superconductor contains 0.44728 mmol  $\text{Cu}^{3+}$ , we can say

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

$$\frac{\text{mol Cu}^{3+}/\text{mol solid}}{\text{gram solid}/\text{mol solid}} = \frac{2c}{760.37 + 15.9994(8 + b + c)}$$

$$\frac{\text{mol Cu}^{3+}}{\text{gram solid}} = \frac{2c}{760.37 + 15.9994(8 + b + c)} = 4.4728 \times 10^{-4} \quad (4)$$

Substituting  $b = 0.9997c$  in the denominator of (4) allows us to solve for  $c$ :

$$\frac{2c}{760.37 + 15.9994(8 + 1.9997c)} = 4.4728 \times 10^{-4} \Rightarrow c = 0.2001$$

$$\Rightarrow b = 0.9997c = 0.2000$$

The average oxidation numbers are  $\text{Bi}^{3.2000+}$  and  $\text{Cu}^{2.2001+}$  and the formula of the compound is  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.4001}$ , since the oxygen stoichiometry derived at the beginning of the solution is  $x = 8 + b + c$ .

(b) Propagation of error:

Expt A: 102.3 ( $\pm 0.2$ ) mg compound consumed 0.0915 ( $\pm 0.0007$ ) mmol  $\text{Cu}^+$

Expt B: 94.6 ( $\pm 0.2$ ) mg compound consumed 0.0423 ( $\pm 0.0007$ ) mmol  $\text{Fe}^{2+}$

Normalizing to 1 gram of superconductor gives

$$\text{Expt A: mmol Bi}^{4+} + \text{mmol Cu}^{3+} \text{ in 1 g of superconductor}$$

$$= \frac{0.0915 (\pm 0.0007)}{0.1023 (\pm 0.0002)} = 0.89443 (\pm 0.00706) \frac{\text{mmol}}{\text{gram}}$$

$$\text{Expt B: mmol Bi}^{4+} \text{ in 1 g of superconductor}$$

$$= \frac{0.0423 (\pm 0.0007)}{0.0946 (\pm 0.0002)} = 0.44715 (\pm 0.00746) \frac{\text{mmol}}{\text{gram}}$$

$$\frac{\text{mmol Cu}^{3+}}{\text{g superconductor}} = 0.89443 (\pm 0.00706) - 0.44715 (\pm 0.00746)$$

$$= 0.44728 (\pm 0.01027)$$

$$\frac{b}{c} = \frac{0.44715 (\pm 0.00746)}{0.44728 (\pm 0.01027)} = 0.9997 (\pm 0.0284)$$

$$\frac{2c}{760.37 + 15.9994(8 + [1.9997 (\pm 0.0284)]c)} = 4.4728 (\pm 0.1027) \times 10^{-4}$$

$$[4471.47 (\pm 102.7)]c = 888.365 + [31.9994 (\pm 0.445)]c$$

$$\Rightarrow c = 0.2001 (\pm 0.0046)$$

The relative uncertainty in  $b$  just given as  $0.00746/0.44715$  is smaller than the relative uncertainty in  $c$ , which is  $0.01027/0.44728$ .

$$\text{Uncertainty in } b = \frac{0.00746/0.44715}{0.01027/0.44728} \text{ (uncertainty in } c\text{)}$$

$$= \frac{0.00746/0.44715}{0.01027/0.44728} (\pm 0.0046) = \pm 0.0033$$

$$\Rightarrow b = 0.2000 (\pm 0.0033)$$

The average oxidation numbers are  $\text{Bi}^{+3.2000} (\pm 0.0033)$  and  $\text{Cu}^{+2.2001} (\pm 0.0046)$  and the formula of the compound is  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.4001} (\pm 0.0057)$ .

## CHAPTER 16

### ELECTROANALYTICAL TECHNIQUES

**16-1.** We observe that the silver electrode requires  $\sim 0.5$  V more negative potential than the platinum electrode for reduction of  $\text{H}_3\text{O}^+$  to  $\text{H}_2$ . The extra voltage needed to liberate  $\text{H}_2$  at the silver surface is the overpotential required to overcome the activation energy for the reaction. In Table 16-1, we see that the difference in overpotential between Pt and Ag is  $\sim 0.5$  V for a current density of  $100 \text{ A/m}^2$ .

**16-2.**  $(0.100 \text{ mol})(96\,485 \text{ C/mol}) = 9.648 \times 10^3 \text{ C}$

$$(9.648 \times 10^3 \text{ C})/(1.00 \text{ C/s}) = 9.648 \times 10^3 \text{ s} = 2.68 \text{ h}$$

**16-3.**  $E^\circ = -\Delta G^\circ/2F = -237.13 \times 10^3/[(2)(964\,85)] = -1.228\,8 \text{ V}$

“Standard” means that reactants and products are in their standard states (1 bar for gases, pure liquid for water, unit activity for  $\text{H}^+$  and  $\text{OH}^-$ ).

**16-4.** (a)  $E = E(\text{cathode}) - E(\text{anode})$

$$= \left\{ E^\circ(\text{cathode}) - 0.059\,16 \log P_{\text{H}_2}^{1/2} [\text{OH}^-] \right\}$$

$$- \left\{ E^\circ(\text{anode}) - 0.059\,16 \log [\text{Br}^-] \right\}$$

(remember to write both reactions as reductions)

$$= \{-0.828 - 0.059\,16 \log (1.0)^{1/2} [0.10]\}$$

$$- \{1.078 - 0.059\,16 \log [0.10]\} = -1.906 \text{ V}$$

(b) Ohmic potential =  $I R = (0.100 \text{ A})(2.0 \Omega) = 0.20 \text{ V}$

(c)  $E = E(\text{cathode}) - E(\text{anode}) - I R - \text{Overpotentials}$

$$= -1.906 - 0.20 - (0.20 + 0.40) = -2.71 \text{ V}$$

(d)  $E(\text{cathode}) = E^\circ(\text{cathode}) - 0.059\,16 \log P_{\text{H}_2}^{1/2} [\text{OH}^-]_s$

$$= -0.828 - 0.059\,16 \log (1.0)^{1/2} [1.0] = -0.828 \text{ V}$$

$$E(\text{anode}) = E^\circ(\text{anode}) - 0.059\,16 \log [\text{Br}^-]_s$$

$$= 1.078 - 0.059\,16 \log [0.010] = 1.196 \text{ V}$$

$$E = E(\text{cathode}) - E(\text{anode}) - I R - \text{Overpotentials}$$

$$= -0.828 - 1.196 - 0.20 - (0.20 + 0.40) = -2.82 \text{ V}$$

**16-5.**  $V_2$  is the voltage between the working and reference electrodes, which is held constant. Working: —○ Reference: → Auxiliary: —|

**16-6.** (a) For every mole of Hg produced, one mole of electrons flows.

$$1.00 \text{ mL Hg} = 13.53 \text{ g Hg} = 0.067\,45 \text{ mol Hg} = 0.067\,45 \text{ mol e}^-.$$

$$(0.067\ 45 \text{ mol}) (96\ 485 \text{ C/mol}) = 6\ 508 \text{ C.}$$

$$\text{Work} = q \cdot E = (6\ 508 \text{ C}) (1.02 \text{ V}) = 6.64 \times 10^3 \text{ J.}$$

- (b) The power is  $0.209 \text{ J/min} = 0.003\ 48 \text{ J/s.}$

$$P = I^2R \Rightarrow I = \sqrt{P/R} = \sqrt{(0.003\ 48 \text{ W})/(100 \Omega)} = 5.902 \text{ mA.}$$

In 1 h the total charge flowing through the circuit is

$$(5.902 \times 10^{-3} \text{ C/s}) (3\ 600 \text{ s}) = 21.25 \text{ C}/(96\ 485 \text{ C/mol})$$

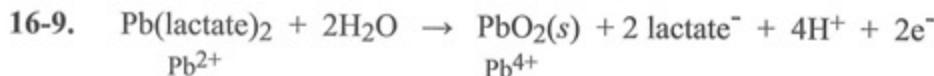
$$= 2.202 \times 10^{-4} \text{ mol of e}^-/\text{h} = 1.101 \times 10^{-4} \text{ mol of Cd/h}$$

$$= 0.012\ 4 \text{ g Cd/h.}$$

- 16-7.** Hydroxide generated at the cathode and  $\text{Cl}^-$  in the anode compartment cannot cross the membrane.  $\text{Na}^+$  from seawater crosses from the anode to the cathode to preserve charge balance. Therefore,  $\text{NaOH}$  can be formed free from  $\text{Cl}^-$ .

- 16-8.**  $E = E(\text{cathode}) - E(\text{anode}) - IR - \text{overpotentials}$

Suppose that the open-circuit voltage of each cell is  $E(\text{cathode}) - E(\text{anode}) = 2.2 \text{ V}$  when no current flows. Ohmic loss and overpotentials for the two half-reactions decrease the output of the cell by 0.2 V, giving a net cell voltage of 2.0 V when the cell is delivering current. The cell can be recharged at very low current flow by applying just over 2.2 V in the opposite direction to reverse the cell chemistry. To charge at a significant rate requires additional voltage to overcome ohmic loss and overpotentials. The recharge requires  $\sim 0.2 \text{ V}$  more than open-circuit voltage, or  $\sim 2.4 \text{ V}$ . Electrical losses [ $IR$ , overpotentials, and concentration polarization in the terms  $E(\text{cathode})$  and  $E(\text{anode})$ ] always decrease the magnitude of the voltage that can be delivered by a cell and increase the magnitude of the voltage required to reverse the spontaneous cell reaction.

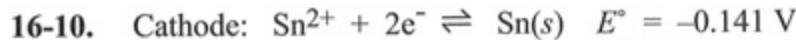


Lead is oxidized to  $\text{PbO}_2$  at the anode.

The mass of lead lactate (FM 385.3) giving 0.111 1 g of  $\text{PbO}_2$

(FM = 239.2) is  $(385.3/239.2)(0.111\ 1 \text{ g}) = 0.179\ 0 \text{ g.}$

$$\% \text{ Pb} = \frac{0.179\ 0}{0.326\ 8} \times 100 = 54.77\%$$



$$E(\text{cathode, vs S.H.E.}) = -0.141 - \frac{0.05916}{2} \log \frac{1}{1.0 \times 10^{-8}} = -0.378 \text{ V}$$

$$E(\text{cathode, vs S.C.E.}) = -0.378 - 0.241 = -0.619 \text{ V}$$

The voltage will be more negative if concentration polarization occurs.

Concentration polarization means that  $[\text{Sn}^{2+}]_s < 1.0 \times 10^{-8} \text{ M}$ .

- 16-11.** When 99.99% of Cd(II) is reduced, the formal concentration will be  $1.0 \times 10^{-5} \text{ M}$ , and the predominant form is  $\text{Cd}(\text{NH}_3)_4^{2+}$ .

$$\beta_4 = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = \frac{(1.0 \times 10^{-5})}{[\text{Cd}^{2+}](1.0)^4} \Rightarrow [\text{Cd}^{2+}] = 2.8 \times 10^{-12} \text{ M}$$



$$E(\text{cathode}) = -0.402 - \frac{0.05916}{2} \log \frac{1}{[\text{Cd}^{2+}]} = -0.744 \text{ V}$$

- 16-12.** Ni deposited =  $(0.4798 \text{ g} - 0.4775 \text{ g}) = 2.3 \text{ mg} = 39.19 \mu\text{mol Ni}$  which would require  $(39.19 \times 10^{-6} \text{ mol Ni})(2 \text{ e}^-/\text{Ni})(96485 \text{ C/mol}) = 7.562 \text{ C}$ . Percentage of current going to reduction of  $\text{Ni}^{2+} = 100 \times \frac{7.562 \text{ C}}{8.082 \text{ C}} = 94\%$ . The remainder went into reduction of  $\text{H}^+$  to  $\text{H}_2$ .

- 16-13.** When excess  $\text{Br}_2$  appears in the solution, current flows at a low applied potential difference (0.25 V) in the detector circuit by virtue of the reactions



- 16-14.** A mediator shuttles electrons between analyte and the electrode. After being oxidized or reduced by analyte, the mediator is regenerated at the electrode.

- 16-15.** (a)  $0.005 \text{ C/s} \times 0.1 \text{ s} = 0.0005 \text{ C}$

$$\frac{0.0005 \text{ C}}{96485 \text{ C/mol}} = 5.2 \times 10^{-9} \text{ mol e}^-$$

- (b) A 0.01 M solution of a two-electron reductant delivers 0.02 moles of electrons/liter.

$$\frac{5.2 \times 10^{-9} \text{ moles}}{0.02 \text{ moles/liter}} = 2.6 \times 10^{-7} \text{ L} = 0.00026 \text{ mL} = 0.26 \mu\text{L}$$

- 16-16.** (a)  $\text{mol e}^- = \frac{I \cdot t}{F} = \frac{(5.32 \times 10^{-3} \text{ C/s})(964 \text{ s})}{96485 \text{ C/mol}} = 5.32 \times 10^{-5} \text{ mol}$

(b) One mol  $e^-$  reacts with  $\frac{1}{2}$  mol  $Br_2$ , which reacts with  $\frac{1}{2}$  mol cyclohexene  
 $\Rightarrow 2.66 \times 10^{-5}$  mol cyclohexene.

$$(c) 2.66 \times 10^{-5} \text{ mol}/5.00 \times 10^{-3} \text{ L} = 5.32 \times 10^{-3} \text{ M}$$

**16-17.**  $2I^- \rightarrow I_2 + 2e^- \Rightarrow$  one mole of  $I_2$  is created when two moles of electrons flow.  
 $(812 \text{ s})(52.6 \times 10^{-3} \text{ C/s})/(96\ 485 \text{ C/mol}) = 0.442\ 7 \text{ mmol of } e^- = 0.221\ 3 \text{ mmol of } I_2$ . Therefore, there must have been  $0.221\ 3 \text{ mmol of H}_2\text{S (FM 34.08)} = 7.542 \text{ mg of H}_2\text{S}/50.00 \text{ mL} = 7.542 \times 10^3 \mu\text{g of H}_2\text{S}/50.00 \text{ mL} = 151 \mu\text{g/mL}$ .



Electron flow =

$$\left(4 \frac{\text{electrons}}{C_6H_5N=NC_6H_5}\right)\left(25.9 \frac{\text{nmol}}{\text{s}}\right)\left(96\ 485 \frac{\text{C}}{\text{mol}}\right) = 1.00 \times 10^{-2} \text{ C/s}$$

$$\text{current density} = \frac{1.00 \times 10^{-2} \text{ A}}{1.00 \times 10^{-4} \text{ m}^2} = 1.00 \times 10^2 \text{ A/m}^2$$

$$\Rightarrow \text{overpotential} = 0.85 \text{ V}$$

$$(b) E(\text{cathode}) = 0.100 - 0.059\ 16 \log \frac{[Ti^{3+}]_s}{[TiO^{2+}]_s[H^+]^2}$$

$$= 0.100 - 0.059\ 16 \log \frac{[0.10]}{[0.050][0.10]^2} = -0.036 \text{ V}$$



$$E(\text{anode}) = 1.229 - \frac{0.059\ 16}{4} \log \frac{1}{P_{O_2}[H^+]^4}$$

$$= 1.229 - \frac{0.059\ 16}{4} \log \frac{1}{(0.20)[0.10]^4} = 1.160 \text{ V}$$

$$(d) E = E(\text{cathode}) - E(\text{anode}) - IR - \text{Overpotential}$$

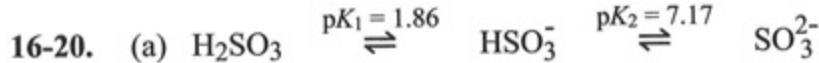
$$= -0.036 - 1.160 - (1.00 \times 10^{-2} \text{ A})(52.4 \Omega) - 0.85 = -2.57 \text{ V}$$

$$(16-19) F = \frac{\text{coulombs}}{\text{mol}} = \frac{I \cdot t}{\text{mol}}$$

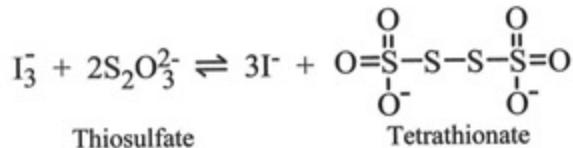
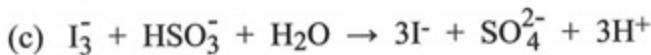
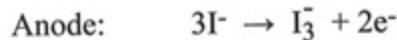
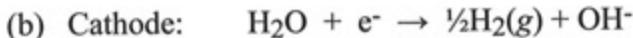
$$= \frac{[0.203\ 639\ 0(\pm 0.000\ 000\ 4) \text{ A}][18\ 000.075 (\pm 0.010) \text{ s}]}{[4.097\ 900 (\pm 0.000\ 003) \text{ g}]/[107.868\ 2 (\pm 0.000\ 2) \text{ g/mol}]}$$

$$= \frac{[0.203\ 639\ 0(\pm 1.96 \ 10^{-4} \ %)][18\ 000.075 (\pm 5.56 \ 10^{-5} \ %)]}{[4.097\ 900 (\pm 7.32 \ 10^{-5} \ %)][107.868\ 2 (\pm 1.85 \ 10^{-4} \ %)]}$$

$$= 9.648\ 667 \times 10^4 (\pm 2.85 \times 10^{-4} \ %) = 964\ 86.67 \pm 0.28 \text{ C/mol}$$



$\text{H}_2\text{SO}_3$  is predominant below pH 1.86.  $\text{HSO}_3^-$  dominates between pH 1.86 and 7.17.  $\text{SO}_3^{2-}$  is dominant above pH 7.17.



- (d) In Step 3,  $\text{I}_3^-$  was generated by a current of 10.0 mA ( $= 10.0 \times 10^{-3}$  C/s) for 4.00 min ( $= 240$  s).

$$\text{charge} = I \cdot t = (10.0 \times 10^{-3} \text{ C/s})(240 \text{ s}) = 2.40 \text{ C}$$

$$\text{mol e}^- = I/F = (2.40 \text{ C})/(96485 \text{ C/mol}) = 24.87 \mu\text{mol e}^-$$

The anode reaction generates  $\frac{1}{2}$  mol  $\text{I}_3^-$  for 1 mol  $\text{e}^-$ . Therefore,  $24.87 \mu\text{mol e}^-$  will generate  $\frac{1}{2}(24.87) = 12.44 \mu\text{mol I}_3^-$ .

In Step 5, 0.500 mL of 0.050 M thiosulfate =  $25.35 \mu\text{mol S}_2\text{O}_3^{2-}$ . But 2 mol  $\text{S}_2\text{O}_3^{2-}$  consume 1 mol  $\text{I}_3^-$ . Therefore,  $25.35 \mu\text{mol S}_2\text{O}_3^{2-}$  consume  $\frac{1}{2}(25.35) = 12.68 \mu\text{mol I}_3^-$ .

We added excess  $\text{S}_2\text{O}_3^{2-}$  in Step 5 and consumed the excess in Step 6. In Step 6, we had to generate  $\text{I}_3^-$  at 10.0 mA for 131 s to react with excess  $\text{S}_2\text{O}_3^{2-}$ .

$$\text{charge} = I \cdot t = (10.0 \times 10^{-3} \text{ C/s})(131 \text{ s}) = 1.31 \text{ C}$$

$$\text{mol e}^- = I/F = (1.31 \text{ C})/(96485 \text{ C/mol}) = 13.58 \mu\text{mol e}^-$$

$$\text{mol I}_3^- = \frac{1}{2}(13.58) = 6.79 \mu\text{mol I}_3^-$$

Here is where we are so far:

Step 3:  $12.44 \mu\text{mol I}_3^-$  were generated.

Step 4:  $x \mu\text{mol I}_3^-$  were consumed by sulfite in wine.

Step 5: We added enough  $\text{S}_2\text{O}_3^{2-}$  to consume  $12.68 \mu\text{mol I}_3^-$ .

Step 6: We had to generate  $6.79 \mu\text{mol I}_3^-$  to consume excess  $\text{S}_2\text{O}_3^{2-}$  from

Step 5. Therefore,  $\text{I}_3^-$  left after Step 4 =  $12.68 - 6.79 = 5.89 \mu\text{mol I}_3^-$ .

We began with  $12.44 \mu\text{mol I}_3^-$  and  $5.89 \mu\text{mol I}_3^-$  were left after reaction with sulfite in wine. Therefore, sulfite in wine consumed  $12.44 - 5.89 = 6.55 \mu\text{mol I}_3^-$ . But 1 mol  $\text{I}_3^-$  reacts with 1 mol sulfite. Therefore, the wine contained  $6.55 \mu\text{mol}$  sulfite in the 2.00 mL injected for analysis.

The wine sample prepared in Step 1 consisted of 9.00 mL wine diluted to 10.00 mL. Therefore, the original wine contained  $10.00/9.00$  of the amount found in the analysis. That is, 2.000 mL of pure wine contains  $(10.00/9.00)(6.55 \mu\text{mol sulfite}) = 7.28 \mu\text{mol sulfite}$ .

$$\text{sulfite in wine} = \frac{7.28 \mu\text{mol sulfite}}{2.00 \text{ mL}} = 3.64 \text{ mM}$$

This problem left out a description of the blank titration that should be done in a real analysis. There are components in wine in addition to sulfite that could react with  $\text{I}_3^-$ . For the blank titration, 1 M formaldehyde is added to the wine to bind all sulfite. The sulfite-formaldehyde adduct is not decomposed in 2 M NaOH and does not react with  $\text{I}_3^-$ . The blank titration consists of taking this formaldehyde/wine solution through the entire procedure. We subtract  $\text{I}_3^-$  consumed by the blank from  $\text{I}_3^-$  consumed by the wine without formaldehyde.

- 16-21.** (a) Balance carbon:  $B = c$ ; balance halogen:  $C = x$ ; balance nitrogen:  $D = n$   
 Balance oxygen:  $o + A = 2B \Rightarrow o + A = 2c \Rightarrow A = 2c - o$   
 Balance hydrogen:  $h + 2A = 3D + E \Rightarrow h + 2(2c - o) = 3n + E$   
 $\Rightarrow E = h + 4c - 2o - 3n$   
 Charge balance,  $F = E - C = h + 4c - 2o - 3n - c = h - c/2 + o - 3n$
- (b) To consume  $\text{Fe}^\cdot$  requires  $F/4 \text{ O}_2$ , because each  $\text{O}_2$  consumes  $4\text{e}^\cdot$ .
- (c)  $F = (9.43 \times 10^{-3} \text{ C})/(9.6485 \times 10^4 \text{ C/mol}) = 9.774 \times 10^{-8} \text{ mol e}^\cdot$   
 $\text{mol O}_2 = F/4 = 2.223 \times 10^{-8} \text{ mol}$
- (d) The mass of  $\text{O}_2$  in (c) is  $(2.223 \times 10^{-8} \text{ mol})(32.00 \text{ g/mol}) = 7.114 \times 10^{-7} \text{ g}$ .  
 This much  $\text{O}_2$  was required to react with 13.5  $\mu\text{L}$  of sample. The mass of  $\text{O}_2$  that would react with 1 L of sample is  $(7.114 \times 10^{-7} \text{ g})/(13.5 \times 10^{-6} \text{ L}) = 0.0527 \text{ g/L} = 52.7 \text{ mg/L}$ .
- (e) The balanced equation oxidation half-reaction is  
 $\text{C}_9\text{H}_6\text{NO}_2\text{ClBr}_2 + 16\text{H}_2\text{O} \rightarrow 9\text{CO}_2 + 3\text{X}^\cdot + \text{NH}_3 + 35\text{H}^+ + 32\text{e}^\cdot$ .

The observed number of electrons in the reaction was  $9.774 \times 10^{-8}$  mol e<sup>-</sup>, so there must have been  $(9.774 \times 10^{-8}$  mol e<sup>-</sup>)/(32 mol e<sup>-</sup>/mol C<sub>9</sub>H<sub>6</sub>NO<sub>2</sub>ClBr<sub>2</sub>) =  $3.054 \times 10^{-9}$  mol C<sub>9</sub>H<sub>6</sub>NO<sub>2</sub>ClBr<sub>2</sub> in 13.5 μL. The molarity of C<sub>9</sub>H<sub>6</sub>NO<sub>2</sub>ClBr<sub>2</sub> is  $(3.054 \times 10^{-9}$  mo)/(13.5 × 10<sup>-6</sup> L) =  $2.26 \times 10^{-4}$  M.

- 16-22.** The Clark electrode measures dissolved oxygen by reducing it to H<sub>2</sub>O at a gold tip on a platinum electrode held at -0.75 V with respect to Ag|AgCl. The opening of the body of the electrode is filled with a 10- to 40-μm-long plug of silicone rubber that is permeable to O<sub>2</sub>. Current is proportional to the concentration of dissolved O<sub>2</sub> in the external medium. The electrode needs to be calibrated in solutions of known O<sub>2</sub> concentration.
- 16-23.** (a) The glucose monitor has a test strip with two carbon indicator electrodes and a silver-silver chloride reference electrode. Indicator electrode 1 is coated with glucose oxidase and a mediator. When a drop of blood is placed on the test strip, glucose from the blood is oxidized near indicator electrode 1 by mediator to gluconolactone and the mediator is reduced. With a potential of +0.2 V (with respect to the Ag|AgCl electrode) on the indicator electrode, reduced mediator is re-oxidized at the indicator electrode. The current between indicator electrode 1 and the reference electrode is proportional to the rate of oxidation of the mediator, which is proportional to the concentration of glucose plus any interfering species in the blood. Indicator electrode 2 has mediator, but no glucose oxidase. Current measured between indicator electrode 2 and the reference electrode is proportional to the concentration of interfering species in the blood. The difference between the two currents is proportional to the concentration of glucose in the blood.
- (b) In the absence of a mediator, the rate of oxidation of glucose depends on the concentration of O<sub>2</sub> in the blood. If [O<sub>2</sub>] is low, the current will be low and the monitor will give an incorrect, low reading for the glucose concentration. A mediator such as 1,1'-dimethylferrocene can replace O<sub>2</sub> in the glucose oxidation and be subsequently reduced at the indicator electrode. The concentration of mediator is constant and high enough, so variations in electrode current are due mainly to variations in glucose concentration. Also, by lowering the required electrode potential for oxidation of the mediator, there is less possible interference by other species in the blood.

- (c) Glucose oxidase is replaced by glucose dehydrogenase, which does not use O<sub>2</sub> as a reactant. The enzyme oxidizes glucose and reduces the PQQ cofactor to PQQH<sub>2</sub>. PQQH<sub>2</sub> is oxidized back to PQQ by a nearby Os<sup>3+</sup> bound to the polymer chain. A nearby Os<sup>2+</sup> can exchange electrons with the Os<sup>3+</sup>. By moving from Os to Os, electrons eventually reach the carbon electrode. The coulometric sensor measures the total number of electrons needed to oxidize all of the glucose in the small blood sample.
- (d) Amperometry measures current during the enzyme-catalyzed oxidation of glucose. Current is proportional to the rate of the oxidation reaction. The rates of most chemical reactions increase with increasing temperature. Therefore, the current will increase with increasing temperature of the blood sample. Coulometry measures the total number of electrons released in the oxidation. Glucose releases 2 electrons per molecule, regardless of temperature. The coulometric signal should have no temperature dependence.
- (e) 1.00 g glucose/L = 5.55 mM glucose. A volume of  $0.300 \times 10^{-6}$  L contains 1.665 nmol glucose. Each mole of glucose releases 2e<sup>-</sup> and 2H<sup>+</sup> during oxidation. Therefore,  $2 \times 1.665 \text{ nmol} = 3.33 \text{ nmol e}^-$  are released. The charge is  $Q = nF = (3.33 \times 10^{-9} \text{ mol})(96\,485 \text{ C/mol}) = 321 \mu\text{C}$ .

**16-24.**  $\omega$  is the rotation rate in radians per second. We need to convert rpm (revolutions per minute) to radians per second.

$$\left(2.00 \times 10^3 \frac{\text{revolutions}}{\text{min}}\right) \left(\frac{1 \text{ min}}{60 \text{ s}}\right) \left(\frac{2\pi \text{ radians}}{\text{revolution}}\right) = 209 \text{ rad/s} = 209 \text{ s}^{-1}$$

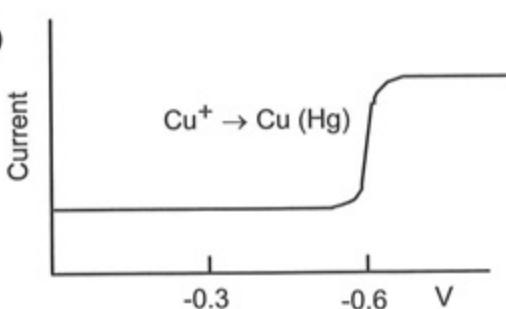
(because radian is a dimensionless unit)

$$\begin{aligned}\delta &= 1.61D^{1/3}v^{1/6}\omega^{-1/2} \\ &= 1.61(2.5 \times 10^{-9} \text{ m}^2/\text{s})^{1/3}(1.1 \times 10^{-6} \text{ m}^2/\text{s})^{1/6}(209 \text{ rad/s})^{-1/2} = 1.53 \times 10^{-5} \text{ m}\end{aligned}$$

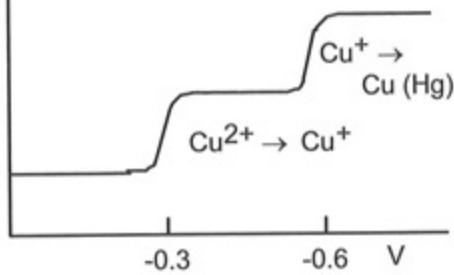
To calculate current density, we need to express the concentration of the species reacting at the electrode in mol/m<sup>3</sup> instead of mol/L. Since 1 L is the volume of a 10-cm cube, there are 1 000 L in 1 m<sup>3</sup>. The concentration of K<sub>4</sub>Fe(CN)<sub>6</sub> is 50.0 mM =  $\left(0.050 \text{ mol/L}\right)\left(1 \text{ m}^3\right) = 50.0 \text{ mol/m}^3$ .

$$\begin{aligned}\text{Current density} &= 0.62nFD^{2/3}v^{-1/6}\omega^{1/2}C_0 \\ &= 0.62(1)\left(96\,485 \frac{\text{C}}{\text{mol}}\right)\left(2.5 \times 10^{-9} \frac{\text{m}^2}{\text{s}}\right)^{2/3}\left(1.1 \times 10^{-6} \frac{\text{m}^2}{\text{s}}\right)^{-1/6}\left(209 \frac{1}{\text{s}}\right)^{1/2}\left(50.0 \frac{\text{mol}}{\text{m}^3}\right) \\ &= 7.84 \times 10^2 \frac{\text{C}}{\text{m}^2 \cdot \text{s}} = 7.84 \times 10^2 \frac{\text{A}}{\text{m}^2}\end{aligned}$$

16-25. (a)



(b)



- (c) The potential for the reaction  $\text{Cu(I)} \rightarrow \text{Cu(Hg)}$  will change if Pt is used, since the product obviously cannot be copper amalgam.

16-26. (a) Charging current arises from charging or discharging of the electric double layer at the electrode-solution interface. Faradaic current arises from oxidation or reduction reactions.

- (b) Charging current decays more rapidly than Faradaic current. If we wait 1 s after a potential step, the charging current decays to near zero and the Faradaic current is still significant. The ratio of the desired signal (Faradaic current) to the undesired background (charging current) is larger at 1 s than it was at earlier times. If we wait too long, both signals become too small to measure.

- (c) In square wave voltammetry, an anodic pulse follows each cathodic pulse and the signal is the difference between the two. The anodic pulse oxidizes the product of each cathodic pulse, thereby replenishing the electroactive species at the electrode surface for the next pulse. The concentration of analyte available at the electrode surface is therefore greater in square wave voltammetry.

16-27. Electrons flowing in 3.4 min =

$$\frac{(14 \times 10^{-6} \text{ C/s})(60 \text{ s/min})(3.4 \text{ min})}{96485 \text{ C/mol}} = 2.96 \times 10^{-8} \text{ mol e}^-$$

For the reaction  $\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd(in Hg)}$ ,

$$\text{moles of Cd}^{2+} = \frac{1}{2} \text{ moles of e}^- = 1.48 \times 10^{-8} \text{ mol}$$

$$\text{moles of Cd}^{2+} \text{ in } 25 \text{ mL of } 0.50 \text{ mM solution} = 1.25 \times 10^{-5} \text{ mol}$$

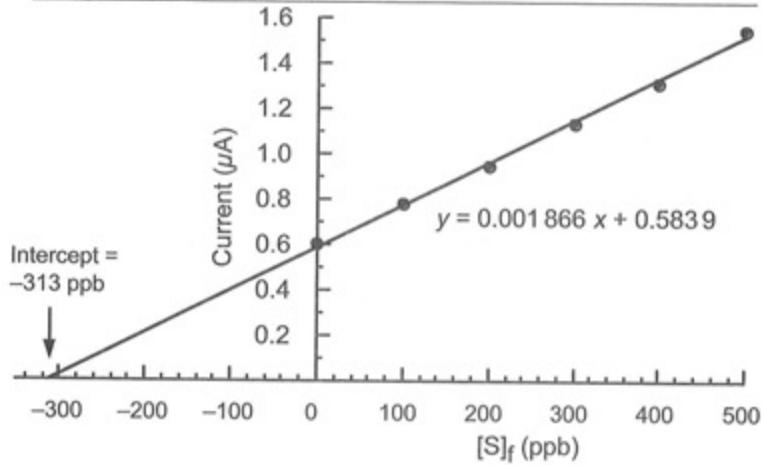
$$\text{percentage of Cd}^{2+} \text{ reduced} = \frac{1.48 \times 10^{-8}}{1.25 \times 10^{-5}} \times 100 = 0.118\%$$

16-28.  $\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$

$$\frac{x(\text{mM})}{3.00 \left( \frac{2.00}{52.00} \right) + x \left( \frac{50.0}{52.0} \right)} = \frac{0.37 \mu\text{A}}{0.80 \mu\text{A}} \Rightarrow x = 0.096 \text{ mM}$$

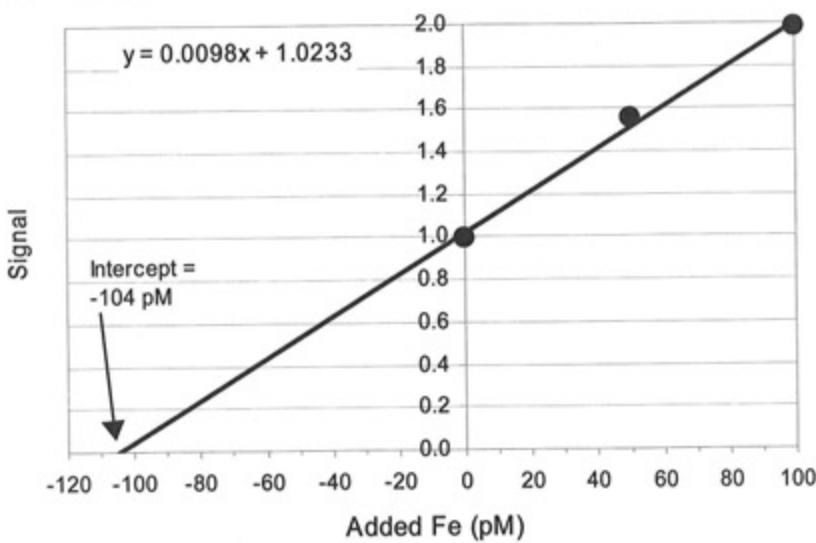
- 16-29. In anodic stripping voltammetry, analyte is reduced and concentrated at the working electrode at a controlled potential for a constant time. The potential is then ramped in a positive direction to reoxidize the analyte, during which time current is measured. The height of the oxidation wave is proportional to the original concentration of analyte. Stripping is the most sensitive voltammetric technique because analyte is concentrated from a dilute solution. The longer the period of concentration, the more sensitive is the analysis.
- 16-30. (a) Concentration (deposition) stage:  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s)$   
 (b) Stripping stage:  $\text{Cu}(s) \rightarrow \text{Cu}^{2+} + 2e^-$   
 (c) All solutions were made up to the same volume, so  $[X]_i = [X]_f \equiv x$ . Prepare a graph of  $I$  vs.  $[S]_f$  using data measured from the figure in the problem. The intercept is at -313 ppb, so the original concentration of  $\text{Cu}^{2+}$  is 313 ppb.

Added standard (ppb)	Current ( $\mu\text{A}$ )
0	0.599
100	0.774
200	0.943
300	1.128
400	1.314
500	1.544



16-31.

	A	B	C	D	E
1	Standard Addition Constant Volume Least-Squares Spreadsheet				
2	x	y			
3	Added Fe(III)	Relative			
4	(pM)	peak height			
5	0	1.00			
6	50	1.56			
7	100	1.98			
8	B10:C12 = LINEST(B5:B7,A5:A7,TRUE,TRUE)				
9		LINEST output:			
10	m	0.0098	1.0233	b	
11	s <sub>m</sub>	0.0008	0.0522	s <sub>b</sub>	
12	R <sup>2</sup>	0.9932	0.0572	s <sub>y</sub>	
13	x-intercept = -b/m =	-104.422			
14	n =	3	B14 = COUNT(A6:A7)		
15	Mean y =	1.513	B15 = AVERAGE(B5:B7)		
16	÷(x <sub>i</sub> - mean x) <sup>2</sup> =	5000	B16 = DEVSQ(A5:A7)		
17	Std deviation of				
18	x-intercept =	13.174			
19	B18 = (C12/ABS(B10))*SQRT((1/B14) + B15^2/(B10^2*B16))				



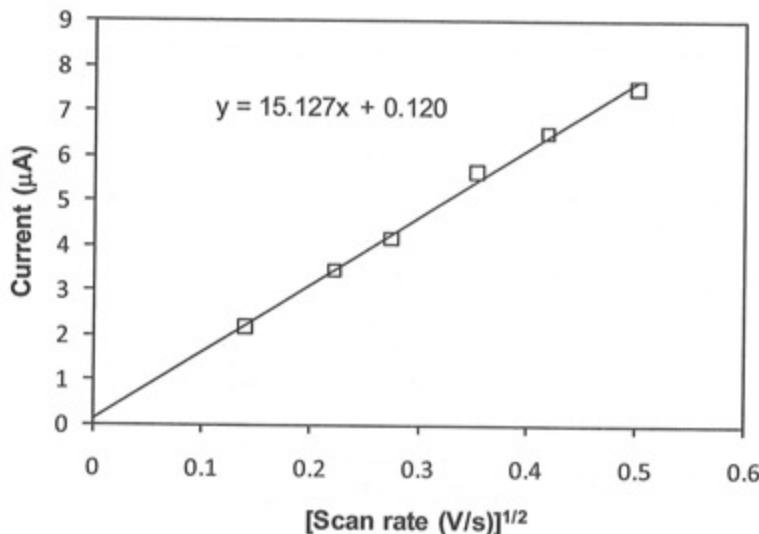
Cells B13 and B18 of the spreadsheet tell us that  $[Fe(III)] = 104 \pm 13 \text{ pM}$ .

16-32. Peak B:  $RNHOH \rightarrow RNO + 2H^+ + 2e^-$

Peak C:  $RNO + 2H^+ + 2e^- \rightarrow RNHOH$

There was no RNO present before the initial scan.

16-33.



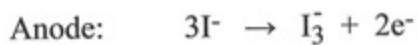
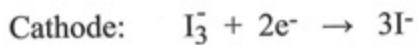
$$I_p = (2.69 \times 10^8)n^{3/2}ACD^{1/2}v^{1/2}$$

$$\text{slope} = (2.69 \times 10^8)n^{3/2}ACD^{1/2}$$

$$\begin{aligned}\Rightarrow D &= \frac{\text{slope}^2}{(2.69 \times 10^8)^2 n^3 A^2 C^2} \\ &= \frac{(15.1 \times 10^{-6} \text{ A}/\sqrt{\text{V}/\text{s}})^2}{(2.69 \times 10^8)^2 1^3 (0.0201 \times 10^{-4} \text{ m}^2)^2 (1.00 \times 10^{-3} \text{ M})^2} = 7.8 \times 10^{-10} \text{ m}^2/\text{s}\end{aligned}$$

- 16-34. Microelectrodes fit into small places, are useful in nonaqueous solution (because of small ohmic losses), and allow rapid voltage scans (because of small capacitance), which permits the study of short-lived species. The low capacitance gives a low background charging current, which increases the sensitivity to analyte by orders of magnitude.
- 16-35. The Nafion membrane permits neutral and cationic species to pass through to the electrode, but excludes anions. It reduces the background signal from ascorbate anion, which would otherwise swamp the signal from dopamine.
- 16-36.  $\text{ROH} + \text{SO}_2 + \text{B} \rightarrow \text{BH}^+ + \text{ROSO}_2^-$   
 $\text{H}_2\text{O} + \text{I}_2 + \text{ROSO}_2^- + 2\text{B} \rightarrow \text{ROSO}_3^- + 2\text{BH}^+\text{I}^-$
- One mole of  $\text{H}_2\text{O}$  plus one mole of  $\text{I}_2$  are required for the oxidation of the alkyl sulfite to an alkyl sulfate in the second reaction.

**16-37.** The bipotentiometric detector maintains a constant current ( $\sim 10 \mu\text{A}$ ) between two detector electrodes, while measuring the voltage needed to sustain that current. Before the equivalence point, the solution contains  $\text{I}^-$ , but little  $\text{I}_2$ . To maintain a current of  $10 \mu\text{A}$ , the cathode potential must be negative enough to reduce some component of the solvent system (perhaps  $\text{CH}_3\text{OH} + \text{e}^- \rightleftharpoons \text{CH}_3\text{O}^- + \frac{1}{2}\text{H}_2(g)$ ). At the equivalence point, excess  $\text{I}_2$  suddenly appears and current can be carried at low voltage by the reactions below. The abrupt voltage drop marks the end point.



## CHAPTER 17

### FUNDAMENTALS OF SPECTROPHOTOMETRY

- 17-1.** (a) double                    (b) halve                    (c) double
- 17-2.** (a)  $E = h\nu = hc/\lambda = (6.6262 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m s}^{-1})/(650 \times 10^{-9} \text{ m})$   
 $= 3.06 \times 10^{-19} \text{ J/photon} = 184 \text{ kJ/mol}$
- (b) For  $\lambda = 400 \text{ nm}$ ,  $E = 299 \text{ kJ/mol}$ .
- 17-3.**  $v = c/\lambda = 2.9979 \times 10^8 \text{ m s}^{-1}/562 \times 10^{-9} \text{ m} = 5.33 \times 10^{14} \text{ Hz}$   
 $\tilde{\nu} = 1/\lambda = 1.78 \cdot 10^6 \text{ m}^{-1} (1 \text{ m}/100 \text{ cm}) = 1.78 \cdot 10^4 \text{ cm}^{-1}$   
 $E = h\nu = (6.6262 \times 10^{-34} \text{ J s})(5.33 \times 10^{14} \text{ s}^{-1}) = 3.53 \times 10^{-19} \text{ J/photon}$   
 $= 213 \text{ kJ/mol}$  (after multiplication by Avogadro's number).
- 17-4.** Microwave energies correspond to molecular rotation energies. Infrared energies correspond to vibrational energies. Visible light can promote electrons to excited states (in colored compounds). Ultraviolet light also promotes electrons and can even break chemical bonds.
- 17-5.** From the definition of index of refraction, we can write
- $$c_{\text{vacuum}} = n \cdot c_{\text{air}}$$
- $$\lambda_{\text{vacuum}} \cdot v = n \cdot \lambda_{\text{air}} \cdot v$$
- $$\lambda_{\text{air}} = \lambda_{\text{vacuum}}/n$$
- $$v = c/\lambda_{\text{vacuum}} = 5.088\,491\,0 \text{ and } 5.083\,335\,8 \times 10^{14} \text{ Hz}$$
- $$\lambda_{\text{air}} = \lambda_{\text{vacuum}}/n = 588.985\,54 \text{ and } 589.582\,86 \text{ nm}$$
- $$\tilde{\nu}_{\text{air}} = 1/\lambda_{\text{air}} = 1.697\,834\,5 \text{ and } 1.696\,114\,4 \cdot 10^4 \text{ cm}^{-1}$$
- 17-6.** Transmittance ( $T$ ) is the fraction of incident light that is transmitted by a substance:  $T = P/P_0$ , where  $P_0$  is incident irradiance and  $P$  is transmitted irradiance. Absorbance is logarithmically related to transmittance:  $A = -\log T$ . When all light is transmitted, absorbance is zero. When no light is transmitted, absorbance is infinite. Absorbance is proportional to concentration. Molar absorptivity is the constant of proportionality between absorbance at a particular wavelength and the product  $cb$ , where  $c$  is concentration and  $b$  is pathlength.
- 17-7.** An absorption spectrum is a graph of absorbance vs. wavelength.
- 17-8.** The color of transmitted light is the complement of the color that is absorbed. If blue-green light is absorbed, red light is transmitted.

17-9.	Absorption Curve	peak (nm)	Predicted color (Table 17-1)	Observed color
	A	760	green	green
	B	700	green	blue-green
	C	600	blue	blue
	D	530	violet	violet
	E	500	red or purple red	red
	F	410	green-yellow	yellow

17-10. If absorbance is too high, too little light reaches the detector for accurate measurement. If absorbance is too low, there is too little difference between sample and reference for accurate measurement.

17-11.  $\epsilon = A/bc = 0.822/[(1.00 \text{ cm})(2.31 \times 10^{-5} \text{ M})] = 3.56 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$

17-12. Violet blue, according to Table 17-1.

17-13. [Fe] in reference cell =  $\left(\frac{10.0}{50.0}\right)(6.80 \cdot 10^{-4}) = 1.36 \times 10^{-4} \text{ M}$ . Setting the absorbances of sample and reference equal to each other gives  $\epsilon_s b_s c_s = \epsilon_r b_r c_r$ . But  $\epsilon_s = \epsilon_r$ , so  $(2.48 \text{ cm})c_s = (1.00 \text{ cm})(1.36 \times 10^{-4} \text{ M}) \Rightarrow c_s = 5.48 \times 10^{-5} \text{ M}$ . This is a 1/4 dilution of runoff, so [Fe] in runoff =  $2.19 \times 10^{-4} \text{ M}$ .

17-14. (a) Measured from graph:

$$\sigma \approx 1.3 \times 10^{-20} \text{ cm}^2 \text{ at } 325 \text{ nm} \quad \sigma \approx 3.5 \times 10^{-19} \text{ cm}^2 \text{ at } 300 \text{ nm}$$

at 325 nm:  $T = e^{-(8 \times 10^{18} \text{ cm}^{-3})(1.3 \times 10^{-20} \text{ cm}^2)(1 \text{ cm})} = 0.90$

$$A = -\log T = 0.045$$

at 300 nm:  $T = e^{-(8 \times 10^{18} \text{ cm}^{-3})(3.5 \times 10^{-19} \text{ cm}^2)(1 \text{ cm})} = 0.061$

$$A = -\log T = 1.22$$

(b)  $T = e^{-n\sigma b} \quad 0.14 = e^{-(8 \times 10^{18} \text{ cm}^{-3})\sigma(1 \text{ cm})}$

$$\Rightarrow \sigma = 2.4576 \times 10^{-19} \text{ cm}^2$$

If  $n$  is decreased by 1%,  $T = e^{-(7.92 \times 10^{18} \text{ cm}^{-3})(2.4576 \times 10^{-19} \text{ cm}^2)(1 \text{ cm})}$

$$= 0.1428$$

Increase in transmittance is  $\frac{0.1428 - 0.14}{0.14} = 2.0\%$ .

Note that the fractional increase in transmittance is greater than the fractional decrease in ozone concentration.

$$(c) T_{\text{winter}} = e^{-(290 \text{ D.U.})(2.69 \times 10^{16} \text{ molecules/cm}^3/\text{D.U.})(2.5 \times 10^{-19} \text{ cm}^2)(1 \text{ cm})} \\ = 0.142$$

$$T_{\text{summer}} = e^{-(350)(2.69 \times 10^{16})(2.5 \times 10^{-19})(1)} = 0.095$$

Fractional increase in transmittance is  $(0.142 - 0.095) / (0.095) = 49\%$ .

- 17-15.** Neocuproine reacts with Cu(I) and prevents it from forming a complex with ferrozine that would give a false positive result in the analysis of iron.

**17-16.** (a)  $c = A/\epsilon b = 0.427/[(6130 \text{ M}^{-1} \text{ cm}^{-1})(1.000 \text{ cm})] = 6.97 \times 10^{-5} \text{ M}$

(b) The sample had been diluted  $\times 10 \Rightarrow 6.97 \times 10^{-4} \text{ M}$ .

(c)  $\frac{x \text{ g}}{(292.16 \text{ g/mol})(5.00 \times 10^{-3} \text{ L})} = 6.97 \times 10^{-4} \text{ M} \Rightarrow x = 1.02 \text{ mg}$

- 17-17.** Yes

**17-18.** (a)  $\epsilon = \frac{A}{cb} = \frac{0.267 - 0.019}{(3.15 \times 10^{-6} \text{ M})(1.000 \text{ cm})} = 7.87 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$

(b)  $c = \frac{A}{\epsilon b} = \frac{0.175 - 0.019}{(7.87 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})(1.000 \text{ cm})} = 1.98 \times 10^{-6} \text{ M}$

- 17-19.** (a) The absorbance due to the colored product from nitrite added to sample C is  $0.967 - 0.622 = 0.345$ . The concentration of colored product due to added nitrite in sample C is  $\frac{(7.50 \times 10^{-3} \text{ M})(10.0 \times 10^{-6} \text{ L})}{0.054 \text{ L}} = 1.389 \times 10^{-6} \text{ M}$ .

$$\epsilon = A/bc = 0.345/[(1.389 \times 10^{-6})(5.00)] = 4.97 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$$

- (b)  $7.50 \times 10^{-8} \text{ mol}$  of nitrite (from  $10.0 \mu\text{L}$  added to sample C) gives

$$A = 0.345. \text{ In sample B, } x \text{ mole of nitrite in food extract gives}$$

$$A = 0.622 - 0.153 = 0.469.$$

$$\frac{x \text{ mol}}{7.50 \times 10^{-8} \text{ mol}} = \frac{0.469}{0.345} \Rightarrow x = 1.020 \times 10^{-7} \text{ mol NO}_2^- = 4.69 \mu\text{g}$$

- 17-20.** (a) Prior to the equivalence point, all added Fe(III) binds to the protein to form a red complex whose absorbance is measured in the figure. After the equivalence point, there are no more binding sites available on the protein. The slight increase in absorbance arises from the color of the iron titrant.

(b)  $163 \times 10^{-6} \text{ L} \times 1.43 \times 10^{-3} \text{ M Fe(III)} = 2.33 \times 10^{-7} \text{ mol Fe(III)}$

(c)  $1.17 \times 10^{-7} \text{ mol transferrin in } 2.00 \times 10^{-3} \text{ L} \Rightarrow 5.83 \times 10^{-5} \text{ M transferrin}$

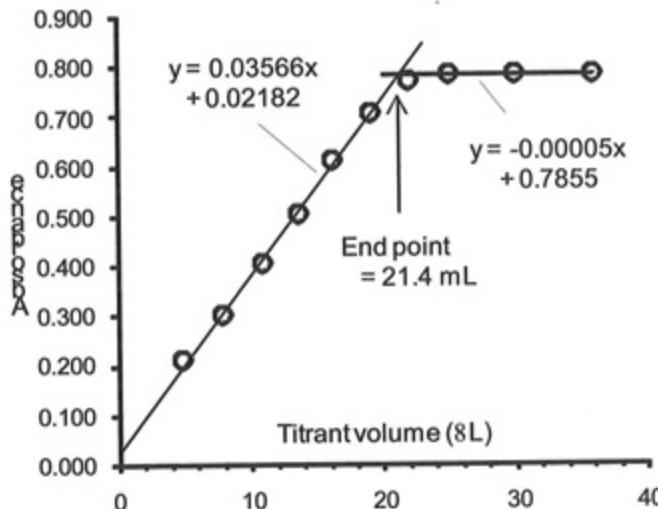
**17-21.** Theoretical equivalence point =

$$\frac{\left(2 \frac{\text{mol Ga}}{\text{mol transferrin}}\right) \left(\frac{0.00357 \text{ g transferrin}}{81000 \text{ g transferrin/mol transferrin}}\right)}{0.00664 \frac{\text{mol Ga}}{\text{L}}} = 13.3 \mu\text{L}$$

Observed end point  $\approx$  intersection of lines taken from first 6 points and last 4 points in the following graph = 12.2  $\mu\text{L}$ , corresponding to  $\frac{12.2}{13.3} = 91.7\%$  of 2 Ga/transferrin = 1.83 Ga/transferrin. In the absence of oxalate, there is no evidence for specific binding of Ga to the protein, since the slope of the curve is small and does not change near 1 or 2 Ga/transferrin.

- 17-22.** (a) In the graph below, least-squares lines were put through the first 6 points and the last 3 points. Their intersection is the estimated end point of 21.4  $\mu\text{L}$ . The moles of TCNQ in the titration are  $(0.700 \text{ mL})(1.00 \times 10^{-4} \text{ M TCNQ}) = 70.0 \text{ nmol TCNQ}$ . This many moles of Au(0) are present in 21.4  $\mu\text{L}$  of nanoparticle solution. The mass of nanoparticles in 21.4  $\mu\text{L}$  is  $(21.4 \mu\text{L})(1.43 \text{ g/L}) = 30.6 \mu\text{g}$  nanoparticles. To find the moles of Au(0) in 1.00 g of nanoparticles, set up a proportion:

$$\frac{70.0 \times 10^{-9} \text{ mol Au(0)}}{30.6 \times 10^{-6} \text{ g nanoparticles}} = \frac{x \text{ mol Au(0)}}{1.00 \text{ g nanoparticles}} \Rightarrow x = 2.29 \text{ mmol Au(0)}$$



- (b) 1.00 g of nanoparticles is estimated to contain 0.25 g  $\text{C}_{12}\text{H}_{25}\text{S}$  (FM 201.40), which is 1.24 mmol  $\text{C}_{12}\text{H}_{25}\text{S}$ .

- (c) From (a), the mass of Au(0) in 1.00 g is  $(2.29 \text{ mmol Au}(0)(196.97 \text{ g/mol}) = 0.451 \text{ g}$ . The mass of Au(I) is estimated as the difference  $1.00 - 0.451 - 0.25 = 0.299 \text{ g} = 1.52 \text{ mmol Au(I)}$ . The calculated mole ratio Au(I):C<sub>12</sub>H<sub>25</sub>S is  $1.52/1.24 = 1.23$ . Ideally, this mole ratio should be 1.00.

- 17-23.**  $n \rightarrow \pi^*(T_1)$ :

$$E = h\nu = h\frac{c}{\lambda} = (6.6261 \times 10^{-34} \text{ J}\cdot\text{s}) \frac{2.9979 \times 10^8 \text{ s}^{-1}}{397 \times 10^{-9} \text{ m}} = 5.00 \times 10^{-19} \text{ J}$$

To convert to J/mol, multiply by Avogadro's number:

$$5.00 \times 10^{-19} \text{ J/molecule} \times 6.022 \times 10^{23} \text{ molecules/mol} = 301 \text{ kJ/mol.}$$

- $n \rightarrow \pi^*(S_1)$ :

$$E = (6.6261 \times 10^{-34} \text{ J}\cdot\text{s}) \frac{2.9979 \times 10^8 \text{ s}^{-1}}{355 \times 10^{-9} \text{ m}} = 5.60 \times 10^{-19} \text{ J} = 337 \text{ kJ/mol.}$$

The difference between the T<sub>1</sub> and S<sub>1</sub> states is  $337 - 301 = 36 \text{ kJ/mol}$ .

- 17-24.** Fluorescence is emission of light with no change in the electronic spin state of the molecule (for example, singlet  $\rightarrow$  singlet). In phosphorescence, the electronic spin does change during emission (for example, triplet  $\rightarrow$  singlet). Phosphorescence is less probable, so molecules spend more time in the excited state prior to phosphorescence than to fluorescence. That is, phosphorescence has a longer lifetime than fluorescence. Phosphorescence also comes at lower energy (longer wavelength) than fluorescence, because the triplet excited state is at lower energy than the singlet excited state.

- 17-25.** Luminescence is light given off after a molecule absorbs light. Chemiluminescence is light given off by a molecule created in an excited state in a chemical reaction.

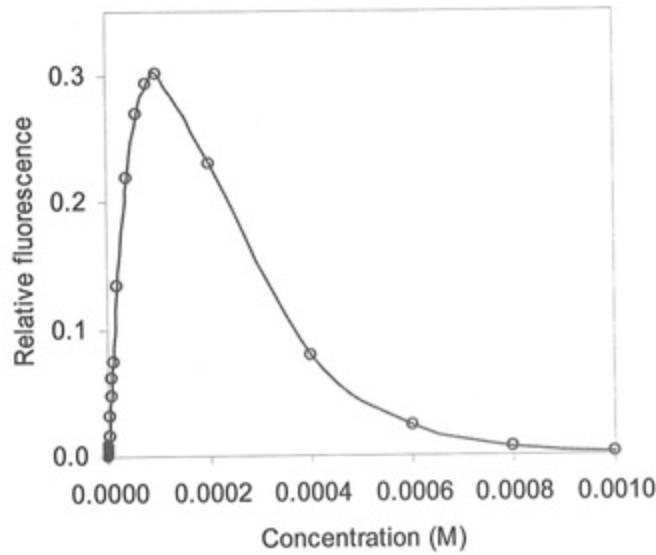
- 17-26.** In Rayleigh scattering, electrons in molecules oscillate at the frequency of incoming radiation and emit that same frequency in all directions. The time scale is  $\sim 10^{-15} \text{ s}$  for visible light. In Raman scattering, molecules extract a quantum of vibrational energy from incoming light and scatter light with less energy than the incoming light. Again, the time scale is  $\sim 10^{-15} \text{ s}$  for visible light. Fluorescence occurs in  $10^{-8}$  to  $10^{-4} \text{ s}$ , which is  $10^7$  to  $10^{11}$  times longer than scattering.

- 17-27.** Phosphorescence is emitted at longer wavelength than fluorescence. Absorption is at shortest wavelength.

- 17-28.** In an excitation spectrum, the exciting wavelength ( $\lambda_{\text{ex}}$ ) is varied while the detector wavelength ( $\lambda_{\text{em}}$ ) is fixed. In an emission spectrum,  $\lambda_{\text{ex}}$  is held constant and  $\lambda_{\text{em}}$  is varied. The excitation spectrum resembles an absorption spectrum because emission intensity is proportional to absorption of the exciting radiation.
- 17-29.** The spreadsheet computes relative fluorescence given by

$$\text{relative intensity} = \frac{I}{k'P_0} = 10^{-\varepsilon_{\text{ex}} b_1 c} (1 - 10^{-\varepsilon_{\text{ex}} b_2 c}) 10^{-\varepsilon_{\text{em}} b_3 c}.$$

	A	B	C
1	Anthracene fluorescence response		
2			
3	$\varepsilon_{\text{ex}} =$	9000	$M^{-1} cm^{-1}$
4	$\varepsilon_{\text{em}} =$	50	$M^{-1} cm^{-1}$
5			
6	$b_1 =$	0.3	cm
7	$b_2 =$	0.4	cm
8	$b_3 =$	0.5	cm
9			
10	Relative fluorescence		
11			
12	c (M)	$I/k'P_0$	Intensity/c
13	1.E-08	8.288E-05	8288
14	2.E-08	0.0001658	8288
15	4.E-08	0.0003314	8286
16	6.E-08	0.000497	8284
17	8.E-08	0.0006626	8282
18	1.E-07	0.0008281	8281
19	2.E-07	0.0016544	8272
20	4.E-07	0.0033019	8255
21	6.E-07	0.0049426	8238
22	8.E-07	0.0065764	8221
23	1.E-06	0.0082034	8203
24	2.E-06	0.0162369	8118
25	4.E-06	0.0318052	7951
26	6.E-06	0.0467266	7788
27	8.E-06	0.0610222	7628
28	1.E-05	0.0747124	7471
29	2.E-05	0.1347552	6738
30	4.E-05	0.2195664	5489
31	6.E-05	0.2689283	4482
32	8.E-05	0.2934519	3668
33	1.E-04	0.300872	3009
34	2.E-04	0.2307768	1154
35	4.E-04	0.0783318	196
36	6.E-04	0.0230136	38
37	8.E-04	0.0065982	8
38	1.E-03	0.0018832	2



Fluorescence increases with concentration and then decreases because of self-absorption. Most of the absorption occurs at the excitation wavelength, and a little comes at the emission wavelength. Column C of the spreadsheet gives the relative fluorescence intensity divided by concentration. If intensity were proportional to concentration, then column C would be constant. We see that it is constant at low concentration, and falls by ~5% at ~5  $\mu M$ . The calibration curve in the text goes up to 0.6  $\mu M$ , which is in the linear range.

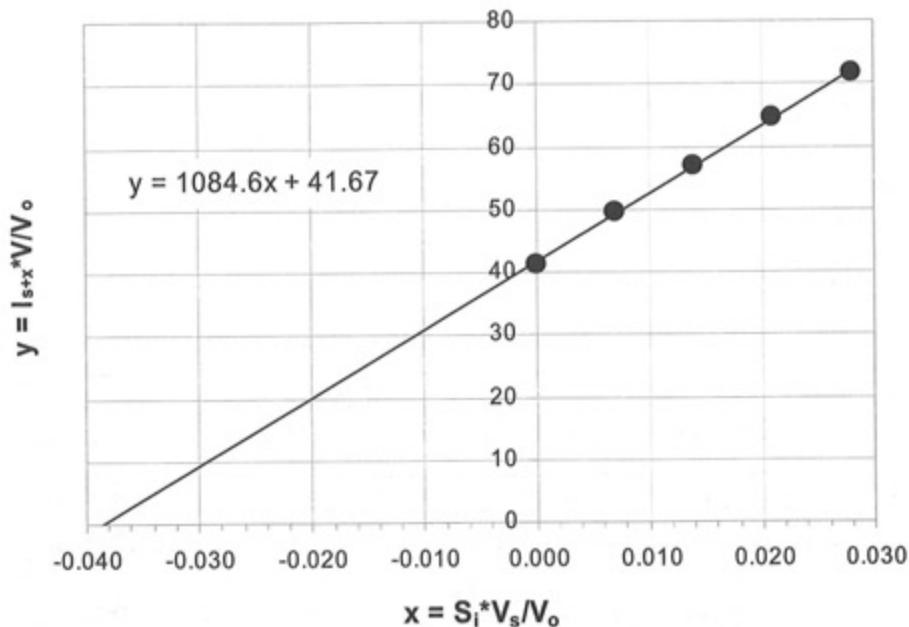
17-30. The equation for standard addition is

$$I_{S+X} \left( \frac{V}{V_0} \right) = I_X + \frac{I_X}{[X]_i} [S]_i \left( \frac{V_s}{V_0} \right)$$

Function to plot  
 on y-axis                  Function to plot  
 on x-axis

where  $V_0$  is the volume of unknown in the cuvet (2.00 mL),  $V_s$  is the volume of standard added (0 to 40  $\mu$ L),  $V$  is the total volume of unknown plus added standard,  $[S]_i$  is the initial concentration of standard (1.40  $\mu$ g Se/mL),  $[X]_i$  is the initial concentration of unknown in the 2.00-mL solution,  $I_X$  is the fluorescence intensity from the unknown, and  $I_{S+X}$  is the fluorescence intensity from the unknown plus standard addition. We make a graph of  $I_{S+X} V/V_0$  versus  $[S]_i V_s/V_0$  in the following spreadsheet.

	A	B	C	D	E	F
1	Standard Addition Variable Volume Least-Squares Spreadsheet					
2						
3	$V_0$ (mL) =	$V_s$ (mL) =		x		y
4	2.00	volume				
5	$[S]_i$ ( $\mu$ g/mL) =	standard	Total volume	x-axis function	$I(s+x) =$	y-axis function
6	1.40	added	$V = V_0 + V_s$	$S_i * V_s / V_0$	signal	$I(s+x) * V / V_0$
7		0.0000	2.000	0.00000	41.4	41.4
8		0.0100	2.010	0.00700	49.2	49.4
9		0.0200	2.020	0.01400	56.4	57.0
10		0.0300	2.030	0.02100	63.8	64.8
11		0.0400	2.040	0.02800	70.3	71.7
12						
13	<code>B16:D18 = LINEST(F7:F11,D7:D11,TRUE,TRUE)</code>					
14						
15	LINEST output:					
16	m	1084.6	41.670	b		
17	$s_m$	14.9	0.255	$s_b$		
18	$R^2$	0.9994	0.330	$s_y$		
19	x-intercept					
20	= -b/m =	-0.03842				
21						
22	n =	5	B22 = COUNT(B7:B11)			
23	Mean y =	56.8546	B23 = AVERAGE(F7:F11)			
24	$\sum (x_i - \text{mean } x)^2 =$	0.00049	B24 = DEVSQ(D7:D11)			
25						
26	Std deviation of					
27	x-intercept =	0.000732				
28	<code>B27 = (C18/ABS(B16))*SQRT((1/B22) + B23^2/(B16^2*B24))</code>					



The  $x$ -intercept is found from the equation of the straight line by setting  $y = 0$ :  
 $0 = 1084.6x + 41.67 \Rightarrow x = -0.038\ 42$ . The concentration of Se in the unknown is  $0.038\ 42\ \mu\text{g/mL}$ . All Se from  $0.108\ \text{g}$  of Brazil nuts was dissolved in  $10.0\ \text{mL}$  of solvent, which contained  $(10.0\ \text{mL})(0.038\ 42\ \mu\text{g/mL}) = 0.384\ 2\ \mu\text{g Se}$ . The wt% Se in the nuts is  $100 \times (0.384\ 2 \times 10^{-6}\ \text{g}/0.108\ \text{g}) = 3.56 \times 10^{-4}$  wt%.

The standard deviation of the  $x$ -intercept is

$$\text{Standard deviation of } x\text{-intercept} = \frac{s_y}{|m|} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{m^2 \sum(x_i - \bar{x})^2}}$$

where  $s_y$  is the standard deviation of  $y$ ,  $m$  is the slope,  $n$  is the number of data points ( $= 5$ ),  $\bar{y}$  is the mean value of  $y$  for the 5 points,  $x_i$  are individual values of  $x$ , and  $\bar{x}$  is the mean value of  $x$  for the 5 points. Cell B27 of the spreadsheet gives a standard deviation of  $0.000\ 732$  for the  $x$ -intercept.

The relative uncertainty in the intercept is  $0.000\ 732/0.038\ 42 = 1.91\%$ . This is the relative uncertainty in wt% Se if other sources of error are insignificant.

Uncertainty in wt% =  $(0.0191)(3.56 \times 10^{-4}\ \text{wt}\%) = 6.8 \times 10^{-6}\ \text{wt}\%$ . Answer =  $3.56 (\pm 0.068) \times 10^{-4}\ \text{wt}\%$ .

The confidence interval is  $\pm t \times (\text{standard deviation})$  where  $t$  is Student's  $t$  (Table 4-2) for  $n - 2 = 3$  degrees of freedom. The 95% confidence interval is  $\pm(3.182)(0.068 \times 10^{-4}\ \text{wt}\%) = \pm 0.22 \times 10^{-4}\ \text{wt}\%$ . The value  $t = 3.182$  was taken from Table 4-2 for 3 degrees of freedom. Answer =  $3.56 (\pm 0.22) \times 10^{-4}\ \text{wt}\%$ .

## CHAPTER 18

### APPLICATIONS OF SPECTROPHOTOMETRY

- 18-1.** Putting  $b = 0.100 \text{ cm}$  into the determinants gives

$$[X] = \frac{\begin{vmatrix} 0.233 & 387 \\ 0.200 & 642 \\ 1640 & 387 \\ 399 & 642 \end{vmatrix}}{\begin{vmatrix} 1640 & 0.233 \\ 399 & 0.200 \\ 1640 & 387 \\ 399 & 642 \end{vmatrix}} = 8.03 \times 10^{-5} \text{ M} \quad [Y] = \frac{\begin{vmatrix} 1640 & 0.233 \\ 399 & 0.200 \\ 1640 & 387 \\ 399 & 642 \end{vmatrix}}{\begin{vmatrix} 1640 & 0.233 \\ 399 & 0.200 \\ 1640 & 387 \\ 399 & 642 \end{vmatrix}} = 2.62 \times 10^{-4} \text{ M}$$

The spreadsheet solution looks like this, with answers in column F:

	A	B	C	D	E	F	G
1	Analysis of a mixture by spreadsheet matrix operations						
2							
3	Wavelength	Coefficient Matrix		Absorbance	Concentrations		
4				of unknown		in mixture	
5	272	1640	387	0.233		8.034E-05	<-[X]
6	327	399	642	0.2		2.616E-04	<-[Y]
7		K		A		C	

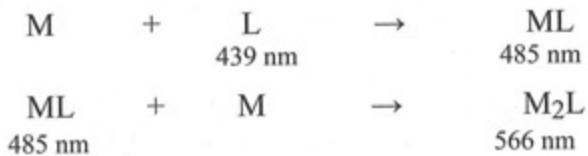
- 18-2.**

	A	B	C	D	E	F	G	H
1	Analysis of a Mixture When You Have More Data Points than Components of the Mixture							
2				Measured			Calculated	
3				Absorbance			Absorb-	
4	Wave-	Absorbance of Standard		of Mixture	Molar Absorptivity		Aabsorb-	
5	length	MnO <sub>4</sub>	Cr <sub>2</sub> O <sub>7</sub>	Am	MnO <sub>4</sub>	Cr <sub>2</sub> O <sub>7</sub>	Acalc	[Acalc-Am] <sup>2</sup>
6	266	0.042	0.410	0.766	420.0	4100.0	0.7650	1.017E-06
7	288	0.082	0.283	0.571	820.0	2830.0	0.5723	1.763E-06
8	320	0.168	0.158	0.422	1680.0	1580.0	0.4217	1.132E-07
9	350	0.125	0.318	0.672	1250.0	3180.0	0.6706	2.050E-06
10	360	0.056	0.181	0.366	560.0	1810.0	0.3690	9.106E-06
11							sum =	1.405E-05
12	Standards	Concentrations in the mixture						
13	[Mn](M)=	(to be found by Solver)						
14	1.00E-04		[MnO <sub>4</sub> ] =	8.356E-05				
15	[Cr](M)=		[Cr <sub>2</sub> O <sub>7</sub> ] =	1.780E-04				
16	1.00E-04							
17	Pathlength	E6 = B6/(\$A\$19*\$A\$14)						
18	(cm) =	F6 = C6/(\$A\$19*\$A\$16)						
19	1.000	G6 = E6*\$A\$19*\$D\$14+F6*\$A\$19*\$D\$15						
20		H6 = (G6-D6) <sup>2</sup>						

- 18-3.** If the spectra of two compounds with a constant total concentration cross at any wavelength, all mixtures with the same total concentration will go through that same point, called an isosbestic point. The appearance of isosbestic points in a

chemical reaction is good evidence that we are observing one main species being converted to one other major species.

- 18-4.** As  $\text{VO}^{2+}$  is added (traces 1-9), the peak at 439 decreases and a new one near 485 nm develops, with an isosbestic point at 457 nm. When  $\text{VO}^{2+}/\text{xylene orange} > 1$ , the peak near 485 nm decreases and a new one at 566 nm grows in, with an isosbestic point at 528 nm. This sequence is logically interpreted by the sequence



where M is vanadyl ion and L is xylenol orange. The structure of xylenol orange in Table 11-3 shows that it has metal-binding groups on both ends of the molecule, and could form an  $M_2L$  complex.

- 18-5.** Convert  $T$  to  $A$  ( $= -\log T$ ) and then convert  $A$  to  $\varepsilon$  ( $= A/bc = A/[(0.005)(0.01)]$ )

	Absorbance		$\varepsilon (\text{M}^{-1} \text{ cm}^{-1})$	
	2022	1993 $\text{cm}^{-1}$	2022	1993 $\text{cm}^{-1}$
A	0.5086	0.09854	A	10170
B	0.01144	0.6990	B	228.8

For the mixture,  $A_{2022} = -\log(0.340) = 0.4685$  and  $A_{1993} = -\log(0.383) = 0.4168$ . Equation 18-6 gives  $[A] = 9.11 \times 10^{-3}$  M and  $[B] = 4.68 \times 10^{-3}$  M.

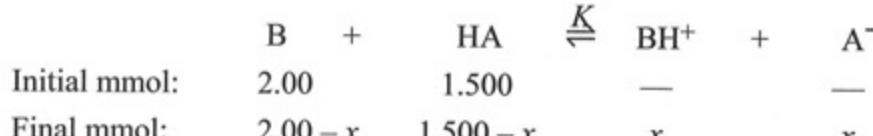
18-6.

	A	B	C	D	E	F	G	H							
1	Solving Simultaneous Linear Equations with Excel Matrix Operations														
2															
3	Wavelength	Coefficient Matrix			Absorbance	Concentrations									
4		TB	STB	MTB	of unknown	in mixture									
5	455	4800	11100	18900	0.412	1.2194E-05	<-[TB]								
6	485	7350	11200	11800	0.350	9.2953E-06	<-[STB]								
7	545	36400	13900	4450	0.632	1.3243E-05	<-[MTB]								
8		K			A	C									
9															
10	1. Highlight block of blank cells required for solution (G5:G7)														
11	2. Type the formula "= MMULT(MINVERSE(B5:D7),E5:E7)"														
12	3. Press CONTROL+SHIFT+ENTER on a PC or COMMAND+RETURN on a Mac														
13	4. The answer appears in cells G5:G7														

## 18-7.

	A	B	C	D	E	F	G	H	I
1	Solving 4 Simultaneous Linear Equations with Excel Matrix Operations								
2	Wave-								
3	length	Coefficient Matrix		Ethyl-	Absorbance		Conc. in		
4	(μm)	p-xylene	m-xylene	o-xylene	benzene	of unknown	mixture		
5	12.5	1.5020	0.0514	0	0.0408	0.1013	0.0627	p-xylene	
6	13.0	0.0261	1.1516	0	0.0820	0.09943	0.0795	m-xylene	
7	13.4	0.0342	0.0355	2.532	0.2933	0.2194	0.0759	o-xylene	
8	14.3	0.0340	0.0684	0	0.3470	0.03396	0.0761	Ethylbz	
9		K			A		C		
10									
11	1. Highlight block of blank cells required for solution (H5:H8)								
12	2. Type the formula "= MMULT(MINVERSE(B5:E8),F5:F8)"								
13	3. Press CONTROL+SHIFT+ENTER on a PC or COMMAND+RETURN on a Mac								
14	4. The answer appears in cells H5:H8								

- 18-8. The quantity of HIn is small compared to aniline and sulfanilic acid. Calling aniline B and sulfanilic acid HA, we can write



$$K = \frac{K_a K_b}{K_w} = \frac{(10^{-3.232})(K_w/10^{-4.601})}{K_w} = 23.39$$

$$\frac{x^2}{(2.00 - x)(1.500 - x)} = 23.39 \Rightarrow x = 1.372 \text{ mmol}$$

$$\text{pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 4.601 + \log \frac{2.00 - 1.372}{1.372} = 4.26$$

For HIn we can write:

$$\text{absorbance} = 0.110 = (2.26 \times 10^4)(5.00) [\text{HIn}] + (1.53 \times 10^4)(5.00)[\text{In}^-].$$

Substituting  $[\text{HIn}] = 1.23 \times 10^{-6} - [\text{In}^-]$  gives  $[\text{In}^-] = 7.94 \times 10^{-7}$  and

$[\text{HIn}] = 4.36 \times 10^{-7}$ . The Henderson-Hasselbalch equation for HIn is therefore

$$\text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \Rightarrow 4.26 = \text{p}K_{\text{HIn}} + \log \frac{7.94 \times 10^{-7}}{4.36 \times 10^{-7}} \Rightarrow \text{p}K_{\text{HIn}} = 4.00.$$

- 18-9. (a)  $A_{620} = \epsilon_{620}^{\text{HIn}^-} b[\text{HIn}^-] + \epsilon_{620}^{\text{In}^{2-}} b[\text{In}^{2-}]$

$$A_{434} = \epsilon_{434}^{\text{HIn}^-} b[\text{HIn}^-] + \epsilon_{434}^{\text{In}^{2-}} b[\text{In}^{2-}]$$

The solution of these two equations is given by Equation 18-6 in the text:

$$[\text{HIn}^-] = \frac{1}{D} (A_{620} \epsilon_{434}^{\text{In}^{2-}} b - A_{434} \epsilon_{620}^{\text{In}^{2-}} b)$$

$$[\text{In}^{2-}] = \frac{1}{D} (A_{434}\epsilon_{620}^{\text{HIn}^-} b - A_{620}\epsilon_{434}^{\text{HIn}^-} b)$$

$$\text{where } D = b^2 (\epsilon_{620}^{\text{HIn}^-} \epsilon_{434}^{\text{In}^{2-}} - \epsilon_{620}^{\text{In}^{2-}} \epsilon_{434}^{\text{HIn}^-})$$

Dividing the expression for  $[\text{In}^{2-}]$  by the expression for  $[\text{HIn}^-]$  gives

$$\frac{[\text{In}^{2-}]}{[\text{HIn}^-]} = \frac{A_{434}\epsilon_{620}^{\text{HIn}^-} - A_{620}\epsilon_{434}^{\text{HIn}^-}}{A_{620}\epsilon_{434}^{\text{In}^{2-}} - A_{434}\epsilon_{620}^{\text{In}^{2-}}}$$

Dividing numerator and denominator on the right side by  $A_{434}$  gives

$$\frac{[\text{In}^{2-}]}{[\text{HIn}^-]} = \frac{\epsilon_{620}^{\text{HIn}^-} - R_A \epsilon_{434}^{\text{HIn}^-}}{R_A \epsilon_{434}^{\text{In}^{2-}} - \epsilon_{620}^{\text{In}^{2-}}} = \frac{R_A \epsilon_{434}^{\text{HIn}^-} - \epsilon_{620}^{\text{HIn}^-}}{\epsilon_{620}^{\text{In}^{2-}} - R_A \epsilon_{434}^{\text{In}^{2-}}}$$

- (b) Mass balance for indicator:  $[\text{HIn}^-] + [\text{In}^{2-}] = F_{\text{In}}$

Dividing both sides by  $[\text{HIn}^-]$  gives

$$\frac{[\text{HIn}^-]}{[\text{HIn}^-]} + \frac{[\text{In}^{2-}]}{[\text{HIn}^-]} = \frac{F_{\text{In}}}{[\text{HIn}^-]} \Rightarrow 1 + R_{\text{In}} = \frac{F_{\text{In}}}{[\text{HIn}^-]} \Rightarrow [\text{HIn}^-] = \frac{F_{\text{In}}}{R_{\text{In}} + 1}$$

Acid dissociation constant of indicator:

$$K_{\text{In}} = \frac{[\text{In}^{2-}][\text{H}^+]}{[\text{HIn}^-]}$$

Substituting  $F_{\text{In}}/(R_{\text{In}} + 1)$  for  $[\text{HIn}^-]$  gives

$$K_{\text{In}} = \frac{[\text{In}^{2-}][\text{H}^+](R_{\text{In}} + 1)}{F_{\text{In}}} \Rightarrow [\text{In}^{2-}] = \frac{K_{\text{In}} F_{\text{In}}}{[\text{H}^+](R_{\text{In}} + 1)}$$

- (c) Equation A in the problem defines  $R_{\text{In}}$  as  $[\text{In}^{2-}]/[\text{HIn}^-]$ . So,

$$K_{\text{In}} = \frac{[\text{In}^{2-}][\text{H}^+]}{[\text{HIn}^-]} = R_{\text{In}}[\text{H}^+] \Rightarrow [\text{H}^+] = K_{\text{In}}/R_{\text{In}}$$

- (d) From the acid dissociation reaction of carbonic acid, we can write

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2(aq)]} \Rightarrow [\text{HCO}_3^-] = \frac{K_1[\text{CO}_2(aq)]}{[\text{H}^+]}$$

From the acid dissociation reaction of bicarbonate, we can write

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \Rightarrow [\text{CO}_3^{2-}] = \frac{K_2[\text{HCO}_3^-]}{[\text{H}^+]}$$

Substituting in the expression for  $[\text{HCO}_3^-]$  gives

$$[\text{CO}_3^{2-}] = \frac{K_1 K_2 [\text{CO}_2(aq)]}{[\text{H}^+]^2}$$

- (e) Charge balance:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HIn}^-] + 2[\text{In}^{2-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

$$F_{Na} + [H^+] = \frac{K_w}{[H^+]} + \frac{F_{In}}{R_{In} + 1} + 2 \frac{K_{In} F_{In}}{[H^+] (R_{In} + 1)} + \frac{K_1 [CO_2(aq)]}{[H^+]} + 2 \frac{K_1 K_2 [CO_2(aq)]}{[H^+]^2}$$

- (f) From part (c) we know that  $[H^+] = K_{In}/R_{In}$ . We calculate  $R_{In}$  from part (a):

$$R_{In} = \frac{R_A \epsilon_{434}^{HIn^-} - \epsilon_{620}^{HIn^-}}{\epsilon_{620}^{In^{2-}} - R_A \epsilon_{434}^{In^{2-}}} = \frac{(2.84)(8.00 \cdot 10^3) - (0)}{(1.70 \cdot 10^4) - (2.84)(1.90 \cdot 10^3)} = 1.958$$

$$[H^+] = K_{In}/R_{In} = (2.0 \times 10^{-7})/1.958 = 1.02 \times 10^{-7} M$$

Substituting this value of  $[H^+]$  into the mass balance in part (e) produces an equation in which the only unknown is  $[CO_2(aq)]$ :

$$\begin{aligned} F_{Na} + [H^+] &= \frac{K_w}{[H^+]} + \frac{F_{In}}{R_{In} + 1} + 2 \frac{K_{In} F_{In}}{[H^+] (R_{In} + 1)} + \frac{K_1 [CO_2(aq)]}{[H^+]} + 2 \frac{K_1 K_2 [CO_2(aq)]}{[H^+]^2} \\ 92.0 \times 10^{-6} + 1.02 \times 10^{-7} &= \frac{(6.7 \times 10^{-15})}{(1.02 \times 10^{-7})} + \frac{(50.0 \times 10^{-6})}{1.958 + 1} + 2 \frac{(2.0 \times 10^{-7})(50.0 \times 10^{-6})}{(1.02 \times 10^{-7})(1.958 + 1)} \\ &\quad + \frac{(3.0 \times 10^{-7})[CO_2(aq)]}{(1.02 \times 10^{-7})} + 2 \frac{(3.0 \times 10^{-7})(3.3 \times 10^{-11})[CO_2(aq)]}{(1.02 \times 10^{-7})^2} \\ 9.21 \times 10^{-5} &= 6.56 \times 10^{-8} + 1.69 \times 10^{-5} + 6.62 \times 10^{-5} + \\ &\quad + 2.94 [CO_2(aq)] + 0.0019 [CO_2(aq)] \\ \Rightarrow [CO_2(aq)] &= 3.04 \times 10^{-6} M \end{aligned}$$

- (g) The ions in solution are  $Na^+$ ,  $HIn^-$ ,  $In^{2-}$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $H^+$ , and  $OH^-$ . We know that  $[Na^+] = 92.0 \mu M$  and  $[H^+] = 0.10 \mu M$ . If the total cation charge is  $92.1 \mu M$ , the total anion charge must be  $92.1 \mu M$ , and the ionic strength must be  $\sim 92 \mu M \approx 10^{-4} M$ . (The ionic strength is not exactly  $92.1 \mu M$  because some anions have a charge of -2, which will increase the ionic strength from  $92.1 \mu M$ .) An ionic strength of  $10^{-4} M$  is low enough that the activity coefficients are close to 1.00.

We can calculate the exact ionic strength from the following expressions derived above:

$$[OH^-] = \frac{K_w}{[H^+]} = 0.07 \mu M$$

$$[HIn^-] = \frac{F_{In}}{R_{In} + 1} = 16.9 \mu M; [In^{2-}] = \frac{K_{In} F_{In}}{[H^+] (R_{In} + 1)} = 33.1 \mu M$$

$$[HCO_3^-] = \frac{K_1 [CO_2(aq)]}{[H^+]} = 2.94 [CO_2(aq)] = 8.9 \mu M$$

$$[\text{CO}_3^{2-}] = \frac{K_1 K_2 [\text{CO}_2(aq)]}{[\text{H}^+]^2} = 0.0019 [\text{CO}_2(aq)] = 0.003 \mu\text{M}$$

$$\text{Ionic strength} = \frac{1}{2} \sum_i c_i z_i^2 =$$

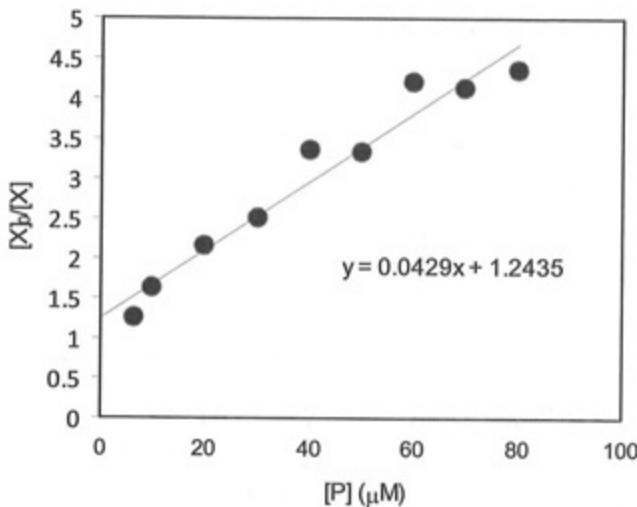
$$\frac{1}{2} \left\{ [\text{Na}^+] \cdot 1^2 + [\text{H}^+] \cdot 1^2 + [\text{OH}^-] \cdot 1^2 + [\text{In}^{2-}] \cdot 2^2 + [\text{HCO}_3^-] \cdot 1^2 + [\text{CO}_3^{2-}] \cdot 2^2 \right\} \\ = 125 \mu\text{M}$$

- 18-10.** The Scatchard plot is a graph of  $[\text{PX}]/[\text{X}]$  versus  $[\text{PX}]$ . Data in the following spreadsheet are plotted in the figure in the textbook. The slope is  $-4.0 \times 10^9 \text{ M}^{-1}$ , giving a binding constant  $K = 4.0 \times 10^9 \text{ M}^{-1}$ . The fraction of saturation in column E is  $S = [\text{PX}]/P_0$ , where  $P_0 = 10.0 \text{ nM}$ .  $S$  ranges from 0.29 to 0.84.

	A	B	C	D	E	F
1	Data for Scatchard plot				$P_0 =$	10 nM
2					Fraction of saturation	
3	$[\text{PX}] (\text{nM})$	$[\text{X}] (\text{nM})$	$[\text{PX}]/[\text{X}]$		$= [\text{PX}]/P_0$	
4	2.87	0.120	24.0		0.29	
5	3.80	0.192	19.8		0.38	
6	4.66	0.296	15.7		0.47	
7	5.54	0.450	12.3		0.55	
8	6.29	0.731	8.61		0.63	
9	6.77	1.22	5.54		0.68	
10	7.52	1.50	5.02		0.75	
11	8.45	3.61	2.34		0.84	

- 18-11. (a)**

	A	B	C	D	E	F	G
1	Estradiol - Albumin Scatchard Plot						
2	abscissa	ordinate					
3	$P (\text{nM})$	$X_0/X$		Highlight cells B15:C17			
4	6.3	1.26		Type			
5	10.0	1.62		$=\text{LINEST}(B4:B12,A4:A12,\text{TRUE},\text{TRUE})$			
6	20.0	2.16		Press CTRL+SHIFT+ENTER (on PC)			
7	30.0	2.51		Press COMMAND+RETURN (on Mac)			
8	40.0	3.34					
9	50.0	3.33		Student's t (95% confidence,			
10	60.0	4.19		7 degrees of freedom) =			
11	70.0	4.13		2.364624 = $\text{TINV}(0.05, 7)$			
12	80.0	4.36		95% confidence interval =			
13				0.008248 = $t^* s_m = D11 * B16$			
14	LINEST output						
15	m	0.042885	1.243476	b			
16	$s_m$	0.003488	0.166224	$s_b$			
17	$R^2$	0.955742	0.259413	$s_y$			



The slope is 0.042 88 with a standard deviation of 0.003 49 in cells B15 and B16. However, the units on the abscissa are  $\mu\text{M}$ , so the slope is really  $(0.042\ 88 \pm 0.003\ 49)/10^{-6}\ \text{M}^{-1} = (4.288 \pm 0.349) \times 10^4\ \text{M}^{-1}$ . To find the 95% confidence interval, we need Student's  $t$  for  $9 - 2 = 7$  degrees of freedom, which is  $t = 2.365$  in cell D11. The 95% confidence interval is  $(0.349)(2.365) = 0.825$ . The final result is  $K = (4.3 \pm 0.8) \times 10^4\ \text{M}^{-1}$ .

- (b) Estradiol is X. The quotient  $[X]_0/[X]$  is 1.26 at the first point and 4.36 at the last point. The fraction of free estradiol is  $[X]/[X]_0 = 1/1.26 = 0.79$  at the first point and  $1/4.36 = 0.23$  at the last point. The fraction of bound estradiol is  $1 - 0.79 = 0.21$  at the first point and  $1 - 0.23 = 0.77$  at the last point.

- 18-12.** (a) We will make the substitutions  $[\text{complex}] = A/\epsilon$  and  $[\text{I}_2] = [\text{I}_2]_{\text{tot}} - [\text{complex}]$  in the equilibrium expression:

$$K = \frac{[\text{complex}]}{[\text{I}_2][\text{mesitylene}]} = \frac{A/\epsilon}{([\text{I}_2]_{\text{tot}} - [\text{complex}])[\text{mesitylene}]}$$

$$K[\text{I}_2]_{\text{tot}} - K[\text{complex}] = \frac{A}{\epsilon[\text{mesitylene}]}$$

Making the substitution  $[\text{complex}] = A/\epsilon$  once more on the left-hand side gives

$$K[\text{I}_2]_{\text{tot}} - \frac{KA}{\epsilon} = \frac{A}{\epsilon[\text{mesitylene}]}$$

Multiplying both sides by  $\epsilon$  and dividing by  $[\text{I}_2]_{\text{tot}}$  gives the desired result:

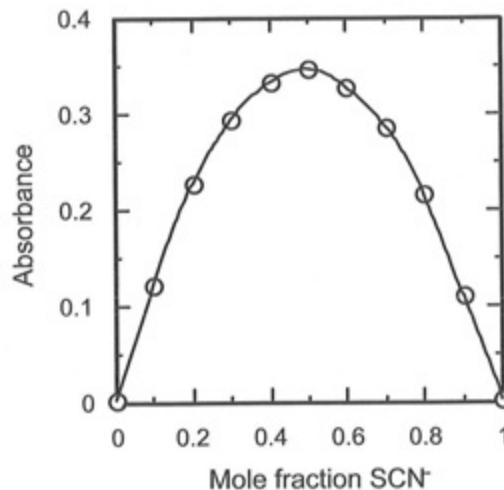
$$\epsilon K - \frac{KA}{[\text{I}_2]_{\text{tot}}} = \frac{A}{[\text{I}_2]_{\text{tot}}[\text{mesitylene}]}$$

- (b) The graph of  $A/([mesitylene][I_2]_{tot})$  versus  $A/[I_2]_{tot}$  is an excellent straight line with a slope of  $-0.464$  and an intercept of  $4.984 \times 10^3$ . Since slope =  $-K$ , the equilibrium constant is  $0.464$ . The molar absorptivity is  $\epsilon = \text{intercept}/K \Rightarrow \epsilon = 1.074 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .

- 18-13.** After running Solver, the average value of  $K$  in cell E10 is  $0.464$  and  $\epsilon = 1.073 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . The Scatchard plot in the previous problem gave  $K = 0.464$  and  $\epsilon = 1.074 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .

	A	B	C	D	E
1	Equilibrium constant for reaction of $I_2$ with mesitylene				
2					
3	[Mesitylene] (M)	[ $I_2$ ]tot (M)	A	[Complex] = A/ $\epsilon$	$K_{eq}$
4	1.6900	7.82E-05	0.369	3.437E-05	0.46443
5	0.9218	2.56E-04	0.822	7.657E-05	0.46349
6	0.6338	3.22E-04	0.787	7.331E-05	0.46439
7	0.4829	3.57E-04	0.703	6.549E-05	0.46473
8	0.3900	3.79E-04	0.624	5.813E-05	0.46480
9	0.3271	3.93E-04	0.556	5.179E-05	0.46353
10				Average =	0.46423
11	Guess for $\epsilon$ :			Standard Dev =	0.00058
12	1.073E+04			Stdev/Average =	0.00125
13					
14	D4 = C4/\$A\$12				
15	E4 = D4/(A4*(B4-D4)) = [complex]/([Mesitylene][Free $I_2$ ])				
16	E10 = AVERAGE(E4:E9)				
17	E11 = STDEV(E4:E9)				
18	E12 = E11/E10				
19	Use Solver to vary $\epsilon$ (cell A12) until cell E12 is minimized				

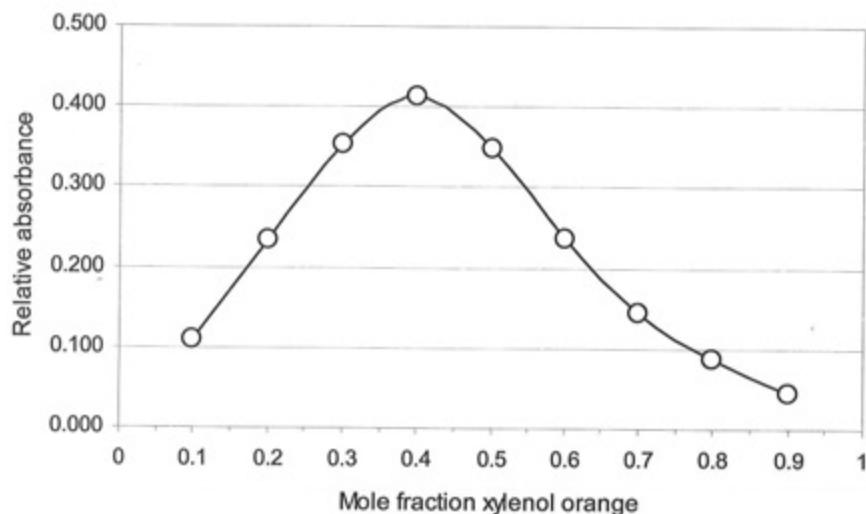
- 18-14.** (a) Maximum absorbance occurs at  $X_{SCN^-} = 0.500$   
 $\Rightarrow$  stoichiometry = 1 : 1 ( $n = 1$ )



- (b) The curved maximum indicates that the equilibrium constant is not very large.
- (c) The different acid concentrations give both solutions the same ionic strength ( $= 16.0 \text{ mM}$ ).
- 18-15.** The Job plot peak is at a xylenol orange mole fraction of 0.40, suggesting the stoichiometry  $(\text{xylene orange})_2\text{Zr}_3$  which has a mole fraction of

$$\frac{\text{xylene orange}}{\text{xylene orange} + \text{Zr(IV)}} = \frac{2}{2+3} = 0.4$$

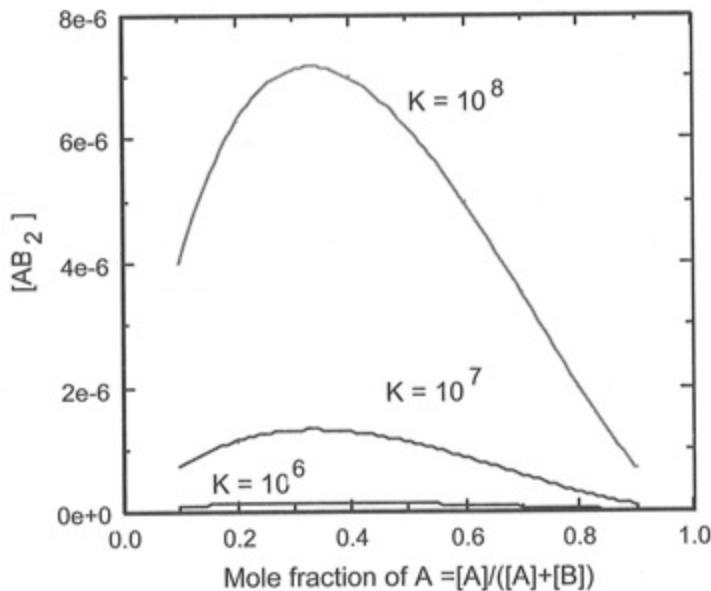
The plot could have been improved by obtaining data points at mole fractions of 0.35 and 0.45 to verify the location of the maximum.



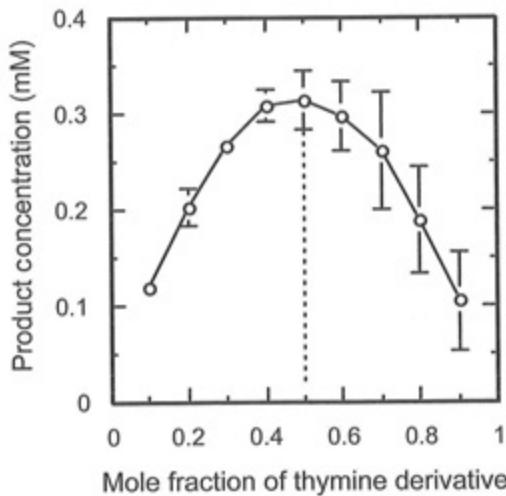
- 18-16.** (a) Here are the results:

[A] <sub>total</sub>	[B] <sub>total</sub>	[AB <sub>2</sub> ]			Mole fraction A
		$K = 10^6$	$K = 10^7$	$K = 10^8$	
1e-5	9e-5	8.01e-8	7.27e-7	4.02e-6	0.1
2e-5	8e-5	1.26e-7	1.14e-6	6.26e-6	0.2
2.5e-5	7.5e-5	1.39e-7	1.25e-6	6.83e-6	0.25
3e-5	7e-5	1.45e-7	1.30e-6	7.12e-6	0.3
3.33e-5	6.67e-5	1.46e-7	1.31e-6	7.17e-6	0.333
4e-5	6e-5	1.42e-7	1.28e-6	6.99e-6	0.4
5e-5	5e-5	1.23e-7	1.12e-6	6.20e-6	0.5
6e-5	4e-5	9.49e-8	8.66e-7	4.97e-6	0.6
7e-5	3e-5	6.24e-8	5.78e-7	3.51e-6	0.7
8e-5	2e-5	3.18e-8	3.00e-7	2.00e-6	0.8
9e-5	1e-5	8.97e-9	8.68e-8	6.70e-7	0.9

- (b) The maximum occurs at a mole fraction of  $A = 1/3$ , since the stoichiometry is 1:2. The greater the equilibrium constant, the greater the extent of reaction and the steeper the curve. When the equilibrium constant is too small, the curve is so shallow that it does not at all resemble two intersecting lines.



- 18-17.** The mole fraction of thymine varies from 0.10 to 0.90 in increments of 0.10 as we go down the table. Job's plot reaches a broad peak at a mole fraction of 0.50, which is consistent with 1:1 complex formation. Job's plot gives us no information on the structure of the product except for its stoichiometry.



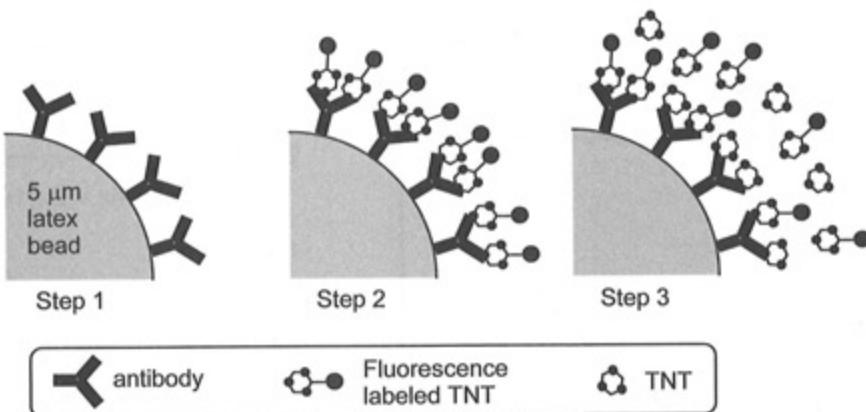
- 18-18.** In *flow injection analysis*, unknown is injected into a continuously flowing stream that could contain a reagent which reacts with analyte. Alternatively, one or more reagents can be added to the flow downstream of sample injection. The sample and reagents travel through a coil in which mixing and reaction occur. Absorbance or fluorescence or some other property of the flowing stream is measured in the detector. In general, reactants and products do not reach equilibrium in flow injection analysis. The precision of the result depends on executing the same process in a very repeatable manner.

In *sequential injection*, unknown and one or more reagents are sequentially injected under computer control into a holding coil. There is not a continuous flow. At an appropriate time, flow is reversed and the mixture is directed through a detector. As in flow injection analysis, equilibrium is generally not reached and precision depends on repeatability of the sequence of steps.

The principal difference between flow injection and sequential injection is that there is continuous flow in the former and there is a sequence of steps without continuous flow in the latter. Sequential injection uses less reagent and generates less waste than flow injection. Sequential injection is called “lab-on-a-valve” because sample, reagents, and product all flow through a central multi-port valve.

- 18-19.** Each molecule of analyte bound to antibody 1 also binds one molecule of antibody 2 that is linked to one enzyme molecule. Each enzyme molecule catalyzes many cycles of reaction in which a colored or fluorescent product is created. Therefore, many product molecules are created for every analyte molecule.
- 18-20.** In time-resolved emission measurements, the short-lived background fluorescence decays to near zero prior to recording emission from the lanthanide ion. By reducing background signal, the signal-to-noise ratio is increased. Also, the wavelength of the lanthanide emission is longer than the wavelength of much of the background emission.

18-21.



In Step 1, antibodies for TNT are attached to latex beads. In Step 2, the antibody is saturated with a fluorescent derivative of TNT. Excess fluorescent derivative is removed. In Step 3, the beads are incubated with TNT, which displaces some fluorescent derivative from binding sites on the antibodies. The suspension of beads is then injected into the flow cytometer. As each bead passes in front of the detector, it is excited by a laser and its fluorescence is measured. The graph in the textbook shows median bead fluorescence versus TNT concentration in a series of standards. The more TNT in the standard, the less fluorescence remains associated with the beads.

- 18-22. The graph of  $K_{sv}$  versus pH has a plateau at low pH near  $K_{sv} \approx 100$  and a plateau at high pH near  $K_{sv} \approx 1350$ . The quencher, 2,6-dimethylphenol, is a weak acid whose  $pK_a$  is expected to be near 10. A logical interpretation is that the basic form,  $A^-$ , is a strong quencher with  $K_{sv} \approx 1350$ , and the acidic form, HA, is a weak quencher with  $K_{sv} \approx 100$ . We estimate  $pK_a$  as the midpoint in the curve at  $K_{sv} \approx (1350 - 100)/2 = 625$ . At this point,  $pH \approx 10.8$ , which is our estimate for  $pK_a$ . The literature value is 10.63.

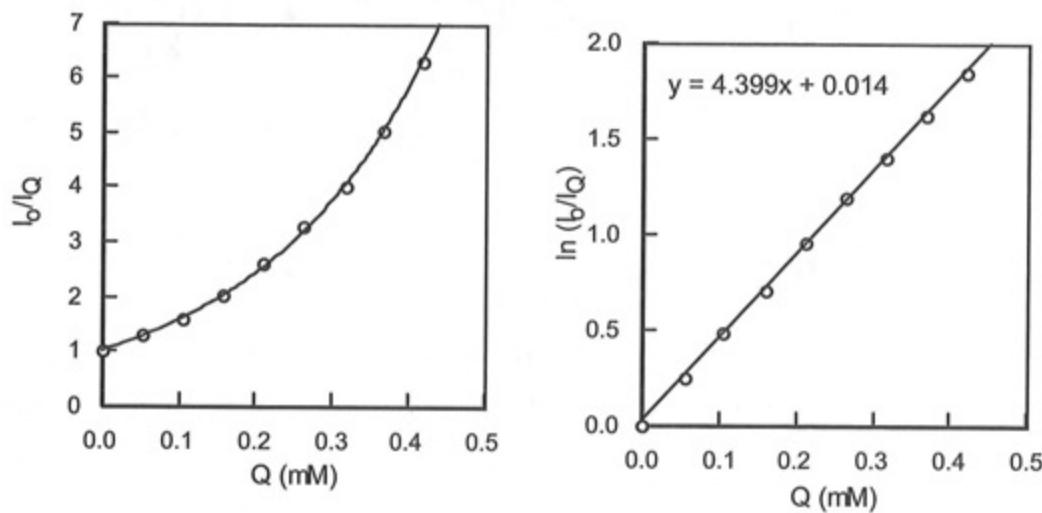
The smooth curve in the graph is a least-squares fit to the equation

$$K_{sv} = K_{sv}^{\text{HA}} \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_a} \right) + K_{sv}^{A^-} \left( \frac{K_a}{[\text{H}^+] + K_a} \right)$$

Fraction in form HA      Fraction in form  $A^-$   
 Quenching by HA      Quenching by  $A^-$

The least-squares fit gave  $K_{sv}^{\text{HA}} = 69.0 \text{ M}^{-1}$ ,  $K_{sv}^{A^-} = 1370 \text{ M}^{-1}$ , and  $pK_a = 10.78$ .

- 18-23.** (a) The following graph at the left shows that the Stern-Volmer equation is not obeyed. If it were obeyed, the graph would be linear.



- (b) The graph at the right above shows that Equation 4 is obeyed. Ideally, the intercept should be zero. The slope of the graph is  $N_{av}/([S] - [CMC])$ .

Given that  $[Q]$  was expressed in mM, we will express  $[S]$  and  $[CMC]$  in mM:  $4.399 = N_{av} / ([20.8] - [8.1]) \rightarrow N_{av} = 55.9$

- (c)  $[M] = ([S] - [CMC]) / N_{av} = ([20.8] - [8.1]) / 55.9 = 0.227 \text{ mM}$   
 $\bar{Q} = [Q]/[M] = 0.200 \text{ mM} / 0.227 \text{ mM} = 0.881 \text{ molecules per micelle}$

(d)  $P_n = \frac{\bar{Q}^n}{n!} e^{-\bar{Q}}$ . For  $n = 0$ ,  $P_0 = e^{-0.881} = 0.414$

$$P_1 = \frac{(0.881)^1}{1!} e^{-0.881} = 0.365 \quad P_2 = \frac{(0.881)^2}{2!} e^{-0.881} = 0.161$$

## CHAPTER 19

### SPECTROPHOTOMETERS

- 19-1.** The light source provides ultraviolet, visible, or infrared radiation. The monochromator selects a narrow band of wavelengths to pass on to the sample. As the experiment progresses, the monochromator scans through a desired range of wavelengths. The beam chopper is a rotating mirror that alternately directs light to the sample or reference. The sample cuvet holds the sample of interest. The reference cuvet is an identical cell containing pure solvent or a reagent blank. The mirror after the reference cuvet and the semitransparent mirror after the sample cuvet pass both beams of light through to the detector, which could be a photomultiplier tube that generates an electric current proportional to the photon irradiance. The amplifier increases the detector signal for display.
- 19-2.** An excited state of the lasing material is pumped to a high population by light, an electric discharge, or other means. Photons emitted when the excited state decays to a less populated lower state stimulate emission from other excited molecules. The stimulated emission has the same energy and phase as the incident photon. In the laser cavity, most light is retained by reflective end mirrors. Some light is allowed to escape from one end. Properties of laser light: monochromatic, bright, collimated, polarized, coherent
- 19-3.** Deuterium. Silicon carbide globar.
- 19-4.** Resolution increases in proportion to the number of grooves that are illuminated and to the diffraction order. The number of grooves can be increased with a more finely ruled grating (closer grooves) and with a longer grating. The diffraction order is optimized by appropriate choice of the blaze angle of the grating.
- Dispersion is proportional to the diffraction order and inversely proportional to the spacing between lines in the grating. The closer the lines, the greater the dispersion.
- The optimum wavelength selected by a grating is the one for which the diffraction condition  $n\lambda = d(\sin \theta + \sin \phi)$  is satisfied by specular reflection when the angle of incidence is equal to the angle of reflection ( $\alpha = \beta$ ).
- 19-5.** A filter removes higher order diffraction (different wavelengths) at the same angle as the desired diffraction.

- 19-6. Advantage - increased ability to resolve closely spaced spectral peaks.  
Disadvantage - more noise because less light reaches detector.
- 19-7. (a) A photomultiplier tube has a photosensitive cathode that emits an electron when struck by a photon. Electrons from the cathode are accelerated by a positive electric potential toward the first dynode. When an accelerated electron strikes the dynode, more electrons are emitted from the dynode. This multiplication process continues through several successive dynodes until  $\sim 10^6$  electrons are finally collected at the anode for each photon striking the photocathode. The signal is the current measured at the anode.
- (b) Each photodiode in a linear array has *p*-type silicon on a substrate of *n*-type silicon. Reverse bias draws electrons and holes away from the junction, which is a depletion region with few electrons and holes. The junction acts as a capacitor, with charge on either side of the depletion region. At the beginning of a measurement cycle, each diode is fully charged. Free electrons and holes created when radiation is absorbed in the semiconductor migrate to regions of opposite charge, partially discharging the capacitor. Charge left in each capacitor is measured at the end of a collection cycle by measuring the current needed to recharge each capacitor.
- (c) A charge coupled device is made from *p*-doped Si on an *n*-doped substrate. The structure is capped with an insulating layer of  $\text{SiO}_2$ , on top of which is a two-dimensional pattern of conducting Si electrodes. When light is absorbed in the *p*-doped region, an electron is introduced into the conduction band and a hole is left in the valence band. The electron is attracted to the region beneath the positive electrode, where it is stored. The hole migrates to the *n*-doped substrate, where it combines with an electron. Each electrode can store  $\sim 10^5$  electrons. After the desired observation time, electrons stored in each pixel of the top row of the array are moved into a serial register at the top and then moved, one pixel at a time, to the top right position, where the charge is read out. Then the next row is moved up and read out, and the sequence is repeated until the entire array has been read.
- 19-8. DTGS has a permanent electric polarization. That is, one face of the crystal has a positive charge and the opposite face has a negative charge. When the temperature of the crystal changes by absorption of infrared light, the polarization

(the voltage difference between the two faces) changes. The change in voltage is the detector signal.

**19-9.** (a)  $n\lambda = d(\sin \theta + \sin \phi)$

$$1 \cdot 600 \times 10^{-9} \text{ m} = d(\sin 40^\circ + \sin (-30^\circ)) \Rightarrow d = 4.20 \times 10^{-6} \text{ m}$$

$$\text{Lines/cm} = 1/(4.20 \times 10^{-4} \text{ cm}) = 2.38 \times 10^3 \text{ lines/cm}$$

(b)  $\lambda = 1/(1000 \text{ cm}^{-1}) = 10^{-3} \text{ cm} \Rightarrow d = 7.00 \times 10^{-3} \text{ cm} \Rightarrow 143 \text{ lines/cm}$

**19-10.**  $10^3$  grooves/cm means  $d = 10^{-5} \text{ m} = 10 \mu\text{m}$

$$\text{Dispersion} = \frac{n}{d \cos \phi} = \frac{1}{(10 \mu\text{m}) \cos 10^\circ} = 0.102 \frac{\text{radians}}{\mu\text{m}}$$

$$0.102 \frac{\text{radians}}{\mu\text{m}} \times \frac{180^\circ}{\pi \text{ radians}} = 5.8^\circ/\mu\text{m}$$

**19-11.** (a) Resolution =  $\frac{\lambda}{\Delta\lambda} = \frac{512.245}{0.03} = 1.7 \times 10^4$

(b)  $\Delta\lambda = \frac{\lambda}{10^4} = \frac{512.23}{10^4} = 0.05 \text{ nm}$

(c) Resolution =  $nN = (4)(8.00 \text{ cm} \times 1850 \text{ cm}^{-1}) = 5.9 \times 10^4$

(d) 250 lines/mm =  $4 \mu\text{m}/\text{line} = d$

$$\frac{\Delta\phi}{\Delta\lambda} = \frac{n}{d \cos \phi} = \frac{1}{(4 \mu\text{m}) \cos 3^\circ} = 0.250 \frac{\text{radians}}{\mu\text{m}} = 14.3^\circ/\mu\text{m}$$

For  $\Delta\lambda = 0.03 \text{ nm}$ ,  $\Delta\phi = (14.3^\circ/\mu\text{m})(3 \times 10^{-5} \mu\text{m}) = 4.3 \times 10^{-4}$  degrees.

For 30th order diffraction, the dispersion will be 30 times greater, or  $0.013^\circ$ .

**19-12.** (a) True transmittance =  $10^{-1.500} = 0.0316$ . With 0.50% stray light, the apparent transmittance is

$$\text{Apparent transmittance} = \frac{P+S}{P_0+S} = \frac{0.0316 + 0.0050}{1 + 0.0050} = 0.0364$$

The apparent absorbance is  $-\log 0.0364 = 1.439$ .

(b) Apparent absorbance = 1.999

$$\text{Apparent transmittance} = 10^{-1.999} = 0.01002305$$

$$\text{Apparent transmittance} = \frac{P+S}{P_0+S} = \frac{0.01002305}{1+0.0050} = 0.01002305$$

$$\Rightarrow S = 2.328 \times 10^{-5} \text{ or } 0.002328\%$$

(c) For true absorbance = 2,

$$\text{Apparent transmittance} = \frac{P+S}{P_0+S} = \frac{0.0100000005}{1+0.00000005} = 0.01000049$$

Apparent absorbance is  $-\log T = -\log(0.010\ 000\ 49) = 1.999\ 978$

Absorbance error =  $2 - 1.999\ 978 = 0.000\ 022$

For true absorbance = 3,

$$\text{Apparent transmittance} = \frac{P + S}{P_0 + S} = \frac{0.001 + 0.000\ 000\ 5}{1 + 0.000\ 000\ 5} = 0.001\ 000\ 495$$

Apparent absorbance is  $-\log T = -\log(0.001\ 000\ 495) = 2.999\ 785$

Absorbance error =  $3 - 2.999\ 785 = 0.000\ 215$

$$19-13. \quad b = \frac{30}{2.1} \left( \frac{1}{1906 - 698 \text{ cm}^{-1}} \right) = 0.1242 \text{ mm}$$

(Air between the plates has refractive index of 1.)

$$19-14. \quad M = \sigma T^4 = [5.6698 \times 10^{-8} \text{ W}/(\text{m}^2 \text{K}^4)] T^4$$

$T(\text{K})$	$M(\text{W}/\text{m}^2)$
77	1.99
298	447

$$19-15. \quad (\text{a}) \quad M_\lambda = \frac{2\pi hc^2}{\lambda^5} \left( \frac{1}{e^{hc/\lambda kT} - 1} \right)$$

at  $T = 1000 \text{ K}$ :

$\lambda (\mu\text{m})$	$M_\lambda (\text{W}/\text{m}^3)$
2.00	$8.79 \times 10^9$
10.00	$1.164 \times 10^9$

$$(\text{b}) \quad M_\lambda \Delta \lambda = (8.79 \times 10^9 \text{ W}/\text{m}^3)(0.02 \times 10^{-6} \text{ m}) = 1.8 \times 10^2 \text{ W}/\text{m}^2 \text{ at } 2.00 \mu\text{m}$$

$$(\text{c}) \quad M_\lambda \Delta \lambda = (1.164 \times 10^9 \text{ W}/\text{m}^3)(0.02 \times 10^{-6} \text{ m}) = 2.3 \times 10^1 \text{ W}/\text{m}^2 \text{ at } 10.00 \mu\text{m}$$

(d) at  $T = 100 \text{ K}$ :

$\lambda (\mu\text{m})$	$M_\lambda (\text{W}/\text{m}^3)$
2.00	$6.69 \times 10^{-19}$
10.00	$2.111 \times 10^3$

$$\frac{M_{2.00 \mu\text{m}}}{M_{10.00 \mu\text{m}}} = \frac{8.79 \times 10^9 \text{ W}/\text{m}^3}{1.164 \times 10^9 \text{ W}/\text{m}^3} = 7.55 \text{ at } 1000 \text{ K}$$

$$\frac{M_{2.00 \mu\text{m}}}{M_{10.00 \mu\text{m}}} = \frac{6.69 \times 10^{-19} \text{ W}/\text{m}^3}{2.111 \times 10^3 \text{ W}/\text{m}^3} = 3.17 \times 10^{-22} \text{ at } 100 \text{ K}$$

At 100 K, there is virtually no emission at  $2.00 \mu\text{m}$  compared to  $10.00 \mu\text{m}$ , whereas at 1000 K, there is a great deal of emission at both wavelengths.

$$\begin{aligned}
 19-16. \quad A &= \frac{L}{c \ln 10} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) \\
 &= \frac{0.210 \text{ m}}{(3.00 \times 10^8 \text{ m/s}) \ln 10} \left( \frac{1}{16.06 \times 10^{-6} \text{ s}} - \frac{1}{18.52 \times 10^{-6} \text{ s}} \right) = 2.51 \times 10^{-6}
 \end{aligned}$$

19-17.  $n_1 \sin \theta_1 = n_2 \sin \theta_2$ , where  $n_1 = 1.50$  and  $n_2 = 1.33$

- (a) If  $\theta_1 = 30^\circ$ ,  $\theta_2 = 34^\circ$
- (b) If  $\theta_1 = 0^\circ$ ,  $\theta_2 = 0^\circ$  (no refraction)

19-18. Light inside the fiber strikes the wall at an angle greater than the critical angle for total reflection. Therefore, all light is reflected back into the core and continues to be reflected from wall-to-wall as it moves along the fiber. If the bending angle is not too great, the angle of incidence will still exceed the critical angle and light will not leave the core.

19-19. When traveling from medium 1 into medium 2, the critical angle for total internal reflection is  $\sin \theta_{\text{critical}} = n_2/n_1$ , where  $n_i$  is the refractive index of medium i.

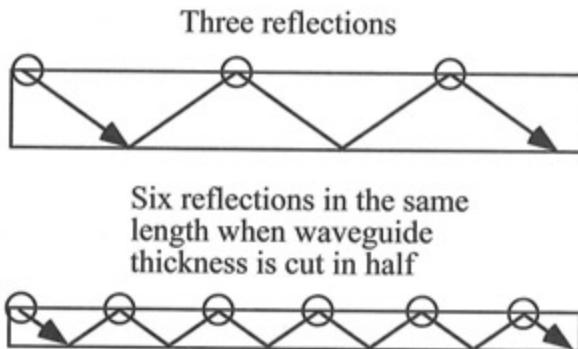
For the solvent/silica interface,  $n_1 = 1.50$  and  $n_2 = 1.46$ , so  $\sin \theta_{\text{critical}} = 1.46/1.5 = 0.9733$ .  $\theta_{\text{critical}} = \sin^{-1}(0.9733) = 1.339$  radians from the Excel function ASIN(0.9733). Degrees =  $180 \times \frac{\text{radians}}{\pi} = 180 \times \frac{1.339}{\pi} = 76.7^\circ$ .

For the silica/air interface,  $n_1 = 1.45$  and  $n_2 = 1.00$ , so  $\sin \theta_{\text{critical}} = 1.00/1.45 = 0.6849$ .  $\theta_{\text{critical}} = \sin^{-1}(0.6849) = 0.7545$  radians. Degrees =  $180 \times \frac{0.7545}{\pi} = 43.2^\circ$ .

The angle in the photograph is  $\sim 55^\circ$ , which exceeds the critical angle at the silica/air interface but does not exceed the critical angle at the solvent/silica interface. Total internal reflection in the photo must be from the silica/air interface.

19-20. Light is transmitted through the diamond crystal waveguide by total internal reflection at the upper and lower surfaces. The upper surface is in contact with a fluid channel containing sorbent beads that retain caffeine from a soft drink flowing through the channel. Caffeine in the beads absorbs some of the evanescent wave from the totally internally reflected radiation, decreasing the radiant power transmitted through the waveguide. The integrated area of the absorption spectrum of transmitted power is proportional to the concentration of caffeine in the soft drink.

- 19-21.** Sensitivity increases as the number of reflections inside the waveguide increases, because there is some attenuation at each reflection. For a constant angle of incidence, the number of reflections increases as the thickness of the waveguide decreases.



- 19-22.** (a) The value of  $\theta_i$ , called the critical angle ( $\theta_c$ ), is such that  $(n_1/n_2)\sin \theta_c = 1$ . For  $n_1 = 1.52$  and  $n_2 = 1.50$ ,  $\theta_c = 80.7^\circ$ . That is,  $\theta$  must be  $\geq 80.7^\circ$  for total internal reflection.  
 (b)  $\frac{\text{power out}}{\text{power in}} = 10^{-\ell(\text{dB/m})/10} = 10^{-(20.0 \text{ m})(0.0100 \text{ dB/m})/10} = 0.955$

- 19-23.** (a)  $n_{\text{core}} \sin \theta_i = n_{\text{cladding}} \sin \theta_r$   
 For total reflection,  $\sin \theta_r \geq 1 \Rightarrow \sin \theta_i \geq \frac{n_{\text{cladding}}}{n_{\text{core}}}$   
 For  $n_{\text{cladding}} = 1.400$  and  $n_{\text{core}} = 1.600$ ,  $\sin \theta_i \geq \frac{1.400}{1.600} \Rightarrow \theta_i \geq 61.04^\circ$   
 (b) For  $n_{\text{cladding}} = 1.400$  and  $n_{\text{core}} = 1.800$ ,  $\theta_i \geq 51.06^\circ$

- 19-24.** Angle of incidence = angle of reflection =  $45^\circ$ . Angle of refraction  $\equiv \theta$ .  
 $n_{\text{prism}} \sin 45^\circ = n_{\text{air}} \sin \theta$ . If total reflection occurs, there is no refracted light.  
 This happens if  $\sin \theta > 1$ , or  $\frac{n_{\text{prism}} \sin 45^\circ}{n_{\text{air}}} > 1$ . Using  $n_{\text{air}} = 1$  gives  
 $n_{\text{prism}} > \sqrt{2}$ . As long as  $n_{\text{prism}} > \sqrt{2}$ , no light will be transmitted through the prism and all light will be reflected.

- 19-25.** (a) The Teflon tube acts as an optical fiber because the internal solution has a higher refractive index (1.33) than the walls (1.29). The tube is a 4.5-m-long sample cell that can be conveniently coiled to fit in a reasonable volume and guide the incident radiation all the way through the tube. The long pathlength allows us to obtain a measurable absorbance for a very low

concentration of analyte.

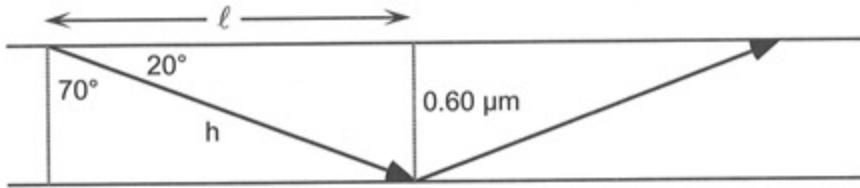
(b)  $n_{\text{core}} \sin \theta_i = n_{\text{cladding}} \sin \theta_r$

For total reflection,  $\sin \theta_r \geq 1 \Rightarrow \sin \theta_i \geq \frac{n_{\text{cladding}}}{n_{\text{core}}}$

For  $n_{\text{cladding}} = 1.29$  and  $n_{\text{core}} = 1.33$ ,  $\sin \theta_i \geq \frac{1.29}{1.33} \Rightarrow \theta_i \geq 76^\circ$

(c)  $A = \epsilon bc = (4.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})(450 \text{ cm})(1.0 \times 10^{-9} \text{ M}) = 0.020$

- 19-26.** (a) The following diagram shows the path of a light wave through the waveguide. The length of one bounce,  $\ell$ , satisfies the equation  $(0.60 \mu\text{m})/\ell = \tan 20^\circ$ , giving  $\ell = 1.648 \mu\text{m}$ . The hypotenuse of the triangle,  $h$ , satisfies the equation  $(0.60 \mu\text{m})/h = \sin 20^\circ$ , giving  $h = 1.754 \mu\text{m}$ . The number of intervals of length  $\ell$  in 3.0 cm is  $(3.0 \text{ cm})/(1.648 \mu\text{m}) = 1.820 \times 10^4$ . Therefore, the pathlength covered by the light is  $h \times (1.820 \times 10^4) = 3.19 \text{ cm}$ .



$$\frac{\text{power out}}{\text{power in}} = 10^{-\ell(\text{dB/m})/10} = 10^{-(3.19 \text{ cm})(0.050 \text{ dB/cm})/10} = 0.964$$

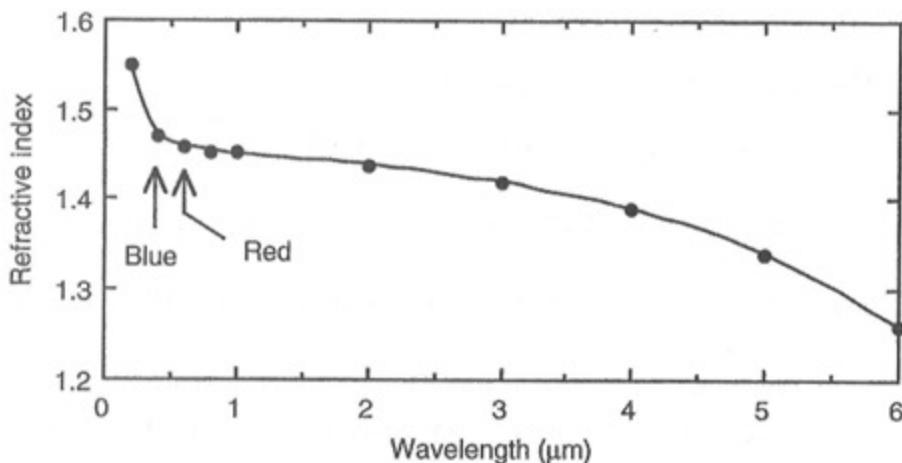
- (b) Wavelength =  $\lambda_0/n$ , where  $\lambda_0$  is the wavelength in vacuum and  $n$  is the refractive index. Wavelength =  $(514 \text{ nm})/1.5 = 343 \text{ nm}$ . The frequency is unchanged from that in vacuum:

$$\nu = c/\lambda = (2.9979 \times 10^8 \text{ m/s})/(514 \times 10^{-9} \text{ m}) = 5.83 \times 10^{14} \text{ Hz}$$

**19-27.** (a)

$\lambda (\mu\text{m})$	$n$	$\lambda (\mu\text{m})$	$n$
0.2	1.5505	2	1.4381
0.4	1.4701	3	1.4192
0.6	1.4580	4	1.3890
0.8	1.4533	5	1.3405
1	1.4504	6	1.2580

- (b)  $dn/d\lambda$  is greater for blue light ( $\sim 400 \text{ nm}$ ) than for red light ( $\sim 600 \text{ nm}$ )



- 19-28. (a)  $\Delta = \pm 2 \text{ cm}$   
 (b) Resolution refers to the ability to distinguish closely spaced peaks.  
 (c) Resolution  $\approx 1/\Delta = 0.5 \text{ cm}^{-1}$   
 (d)  $\delta = 1/(2\Delta\nu) = 1/(2 \times 2000 \text{ cm}^{-1}) = 2.5 \mu\text{m}$
- 19-29. The background transform gives the incident irradiance  $P_0$ . The sample transform gives the transmitted irradiance  $P$ . Transmittance is  $P/P_0$ , not  $P-P_0$ .
- 19-30. White noise is independent of frequency. One source is random motion of charge carriers in electronic circuits.  $1/f$  noise decreases with increasing frequency. Drift and flicker of the lamp of a spectrophotometer are sources of  $1/f$  noise. Line noise results from disturbances at discrete frequencies. The 60 Hz wall frequency is the most common electromagnetic disturbance seen in electronic instruments.
- 19-31. In beam chopping, the beam is alternately directed through the sample and reference cells. Slow drift of source intensity should be cancelled because the intensity seen by the sample and reference are almost the same. More rapid flicker of the lamp might not be cancelled.
- 19-32. The difference voltage is ideally very close to zero if the sample and reference are the same because the same lamp intensity goes through each compartment. If the sample absorbs some radiation, the difference voltage should respond to sample absorption with very little noise from source flicker.

- 19-33.** To increase the ratio from 8 to 20 (a factor of  $20/8 = 2.5$ ) requires  $2.5^2 = 6.25 \approx 7$  scans.

**19-34.** (a)  $(100 \pm 1) + (100 \pm 1) = 200 \pm \sqrt{2}$ , since  $e = \sqrt{e_1^2 + e_2^2} = \sqrt{1^2 + 1^2} = \sqrt{2}$

(b)  $(100 \pm 1) + (100 \pm 1) + (100 \pm 1) + (100 \pm 1) = 400 \pm 2$ , since  
 $e = \sqrt{1^2 + 1^2 + 1^2 + 1^2} = 2$ . The signal-to-noise ratio is  $400:2 = 200:1$ .

- (c) The initial measurement has signal/noise = 100/1.

Averaging  $n$  measurements gives

$$\text{average signal} = \frac{n \cdot 100}{n} = 100$$

$$\text{average noise} = \frac{\sqrt{n}}{n} = 1/\sqrt{n}$$

$$\frac{\text{average signal}}{\text{average noise}} = \frac{100}{1/\sqrt{n}} = 100\sqrt{n},$$

which is  $\sqrt{n}$  times greater than the original value of signal/noise.

- 19-35.** The theoretical signal-to-noise (S/N) ratio should increase in proportion to the square root of the number of cycles that are averaged.

Number of cycles = $n$	$\sqrt{n}$	Predicted relative S/N ratio
1	1	$\equiv 1$
100	10.00	10.00
300	17.32	17.32
1 000	31.62	31.62

If the observed S/N = 60.0 for the average of 1 000 cycles, then the predicted S/N for the other experiments are shown in the following table:

Number of cycles	Predicted S/N ratio	Observed S/N ratio
1 000	60.0 (observed)	60.0
300	$60.0 \left( \frac{17.32}{31.62} \right) = 32.9$	35.9
100	$60.0 \left( \frac{10.00}{31.62} \right) = 19.0$	20.9
1	$60.0 \left( \frac{1}{31.62} \right) = 1.90$	1.95

## CHAPTER 20

### ATOMIC SPECTROSCOPY

- 20-1.** Temperature is more critical in emission spectroscopy, because the small population of the excited state varies substantially as the temperature is changed. The population of the ground state does not vary much.
- 20-2.** Furnaces give increased sensitivity and require smaller sample volumes, but give poorer reproducibility with manual sample introduction. Automated sample introduction gives good precision.
- 20-3.** Drying ( $\sim 20\text{--}100^\circ\text{C}$ ) removes water from the sample. Ashing ( $\sim 100\text{--}500^\circ\text{C}$ ) is intended to remove as much matrix as possible without evaporating analyte. Atomization ( $\sim 500\text{--}2\,000^\circ\text{C}$ ) vaporizes analyte (and most of the rest of the sample) for the atomic absorption measurement. For some samples, ashing temperatures might be much higher than  $500^\circ\text{C}$  to remove more of the matrix, but it must be demonstrated that the ashing does not remove analyte.
- 20-4.** The plasma operates at higher temperature than a flame and the environment is Ar, not combustion gases. The plasma decreases chemical interference (such as oxide formation) and allows emission instead of absorption to be used. Lamps are not required and simultaneous multi-element analysis is possible. Self-absorption is reduced in the plasma because the temperature is more uniform. Disadvantages of the plasma are increased cost of equipment and operation.
- 20-5.** Doppler broadening occurs because an atom moving toward the radiation source sees a higher frequency than one moving away from the source. Increasing temperature gives increased speeds (more broadening) and increased mass gives decreased speeds (less broadening).
- 20-6.** (a) A beam chopper alternately blocks or exposes the lamp to the flame and detector. When the lamp is blocked, signal is due to background. When the lamp is exposed, signal is due to analyte plus background. The difference is the desired analytical signal.
- (b) The flame or furnace is alternately exposed to a D<sub>2</sub> lamp and the hollow-cathode lamp. Absorbance from the D<sub>2</sub> lamp is due to background. Absorbance from the hollow-cathode lamp is due to analyte plus background. The difference is the desired signal.

- (c) When a magnetic field parallel to the viewing direction is applied to the furnace, the analytical signal is split into two components that are separated from the analytical wavelength, and one component at the analytical wavelength. The component at the analytical wavelength is not observed because of its polarization. The other two components have the wrong wavelength to be observed. Analyte is essentially “invisible” to the detector when the magnetic field is applied, and only background is seen. Corrected signal is that observed without a field minus that observed with the field.
- 20-7.** Spectral interference refers to the overlap of analyte signal with signals due to other elements or molecules in the sample or with signals due to the flame or furnace. Chemical interference occurs when a component of the sample decreases the extent of atomization of analyte through some chemical reaction. Isobaric interference is the overlap of different species with nearly the same mass-to-charge ratio in a mass spectrum. Ionization interference refers to a loss of analyte atoms through ionization.
- 20-8.** La<sup>3+</sup> acts as releasing agent by binding tightly to PO<sub>4</sub><sup>3-</sup> and freeing Pb<sup>2+</sup>.
- 20-9.**
- A collision cell guides ions to the entrance of the mass separator and reduces the spread of ion kinetic energies by a factor of 10.
  - A dynamic reaction cell contains a reactive gas such as NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO, or O<sub>2</sub> and its electric field is configured to select lower and upper masses of ions to pass through the cell. Plasma species which interfere with some elements can be reduced by as many as 9 orders of magnitude by reactions such as electron transfer (<sup>40</sup>Ar<sup>16</sup>O<sup>+</sup> + NH<sub>3</sub> → NH<sub>3</sub><sup>+</sup> + Ar + O) and proton transfer (<sup>40</sup>ArH<sup>+</sup> + NH<sub>3</sub> → NH<sub>4</sub><sup>+</sup> + Ar). The reactive gas can also be used to shift the analyte signal from a position at which interference occurs (for example, <sup>40</sup>Ar<sup>16</sup>O<sup>+</sup> interferes with <sup>56</sup>Fe<sup>+</sup>) to one where there is no interference (<sup>56</sup>Fe<sup>+</sup> + N<sub>2</sub>O → <sup>56</sup>Fe<sup>16</sup>O<sup>+</sup> + N<sub>2</sub>).
  - When <sup>87</sup>Sr<sup>+</sup> is converted to <sup>87</sup>Sr<sup>19</sup>F<sup>+</sup>, which has a mass of 106, it no longer overlaps with <sup>87</sup>Rb<sup>+</sup> in the mass spectrum.
- 20-10.** The extent to which an element is ablated, transported to the plasma, and atomized depends on the matrix in which it is found. Different elements in a given matrix might not behave in the same manner. The most reliable calibration

is for the analyte of interest to be measured in the same matrix as the unknown—if that is possible.

- 20-11.** In the excitation spectrum, we are looking at emission over a band of wavelengths 1.6 nm wide, while exciting the sample with different narrow bands (0.03 nm) of laser light. The sample absorbs light only when the laser frequency coincides with the atomic frequency. Therefore, emission is observed only when the narrow laser line is in resonance with the atomic levels. In the emission spectrum, the sample is excited by a fixed laser frequency and then emits radiation. The monochromator bandwidth is not narrow enough to discriminate between emission at different wavelengths, so a broad envelope is observed.

- 20-12.** For Pb:

$$\begin{aligned} \left(104 \pm 17 \frac{\text{pg Pb}}{\text{g snow}}\right) \left(11.5 \frac{\text{g snow}}{\text{cm}^2}\right) &= 1196 \pm 196 \frac{\text{pg Pb}}{\text{cm}^2} \\ \left(1196 \pm 196 \frac{\text{pg Pb}}{\text{cm}^2}\right) \left(\frac{1 \text{ ng}}{1000 \text{ pg}}\right) &= 1.2 \pm 0.2 \frac{\text{ng Pb}}{\text{cm}^2} \end{aligned}$$

Similarly, we multiply each of the other concentrations by 11.5 g snow/cm<sup>2</sup> to find Tl:  $0.005 \pm 0.001$ ; Cd:  $0.04 \pm 0.01$ ; Zn:  $2.0 \pm 0.3$ ; Al:  $7 (\pm 2) \times 10^1 \text{ ng/cm}^2$ .

**20-13.**  $\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{3.371 \times 10^{-19} \text{ J}} = 5.893 \times 10^{-7} \text{ m} = 589.3 \text{ nm}$

- 20-14.** We derive the value for 6 000 K as follows:

$$\begin{aligned} \Delta E = h\nu &= \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34} \text{ J}\cdot\text{s})(2.9979 \times 10^8 \text{ m/s})}{500 \times 10^{-9} \text{ m}} = 3.97 \times 10^{-19} \text{ J} \\ \frac{N^*}{N_0} &= \frac{g^*}{g_0} e^{-\Delta E/kT} = \frac{g^*}{g_0} e^{-(3.97 \times 10^{-19} \text{ J})/(1.381 \times 10^{-23} \text{ J/K})(6000 \text{ K})} = \frac{g^*}{g_0} (8.3 \times 10^{-3}) \end{aligned}$$

If  $g^*/g_0 = 3$ , then  $N^*/N_0 = 3 (8.3 \times 10^{-3}) = 0.025$ .

- 20-15.** Doppler linewidth:  $\Delta\lambda = \lambda (7 \times 10^{-7}) \sqrt{T/M}$

For  $\lambda = 589 \text{ nm}$ ,  $M = 23$  (sodium) at  $T = 2000 \text{ K}$ ,

$$\Delta\lambda = (589 \text{ nm})(7 \times 10^{-7}) \sqrt{(2000)/23} = 0.0038 \text{ nm}$$

For  $\lambda = 254 \text{ nm}$ ,  $M = 201$  (mercury) at  $T = 2000 \text{ K}$ ,

$$\Delta\lambda = (254 \text{ nm})(7 \times 10^{-7}) \sqrt{(2000)/201} = 0.00056 \text{ nm}$$

- 20-16.** (a)  $\Delta E = h\nu = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34} \text{ J}\cdot\text{s})(2.9979 \times 10^8 \text{ m/s})}{422.7 \times 10^{-9} \text{ m}}$   
 $= 4.699 \times 10^{-19} \text{ J/molecule} = 283.0 \text{ kJ/mol}$
- (b)  $\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E/kT} = 3e^{-(4.699 \times 10^{-19} \text{ J})/(1.381 \times 10^{-23} \text{ J/K})(2500\text{K})} = 3.67 \times 10^{-6}$
- (c) At 2515 K,  $N^*/N_0 = 3.98 \times 10^{-6} \Rightarrow 8.4\%$  increase from 2500 to 2515 K
- (d) At 6000 K,  $N^*/N_0 = 1.03 \times 10^{-2}$

20-17. Element:	Na	Cu	Br
Excited state energy (eV):	2.10	3.78	8.04
Wavelength (nm):	591	328	154
Degeneracy ratio ( $g^*/g_0$ ):	3	3	2/3
$N^*/N_0$ at 2600 K in flame:	$2.6 \times 10^{-4}$	$1.4 \times 10^{-7}$	$1.8 \times 10^{-16}$
$N^*/N_0$ at 6000 K in plasma:	$5.2 \times 10^{-2}$	$2.0 \times 10^{-3}$	$1.2 \times 10^{-7}$
Calculations: wavelength = $hc/\Delta E$	$N^*/N_0 = (g^*/g_0) e^{-\Delta E/kT}$		
Br is not readily observed in atomic absorption, because its lowest excited state requires far-ultraviolet radiation for excitation. Nitrogen and oxygen in the air absorb far-ultraviolet energy and would have to be excluded from the optical path. The excited state lies at such high energy that it is not sufficiently populated to provide adequate intensity for optical emission.			

- 20-18.** The dissociation energy of YC is greater than that of BaC, so the equilibrium  $\text{BaC} + \text{Y} \rightleftharpoons \text{Ba} + \text{YC}$  is driven to the right, increasing the concentration of free Ba atoms in the gas phase.

- 20-19.** Area of pit =  $\pi(20 \times 10^{-4} \text{ cm})^2 = 1.26 \times 10^{-5} \text{ cm}^2$   
Power =  $2.4 \times 10^{-3} \text{ J}/10 \times 10^{-9} \text{ s} = 2.4 \times 10^5 \text{ W}$   
Power density =  $2.4 \times 10^5 \text{ W}/1.26 \times 10^{-5} \text{ cm}^2 = 1.9 \times 10^{10} \text{ W/cm}^2 = 20 \text{ GW/cm}^2$   
Ablated mass = volume × density = depth × area × density =  
 $(1 \times 10^{-4} \text{ cm})(1.26 \times 10^{-5} \text{ cm}^2)(4 \text{ g/cm}^3) = 5 \text{ ng}$

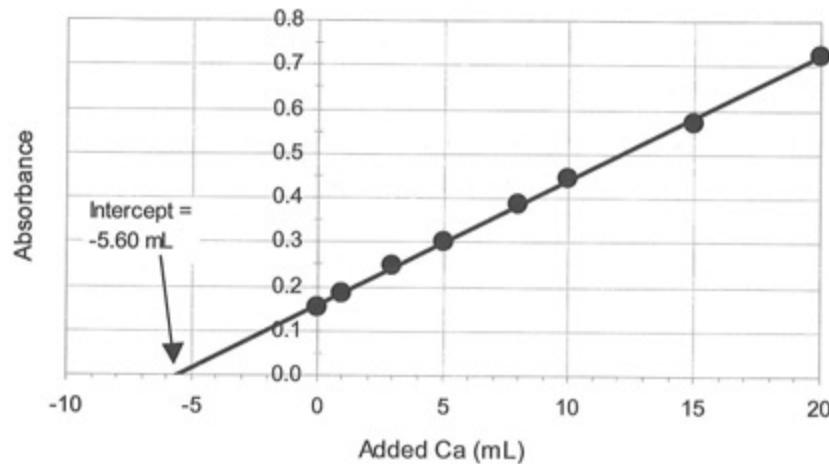
- 20-20.** Analyte and standard are lost in equal proportions, so their ratio remains constant.

20-21.

	A	B	C	D
1	Standard Addition Constant Volume Least-Squares			
2	x	y		
3	Volume added (mL)	Absorbance		
4	0.00	0.151		
5	1.00	0.185		
6	3.00	0.247		
7	5.00	0.300		
8	8.00	0.388		
9	10.00	0.445		
10	15.00	0.572		
11	20.00	0.723		
12	B14:C16 = =LINEST(B4:B11,A4:A11,TRUE,TRUE)			
13	LINEST output:			
14	m	0.0282	0.1579	b
15	s <sub>m</sub>	0.0003	0.0031	s <sub>b</sub>
16	R <sup>2</sup>	0.9993	0.0057	s <sub>y</sub>
17	x-intercept = -b/m =	-5.599		
18	n =	8	= COUNT(A4:A11)	
19	Mean y =	0.376	= AVERAGE(B4:B11)	
20	$\sum(x_i - \text{mean } x)^2 =$	343.5	= DEVSQ(A4:A8)	
21	Std deviation of			
22	x-intercept =	0.1630		
23	B22=(C16/ABS(B14))*SQRT((1/B18) + B19^2/(B14^2*B20))			

The x-intercept is  $-5.60 \pm 0.16$  mL. Standard [Ca] = 20.0  $\mu\text{g Ca/mL}$ . The intercept corresponds to Ca =  $(5.60 \pm 0.16$  mL)(20.0  $\mu\text{g Ca/mL}$ ) =  $112.0 \pm 3.2$   $\mu\text{g}$ . This is the mass of Ca in 5.00 mL of unknown. The total volume of unknown was 100.0 mL, so mass of Ca in total unknown =  $(100.0 \text{ mL}/5.00 \text{ mL})(112.0 \pm 3.2 \mu\text{g Ca}) = 2240 \pm 64 \mu\text{g Ca}$ .

$$\text{wt\% Ca in cereal} = \frac{100 \times (2240 \pm 64 \mu\text{g Ca})}{0.5216 \text{ g cereal}} = 0.429 \pm 0.012 \text{ wt\%}.$$



20-22. (a) [S] in unknown mixture =  $(8.24 \text{ } \mu\text{g/mL}) \left( \frac{5.00}{50.0} \right) = 0.824 \text{ } \mu\text{g/mL}$

Standard mixture has equal concentrations of X and S:

$$\frac{A_X}{[X]} = F \left( \frac{A_S}{[S]} \right) \Rightarrow \frac{0.930}{[X]} = F \left( \frac{1.000}{[S]} \right) \Rightarrow F = 0.930$$

Unknown mixture:

$$\frac{A_X}{[X]} = F \left( \frac{A_S}{[S]} \right) \Rightarrow \frac{1.690}{[X]} = 0.930 \left( \frac{1.000}{[0.824 \text{ mg/mL}]} \right) \Rightarrow [X] = 1.497 \text{ } \mu\text{g/mL}$$

But X was diluted by a factor of  $10.00/50.0$ , so the original concentration in the unknown was  $(1.497 \text{ } \mu\text{g/mL}) \left( \frac{50.0}{10.00} \right) = 7.49 \text{ } \mu\text{g/mL}$ .

(b) Standard mixture has equal concentrations of X and S:

$$\frac{A_X}{[X]} = F \left( \frac{A_S}{[S]} \right) \Rightarrow \frac{0.930}{[3.42]} = F \left( \frac{1.000}{[1.00]} \right) \Rightarrow F = 0.2719$$

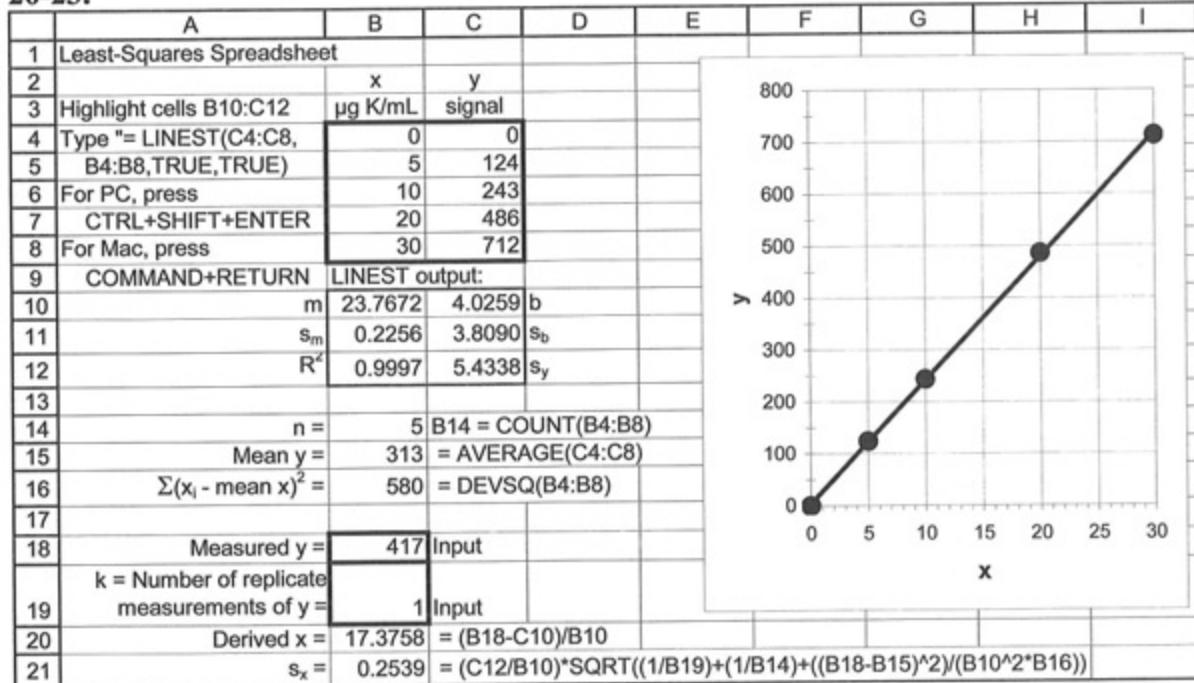
Unknown mixture:

$$\frac{A_X}{[X]} = F \left( \frac{A_S}{[S]} \right) \Rightarrow \frac{1.690}{[X]} = 0.2719 \left( \frac{1.000}{[0.824 \text{ } \mu\text{g/mL}]} \right) \Rightarrow [X] = 5.122$$

$\mu\text{g/mL}$

But X was diluted by a factor of  $10.00/50.0$ , so the original concentration in the unknown was  $(5.122 \text{ } \mu\text{g/mL}) \left( \frac{50.0}{10.00} \right) = 25.6 \text{ } \mu\text{g/mL}$ .

20-23.

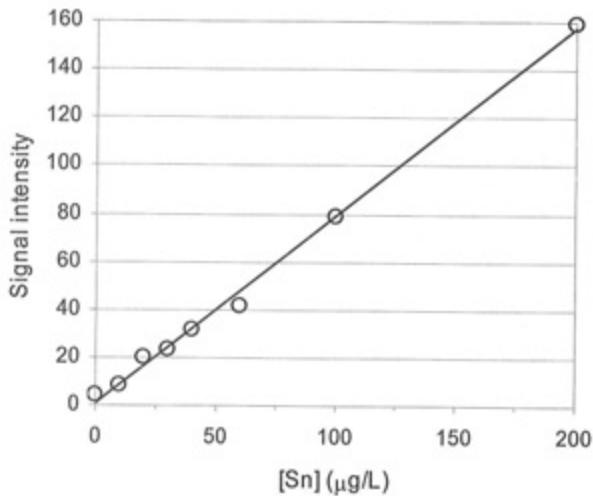


Cells B20 and B21 give us [unknown] =  $17.4 \pm 0.3 \text{ }\mu\text{g/mL}$  for an emission intensity of 417.

- 20-24. (a) CsCl provides Cs atoms which ionize to  $\text{Cs}^+ + e^-$  in the plasma. Electrons in the plasma inhibit ionization of Sn. Therefore, emission from atomic Sn is not lost to emission from  $\text{Sn}^+$ .

(b)

	A	B	C	D	E	F
1	Tin in canned food - <i>Anal. Bioanal. Chem.</i> <b>2002</b> , 374, 235					
2	Calibration data for 189.927 nm					
3						
4	Conc ( $\mu\text{g/L}$ )	Signal intensity			Output from LINEST	
5	0	4.0			slope	intercept
6	10	8.5	Parameter	0.781651	0.863321	
7	20	19.6	Std Dev	0.018508	1.556732	
8	30	23.6	R <sup>2</sup>	0.996648	3.213618	
9	40	31.1				
10	60	41.7				
11	100	78.8				
12	200	159.1				
13						
14	Select cells E6:F8					
15	Enter the formula = LINEST(B5:B12,A5:A12,TRUE,TRUE)					
16	CONTROL+SHIFT+ENTER on PC or COMMAND+RETURN on Mac					



- (c) For the 189.927 nm Sn emission line, spike recoveries are all near 100  $\mu\text{g/L}$ , which is near 100%. None of the elements in the table appears to interfere significantly at 189.927 nm. For the 235.485 nm emission line, interference from an emission line of Fe is so serious that the Sn signal cannot be measured. Several other elements interfere enough to reduce the accuracy of the Sn measurement. These elements include Cu, Mn, Zn, Cr, and, perhaps,

Mg. The 189.927 nm line is clearly the better of the two wavelengths for minimizing interference.

- (d) Limit of detection = minimum detectable concentration =  $3s/m$   
 where  $s$  is the standard deviation of the replicate samples and  $m$  is the slope of the calibration curve. Putting in the values  $s = 2.4$  units and  $m = 0.782$  units per ( $\mu\text{g/L}$ ) gives

$$\text{limit of detection} = \frac{3s}{m} = \frac{3(2.4 \text{ units})}{0.782 \text{ units}/(\mu\text{g/L})} = 9.2 \mu\text{g/L}$$

$$\text{limit of quantitation} = \frac{10s}{m} = \frac{10(2.4 \text{ units})}{0.782 \text{ units}/(\mu\text{g/L})} = 30.7 \mu\text{g/L}$$

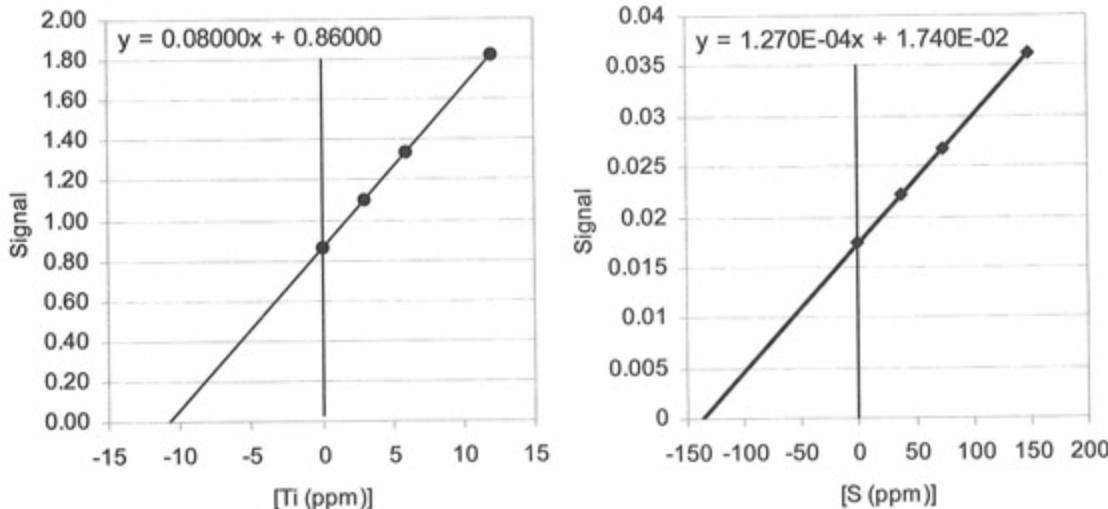
It would be reasonable to quote a limit of detection as 9  $\mu\text{g/L}$  and a limit of quantitation as 31  $\mu\text{g/L}$ .

- (e) A 2-g food sample ends up in a volume of 50 mL. The limit of quantitation is 30.7  $\mu\text{g Sn/L}$  for the solution. A 50-mL volume with Sn at the limit of quantitation contains  $(0.050 \text{ L})(30.7 \mu\text{g Sn/L}) = 1.54 \mu\text{g Sn}$ . The quantity of Sn per unit mass of food is

$$\frac{(1.54 \mu\text{g Sn})(1 \text{ mg}/1000 \mu\text{g})}{(2.0 \text{ g food})(1 \text{ kg}/1000 \text{ g})} = 0.77 \frac{\text{mg Sn}}{\text{kg food}} = 0.77 \text{ ppm}$$

**20-25.** Standard addition graph: plot signal versus Ti or S concentration.

Ti (ppm)	Signal	S (ppm)	Signal
0.00	0.86	0.0	0.0174
3.00	1.10	37.0	0.0221
6.00	1.34	74.0	0.0268
12.00	1.82	148.0	0.0362



Ti standard addition graph: negative intercept =  $0.860/0.0800 = 10.75 \text{ mg/L}$

S standard addition graph: negative intercept =  $0.0174/0.000127 = 137.0 \text{ mg/L}$

Ti atomic mass = 47.867                    S atomic mass = 32.065

$$[\text{Ti}] = (10.75 \text{ mg/L})/(47.867 \text{ g/mol}) = 2.246 \times 10^{-4} \text{ M}$$

$$[\text{S}] = (137.0 \text{ mg/L})/(32.065 \text{ g/mol}) = 4.273 \times 10^{-3} \text{ M}$$

$$[\text{Transferrin}] = [\text{S}]/39 = 1.096 \times 10^{-4} \text{ M}$$

$$\text{Ti/transferrin} = (2.246 \times 10^{-4} \text{ M})/(1.096 \times 10^{-4} \text{ M}) = 2.05$$

## CHAPTER 21

### MASS SPECTROMETRY

- 21-1.** Gaseous molecules are ionized by collisions with 70-eV electrons in the ion source. The ions are accelerated out of the source by a voltage,  $V$ . All ions have nearly the same kinetic energy ( $\frac{1}{2}mv^2$ , where  $m$  is mass and  $v$  is velocity), so the heavier ions have lower velocity. Ions then enter a magnetic field ( $B$ ) and are deflected so they travel through the arc of a circle whose radius is  $(\sqrt{2V(m/z)/e})/B$ , where  $z$  is the number of charges on the ion and  $e$  is the elementary charge. By varying the magnetic field, ions of different  $m/z$  are deflected through the slit leading to the detector. At the detector, ion impacts liberate electrons from a cathode. The electrons are amplified by a series of dynodes (as in a photomultiplier tube). The mass spectrum is a graph of detector signal versus  $m/z$ .
- 21-2.** For the electron impact spectrum, pentobarbital is bombarded by electrons with an energy of 70 electron volts. The molecular ion ( $m/z = 226$ ) produced by the impact has enough energy to break into fragments and little  $M^{+*}$  is observed. Large peaks correspond to the most stable cation fragments. For chemical ionization, pentobarbital reacts with  $\text{CH}_5^+$ , which is a potent proton donor, but does not have excess kinetic energy. The dominant peak is usually  $\text{MH}^+$  ( $m/z = 227$ ). In the case of pentobarbital, some fragmentation is observed even in the chemical ionization spectrum.
- 21-3.**  $1 \text{ dalton (Da)} \equiv 1/12 \text{ of the mass of } ^{12}\text{C} = \left( \frac{(1/12) \times 12 \text{ g/mol (exactly)}}{6.022 \ 14 \times 10^{23} \text{ mol}^{-1}} \right)$   
 $= 1.660 \ 54 \times 10^{-24} \text{ g}$   
 $[5.03 (\pm 0.14) \times 10^{10} \text{ Da}] [1.660 \ 54 \times 10^{-24} \text{ g/Da}]$   
 $= 8.35 (\pm 0.23) \times 10^{-14} \text{ g} = 83.5 (\pm 2.3) \text{ fg}$
- 21-4.** The atomic mass in the periodic table is a weighted average of the masses of all the isotopes of that element. We can estimate the relative abundance of the two major isotopes of Ni from the heights of their mass spectral peaks. The heights of the peaks that I measured from an earlier version of this illustration are 42.6 mm for  $^{58}\text{Ni}$  and 17.1 mm for  $^{60}\text{Ni}$ . The weighted average is

atomic mass

$$\begin{aligned}
 &= ({}^{58}\text{Ni mass})(\% \text{ abundance of } {}^{58}\text{Ni}) + ({}^{60}\text{Ni mass})(\% \text{ abundance of } {}^{60}\text{Ni}) \\
 &= (57.935 \ 3) \left( \frac{42.6}{42.6 + 17.1} \right) + (59.933 \ 2) \left( \frac{17.1}{42.6 + 17.1} \right) = 58.51
 \end{aligned}$$

The atomic mass in the periodic table is 58.69. This main reason for disagreement is that we neglected the existence of  ${}^{61}\text{Ni}$  (1.13% natural abundance),  ${}^{62}\text{Ni}$  (3.59%), and  ${}^{64}\text{Ni}$  (0.90%).

**21-5.** Resolving power =  $\frac{m}{m_{1/2}} = \frac{2846.3}{0.19} = 1.5 \times 10^4$ .

We should be able to barely distinguish two peaks differing by 1 Da at a mass of  $1.5 \times 10^4$  Da. Therefore, we should be able to distinguish two peaks at 10 000 and 10 001 Da.

- 21-6.** The overlap at the base of the peaks is approximately 10% in the mass spectrum. The resolving power is approximately  $m/\Delta m \approx 31/0.010 \approx 3\ 100$ .

- 21-7.** Resolving power by 10% valley formula:  $m/\Delta m = 906.49/0.000\ 45 = 2.0 \times 10^6$   
 Resolving power by half-width formula:  $m/m_{1/2} = 906.49/0.000\ 27 = 3.4 \times 10^6$   
 The mass of an electron, 0.000 55 Da, is greater than the mass difference between the two compounds. The mass difference of the compounds is 82% of the mass of one electron.

**21-8.**  $\text{C}_5\text{H}_7\text{O}^+$ :     $5 \times 12.000\ 00$   
                          $+7 \times \underline{1.007\ 825}$   
                          $+1 \times 15.994\ 91$   
                          $\underline{-e^- \text{ mass}} \quad \underline{-1 \times 0.000\ 55}$   
                          $83.049\ 14$

$\text{C}_6\text{H}_{11}^+$ :     $6 \times 12.000\ 00$   
                          $+11 \times \underline{1.007\ 825}$   
                          $\underline{-e^- \text{ mass}} \quad \underline{-1 \times 0.000\ 55}$   
                          $83.085\ 52$

$\text{C}_6\text{H}_{11}^+$  is a closer match than  $\text{C}_5\text{H}_7\text{O}^+$  to the observed mass of 83.086 5 Da.

**21-9.**  ${}^{31}\text{P}^+ = {}^{31}\text{P} - \text{e}^- = 30.973\ 76 - 0.000\ 55 = 30.973\ 21$  (observed: 30.9735)

To measure  $m/z$ , I enlarged the figure and sketched a Gaussian curve over each signal by eye. I then measured the position of the center of the peak with a millimeter scale ruler.

$$\begin{aligned} {}^{15}\text{N}{}^{16}\text{O}^+ &= {}^{15}\text{N} + {}^{16}\text{O} - \text{e}^- = 15.000\ 11 + 15.994\ 91 - 0.000\ 55 \\ &= 30.994\ 47 \text{ (observed: 30.9946)} \end{aligned}$$

$$\begin{aligned} {}^{14}\text{N}{}^{16}\text{OH}^+ &= {}^{14}\text{N} + {}^{16}\text{O} + {}^1\text{H} - \text{e}^- = \\ &14.003\ 07 + 15.994\ 91 + 1.007\ 82 - 0.000\ 55 = 31.005\ 25 \\ &\quad \text{(observed: 31.0056)} \end{aligned}$$

**21-10.**  ${}^{79}\text{Br}$  abundance  $\equiv a = 0.506\ 9$        ${}^{81}\text{Br}$  abundance  $\equiv b = 0.493\ 1$

$$\text{Abundance of C}_2\text{H}_2{}^{79}\text{Br}_2 = a^2 = 0.256\ 95$$

$$\text{Abundance of C}_2\text{H}_2{}^{79}\text{Br}{}^{81}\text{Br} = 2ab = 0.499\ 90$$

$$\text{Abundance of C}_2\text{H}_2{}^{81}\text{Br}_2 = b^2 = 0.243\ 15$$

$$\text{Relative abundances: M}^+ : \text{M}+1 : \text{M}+2 = 1 : 1.946 : 0.946\ 3$$

Figure 21-7 shows the stick diagram.

**21-11.**  ${}^{10}\text{B}$  abundance  $\equiv a = 0.199$        ${}^{11}\text{B}$  abundance  $\equiv b = 0.801$

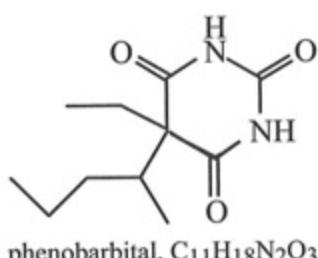
$$\text{Abundance of } {}^{10}\text{B}_2\text{H}_6 = a^2 = 0.039\ 60$$

$$\text{Abundance of } {}^{10}\text{B}{}^{11}\text{BH}_6 = 2ab = 0.3188$$

$$\text{Abundance of } {}^{11}\text{B}_2\text{H}_6 = b^2 = 0.6416$$

$$\text{Relative abundances: M}^+ : \text{M}+1 : \text{M}+2 = 1 : 8.05 : 16.20$$

**21-12.** (a)

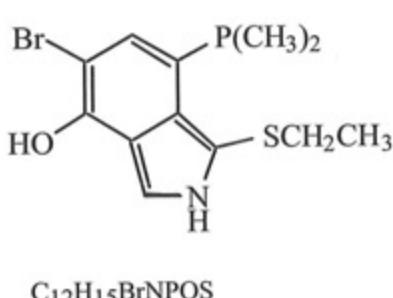


$$\text{R} + \text{DB} = c - h/2 + n/2 + 1$$

$$\text{R} + \text{DB} = 11 - 18/2 + 2/2 + 1 = 4$$

The molecule has one ring + three double bonds.

(b)

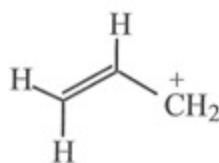


$$\text{R} + \text{DB} = c - h/2 + n/2 + 1$$

$$\text{R} + \text{DB} = 12 - \frac{15+1}{2} + \frac{1+1}{2} + 1 = 6$$

The molecule has two rings + four double bonds. Note that  $h$  includes H + Br, and  $n$  includes N + P. S, like O, does not contribute to the count.

(c)



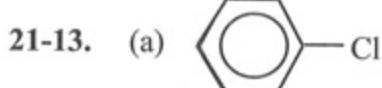
A fragment in a mass spectrum



$R + DB = c - h/2 + n/2 + 1$

$R + DB = 3 - 5/2 + 1 = 1\frac{1}{2} \text{ Huh?}$

We come out with a fraction instead of an integer because the species is an ion in which one C makes three bonds instead of four.



The pair of peaks at  $m/z = 112$  and  $114$  strongly suggest that the molecule contains 1 Cl.

$\text{rings} + \text{double bonds} = c - h/2 + n/2 + 1 = 6 - 6/2 + 1 = 4$ 

$\uparrow$   
h includes H + Cl

$\text{Expected intensity of } M+1 \text{ is } 1.08(6) + 0.012(5) = 6.54\%$ 

carbon      hydrogen

$\text{Observed intensity of } M+1 = 69/999 = 6.9\%$

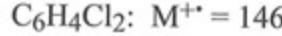
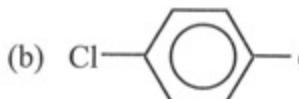
$\text{Expected intensity of } M+2 = 0.0058(6)(5) + 32.0(1) = 32.2\%$ 

carbon      chlorine

$\text{Observed intensity of } M+2 = 329/999 = 32.9\%$

The  $M+3$  peak is the isotopic partner of the  $M+2$  peak.  $M+3$  contains  $^{37}\text{Cl}$  plus either 1  $^{13}\text{C}$  or 1  $^2\text{H}$ . Therefore, the expected intensity of  $M+3$  (relative to  $M+2$ ) is  $1.08(6) + 0.012(5) = 6.54\%$  of predicted intensity of  $M+2 = (0.0654)(32.2) = 2.11\%$  of  $M^{+\bullet}$ .

$\text{Observed intensity of } M+3 = 21/999 = 2.1\%.$



The peaks at  $m/z = 146$ ,  $148$ , and  $150$  look like the isotope pattern from 2 Cl in Figure 21-7.

$\text{rings} + \text{double bonds} = c - h/2 + n/2 + 1 = 6 - 6/2 + 1 = 4$

$\text{Expected intensity of } M+1 \text{ is } 1.08(6) + 0.012(4) = 6.53\%$ 

carbon      hydrogen

$\text{Observed intensity of } M+1 = 56/999 = 5.6\%$

$\text{Expected intensity of } M+2 = 0.0058(6)(5) + 32.0(2) = 64.2\%$ 

carbon      chlorine

Observed intensity of M+2 = 624/999 = 62.5%

The M+3 peak is the isotopic partner of the M+2 peak. M+3 contains 1  $^{35}\text{Cl}$  + 1  $^{37}\text{Cl}$  plus either 1  $^{13}\text{C}$  or 1  $^2\text{H}$ . Therefore, the expected intensity of M+3 (relative to M+2) is  $1.08(6) + 0.012(4) = 6.53\%$  of predicted intensity of M+2 =  $(0.0653)(64.2) = 4.19\%$  of  $\text{M}^{+*}$ .

Observed intensity of M+3 is 33/999 = 3.3%.

Expected intensity of M+4 from  $\text{C}_6\text{H}_4^{37}\text{Cl}_2$  is  $5.11(2)(1) = 10.22\%$  of  $\text{M}^{+*}$ .

The small contribution from  $^{12}\text{C}_4^{13}\text{C}_2\text{H}_4^{35}\text{Cl}^{37}\text{Cl}$  is based on the predicted intensity of M+2. It is  $0.0058(6)(5) = 0.174\%$  of  $64.2\% = 0.11\%$ .

Total expected intensity of M+4 is  $10.22\% + 0.11\% = 10.33\%$  of  $\text{M}^{+*}$

Observed intensity = 99/999 = 9.9%.

Expected intensity of M+5 from  $^{12}\text{C}_5^{13}\text{CH}_4^{37}\text{Cl}_2$  and  $^{12}\text{C}_6\text{H}_3^2\text{H}^{37}\text{Cl}_2$  is based on the predicted intensity of M+4. M+5 should have  $1.08(6) + 0.012(4) = 6.53\%$  of M+4 =  $6.53\%$  of  $10.33\% = 0.67\%$ .

Observed intensity = 5/999 = 0.5%.



The peak at  $m/z = 93$  was chosen as the molecular ion, because it is the tallest peak in the cluster and it has plausible isotope peaks at M+1 and M+2. The significant peak at M-1 could be from loss of 1 H. The tiny stuff at M-2 and M-3 could be noise or, possibly, loss of more than 1 H.

With an odd mass, the nitrogen rule tells us that there are an odd number of N atoms in the molecule.

$$\text{rings} + \text{double bonds} = c - h/2 + n/2 + 1 = 6 - 7/2 + 1/2 + 1 = 4$$

Expected intensity of M+1 is  $1.08(6) + 0.012(7) + 0.369(1) = 6.93\%$   
carbon      hydrogen      nitrogen

Observed intensity of M+1 = 71/999 = 7.1%

Expected intensity of M+2 =  $0.0058(6)(5) = 0.17\%$

Observed intensity of M+2 = 2/999 = 0.2%



There are six strong peaks in an unfamiliar pattern. Given that only elements from Table 21-1 are admissible, we notice that Hg has six significant isotopes. By convention, we take the lightest isotope,  $^{198}\text{Hg}$ , for the molecular ion at  $m/z = 228$ . This leaves just 30 Da for the rest of the

molecule, which could be composed of two methyl groups.

In computing rings + double bonds, we include Hg as a Group 6 atom (like O or S) because it makes 2 bonds.

$$\text{rings} + \text{double bonds} = c - h/2 + n/2 + 1 = 2 - 6/2 + 1 = 0.$$

The peak at  $m/z = 228$  is  $M^{+*} = (\text{CH}_3)_2^{198}\text{Hg}$ .

Small peaks at  $m/z = 227$  and  $226$  could arise from loss of one or two H atoms. If  $(\text{CH}_3)_2^{198}\text{Hg}$  loses H atoms, then all the species at higher mass, such as  $(\text{CH}_3)_2^{199}\text{Hg}$ , will also lose H atoms. That is, each isotopic molecule is going to contribute some intensity to peaks of lower mass. It makes no sense for us to get too carried away with the analysis of the isotopic pattern, because each peak derives intensity from peaks at lower and higher mass.

The peak at  $m/z = 229$  is  $M+1$ , composed mainly of  $(\text{CH}_3)_2^{199}\text{Hg}$ , with some  $(^{12}\text{CH}_3)(^{13}\text{CH}_3)^{198}\text{Hg} + ^{12}\text{C}_2\text{H}_5^2\text{H}^{198}\text{Hg}$ . Just considering Hg, the predicted intensity, based on  $M^+$ , is  $\frac{16.87}{9.97} \times 100 = 169.2\%$  of  $M^{+*}$ . The

observed intensity is  $215/130 = 165\%$  of  $M^{+*}$ . In this calculation, the fraction  $\frac{16.87}{9.97}$  is the ratio of the abundances of  $^{199}\text{Hg}$  to  $^{198}\text{Hg}$ . The peak at  $m/z = 230$  is  $M+2$ , composed mainly of  $(\text{CH}_3)_2^{200}\text{Hg}$ . The predicted  $^{200}\text{Hg}$  isotopic intensity, based on  $M^+$ , is  $\frac{23.10}{9.97} \times 100 = 231.7\%$  of  $M^{+*}$ .

Observed intensity of  $M+2 = 291/130 = 224\%$  of  $M^{+*}$ .

Just considering Hg isotopes, we expect the peaks at  $M$ ,  $M+1$ ,  $M+2$ ,  $M+3$ ,  $M+4$ , and  $M+6$  to have the ratios  $9.97 : 16.87 : 23.10 : 13.18 : 29.86 : 6.87 = 1 : 1.69 : 2.32 : 1.32 : 2.99 : 0.69$ .

Observed intensity ratio =  $1 : 1.65 : 2.24 : 1.29 : 2.81 : 0.64$ .

- (e)  $\text{CH}_2\text{Br}_2$ :  $M^{+*} = 172$

The three peaks at  $m/z = 172$ ,  $174$  and  $176$ , with approximate ratios  $1 : 2 : 1$  looks like the pattern from 2 Br atoms in Figure 21-7.

$$\text{rings} + \text{double bonds} = c - h/2 + n/2 + 1 = 1 - 4/2 + 1 = 0$$

$\uparrow$   
h includes H + Br

Expected intensity of  $M+1$  is  $1.08(1) + 0.012(2) = 1.10\%$   
carbon      hydrogen

Observed intensity of  $M+1 = 12/531 = 2.3\%$ . It is possible that this peak at  $m/z = 173$  also has contributions from  $\text{CH}^{79}\text{Br}^{81}\text{Br}$ . We have no way to compute the intensity at  $m/z = 173$  if some of this peak comes from

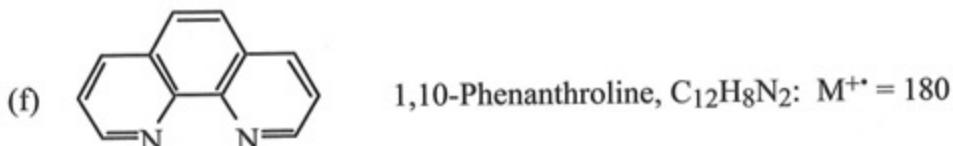
$\text{CH}^{79}\text{Br}^{81}\text{Br}$ . Given this ambiguity, we will just compare the theoretical pattern for 2 Br atoms to the observed pattern:

Theoretical intensity of  $M+2 = 97.3(2) = 194.6\%$

Observed intensity of  $M+2 = 999/531 = 188\%$

Theoretical intensity of  $M+4 = 47.3(2)(1) = 94.6\%$

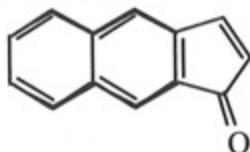
Observed intensity of  $M+4 = 497/531 = 93.6\%$



The strongest peak in the high-mass cluster is at  $m/z = 180$ , which could be the molecular ion. It has plausible isotopic peaks at 181 and 182. The significant peak at  $m/z = 179$  could be from loss of 1 H.

The intensity ratio  $M+1/M^{+*} = 138/999 = 13.8\%$ . We estimate that the number of C atoms is  $13.8/1.08 = 12.8$ .

If the molecule contains 13 C atoms, the formula might be  $\text{C}_{13}\text{H}_8\text{O}$ , which would have  $13 - 8/2 + 1 = 10$  rings plus double bonds. The expected intensity of  $M+1$  would be  $1.08(13) + 0.012(8) + 0.038(1) = 14.2\%$ . The expected intensity of  $M+2$  would be  $0.0058(13)(12) + 0.205(1) = 1.1\%$ . Observed intensity of  $M+2 = 9/999 = 0.9\%$ . The formula  $\text{C}_{13}\text{H}_8\text{O}$  fits the data and a conceivable structure is



If the molecule contains 12 C atoms, the formula might be  $\text{C}_{12}\text{H}_4\text{O}_2$ , which would have  $12 - 4/2 + 1 = 11$  rings plus double bonds. A molecule with this many rings + double bonds would be pretty implausible.

If the molecule contains nitrogen, it must contain an even number of N atoms because the molecule has an even mass. A possible formula is  $\text{C}_{12}\text{H}_8\text{N}_2$ , which would have  $12 - 8/2 + 2/2 + 1 = 10$  rings plus double bonds. This turns out to be the correct formula, and the structure is shown at the beginning of this answer. The predicted intensity of  $M+1$  is  $1.08(12) + 0.012(8) + 0.369(2) = 13.8\%$ , which is exactly equal to the observed intensity. The expected intensity of  $M+2$  is  $0.0058(12)(11) = 0.8\%$ . Observed intensity = 0.9%.

Ferrocene,  $C_{10}H_{10}Fe$ :  $M^{+*} = 186$ 

The strongest peak at high mass is at  $m/z = 186$ , which could be the molecular ion. It has plausible isotopic peaks at 187 and 188. Significant peaks at  $m/z = 184$  and 185 could be from loss of H. Calling  $M^{+*} = 186$ , we find the following ratios of peak intensities:

$M-2$	$M-1$	$M^{+*}$	$M+1$	$M+2$
8.3	1.6	100	13.2	1.0

From the intensity ratio  $M+1/M^{+*} = 13.2\%$ , we could estimate that the number of C atoms 1s  $13.8/1.08 = 12.8$ . From this we could propose formulas like  $C_{13}H_{14}O$  or  $C_{12}H_{10}O_2$ .

Alternatively, noting the significant intensity of  $M-2$ , we could propose that the molecule has Fe in it, which, in fact, it does. For the formula  $C_{10}H_{10}Fe$ , we predict that  $M-2$  will have an intensity of  $\frac{5.845}{91.754} \times 100 = 6.37\%$  of  $M^{+*}$ , which is not terribly far from the observed value of 8.3%. The intensity at  $M+1$  will have a contribution from  $^{57}Fe$  and from  $^{13}C$  and  $^2H$ . The  $^{57}Fe$  contribution is  $2.119/91.754 = 2.31\%$  of  $M^{+*}$ . The other contributions are  $1.08(10) + 0.012(10) = 10.92\%$ . The total intensity predicted at  $M+1$  is 13.23% and the observed intensity is 13.2%. The predicted intensity at  $M+2$  is  $\frac{0.282}{91.754} \times 100$  (from Fe) + 0.005 8(10)(9) (from C) = 0.83%, and the observed intensity is 1.0%.

- 21-14.** The compound is dibromochloromethane:

212	$CH^{81}Br_2^{37}Cl$	94	$CH^{81}Br$
210	$CH^{81}Br_2^{35}Cl + CH^{79}Br^{81}Br^{37}Cl$	93	$C^{81}Br$
208	$CH^{79}Br^{81}Br^{35}Cl + CH^{79}Br_2^{37}Cl$	92	$CH^{79}Br$
206	$CH^{79}Br_2^{35}Cl$	91	$C^{79}Br$
175	$CH^{81}Br_2$	81	$^{81}Br$
173	$CH^{79}Br^{81}Br$	79	$^{79}Br$
171	$CH^{79}Br_2$	50	$CH^{37}Cl$
162	$^{81}Br_2$	49	$C^{37}Cl$
160	$^{79}Br^{81}Br$	48	$CH^{35}Cl$
158	$^{79}Br_2$	47	$C^{35}Cl$
131	$CH^{81}Br^{37}Cl$	37	$^{37}Cl$
129	$CH^{81}Br^{35}Cl + CH^{79}Br^{37}Cl$	35	$^{35}Cl$
127	$CH^{79}Br^{35}Cl$		

**21-15.** The CO<sub>2</sub> that we exhale is derived from oxidation of the food we eat. The chart shows that the group of plants called C<sub>3</sub> plants has less <sup>13</sup>C than the groups called C<sub>4</sub> and CAM plants. If the diet in the United States contains more C<sub>4</sub> and CAM plants and the diet in Europe contains more C<sub>3</sub> plants, then the difference in <sup>13</sup>C content of exhaled CO<sub>2</sub> might be explained.

**21-16.** (a) Mass of proton + electron = 1.007 276 467 + 0.000 548 580  
 $= 1.007\ 825\ 047\ \text{Da}$ . To the number of significant digits in Table 1, the masses of the proton and electron are equal to the mass of <sup>1</sup>H.

(b) mass of proton + neutron + electron  
 $= 1.007\ 276\ 467 + 1.008\ 664\ 916 + 0.000\ 548\ 580 = 2.016\ 489\ 963\ \text{Da}$   
mass of <sup>2</sup>H in table = 2.014 10 Da.

The <sup>2</sup>H atom is 0.002 39 Da lighter than the sum of its elementary particles.

(c) Mass difference = (0.002 39 Da) ( $1.660\ 5 \times 10^{-27}\ \text{kg/Da}$ )  
 $= 3.97 \times 10^{-30}\ \text{kg}$   
 $E = mc^2 = (3.97 \times 10^{-30}\ \text{kg})(2.997\ 9 \times 10^8\ \text{m/s})^2 = 3.57 \times 10^{-13}\ \text{J}$   
 $mc^2$  is the binding energy of a single nucleus. For a mole, the energy is  
 $(3.57 \times 10^{-13}\ \text{J})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 2.15 \times 10^{11}\ \text{J/mol} = 2.15 \times 10^8\ \text{kJ/mol}$ .

(d) Binding energy for atom = (13.6 eV)( $1.602\ 18 \times 10^{-19}\ \text{J/eV}$ ) =  $2.18 \times 10^{-18}\ \text{J}$   
To convert to a mole:  $(2.18 \times 10^{-18}\ \text{J})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 1.31 \times 10^6\ \text{J/mol} = 1.31 \times 10^3\ \text{kJ/mol}$ . The ratio of the nuclear binding energy to the electron binding energy is  $(2.15 \times 10^8\ \text{kJ/mol})/(1.31 \times 10^3\ \text{kJ/mol}) = 1.64 \times 10^5$ .

(e)  $\frac{\text{nuclear binding energy}}{\text{bond energy}} \approx (2.15 \times 10^8\ \text{kJ/mol})/(400\ \text{kJ/mol}) = 5 \times 10^5$

**21-17.**  $^{79}\text{Br}$  abundance  $\equiv a = 0.506\ 9$        $^{81}\text{Br}$  abundance  $+ b = 0.493\ 1$   
Abundance of CH<sup>79</sup>Br<sub>3</sub> =  $a^3 = 0.130\ 25$   
Abundance of CH<sup>79</sup>Br<sub>2</sub><sup>81</sup>Br =  $3a^2b = 0.380\ 10$   
Abundance of CH<sup>79</sup>Br<sup>81</sup>Br<sub>2</sub> =  $3ab^2 = 0.369\ 75$   
Abundance of CH<sup>81</sup>Br<sub>3</sub> =  $b^3 = 0.119\ 90$   
Relative abundances: M<sup>+</sup> : M+1 : M+2 : M+3 = 0.342 7 : 1 : 0.972 8 : 0.315 4

**21-18.**  $^{28}\text{Si}$  abundance  $\equiv a = 0.922\ 30$     $^{29}\text{Si} \equiv b = 0.046\ 83$     $^{30}\text{Si} \equiv c = 0.030\ 87$   
 $(a + b + c)^3 = a^3 + 3a^2b + 3a^2c + 3ab^2 + 6abc + 3ac^2 + b^3 + 3b^2c + 3bc^2 + c^3$

	A	B	C	D
1				
2				
3	Silicon			
4	a =	$a^3 =$	Relative abundance	Composition
5	0.92230	0.784543	1.000000	28Si 28Si 28 Si
6	b =	$3a^2b =$		(mass = 84)
7	0.04683	0.119506	0.152326	28Si 28Si 29 Si
8	c =	$3a^2c =$		(mass = 85)
9	0.03087	0.078778	0.100412	28Si 28Si 30 Si
10		$3ab^2 =$		(mass = 86)
11		0.006068	0.007734	28Si 29Si 29 Si
12		$6abc =$		(mass = 86)
13		0.008000	0.010197	28Si 29Si 30 Si
14		$3ac^2 =$		(mass = 87)
15		0.002637	0.003361	28Si 30Si 30 Si
16		$b^3 =$		(mass = 88)
17		0.000103	0.000131	29Si 29Si 29 Si
18		$3b^2c =$		(mass = 87)
19		0.000203	0.000259	29Si 29Si 30 Si
20		$3bc^2 =$		(mass = 88)
21		0.000134	0.000171	29Si 30Si 30 Si
22		$c^3 =$		(mass = 89)
23		2.9418E-05	0.000037	30Si 30Si 30 Si
24				(mass = 90)
25	Check: sum of terms in column B =			
26		1		

mass:        84        85        86        87        88        89        90  
 intensity:    1    0.1523    0.1081    0.01033    0.00362    0.000171    0.000037

- 21-19. In a double-focusing mass spectrometer, ions ejected from the source pass through an electrostatic sector that selects ions with a narrow band of kinetic energies to continue into the magnetic sector. The electric sector acts as an energy filter and the magnetic sector acts as a momentum filter.
- 21-20. From Box 21-2, we know that an ion of  $m/z = 500$  accelerated through a potential difference of  $V$  volts attains a velocity of  $\sqrt{2zeV/m}$ . We need to express the mass in kg. The footnote of Table 21-1 gives the conversion factor.

$$500 \text{ Da} \times 1.661 \times 10^{-27} \text{ kg/Da} = 8.30 \times 10^{-25} \text{ kg}$$

$$\begin{aligned} \text{velocity} &= \sqrt{\frac{2zeV}{m}} = \sqrt{\frac{2(1)(1.602 \times 10^{-19} \text{ C})(5.00 \times 10^3 \text{ V})}{8.30 \times 10^{-25} \text{ kg}}} \\ &= 4.39 \times 10^4 \text{ m/s} \end{aligned}$$

To figure out the units, remember that work (joules) =  $E \cdot q$  = volts·coulombs. So the product  $C \times V = J = m^2 kg/s^2$ . Putting these units into the square root gives velocity in m/s.

The time needed to travel 2.00 m is  $(2.00\text{ m})/(4.39 \times 10^4\text{ m/s}) = 45.6\text{ }\mu\text{s}$ . If we repeated a cycle each time this heaviest ion reaches the detector, we could collect  $1/(45.6\text{ }\mu\text{s}) = 2.20 \times 10^4$  spectra per second.

If we double the mass in the square root to get up to 1 000 Da, the velocity decreases by  $1/\sqrt{2}$  and the frequency goes down by  $1/\sqrt{2}$  to  $1.56 \times 10^4$  spectra per second.

- 21-21.** The reflectron improves resolving power by ensuring that all ions of the same mass reach the detector grid at the same time. Ions from the ion source have some spread of kinetic energy. Faster ions penetrate deeper into the reflectron and therefore spend more time there before being turned around. The reflectron essentially allows slower ions to catch up to faster ions.

**21-22.** (a)  $\lambda = \frac{kT}{(\sqrt{2}\sigma P)} = \frac{(1.38 \times 10^{-23}\text{ J/K})(300\text{ K})}{(\sqrt{2}(\pi(10^{-9}\text{ m})^2)(10^{-5}\text{ Pa}))} = 93\text{ m}$

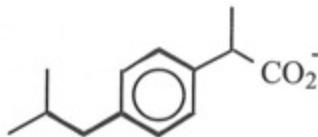
(The answer is in meters if you substitute  $\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}$  for J and  $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$  for Pa from Table 1-2.)

(b)  $\lambda = \frac{kT}{(\sqrt{2}\sigma P)} = \frac{(1.38 \times 10^{-23}\text{ J/K})(300\text{ K})}{(\sqrt{2}(\pi(10^{-9}\text{ m})^2)(10^{-8}\text{ Pa}))} = 93\text{ km}$

- 21-23.** Ions seen in electrospray usually existed in solution prior to electrospray. Atmospheric pressure chemical ionization creates ions in the corona discharge around the high voltage needle.
- 21-24.** In collisionally activated dissociation, ions are accelerated through an electric field and directed into a region with a significant pressure of gas molecules. Collisions transfer enough energy to break molecules into fragments. Collisionally activated dissociation can be conducted “up front” at the entrance to the mass separator, or in the middle section (the collision cell) in tandem mass spectrometry.
- 21-25.** A reconstructed total ion chromatogram shows the current from all ions above a selected mass displayed as a function of time. The chromatogram is “reconstructed” by summing the intensities for all observed values of  $m/z$ . The total ion chromatogram shows everything coming off the column. An extracted

ion chromatogram displays detector current for just one or a few values of  $m/z$  as a function of time. The intensity displayed is extracted from the full mass spectrum recorded at each time interval. A selected ion chromatogram also displays detector current for just one or a small number of  $m/z$  values. However, for a selected ion chromatogram, the detector is not measuring the signal for all values of  $m/z$  in each time interval. The detector is set at just the desired values of  $m/z$  and collects that information for the whole time. The extracted ion chromatogram and the selected ion chromatogram are selective for an analyte of interest (plus anything else that gives a signal at the same  $m/z$ ). The selected ion chromatogram has improved signal-to-noise ratio because the most time is spent detecting signal at the selected mass.

- 21-26.** In selected reaction monitoring, an ion of one  $m/z$  value is selected by the first mass separator. This ion is directed to a collision cell in which it undergoes collisionally activated dissociation to produce fragment ions. One of those fragment ions is then selected by a second mass separator and passed through to the detector. The detector is just responding to one product ion from the selected precursor ion. This technique is called MS/MS because it involves two consecutive mass separation steps. The signal/noise ratio is improved because the noise level is very low. There are few sources of the precursor ion other than the desired analyte, and it is very unlikely that other precursor ions of the selected  $m/z$  can decompose to give the same product ion selected by the second mass separator.
- 21-27.** (a) Ibuprofen can readily dissociate to form a carboxylate anion, so I would choose the negative ion mode. It would be harder to form a cation.



The carboxylate anion should exist in neutral solution, since  $pK_a$  is probably around 4. In sufficiently acidic solution, the carboxylate will be protonated. I would use a neutral chromatography solvent to ensure a good supply of analyte anions.

(b) The formula of the molecular ion,  $M^-$ , is  $C_{13}H_{17}O_2^-$ . The intensity expected at  $M+1$  is  $1.08(13) + 0.012(17) + 0.038(2) = 14.32$ .

carbon	hydrogen	oxygen
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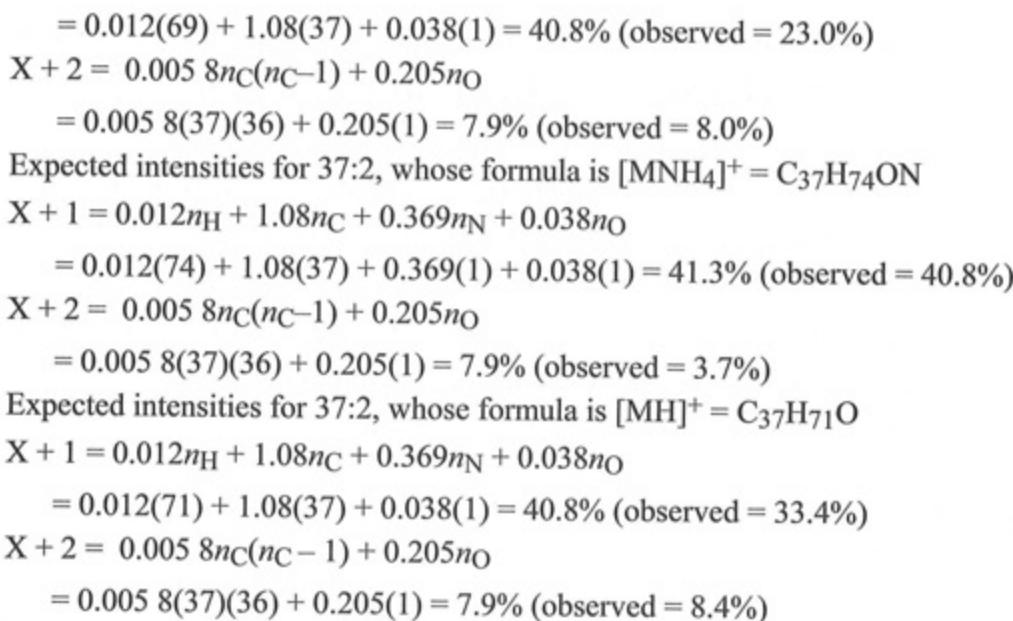
- 21-28.** The analysis follows the same steps as Table 21-3. The work is set out in the following table. Peaks A and B give  $n_A = 12$  and peaks H and I give  $n_H = 19$ . The combination of peaks G and H give  $n_G \approx 21$ , which makes no sense and will be ignored. Assigning peaks A, B, C... as  $n = 12, 13, 14...$  gives the sensible, constant molecular masses in the last column of the table. The mean value, disregarding peak G, is 15 126.

Analysis of electrospray mass spectrum of  $\alpha$ -chain of hemoglobin

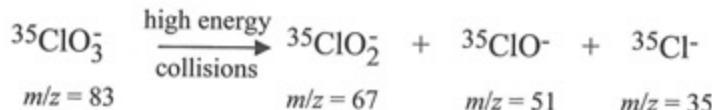
Peak	Observed $m/z$			Charge = $n =$ $\frac{m_{n+1} - 1.008}{m_n - m_{n+1}}$	Molecular mass $= n \times (m_n - 1.008)$
	$\equiv m_n$	$m_{n+1} - 1.008$	$m_n - m_{n+1}$		
A	1 261.5	1 163.6	96.9	12.01 $\approx$ 12	15 126
B	1 164.6	—	—	[13]	15 127
C	—	—	—	[14]	—
D	—	—	—	[15]	—
E	—	—	—	[16]	—
F	—	—	—	[17]	—
G	834.3	796.1	37.2	21.4 [18]	14 999
H	797.1	756.2	39.9	18.95 $\approx$ 19	15 126
I	757.2			[20]	15 124
				mean = 15 100	
				mean without peak G = 15 126	

- 21-29.** The separation between adjacent peaks is 0.27, 0.28, 0.25, 0.24, 0.24, 0.24, 0.27, 0.23, 0.24, 0.25, 0.26, and 0.24  $m/z$  units, giving a mean value of 0.25<sub>1</sub>. If species differing by 1 Da are separated by 0.25<sub>1</sub>  $m/z$  unit, the species must carry 4 charges ( $z = 4$ ). The mass of the tallest peak must be  $4(1 962.12) = 7 848.48$  Da.

- 21-30.** Expected intensities for 37:3, whose formula is  $[MNH_4]^+ = C_{37}H_{72}ON$
- $$\begin{aligned} X + 1 &= 0.012n_H + 1.08n_C + 0.369n_N + 0.038n_O \\ &= 0.012(72) + 1.08(37) + 0.369(1) + 0.038(1) = 41.2\% \text{ (observed = 35.8\%)} \\ X + 2 &= 0.0058n_C(n_C - 1) + 0.205n_O \\ &= 0.0058(37)(36) + 0.205(1) = 7.9\% \text{ (observed = 7.0\%)} \end{aligned}$$
- Expected intensities for 37:3, whose formula is  $[MH]^+ = C_{37}H_{69}O$
- $$X + 1 = 0.012n_H + 1.08n_C + 0.038n_O$$



- 21-31.** Selected reaction monitoring chooses the molecular ion  $\text{ClO}_3^-$  ( $m/z = 83$ ) with the mass separator Q1. In collision cell Q2, this species could possibly undergo the following decomposition:



Quadrupole Q3 selects only  $m/z = 67$ . The measurement is specific for  $\text{ClO}_2^-$  because there are probably few compounds in water producing ions at  $m/z = 83$ , and *very few* of them are likely to decompose into  $m/z = 67$ . None of the species  $\text{ClO}_2^-$ ,  $\text{BrO}_3^-$ , or  $\text{IO}_3^-$  can produce  $m/z = 83$  to be selected by Q1.

- 21-32.** (a) Consider the term  $A_x C_x m_x$ , which applies to the unknown:

$$\begin{aligned}
 A_x C_x m_x &= \left( \frac{\mu\text{mol isotope A}}{\mu\text{mol isotope A} + \mu\text{mol isotope B}} \right) \left( \frac{\mu\text{mol V}}{\text{g unknown}} \right) (\text{g unknown}) \\
 &= \left( \frac{\mu\text{mol isotope A}}{\mu\text{mol isotope A} + \mu\text{mol isotope B}} \right) (\mu\text{mol V}) \\
 &= \left( \frac{\mu\text{mol isotope A}}{\mu\text{mol isotope A} + \mu\text{mol isotope B}} \right) (\mu\text{mol isotope A} + \mu\text{mol isotope B}) \\
 &= \mu\text{mol isotope A in the unknown}.
 \end{aligned}$$

Similarly,  $B_x C_x m_x = \mu\text{mol isotope B in the unknown}$ ,  $A_s C_s m_s = \mu\text{mol isotope A in the spike}$ , and  $B_s C_s m_s = \mu\text{mol isotope B in the unknown}$ .

When we mix the unknown and the spike, the isotope ratio is

$$\begin{aligned}
 R &= \frac{\mu\text{mol A}}{\mu\text{mol B}} = \frac{\mu\text{mol A in unknown} + \mu\text{mol A in spike}}{\mu\text{mol B in unknown} + \mu\text{mol B in spike}} \\
 &= \frac{A_X C_X m_X + A_S C_S m_S}{B_X C_X m_X + B_S C_S m_S}.
 \end{aligned}$$

(b) Cross-multiplying Equation A gives

$$R(B_X C_X m_X + B_S C_S m_S) = A_X C_X m_X + A_S C_S m_S$$

$$RB_X C_X m_X + RB_S C_S m_S = A_X C_X m_X + A_S C_S m_S$$

$$RB_X C_X m_X - A_X C_X m_X = A_S C_S m_S - RB_S C_S m_S$$

$$C_X = \frac{A_S C_S m_S - RB_S C_S m_S}{RB_X m_X - A_X m_X}$$

$$C_X = \left( \frac{C_S m_S}{m_X} \right) \left( \frac{A_S - RB_S}{RB_X - A_X} \right)$$

(c) A =  $^{51}\text{V}$  and B =  $^{50}\text{V}$

Atom fractions in unknown:  $A_X = 0.9975$  and  $B_X = 0.0025$

Atom fractions in spike:  $A_S = 0.6391$  and  $B_S = 0.3609$

$$\begin{aligned}
 C_X &= \left( \frac{C_S m_S}{m_X} \right) \left( \frac{A_S - RB_S}{RB_X - A_X} \right) \\
 &= \left( \frac{(2.2435 \mu\text{mol V/g})(0.41946 \text{ g})}{0.40167 \text{ g}} \right) \left( \frac{0.6391 - (10.545)(0.3609)}{(10.545)(0.0025) - 0.9975} \right) \\
 &= 7.6394 \mu\text{mol V/g}
 \end{aligned}$$

$$\begin{aligned}
 (d) \quad C_X &= \left( \frac{(2.2435 \mu\text{mol V/g})(0.41946 \text{ g})}{0.40167 \text{ g}} \right) \left( \frac{0.6391 - (10.545)(0.3609)}{(10.545)(0.0025) - 0.9975} \right) \\
 &= \left( \frac{(2.2435 \mu\text{mol V/g})(0.41946 \text{ g})}{0.40167 \text{ g}} \right) \left( \frac{0.6391 - 3.8057}{0.02636 - 0.9975} \right) \\
 &= (2.3429) \left( \frac{-3.166}{-0.9711} \right) \\
 &= 7.639 \mu\text{mol V/g}
 \end{aligned}$$

**CHAPTER 22**  
**INTRODUCTION TO ANALYTICAL SEPARATIONS**

- 22-1.** Three extractions with 100 mL are more effective than one extraction with 300 mL.
- 22-2.** Adjust the pH to 3 so the acid is in its neutral form ( $\text{CH}_3\text{CO}_2\text{H}$ ), rather than its anionic form ( $\text{CH}_3\text{CO}_2^-$ ).
- 22-3.** (a) The EDTA complex is anionic ( $\text{AlY}^-$ ), whereas the 8-hydroxyquinoline complex is neutral ( $\text{AlL}_3$ ).
- (b) The EDTA complex is anionic ( $\text{AlY}^-$ ), so we need a hydrophobic cation such as  $(\text{C}_8\text{H}_{17})_3\text{NH}^+$  to try to bring hydrophobic  $\text{AlY}^-$  into the organic solvent.
- 22-4.** The complexation reaction  $m\text{HL} + \text{M}^{m+} \rightleftharpoons \text{ML}_m + m\text{H}^+$  is driven to the right at high pH by consumption of  $\text{H}^+$ . This consumption increases the fraction of metal in the form  $\text{ML}_m$ , which is extracted into organic solvent.
- 22-5.** The form that is extracted into organic solvent is  $\text{ML}_n$ . The formation of  $\text{ML}_n$  is favored by increasing the formation constant ( $\beta$ ).  $\text{ML}_n$  is also favored by increasing  $K_a$ , which increases the fraction of ligand in the form  $\text{L}^-$ . Increasing  $K_L$  decreases the fraction of ligand in the aqueous phase, thereby decreasing the formation of  $\text{ML}_n$ . Increasing  $[\text{H}^+]$  decreases the concentration of  $\text{L}^-$  available for complexation.
- 22-6.** When  $\text{pH} > \text{p}K_{\text{BH}^+}$ , the predominant form is B, which is extracted into the organic phase. When  $\text{pH} > \text{p}K_a$  for HA, the predominant form is  $\text{A}^-$ , which is extracted into the aqueous phase.
- 22-7.** (a)  $\text{S}_{\text{H}_2\text{O}} \rightleftharpoons \text{S}_{\text{CHCl}_3} \quad K = [\text{S}]_{\text{CHCl}_3}/[\text{S}]_{\text{H}_2\text{O}} = 4.0$   
 $[\text{S}]_{\text{CHCl}_3} = K[\text{S}]_{\text{H}_2\text{O}} = (4.0)(0.020 \text{ M}) = 0.080 \text{ M}$
- (b) 
$$\frac{\text{mol S in CHCl}_3}{\text{mol S in H}_2\text{O}} = \frac{(0.080 \text{ M})(10.0 \text{ mL})}{(0.020 \text{ M})(80.0 \text{ mL})} = 0.50$$
- 22-8.** Fraction remaining =  $\left(\frac{V_1}{V_1+KV_2}\right)^n = \left(\frac{80.0}{80.0+(4.0)(10.0)}\right)^6 = 0.088$
- 22-9.** (a) 
$$D = \frac{[\text{B}]_{\text{C}_6\text{H}_6}}{[\text{B}]_{\text{H}_2\text{O}} + [\text{BH}^+]_{\text{H}_2\text{O}}}$$

(b)  $D$  is the quotient of total concentrations in the phases.

$K$  is the quotient of concentrations of neutral species (B) in the phases.

$$(c) D = \frac{K \cdot K_a}{K_a + [H^+]} = \frac{(50.0)(1.0 \times 10^{-9})}{(1.0 \times 10^{-9}) + (1.0 \times 10^{-8})} = 4.5$$

(d)  $D$  will be greater at pH 10 because a greater fraction of B is neutral.

22-10. From Equation 22-12,  $D \approx \frac{[ML_n]_{org}}{[M^{n+}]_{aq}} = K_{extraction} \frac{[HL]_{org}^n}{[H^+]_{aq}^n}$

Comparing this result to Equation 22-13 gives  $K_{extraction} = \frac{K_M \beta K_a^n}{K_L^n}$

Constant	Effect on $K_{extraction}$	Reason
$K_M$	increase	$ML_n$ is more soluble in organic phase.
$\beta$	increase	Ligand binds metal more tightly and $ML_n$ is the organic-soluble form.
$K_a$	increase	Ligand dissociates to $L^-$ more easily, increasing $ML_n$ formation.
$K_L$	decrease	$HL$ is more soluble in organic phase, where it is not available to react with $M^{n+}(aq)$ .

22-11. (a)  $D = K[H^+]/([H^+] + K_a) = 3 \cdot 10^{-4.00}/(10^{-4.00} + 1.52 \times 10^{-5}) = 2.60$  at pH 4.00.

Fraction remaining in water =  $q = V_1/(V_1 + DV_2) = 100/[100 + 2.60(25)] =$

0.606. Therefore, the molarity in water is  $0.606(0.10\text{ M}) = 0.0606\text{ M}$ .

The total moles of solute in the system is  $(0.100\text{ L})(0.10\text{ M}) = 0.010\text{ mol}$ .

The fraction of solute in benzene is 0.394, so the molarity in benzene is

$0.394(0.010\text{ mol})/0.025\text{ L} = 0.16\text{ M}$ .

(b) At pH 10.0:  $D = 1.97 \times 10^{-5}$ ,  $q = 0.999995$ , molarity in water =

$0.10\text{ M}$ , and molarity in benzene =  $2 \times 10^{-6}\text{ M}$ .

22-12.  $D = C/[H^+]^n$ , where  $C = K_M \beta K_a^n [HL]_{org}^n / K_L^n$

$$D_1 = 0.01 = C/[H^+]_1^2 \text{ and } D_2 = 100 = C/[H^+]_2^2$$

$$D_2/D_1 = 10^4 = [H^+]_1^2 / [H^+]_2^2 \Rightarrow [H^+]_1 / [H^+]_2 = 10^2 \Rightarrow \Delta \text{pH} = 2 \text{ pH units}$$

22-13. (a) Since there is so much more dithizone than Cu, it is safe to say that  $[HL]_{org} = 0.1\text{ mM}$ .

$$D = \frac{K_M \beta K_a^n}{K_L^n} \frac{[HL]_{org}^n}{[H^+]_{aq}^n} = \frac{(7 \times 10^4)(5 \times 10^{22})(3 \times 10^{-5})^2}{(1.1 \times 10^4)^2} \frac{(1 \times 10^{-4})^2}{[H^+]^2}$$

$$= 2.6 \times 10^4 \text{ at pH 1 and } 2.6 \times 10^{10} \text{ at pH 4}$$

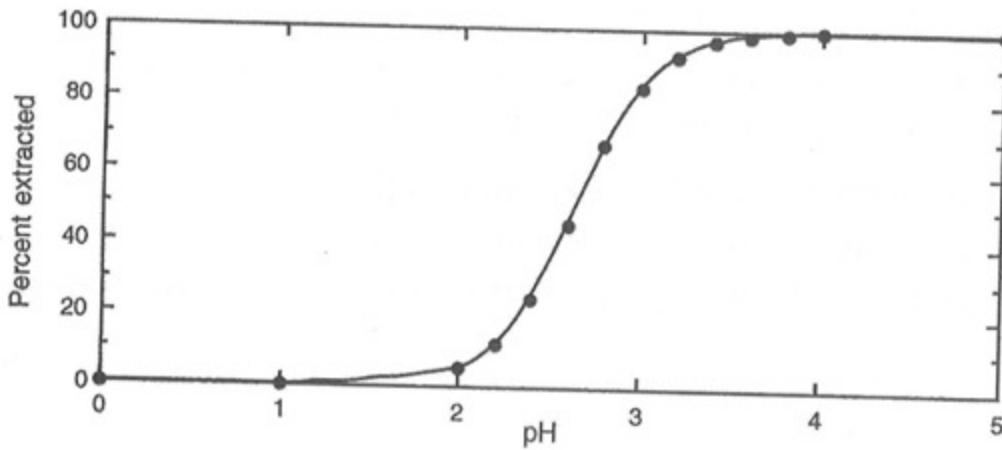
$$(b) q = V_1/(V_1+DV_2) = 100/[100 + 2.6 \times 10^4 (10)] = 3.8 \times 10^{-4}$$

**22-14.** (a)  $D = \frac{[ML_2]_{org}}{[ML_2]_{aq}} = \frac{C_{org}V_{org}}{C_{aq}V_{aq}} \Rightarrow C_{org} = D C_{aq} \frac{V_{aq}}{V_{org}}$

$$\% \text{ extracted} = \frac{100 C_{org}}{C_{aq} + C_{org}} = \frac{100 D C_{aq} \frac{V_{aq}}{V_{org}}}{C_{aq} + D C_{aq} \frac{V_{aq}}{V_{org}}} = \frac{100 D \frac{V_{aq}}{V_{org}}}{1 + D \frac{V_{aq}}{V_{org}}}$$

(b) Spreadsheet for pH dependence of dithizone extraction

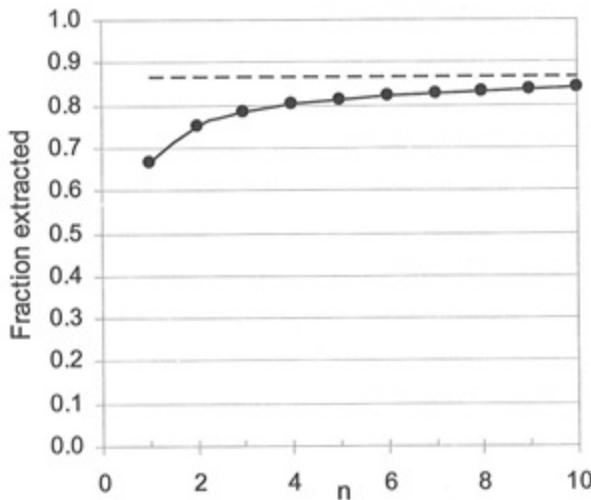
	A	B	C	D	E
1	K(M) =	pH	H	D = Dist.coeff	% extracted
2	70000		1	1.00E-01	2.60E-02
3	Beta =		2	1.00E-02	2.60E+00
4	5E+18		2.2	6.31E-03	6.54E+00
5	Ka =		2.4	3.98E-03	1.64E+01
6	0.00003		2.6	2.51E-03	4.13E+01
7	K(L) =		2.8	1.58E-03	1.04E+02
8	11000		3	1.00E-03	2.60E+02
9	[HL]org =		3.2	6.31E-04	6.54E+02
10	0.00001		3.4	3.98E-04	1.64E+03
11	V(org) =		3.6	2.51E-04	4.13E+03
12	2		3.8	1.58E-04	1.04E+04
13	V(aq) =		4	1.00E-04	2.60E+04
14	100		5	1.00E-05	2.60E+06
15					100.00
16	C2 = 10^-B2				
17	$D2 = (\$A\$2 * \$A\$4 * \$A\$6^2 * \$A\$10^2) / (\$A\$8^2 * C2^2)$				
18	$E2 = (D2 * \$A\$12 / \$A\$14) / (1 + (D2 * \$A\$12 / \$A\$14)) * 100$				



22-15.

	A	B	C	D	E	F
1	Liquid-liquid extraction efficiency					
2						
3	$V_2 =$	50 mL (volume of extraction solvent)				
4	$V_1 =$	50 mL (volume to be extracted)				
5	$K =$	2 (partition coefficient = $[S]_2/[S]_1$ )				
6	Divide $V_2$ into $n$ equal portions for $n$ extractions					
7	Theoretical maximum fraction extracted = $1-q_{\text{limit}} = 1-\exp(-V_2/V_1)K$					
8	$1-q_{\text{limit}} =$	0.864665				
9						
10	$V_2/n$					
11	individual	$q =$	$1-q =$	% of limiting		
12	extraction	fraction	fraction	fraction		
13	$n$	volume	remaining	extracted	extracted	
14	1	50.0	0.333	0.667	77.1	
15	2	25.0	0.250	0.750	86.7	
16	3	16.7	0.216	0.784	90.7	
17	4	12.5	0.198	0.802	92.8	
18	5	10.0	0.186	0.814	94.1	
19	6	8.3	0.178	0.822	95.1	
20	7	7.1	0.172	0.828	95.7	
21	8	6.3	0.168	0.832	96.2	
22	9	5.6	0.164	0.836	96.6	
23	10	5.0	0.162	0.838	97.0	
24	$C14 = (\$B\$4/(\$B\$4+B14*\$B\$5))^{A14}$					
25	$q = [V_1/(V_1 + (V_2/n)K)]^n$					

The theoretical limit for fraction extracted is in cell C8. 95% of the theoretical fraction extracted is  $(0.95)(0.864665) = 0.8214$ . This fraction is exceeded with  $n = 6$  equal extractions.



**22-16.** 1-C, 2-D, 3-A, 4-E, 5-B

**22-17.** The larger the partition coefficient, the greater the fraction of solute in the stationary phase, and the smaller the fraction that is moving through the column.

**22-18.** (a)  $k = \frac{\text{time solute spends in stationary phase}}{\text{time solute spends in mobile phase}} = \frac{t_r - t_m}{t_m} = \frac{t_s}{t_m}$

(b) Fraction of time in mobile phase =  $\frac{t_m}{t_m + t_s} = \frac{t_m}{t_m + kt_m} = \frac{1}{1+k}$

(c)  $R = \frac{t_m}{t_r} = \frac{t_m}{t_m + t_s} = \frac{1}{1+k}$ . Parts (b) and (c) together tell us that

$$\frac{\text{time for solvent to pass through column}}{\text{time for solute to pass through column}} = \frac{\text{time spent by solute in mobile phase}}{\text{total time on column}}$$

**22-19.** (a) Volume per cm of length =  $\pi r^2 \times \text{length} = \pi \left(\frac{0.461 \text{ cm}}{2}\right)^2 (1 \text{ cm}) = 0.167 \text{ mL}$

mobile phase volume =  $(0.390)(0.167 \text{ mL}) = 0.0651 \text{ mL}$  per cm of column

linear flow rate =  $u_x = \frac{1.13 \text{ ml/min}}{0.0651 \text{ mL/cm}} = 17.4 \text{ cm/min}$

(b)  $t_m = (10.3 \text{ cm}) / (17.4 \text{ cm/min}) = 0.592 \text{ min}$

(c)  $k = \frac{t_r - t_m}{t_m} \Rightarrow t_r = kt_m + t_m = 10(0.592) + 0.592 = 6.51 \text{ min}$

**22-20.** (a) Linear flow rate =  $(30.1 \text{ m}) / (2.16 \text{ min}) = 13.9 \text{ m/min.}$

Inner diameter of open tube =  $530 \mu\text{m} - 2(3.1 \mu\text{m}) = 523.8 \mu\text{m}$

$\Rightarrow$  radius =  $261.9 \mu\text{m}$ .

Volume =  $\pi r^2 \times \text{length} = \pi (261.9 \times 10^{-4} \text{ cm})^2 (30.1 \times 10^2 \text{ cm}) = 6.49 \text{ mL}$

Volume flow rate =  $(6.49 \text{ mL}) / (2.16 \text{ min}) = 3.00 \text{ mL/min}$

(b)  $k = \frac{t_r - t_m}{t_m} = \frac{17.32 - 2.16}{2.16} = 7.02$

$k = t_s/t_m$  (where  $t_s$  = time in stationary phase)

$$\begin{aligned} \text{Fraction of time in stationary phase} &= \frac{t_s}{t_s + t_m} = \frac{kt_m}{kt_m + t_m} = \\ &= \frac{k}{k+1} = \frac{7.02}{7.02+1} = 0.875 \end{aligned}$$

(c) Volume of coating  $\approx 2\pi r \times \text{thickness} \times \text{length}$

$$= 2\pi[(261.9 + 1.55) \times 10^{-4} \text{ cm}](3.1 \times 10^{-4} \text{ cm})(30.1 \times 10^2 \text{ cm}) = 0.154 \text{ mL}$$

$$k = K \frac{V_s}{V_m} \Rightarrow 7.02 = K \frac{0.154 \text{ mL}}{6.49 \text{ mL}} \Rightarrow K = \frac{c_s}{c_m} = 295$$

22-21. (a)  $\frac{\text{Large load}}{\text{Small load}} = \left( \frac{\text{Large column radius}}{\text{Small column radius}} \right)^2$   
 $\frac{100 \text{ mg}}{4.0 \text{ mg}} = \left( \frac{\text{Large column diameter}}{0.85 \text{ cm diameter}} \right)^2 \Rightarrow \text{large column diameter} = 4.25 \text{ cm}$

Use a 40-cm-long column with a diameter near 4.25 cm.

- (b) The linear flow rate should be the same. Since the cross-sectional area of the column is increased by a factor of 25, the volume flow rate should be increased by a factor of 25  $\Rightarrow u_v = 5.5 \text{ mL/min.}$
- (c) Volume of small column =  $\pi r^2 \times \text{length} = \pi (0.85/2 \text{ cm})^2 (40 \text{ cm}) = 22.7 \text{ mL}$   
 Mobile phase volume = 35% of column volume = 7.94 mL  
 $\text{Linear flow} = \frac{40 \text{ cm}}{(7.94 \text{ mL})/(0.22 \text{ mL/min})} = 1.11 \text{ cm/min for both columns}$

22-22. (a)  $k = \frac{9.0 - 3.0}{3.0} = 2.0$

(b) Fraction of time solute is in mobile phase =  $\frac{t_m}{t_r} = \frac{3.0}{9.0} = 0.33$

(c)  $K = k \frac{V_m}{V_s} = (2.0) \frac{V_m}{0.10 V_m} = 20$

22-23. Solvent volume per cm of column length =  $(0.15)\pi \left(\frac{0.30 \text{ cm}}{2}\right)^2 = 0.0106 \text{ mL/cm.}$

A volume flow rate of 0.20 mL/min corresponds to a linear flow rate of  $\left(\frac{0.20 \text{ mL/min}}{0.0106 \text{ mL/cm}}\right) = 19 \text{ cm/min.}$

22-24.  $k = K \frac{V_s}{V_m} = 3\left(\frac{1}{5}\right) = \frac{3}{5}$  For  $K = 30, k = 30\left(\frac{1}{5}\right) = 6.$

22-25.  $k = \frac{V_r}{V_m} = \frac{V_r - V_m}{V_m} = \frac{76.2 - 16.6}{16.6} = 3.59$

$$K = k \frac{V_m}{V_s} = (3.59) \frac{16.6}{12.7} = 4.69$$

22-26.  $K = k \frac{V_m}{V_s}$   
 $k = \frac{t_r - t_m}{t_m} = \frac{433 - 63}{63} = 5.87$

$$\frac{V_m}{V_s} = \frac{\pi r^2 \times \text{length}}{2\pi r \times \text{thickness} \times \text{length}} = \frac{(103)^2}{2(103.25) \times 0.5} = 102.8$$

(In the numerator,  $r$  refers to the radius of the open tube =  $1/2 (207 - 1.0)$   $\mu\text{m}$  = 103  $\mu\text{m}$ . In the denominator,  $r$  is the radius at the center of the stationary phase, which is  $103 + \frac{1}{2}(0.5) = 103.25$   $\mu\text{m}$ .)

Therefore, the partition coefficient is  $K = k \frac{V_m}{V_s} = 5.87 (102.8) = 603$ .

$$\begin{aligned}\text{Fraction of time in stationary phase} &= \frac{t_s}{t_s + t_m} = \frac{kt_m}{kt_m + t_m} = \frac{k}{k+1} \\ &= \frac{5.87}{5.87+1} = 0.854\end{aligned}$$

- 22-27.** (a) After 10 cycles, the compounds have passed through a length  $10L$  containing  $10N$  theoretical plates. We are told that  $\gamma = 1.018$ .

$$\text{resolution} = \frac{\sqrt{N}}{4} (\gamma - 1)$$

$$1.60 = \frac{\sqrt{10N}}{4} (1.018 - 1) \Rightarrow N = 1.26 \times 10^4$$

- (b) Plate height =  $H = L/N = 50 \text{ cm}/1.26 \times 10^4 = 4.0 \times 10^{-3} \text{ cm} = 40 \mu\text{m}$

- (c) Resolution is proportional to  $\sqrt{N}$  or  $\sqrt{\text{number of cycles}}$

$$\frac{\text{resolution in 2 cycles}}{\text{resolution in 10 cycles}} = \sqrt{\frac{2}{10}} = 0.447$$

$$\text{resolution in 2 cycles} = 0.447(\text{resolution in 10 cycles}) = 0.447(1.6) = 0.72$$

(observed resolution = 0.71)

- 22-28.** (a) Column 1 (sharper peaks)

- (b) Column 2 (large plate height means fewer plates means broader peaks)

- (c) Column 1 (less overlap between peaks because they are sharper)

- (d) Neither (relative retention ( $= t_r(B)/T_r(A)$ ) is equal for the two columns)

- (e) Compound B (longer retention time)

- (f) Compound B (longer retention time means greater affinity for stationary phase)

- (g)  $\gamma = t_B/t_A = 10/8 = 1.25$

- 22-29.** The linear rate at which solution goes past the stationary phase determines how completely the equilibrium between the two phases is established. This

determines the size of the mass transfer term ( $Cu_x$ ) in the van Deemter equation. The extent of longitudinal diffusion depends on the time spent on the column, which is inversely proportional to linear flow rate.

- 22-30. Smaller plate height gives less band spreading: 0.1 mm
- 22-31. Diffusion coefficients of gases are  $10^4$  times greater than those of liquids. Therefore, longitudinal diffusion occurs much faster in gas chromatography than in liquid chromatography.
- 22-32. The smaller the particle size, the more rapid is equilibration between mobile and stationary phases.
- 22-33. Minimum plate height is at 33 mL/min.
- 22-34. Silanization caps hydroxyl groups to which strong hydrogen bonding can occur.
- 22-35. Isotherms and band shapes are given in Figure 22-21. In overloading, the solute becomes more soluble in the stationary phase as solute concentration increases. This leaves little solute trailing behind the main band, and gives a non-Gaussian shape. Tailing occurs when small quantities of solute are retained more strongly than large quantities. The beginning of the band is abrupt, but the back part trails off slowly as the tightly bound solute is gradually eluted.
- 22-36. With 5.0 mg, the column may be overloaded. That is, the quantity of solute per unit length may be too great for the volume of stationary phase. This leads to the upper nonlinear isotherm in Figure 22-21, which broadens bands and decreases resolution.
- 22-37. Equation 22-26 says that the standard deviation of the band is proportional to  $\sqrt{t}$ . Here is what we know of the rate of diffusion:

time	standard deviation
$t_1$	$\sigma_1 = 1$
$t_2 = t_1 + 20$	$\sigma_2 = 2$
$t_3 = t_1 + 40$	$\sigma_3 = ?$

From the bandwidths at times  $t_1$  and  $t_2$ , we can write

$$\frac{\sigma_2}{\sigma_1} = \sqrt{\frac{t_2}{t_1}} \Rightarrow \frac{2}{1} = \sqrt{\frac{t_1 + 20}{t_1}} \Rightarrow t_1 = \frac{20}{3} \text{ min}$$

$$\text{For time } t_3: \frac{\sigma_3}{\sigma_1} = \sqrt{\frac{t_3}{t_1}} \Rightarrow \frac{\sigma_3}{1} = \sqrt{\frac{\frac{20}{3} + 40}{\frac{20}{3}}} \Rightarrow \sigma_3 = 2.65 \text{ mm}$$

- 22-38.** (a)  $N = \frac{5.55 t_r^2}{w_{1/2}^2} = \frac{5.55 (9.0 \text{ min})^2}{(2.0 \text{ min})^2} = 1.12 \times 10^2 \text{ plates}$
- (b)  $(10 \text{ cm})/(1.12 \times 10^2 \text{ plates}) = 0.89 \text{ mm}$
- 22-39.** (a)  $N = \frac{41.7 (t_r/w_{0.1})^2}{(A/B) + 1.25} = \frac{41.7 (900 \text{ s}/44 \text{ s})^2}{(33 \text{ s}/11 \text{ s}) + (1.25)} = 4.1 \times 10^3 \text{ plates}$
- (b) To use the equation  $N = (t_r/\sigma)^2$ , we need to find the standard deviation of the peak. The width at 1/10 height is  $22 + 22 = 44 \text{ s}$ , which we are told is equal to  $4.297\sigma$ . Therefore,  $\sigma = (44 \text{ s})/4.297 = 10.24 \text{ s}$ .  $N = (t_r/\sigma)^2 = (900 \text{ s}/10.24 \text{ s})^2 = 7.72 \times 10^3 \text{ plates}$ .
- The equation for an asymmetric peak from (a) gives
- $$N = \frac{41.7 (t_r/w_{0.1})^2}{(A/B) + 1.25} = \frac{41.7 (900 \text{ s}/44 \text{ s})^2}{(22 \text{ s}/22 \text{ s}) + (1.25)} = 7.75 \times 10^3 \text{ plates}$$
- 22-40.** Resolution =  $\frac{\Delta t_r}{w} = \frac{5 \text{ min}}{6 \text{ min}} = 0.83$ . This is most like the diagram for a resolution of 0.75.
- 22-41.** Since  $w = 4V_r/\sqrt{N}$ ,  $w$  is proportional to  $V_r$  (if  $N$  is constant).  
 $w_2/w_1 = V_2/V_1 = 127/49 \Rightarrow w_2 = (127/49)(4.0) = 10.4 \text{ mL}$ .
- 22-42.**  $\sigma_{\text{obs}}^2 = \left(\frac{w_{1/2}}{2.35}\right)^2 = \left(\frac{39.6}{2.35}\right)^2 = 283.96 \text{ s}^2$   
 $\Delta t_{\text{injection}} = (0.40 \text{ mL})/(0.66 \text{ mL/min}) = 0.606 \text{ min} = 36.36 \text{ s}$   
 $\sigma_{\text{injection}}^2 = \frac{\Delta t_{\text{injection}}^2}{12} = \frac{36.36^2}{12} = 110.19 \text{ s}^2$   
 $\Delta t_{\text{detector}} = (0.25 \text{ mL})/(0.66 \text{ mL/min}) = 22.73 \text{ s}$   
 $\sigma_{\text{detector}}^2 = (\Delta t)^2_{\text{detector}}/12 = 43.04 \text{ s}^2$   
 $\sigma_{\text{obs}}^2 = \sigma_{\text{column}}^2 + \sigma_{\text{injection}}^2 + \sigma_{\text{detector}}^2$   
 $283.96 = \sigma_{\text{column}}^2 + 110.19 + 43.04 \Rightarrow \sigma_{\text{column}} = 11.43 \text{ s}$   
 $w_{1/2} = 2.35 \sigma_{\text{column}} = 26.9 \text{ s}$

$$22-43. \quad \alpha = \frac{t'_{r2}}{t'_{r1}} = \frac{k_2}{k_1} = \frac{K_2}{K_1} = \frac{18}{15} = 1.20$$

$$k_2 = K_2 \frac{V_s}{V_m} = 18 \left( \frac{1}{3.0} \right) = 6.0 \quad k_1 = 15 \left( \frac{1}{3.0} \right) = 5.0$$

$$k_1 = (t_1 - t_m)/t_m = t_1/t_m - 1 \Rightarrow t_1 = t_m(k_1 + 1) = (1.0 \text{ min})(5.0 + 1) = 6.0 \text{ min}$$

$$k_2 = (t_2 - t_m)/t_m \Rightarrow t_2 = t_m(k_2 + 1) = (1.0 \text{ min})(6.0 + 1) = 7.0 \text{ min}$$

$$\gamma = t_2/t_1 = 7.0/6.0 = 1.167$$

$$\text{Resolution} = \frac{\sqrt{N}}{4} (\gamma - 1)$$

$$1.5 = \frac{\sqrt{N}}{4} (1.167 - 1) \Rightarrow 1.3 \times 10^3 \text{ plates}$$

$$22-44. \quad (a) \quad \gamma = t_2/t_1 = 1.01, 1.05, \text{ or } 1.10$$

$$\text{Resolution} = \frac{\sqrt{N}}{4} (\gamma - 1) \Rightarrow N = \left( \frac{4 \times \text{resolution}}{\gamma - 1} \right)^2$$

resolution	$\gamma$	N
2.0	1.01	640 000
2.0	1.05	25 600
2.00	1.10	6 400

- (b) For the same kind of column,  $N$  can be increased by increasing the column length ( $N \propto \sqrt{L}$ ).  $\gamma$  can be increased by changing solvent and/or stationary phase to change the partition coefficients of the two components.

$$22-45. \quad (a) \quad \text{C}_6\text{HF}_5: \quad t'_r = 12.98 - 1.06 = 11.92 \text{ min.} \quad k = 11.92/1.06 = 11.25$$

$$\text{C}_6\text{H}_6: \quad t'_r = 13.20 - 1.06 = 12.14 \text{ min.} \quad k = 12.14/1.06 = 11.45$$

$$(b) \quad \alpha = 12.14/11.92 = 1.018$$

$$(c) \quad \gamma = t_2/t_1 = 13.20/12.98 = 1.017$$

$$(d) \quad w_{1/2}(\text{C}_6\text{HF}_5) = 0.124 \text{ min; } w_{1/2}(\text{C}_6\text{H}_6) = 0.121 \text{ min}$$

$$\text{C}_6\text{HF}_5: \quad N = \frac{5.55 t_r^2}{w_{1/2}^2} = \frac{5.55 (12.98)^2}{0.124^2} = 6.08 \times 10^4 \text{ plates}$$

$$\text{Plate height} = \frac{30.0 \text{ m}}{6.08 \times 10^4 \text{ plates}} = 0.493 \text{ mm}$$

$$\text{C}_6\text{H}_6: \quad N = \frac{5.55 (13.20)^2}{0.121^2} = 6.60 \times 10^4 \text{ plates}$$

$$\text{Plate height} = \frac{30.0 \text{ m}}{6.60 \times 10^4 \text{ plates}} = 0.455 \text{ mm}$$

(e)  $w(\text{C}_6\text{HF}_5) = 0.220 \text{ min}; w(\text{C}_6\text{H}_6) = 0.239 \text{ min}$

$$\text{C}_6\text{HF}_5: N = \frac{16 t_r^2}{w^2} = \frac{16 (12.98)^2}{0.220^2} = 5.57 \times 10^4 \text{ plates}$$

$$\text{C}_6\text{H}_6: N = \frac{16 (13.20)^2}{0.239^2} = 4.88 \times 10^4 \text{ plates}$$

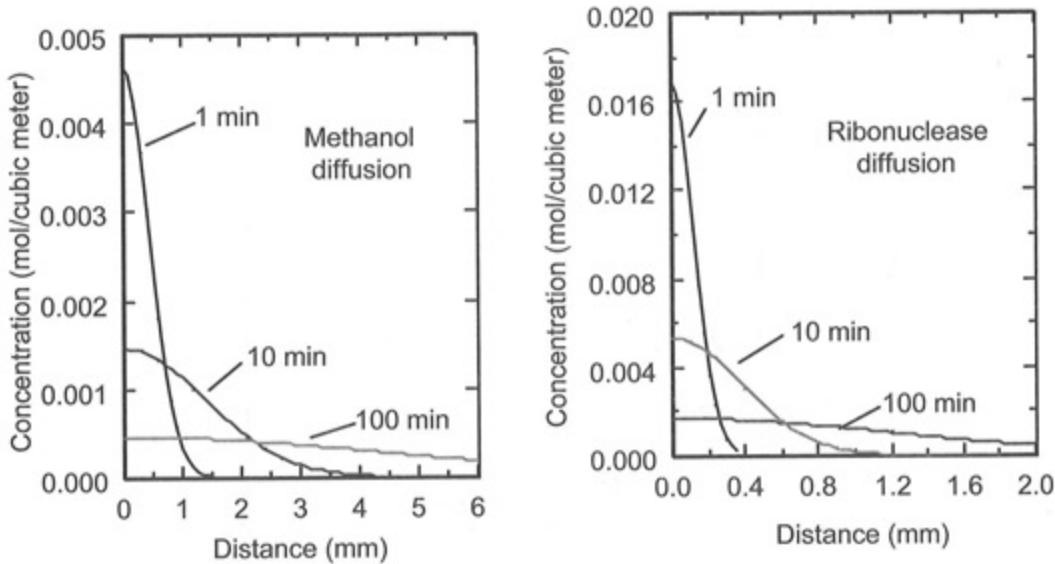
(f) Resolution =  $\frac{\Delta t_r}{w_{\text{av}}} = \frac{13.20 - 12.98}{0.229} = 0.96$

(g)  $N = \sqrt{(5.57 \times 10^4)(4.88 \times 10^4)} = 5.21 \times 10^4 \text{ plates}$

$$\text{Resolution} = \frac{\sqrt{N}}{4} (\gamma - 1) = \frac{\sqrt{5.21 \times 10^4}}{4} (1.017 - 1) = 0.97$$

- 22-46. Initial concentration ( $m$ ) =  $10 \text{ nmol}/(1.96 \times 10^{-3} \text{ m}^2) = 5.09 \times 10^{-6} \text{ mol/m}^2$ . Diffusion will be symmetric about the origin. Only diffusion in the positive direction is computed below for  $t = 60 \text{ s}$ . Other conditions in the graphs are obtained by changing  $t$  and the diffusion coefficient  $D$ .

	A	B	C
1	Diffusion problem		
2		x (m)	c(mol/m <sup>3</sup> )
3	moles =	0	4.637E-03
4	1.00E-08	0.0001	4.518E-03
5	diameter (m) =	0.0002	4.178E-03
6	0.05	0.0003	3.668E-03
7	x-sectional area (m <sup>2</sup> )	0.0004	3.057E-03
8	0.001963495	0.0005	2.418E-03
9	m (mol/m <sup>2</sup> )=	0.0006	1.816E-03
10	5.093E-06	0.0007	1.294E-03
11	D (m <sup>2</sup> /s) =	0.0008	8.758E-04
12	1.600E-09	0.0009	5.625E-04
13	t (s) =	0.001	3.430E-04
14	60	0.0012	1.090E-04
15		0.0014	2.815E-05
16		0.0016	5.901E-06
17		0.0018	1.004E-06
18	A10 = A4/A8	0.002	1.388E-07
19			
20	C3 = (\$A\$10/(SQRT(4*PI()*\$A\$12*\$A\$14)))		
21		*EXP(-(B3^2)/(4*\$A\$12*\$A\$14)))	



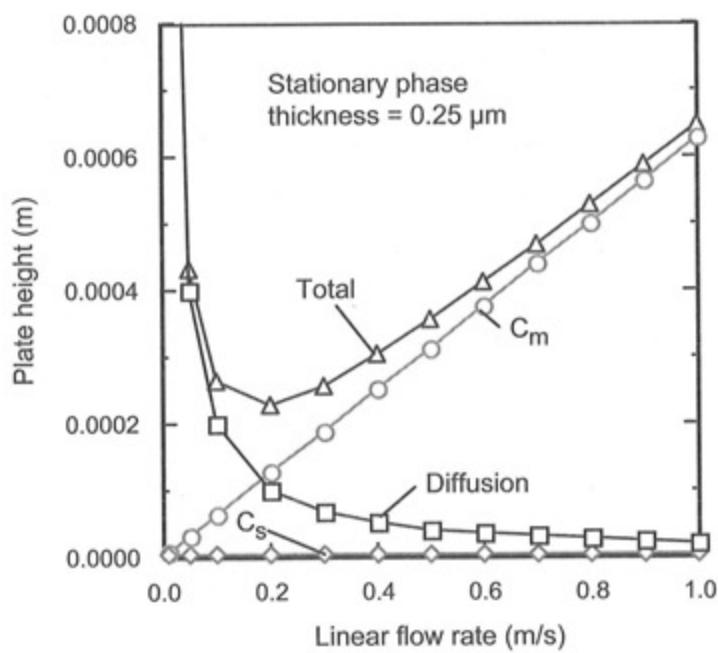
$$\begin{aligned}
 22-47. \quad \text{Plate height} &= H_D + H_{\text{mass transfer}} = \frac{B}{u_x} + (C_s + C_m)u_x \\
 &= \frac{2D_m}{u_x} + \left( \frac{2kd^2}{3(k+1)^2 D_s} + \frac{1+6k+11k^2 r^2}{24(k+1)^2 D_m} \right) u_x
 \end{aligned}$$

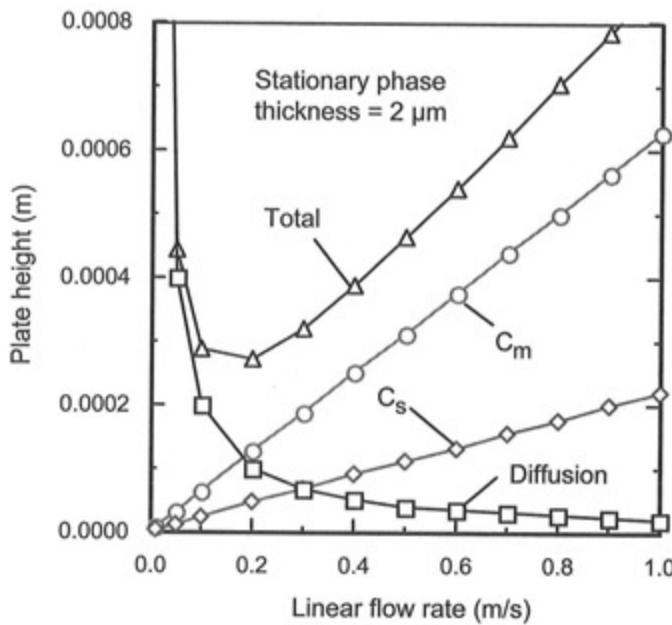
Parameters for 0.25  $\mu\text{m}$  thick stationary phase:

$$D_m = 1.0 \times 10^{-5} \text{ m}^2/\text{s} \quad D_s = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$$

$$d = 2.5 \times 10^{-7} \text{ m} \quad r = 12.5 \times 10^{-4} \text{ m}$$

$$k = 10$$





	A	B	C	D	E	F
1	Plate height calculation for 0.25-μm-thick stationary phase					
2			H(mass transfer)			
3	D <sub>m</sub> =	u <sub>x</sub> (m/s)	H(diffusion)	C <sub>s</sub> term	C <sub>m</sub> term	H (total)
4	0.00001	0.01	2.00E-03	3.44E-08	6.25E-06	2.01E-03
5	D <sub>s</sub> =	0.05	4.00E-04	1.72E-07	3.12E-05	4.31E-04
6	1E-09	0.1	2.00E-04	3.44E-07	6.25E-05	2.63E-04
7	k =	0.2	1.00E-04	6.89E-07	1.25E-04	2.26E-04
8	10	0.3	6.67E-05	1.03E-06	1.87E-04	2.55E-04
9	d (m) =	0.4	5.00E-05	1.38E-06	2.50E-04	3.01E-04
10	2.50E-07	0.5	4.00E-05	1.72E-06	3.12E-04	3.54E-04
11	r (m) =	0.6	3.33E-05	2.07E-06	3.75E-04	4.10E-04
12	1.25E-04	0.7	2.86E-05	2.41E-06	4.37E-04	4.68E-04
13		0.8	2.50E-05	2.75E-06	5.00E-04	5.27E-04
14		0.9	2.22E-05	3.10E-06	5.62E-04	5.88E-04
15		1	2.00E-05	3.44E-06	6.25E-04	6.48E-04
16	C4 = 2*\$A\$4/B4					
17	D4 = 2*\$A\$8*\$A\$10^2*B4/(3*(\$A\$8+1)^2*\$A\$6)					
18	E4 = (1+6*\$A\$8+11*\$A\$8^2)*\$A\$12^2*B4/(24*(\$A\$8+1)^2*\$A\$4)					
19	F4 = C4+D4+E4					

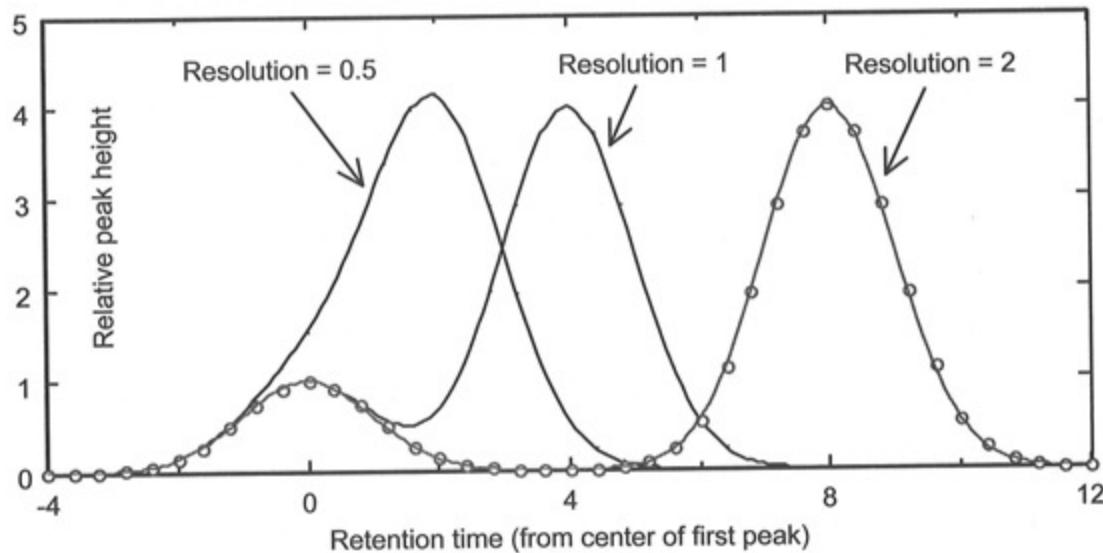
For stationary phase thickness = 0.25 μm, plate height contribution from mass transfer in the stationary phase is negligible, as shown in the first graph. If the stationary phase is 2.0 μm thick, plate height from mass transfer in the stationary phase is not negligible, but it is still less than plate height from mass transfer in the mobile phase. C<sub>s</sub> and total plate height in the second graph are greater than in the first graph. C<sub>m</sub> and longitudinal diffusion terms are unaffected.

**22-48.** Inspection of Equation 4-3 shows that the general form of a Gaussian curve is  $y = Ae^{-(x-x_0)^2/2\sigma^2}$ , where  $A$  is a constant proportional to the area under the curve,  $x_0$  is the abscissa of the center of the peak, and  $\sigma$  is the standard deviation. We can arbitrarily let  $\sigma = 1$ , which means that the width at the base ( $w = 4\sigma$ ) is 4. A peak with an area of 1 centered at the origin is  $y = 1 \cdot e^{-(x)^2/2}$ . A curve of area 4 is  $y = 4 \cdot e^{-(x)^2/2}$ . The resolution is  $\Delta x/w$ . For a resolution of 0.5,  $\Delta x = 0.5 \cdot w = 2$ . That is, the second peak is centered at  $x = 2$  if the resolution is 0.5. Its equation is  $y = 4 \cdot e^{-(x-2)^2/2}$ . Similarly, for a resolution of 1,  $\Delta x = 1 \cdot w = 4$  and the second peak is centered at  $x = 4$ . For a resolution of 2, the second peak is centered at  $x = 8$ . The equations of the curves plotted below are:

$$\text{Resolution} = 0.5: \quad y = 1 \cdot e^{-(x)^2/2} + 4 \cdot e^{-(x-2)^2/2}$$

$$\text{Resolution} = 1: \quad y = 1 \cdot e^{-(x)^2/2} + 4 \cdot e^{-(x-4)^2/2}$$

$$\text{Resolution} = 2: \quad y = 1 \cdot e^{-(x)^2/2} + 4 \cdot e^{-(x-8)^2/2}$$



## CHAPTER 23

### GAS CHROMATOGRAPHY

- 23-1.** (a) Low boiling solutes are separated well at low temperature, and the retention of high boiling solutes is reduced to a reasonable time at high temperature.
- (b) Higher pressure gives higher flow rate. If pressure is increased during a separation, retention times of late-eluting peaks are reduced. The effect is the same as increasing temperature, but high temperatures are not required. Pressure programming reduces the likelihood of decomposing thermally sensitive compounds.
- 23-2.** (a) Packed columns offer high sample capacity, while open tubular columns give better separation efficiency (smaller plate height), shorter analysis time, and increased sensitivity to small quantities of analyte.
- (b) Wall-coated: liquid stationary phase bonded to the wall of column  
Support-coated: liquid stationary phase on solid support on wall of column  
Porous-layer: solid stationary phase on wall of column
- (c) Bonding or cross-linking the stationary phase reduces the tendency for the stationary phase to bleed from the column during use.
- 23-3.** (a) Open tubular columns eliminate the multiple path term ( $A$ ) from the van Deemter equation, decreasing plate height. Also, the lower resistance to gas flow allows longer columns to be used with the same elution time.
- (b) Diffusion of solute in H<sub>2</sub> and He is more rapid than in N<sub>2</sub>. Therefore, equilibration of solute between mobile phase and stationary phase is faster.
- 23-4.** (a) Split injection is the ordinary mode for open tubular columns. It is best for high concentrations of analyte, gas analysis, high resolution, and dirty samples (with an adsorbent packing in the injection liner). Splitless injection is useful for trace analysis (dilute solutions) and for compounds with moderate thermal stability. On-column injection is best for quantitative analysis and for thermally sensitive solutes that might decompose during a high-temperature injection.
- (b) In solvent trapping, the initial column temperature is low enough to condense solvent at the beginning of the column. Solute is very soluble in the solvent and is trapped in a narrow band at the start of the column. In

cold trapping, the initial column temperature is 150° lower than the boiling points of solutes, which condense in a narrow band at the start of the column. In both cases, elution occurs as the column temperature is raised.

- 23-5. (a) All analytes  
(b) Carbon atoms bearing hydrogen atoms  
(c) Molecules with halogens, CN, NO<sub>2</sub>, conjugated C=O  
(d) P and S and other elements selected by wavelength  
(e) P and N (and also hydrocarbons)  
(f) Aromatic and unsaturated compounds  
(g) S  
(h) Most elements (selected individually by wavelength)  
(i) All analytes
- 23-6. The thermal conductivity detector measures changes in the thermal conductivity of the gas stream exiting the column. Any substance other than the carrier gas will change the conductivity of the gas stream. Therefore, the detector responds to all analytes. The flame ionization detector burns eluate in an H<sub>2</sub>/O<sub>2</sub> flame to create CH radicals from carbon atoms (except carbonyl and carboxyl carbons), which then go on to be ionized to a small extent in the flame: CH + O → CHO<sup>+</sup> + e<sup>-</sup>. Most other kinds of molecules do not create ions in the flame and are not detected.
- 23-7. A *reconstructed total ion chromatogram* is created by summing all ion intensities (above a selected value of *m/z*) in each mass spectrum at each time interval during a chromatography experiment. The technique responds to essentially everything eluted from the column and has no selectivity at all.  
In *selected ion monitoring*, intensities at just one or a few values of *m/z* are plotted versus elution time. Only species with ions at those *m/z* values are detected, so the selectivity is much greater than that of the reconstructed total ion chromatogram. The signal-to-noise ratio is increased because ions are collected at each *m/z* for a longer time than would be allowed if the entire spectrum were being scanned.

*Selected reaction monitoring* is most selective. One ion from the first mass separator is passed through a collision cell, where it breaks into several product ions that are separated by a second mass separator. The intensities of one or a few of these product ions are plotted as a function of elution time. The selectivity is high because few species from the column produce the first selected ion and even fewer break into the same fragments in the collision cell. This technique is so selective that it can transform a poor chromatographic separation into a highly specific determination of one component with virtually no interference.

- 23-8. Column (a): hexane < butanol < benzene < 2-pentanone < heptane < octane  
 Column (b): hexane < heptane < butanol < benzene < 2-pentanone < octane  
 Column (c): hexane < heptane < octane < benzene < 2-pentanone < butanol
- 23-9. Column (a): 3, 1, 2, 4, 5, 6; Column (b): 3, 4, 1, 2, 5, 6; Column (c): 3, 4, 5, 6, 2, 1
- 23-10. (a)  $t_r' = 8.4 - 3.7 = 4.7 \text{ min}$ ;  $k = 4.7/3.7 = 1.3$   
 (b)  $k = KV_s/V_m \Rightarrow K = (1.3)(1.4) = 1.8$

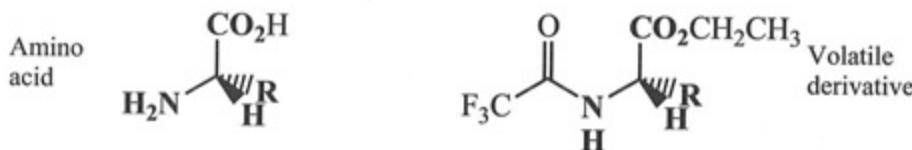
$$23-11. I = 100 \left[ 8 + (9 - 8) \frac{\log(12.0) - \log(11.0)}{\log(14.0) - \log(11.0)} \right] = 836$$

$$23-12. \begin{cases} \log(15.0) = \frac{a}{373} + b \\ \log(20.0) = \frac{a}{363} + b \end{cases} \Rightarrow a = 1.69 \times 10^3 \text{ K} \quad b = -3.36$$

To solve for  $a$ , subtract one equation from the other to eliminate  $b$ . Once you have  $a$ , substitute it back into either equation and solve for  $b$ .

$$\text{At } 353 \text{ K: } \log t_r' = \frac{1.692 \times 10^3}{353} - 3.36 \Rightarrow t_r' = 27.1 \text{ min}$$

- 23-13. Derivatization uses a chemical reaction to convert analyte into a form that is more convenient to separate or easier to detect. In Box 23-1, amino and carboxylate groups of amino acids were converted to covalent derivatives to make the molecules volatile enough to be separated by gas chromatography:



- 23-14.** (a) In solid-phase microextraction, analyte is extracted from a liquid or gas into a thin coating on a silica fiber extended from a syringe. After extraction, the fiber is withdrawn into the syringe. To inject sample into a chromatograph, the metal needle is inserted through the septum and the fiber is extended into the injection port. Analyte slowly evaporates from the fiber in the high-temperature port. Cold trapping is required to condense analyte at the start of the column during slow evaporation from the fiber. If cold trapping were not used, the peaks would be extremely broad because of the slow evaporation from the fiber. During solid-phase microextraction, analyte equilibrates between the unknown and the coating on the fiber. Only a fraction of analyte is extracted into the fiber.
- (b) In stir-bar sorptive extraction, a thick coating on the outside of a glass-coated stirring bar is used in place of a thin coating on a fiber. After extraction, the bar is placed in a thermal desorption tube where analyte is vaporized and cold trapped for chromatography. The volume of the coating is  $\sim 100$  times greater in stir-bar sorptive extraction, so the sensitivity is  $\sim 100$  times higher.
- 23-15.** The idea of purge and trap is to collect *all* of the analyte from the unknown and to inject *all* of the analyte into the chromatography column. Splitless injection is required so analyte is not lost during injection. Any unknown loss of analyte would lead to an error in quantitative analysis.
- 23-16.** The order of decisions is: (1) goal of the analysis, (2) sample preparation method, (3) detector, (4) column, and (5) injection method.
- 23-17.** (a) A thin stationary phase permits rapid equilibration of analyte between the mobile and stationary phases, which reduces the C term in the van Deemter equation. A thin stationary phase in a narrow-bore column gives small plate height and high resolution. In a wide-bore column, the large diameter of the column slows down the rate of mass transfer between the mobile and stationary phases (because it takes time for analyte to diffuse across the diameter of the column), which defeats the purpose of the thin stationary phase.

- (b) Narrow-bore column: plate height =  $1/(5\,000 \text{ m}^{-1}) = 2.0 \times 10^{-4} \text{ m} = 200 \mu\text{m}$ . The area of a length ( $\ell$ ) of the inside wall of the column is  $\pi d\ell$ , where  $d$  is the column diameter. The volume of stationary phase in this length is  $\pi d\ell t$ , where  $t$  is the thickness of the stationary phase. For  $d = 250 \mu\text{m}$ ,  $\ell = 200 \mu\text{m}$ , and  $t = 0.10 \mu\text{m}$ , the volume is  $1.57 \times 10^4 \mu\text{m}^3$ . A density of  $1.0 \text{ g/mL}$  is  $1.0 \text{ g/cm}^3 = 1.0 \text{ g}/(10^4 \mu\text{m})^3 = 1.0 \text{ g}/10^{12} \mu\text{m}^3 = 1 \text{ pg}/\mu\text{m}^3$ . The mass of stationary phase in one theoretical plate is  $(1.57 \times 10^4 \mu\text{m}^3)(1 \text{ pg}/\mu\text{m}^3) = 1.57 \times 10^4 \text{ pg}$ .  $1.0\%$  of this mass is  $= 0.16 \text{ ng}$ .

Wide-bore column: For  $d = 530 \mu\text{m}$ ,  $\ell = 667 \mu\text{m}$ , and  $t = 5.0 \mu\text{m}$ , the volume is  $5.55 \times 10^6 \mu\text{m}^3$ . Mass of stationary phase is  $(5.55 \times 10^6 \mu\text{m}^3)(1 \text{ pg}/\mu\text{m}^3) = 5.55 \times 10^6 \text{ pg}$ .  $1.0\%$  of this mass is  $= 56 \text{ ng}$ .

- 23-18.** Use a narrower column or a longer column (doubling the length increases resolution by  $\sqrt{2}$ ) or try a different stationary phase.
- 23-19.**
- (a) The column on a chip is part of a system intended to be an autonomous environmental monitor. Therefore, it needs to be compact and to require little power and consumables. Air is selected as carrier gas because it can be taken from the atmosphere. Any other carrier gas would require a supply tank which would be heavy, bulky, and would run out of gas. Oxygen from air could degrade the column at elevated temperature. Therefore, the temperature must be kept below the point at which oxidation would occur. Air has impurities which must be removed by a filtration system. The filter is most likely a consumable which eventually needs replacement.
  - (b) The optimum velocity gives the lowest plate height. It is the minimum in each curve. Optimum velocity =  $9.3 \text{ cm/s}$  for air and  $17.6 \text{ cm/s}$  for  $\text{H}_2$ . Plate height at optimum velocity =  $0.036 \text{ cm}$  for air and  $0.051 \text{ cm}$  for  $\text{H}_2$ . (Values come from the original publication. You will probably measure somewhat different values from the figure.)
  - (c) Plates = column length/plate height =  $3.0 \text{ m}/0.036 \text{ cm} = 8\,300$  for air and  $5\,900$  for  $\text{H}_2$
  - (d) Time = column length/optimum velocity =  $3.0 \text{ m}/9.3 \text{ cm/s} = 32 \text{ s}$  for air and  $17 \text{ s}$  for  $\text{H}_2$

- (e) The two terms describe broadening due to the finite time for solute to diffuse through the stationary phase and the mobile phase. If the stationary phase is sufficiently thin, the time for diffusion through the stationary phase (the  $C_s$  term) becomes negligible.
- (f) Acceptable flow rates for  $H_2$  are higher than for air because solutes diffuse through  $H_2$  faster than they diffuse through air. With  $H_2$  carrier, solutes can diffuse from the center of the column to the wall more rapidly than they can with air carrier.

$$23-20. \text{ (a)} \quad S = [\text{pentanol}] = \frac{234 \text{ mg} / 88.15 \text{ g/mol}}{10.0 \text{ mL}} = 0.2655 \text{ M}$$

$$X = [2,3\text{-dimethyl-2-butanol}] = \frac{237 \text{ mg} / 102.17 \text{ g/mol}}{10.0 \text{ mL}} = 0.2320 \text{ M}$$

$$\frac{A_X}{[X]} = F \left( \frac{A_S}{[S]} \right) \Rightarrow \frac{1.00}{[0.2320 \text{ M}]} = F \left( \frac{0.913}{[0.2655 \text{ M}]} \right) \Rightarrow F = 1.253$$

- (b) I estimate the areas by measuring the height and  $w_{1/2}$  in millimeters. Your answer will be different from mine if the figure size in your book is different from that in my manuscript. However, relative peak areas should be the same.

pentanol: height = 40.1 mm;  $w_{1/2} = 3.7$  mm;

$$\text{area} = 1.064 \times \text{peak height} \times w_{1/2} = 158 \text{ mm}^2$$

2,3-dimethyl-2-butanol:

$$\text{height} = 77.0 \text{ mm}; \quad w_{1/2} = 2.0 \text{ mm}; \quad \text{area} = 164 \text{ mm}^2$$

$$(c) \quad \frac{164}{2,3\text{-dimethyl-2-butanol}} = 1.253 \left( \frac{158}{[93.7 \text{ mM}]} \right)$$

$$\Rightarrow [2,3\text{-dimethyl-2-butanol}] = 77.6 \text{ mM}$$

$$23-21. \quad \frac{A_X}{[X]} = F \left( \frac{A_S}{[S]} \right) \Rightarrow \frac{395}{[63 \text{ nM}]} = F \left( \frac{787}{[200 \text{ nM}]} \right) \Rightarrow F = 1.59$$

The concentration of internal standard mixed with unknown is

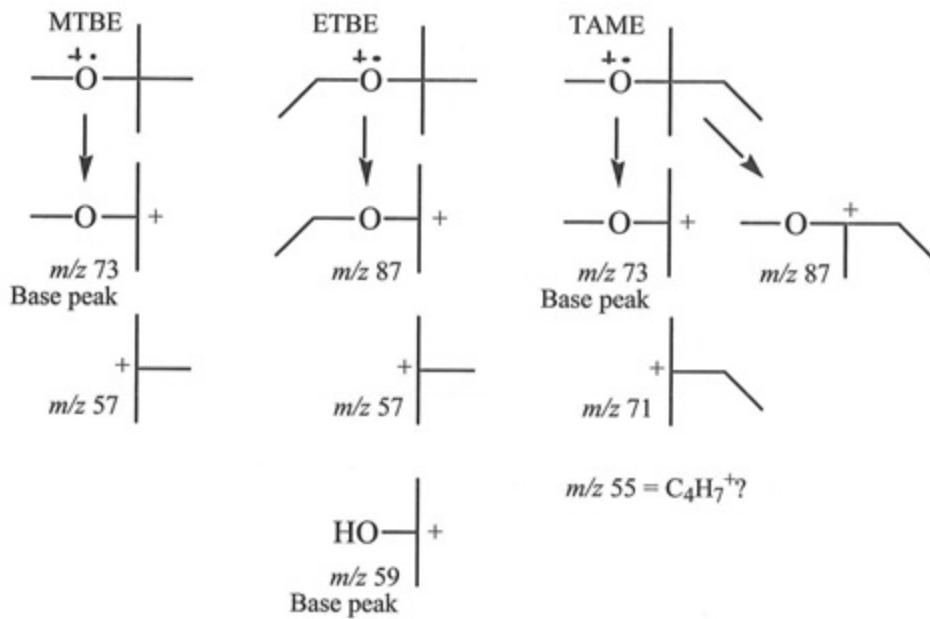
$$\frac{0.100 \text{ mL}}{10.00 \text{ mL}} (1.6 \times 10^{-5} \text{ M}) = 0.16 \mu\text{M}$$

$$\frac{633}{[\text{iodoacetone}]} = 1.59 \left( \frac{520}{[0.16 \mu\text{M}]} \right) \Rightarrow [\text{iodoacetone}] = 0.122 \mu\text{M}$$

$$[\text{iodoacetone}] \text{ in original unknown} = \frac{10.00}{3.00} (0.122 \mu\text{M}) = 0.41 \mu\text{M}$$

$$23-22. \quad I = 100 \left[ (7 + (10 - 7)) \frac{\log (20.0) - \log (12.6)}{\log (22.9) - \log (12.6)} \right] = 932$$

- 23-23.** (a) NaCl lowers the solubility of moderately nonpolar compounds, such as ethers, in water. Adding NaCl increases the fraction of the organic compounds that will be transferred to the extraction fiber.
- (b) Selected ion monitoring is measuring ion abundance for  $m/z$  73. Only three compounds in the extract have appreciable intensity at  $m/z$  73.
- (c) The base peak for both MTBE and TAME is at  $m/z$  73. This mass corresponds to M-15 (loss of  $\text{CH}_3$ ) for MTBE and M-29 (loss of  $\text{C}_2\text{H}_5$ ) for TAME. Loss of the ethyl group bound to carbon in TAME suggests that the methyl group lost from MTBE is also bound to carbon, not to oxygen. If methyl bound to oxygen were easily lost from MTBE and TAME, we would expect to see the ethyl group bound to oxygen lost from ETBE. There is no significant peak at M-29 ( $m/z$  73) in ETBE. The following structures are suggested:



- 23-24.** (a) The vial was heated to increase the vapor pressure of the analyte and the internal standard, so there would be enough in the gas phase (the headspace) to extract a significant quantity with the microextraction fiber.
- (b) At 60°C the analyte and internal standard are cold trapped at the beginning of the column. Since desorption from the fiber takes many minutes, we do not want chromatography to begin until desorption is complete.



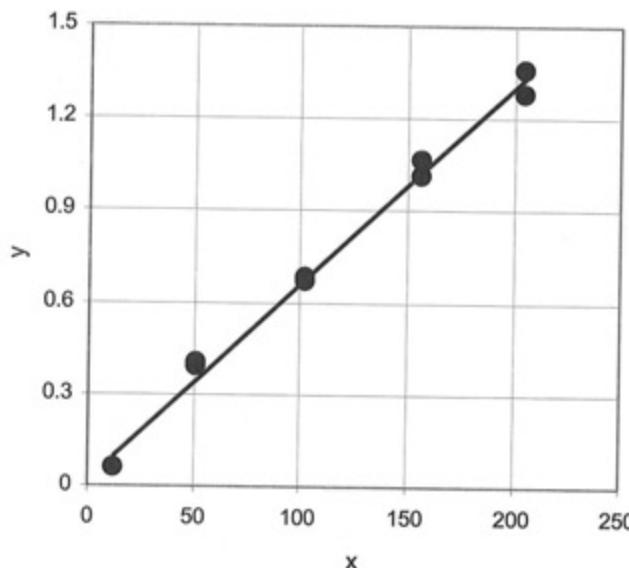
	A	B	C	D	E
1	Least-Squares Spreadsheet				
2					
3		x	y		
4		12	0.056		
5		12	0.059		
6		51	0.402		
7		51	0.391		
8		102	0.684		
9	Highlight cells B16:C18	102	0.669		
10	Type "= LINEST(C4:C13,	157	1.011		
11	B4:B13,TRUE,TRUE)	157	1.063		
12	For PC, press	205	1.278		
13	CTRL+SHIFT+ENTER	205	1.355		
14	For Mac, press				
15	COMMAND+RETURN	LINEST output:			
16	m	0.006401	0.0222	b	
17	s <sub>m</sub>	0.000185	0.0234	s <sub>b</sub>	
18	R <sup>2</sup>	0.9933	0.0409	s <sub>y</sub>	
19					
20	n =	10	B20 = COUNT(B4:B13)		
21	Mean y =	0.6968	B21 = AVERAGE(C4:C13)		
22	$\sum(x_i - \text{mean } x)^2$ =	48554.4	B22 = DEVSQ(B4:B13)		
23					
24	Measured y =	1.25	Input		
25	k = Number of replicate measurements of y =	2	Input		
26	Derived x =	191.83	B26 = (B24-C16)/B16		
27	s <sub>x</sub> =	5.54			
28	B27 = (C18/B16)*SQRT((1/B25)+(1/B20)+((B24-B21)^2)/(B16^2*B22))				

Least-squares parameters are computed in the block B16:C18. In cell B24, we insert the mean y value (1.25) for 2 replicate unknowns. The number of replicates is entered in cell B25. The derived value of x is computed in cell B26 and the uncertainty is computed with Equation 4-27 in cell B27.

Answers for the unknowns:

nonsmoker:  $78 \pm 5 \mu\text{g/L}$

nonsmoker with smoking parents:  $192 \pm 6 \mu\text{g/L}$



23-25. Nitrite:  $[{}^{14}\text{NO}_2^-] = [{}^{15}\text{NO}_2^-](R - R_{\text{blank}}) = [80.0 \mu\text{M}](0.062 - 0.040) = 1.8 \mu\text{M}$   
 Nitrate:  $[{}^{14}\text{NO}_3^-] = [{}^{15}\text{NO}_3^-](R - R_{\text{blank}}) = [800.0 \mu\text{M}](0.538 - 0.058) = 384 \mu\text{M}$

- 23-26. (a) The  $A$  term describing multiple flow paths is 0 for an open tubular column.  
 Multiple paths arise in a packed column when liquid takes different paths through the column.
- (b)  $B = 2D_m$ , where  $D_m$  is the diffusion coefficient of solute in the mobile phase.
- (c)  $C = C_s + C_m$   

$$C_s = \frac{2k}{3(k+1)^2} \frac{d^2}{D_s} \quad C_m = \frac{1+6k+11k^2}{24(k+1)^2} \frac{r^2}{D_m}$$
  
 where  $k$  = retention factor  
 $d$  = thickness of stationary phase  
 $r$  = column radius  
 $D_s$  = diffusion coefficient of solute in the stationary phase  
 $D_m$  = diffusion coefficient of solute in the mobile phase

(d)  $H = B/u_x + Cu_x \quad (u_x = \text{linear velocity})$

Plate height is a minimum at the optimum velocity:

$$\frac{dH}{du_x} = -\frac{B}{u_x^2} + C = 0 \Rightarrow u_x (\text{optimum}) = \sqrt{\frac{B}{C}}$$

The minimum plate height is found by plugging this value of  $u_x$  (optimum) back into the van Deemter equation:

$$H_{\min} = B/u_x + Cu_x = B \sqrt{\frac{C}{B}} + C \sqrt{\frac{B}{C}} = 2\sqrt{BC} = 2\sqrt{B(C_s + C_m)}$$

$$H_{\min} = 2 \sqrt{\left(2D_m\right) \left(\frac{2k}{3(k+1)^2} \frac{d^2}{D_s} + \frac{1+6k+11k^2}{24(k+1)^2} \frac{r^2}{D_m}\right)}$$

$$H_{\min} = 2 \sqrt{\frac{4k}{3(k+1)^2} \frac{d^2 D_m}{D_s} + \frac{(1+6k+11k^2) 2r^2}{24(k+1)^2}}$$

- 23-27. (a) As  $k \rightarrow 0$ ,  $H_{\min}/r = \sqrt{1/3} = 0.58$

$$\text{As } k \rightarrow \infty, H_{\min}/r = \sqrt{\frac{1+6k+11k^2}{3(1+k)^2}} \rightarrow \sqrt{\frac{11k^2}{3k^2}} = \sqrt{\frac{11}{3}} = 1.9$$

- (b) As  $k \rightarrow 0$ ,  $H_{\min} = 0.58 r = 0.058 \text{ mm}$

$$\text{As } k \rightarrow \infty, H_{\min} = 1.9 r = 0.19 \text{ mm}$$

- (c) For  $k = 5.0$ ,  $H_{\min} = r \sqrt{\frac{1+6 \cdot 5.0 + 11 \cdot 25}{3(36)}} = 1.68 r = 0.168 \text{ mm}$

$$\text{Number of plates} = \frac{50 \times 10^3 \text{ mm}}{0.168 \text{ mm/plate}} = 3.0 \times 10^5$$

- (d)  $k = KV_s/V_m$ , where  $V_s$  is the volume of stationary phase and  $V_m$  is the volume of mobile phase. For a length of column,  $\ell$ , the volume of mobile phase is  $\pi r^2 \ell$  and the volume of stationary phase is  $2\pi r t \ell$ . Substituting these volumes into the equation for  $k$  gives  $k = K(2\pi r t \ell)/(\pi r^2 \ell) = 2tK/r$ .

$$k = \frac{2(0.20 \mu\text{m})(1000)}{(100 \mu\text{m})} = 4.0$$

- 23-28. The van Deemter equation has the form

$$H = B/u_x + Cu_x = B/u_x + (C_s + C_m)u_x$$

$$B = 2D_m \quad C_s = \frac{2k}{3(k+1)^2} \frac{d^2}{D_s} \quad C_m = \frac{1+6k+11k^2}{24(k+1)^2} \frac{r^2}{D_m}$$

where  $k$  = retention factor = 8.0

$d$  = thickness of stationary phase =  $3.0 \times 10^{-6} \text{ m}$

$r$  = column radius =  $2.65 \times 10^{-4} \text{ m}$

$D_s$  = diffusion coefficient of solute in the stationary phase

$D_m$  = diffusion coefficient of solute in the mobile phase

Experimentally, we find  $H = (6.0 \times 10^{-5} \text{ m}^2/\text{s})/u_x + (2.09 \times 10^{-3} \text{ s})u_x$ .

Therefore,  $B = 2D_m = (6.0 \times 10^{-5} \text{ m}^2/\text{s})$ , or  $D_m = 3.0 \times 10^{-5} \text{ m}^2/\text{s}$ .

From the second term of the experimental van Deemter equation, we know that

$$C_s + C_m = 2.09 \times 10^{-3} \text{ s} = \frac{2k}{3(k+1)^2} \frac{d^2}{D_s} + \frac{1+6k+11k^2}{24(k+1)^2} \frac{r^2}{D_m}$$

Inserting the known values of all parameters allows us to solve for  $D_s$ :

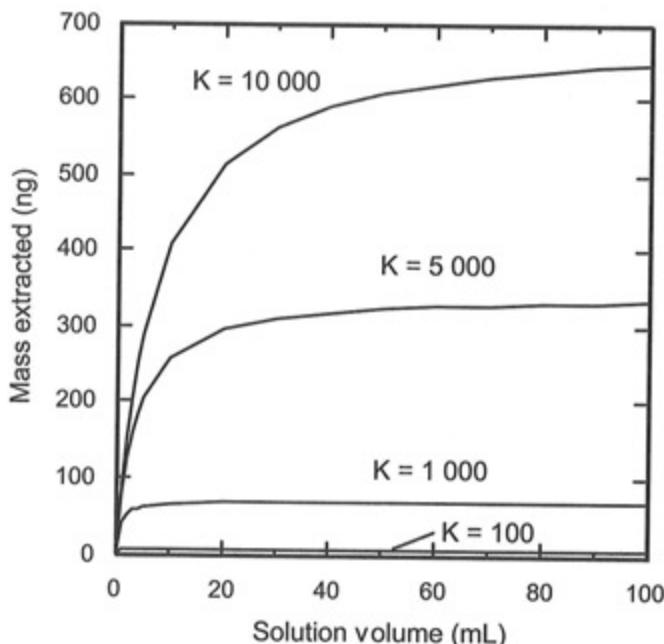
$$2.09 \times 10^{-3} \text{ s} =$$

$$\frac{2(8.0)}{3((8.0) + 1)^2} \frac{(3.0 \times 10^{-6} \text{ m})^2}{D_s} + \frac{1 + 6(8.0) + 11(8.0)^2}{24((8.0) + 1)^2} \frac{(2.65 \times 10^{-4} \text{ m})^2}{(3.0 \times 10^{-5} \text{ m}^2/\text{s})}$$

$$\Rightarrow D_s = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$$

The diffusion coefficient in the mobile phase is  $(3.0 \times 10^{-5} \text{ m}^2/\text{s})/(5.0 \times 10^{-10} \text{ m}^2/\text{s}) = 6.0 \times 10^4$  times greater than the diffusion coefficient in the stationary phase. This makes sense, because it is easier for solute to diffuse through He gas than through a viscous liquid phase.

23-29. (a)



Mass of analyte extracted by solid phase microextraction

K = partition coefficient =	V <sub>s</sub> (mL)	m (ng)
1.00E+02	0	0.000
V <sub>f</sub> = volume of film (mL) =	1	6.455
6.90E-04	2	6.670
C <sub>0</sub> = initial concentration in solution (μg/ mL) =	3	6.745
0.1	4	6.783
10	5	6.806
50	10	6.853
100	50	6.890
1000	100	6.895
<b>C4 = 1000 * (\$A\$5 * \$A\$8 * \$A\$13 * B4) / (\$A\$5 * \$A\$8 + B4)</b>		

$$(b) m = \frac{KV_f c_0 V_s}{KV_f + V_s} \quad \text{If } V_s \gg KV_f, m = KV_f c_0$$

For  $V_f = 6.9 \times 10^{-4}$  mL and  $c_0 = 0.1$  µg/mL,  $m \rightarrow (6.9 \times 10^{-5})(K)$  µg

For  $K = 100$ ,  $m \rightarrow 6.9$  ng, which agrees with the graph.

For  $K = 10\,000$ ,  $m \rightarrow 690$  ng, which is where the graph is heading, but it will require about 1 liter of solution to attain the limiting concentration in the fiber.

- (c) The spreadsheet tells us that when  $K = 100$ , 6.85 ng have been extracted into the fiber and when  $K = 10\,000$ , 408 ng have been extracted into the fiber. The total analyte in 10.0 mL is  $(0.10 \text{ }\mu\text{g/mL})(10.0 \text{ mL}) = 1.0 \text{ }\mu\text{g}$ . The fraction extracted for  $K = 100$  is  $6.86 \text{ ng}/1.0 \text{ }\mu\text{g} = 0.0069$  (or 0.69%). The fraction extracted for  $K = 10\,000$  is 0.41 (or 41%).

**23-30.** (a) For the formula  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_6$ ,

rings + double bonds =  $c - h/2 + n/2 + 1 = 9 - (4+6)/2 + 2/2 + 1 = 6$ , which agrees with the structure that has 2 rings + 4 double bonds.

- (b) Nominal mass = integer mass of the species with the most abundant isotope of each of the constituent atoms. For  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_6$ , nominal mass =  $(9 \times 12) + (4 \times 1) + (2 \times 14) + (6 \times 35) = 350$ .
- (c) The sequence  $m/z$  350, 315, 280, 245, and 210 corresponds to successive losses of mass 35 Da. A logical assignment is  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_6^+$ ,  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_5^+$ ,  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_4^+$ ,  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_3^+$ ,  $\text{C}_9\text{H}_4\text{N}_2\text{Cl}_2^+$ .

(d) Here is the spreadsheet for 5 Cl atoms:

	A	B	C	D	E
1	Isotopic abundance from binomial distribution				
2					
3	$^{35}\text{Cl} =$	0.7577	natural abundance		
4	$^{37}\text{Cl} =$	0.2423	natural abundance		
5	n =	5			
6					
7	$^{35}\text{Cl}$	Formula	Mass	Abundance	Relative abundance
8	5	$^{35}\text{Cl}_5^{37}\text{Cl}_0$	M	0.24974	62.54
9	4	$^{35}\text{Cl}_4^{37}\text{Cl}_1$	M+2	0.39931	100.00
10	3	$^{35}\text{Cl}_3^{37}\text{Cl}_2$	M+4	0.25539	63.96
11	2	$^{35}\text{Cl}_2^{37}\text{Cl}_3$	M+6	0.08167	20.45
12	1	$^{35}\text{Cl}_1^{37}\text{Cl}_4$	M+8	0.01306	3.27
13	0	$^{35}\text{Cl}_0^{37}\text{Cl}_5$	M+10	0.00084	0.21
14	$\text{D8} = \text{BINOMDIST}(\text{A8}, \$\text{B\$5}, \$\text{B\$3}, \text{FALSE})$				
15	$\text{E8} = 100 * \text{D8} / \text{MAX}(\text{\$D\$8:\$D\$13})$				

And here are the results for species with 6, 5, 4, 3, 2, and 1 Cl atom. The predicted patterns are in reasonable agreement with the observed amplitudes of the clusters of peaks at  $m/z$  350, 315, 280, 245, and 210.

	Predicted relative abundance					
	$\text{Cl}_6$	$\text{Cl}_5$	$\text{Cl}_4$	$\text{Cl}_3$	$\text{Cl}_2$	$\text{Cl}_1$
M	52.12	62.54	78.18	100.00	100.00	100.00
M+2	100.00	100.00	100.00	95.94	63.96	31.98
M+4	79.95	63.96	47.97	30.68	10.23	
M+6	34.09	20.45	10.23	3.27		
M+8	8.18	3.27	0.82			
M+10	1.05	0.21				
M+12	0.06					

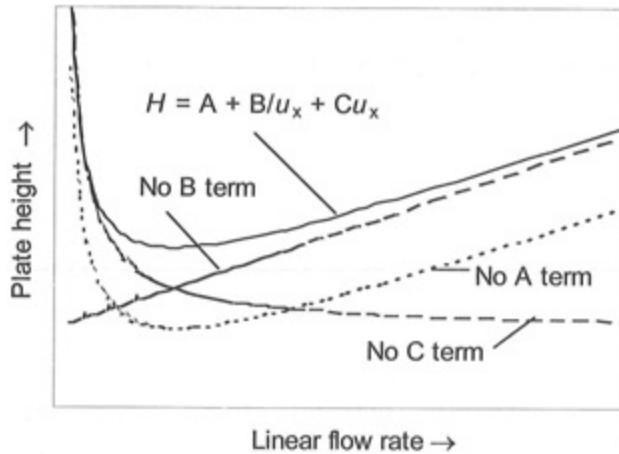
## CHAPTER 24

### HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

- 24-1.** (a) In reversed-phase chromatography, the solutes are nonpolar and more soluble in a nonpolar mobile phase. In normal-phase chromatography, the solutes are polar and more soluble in a polar mobile phase.
- (b) A gradient of increasing pressure gives increasing solvent density, which gives increasing eluent strength in supercritical fluid chromatography.
- 24-2.** Solvent is competing with solute for adsorption sites. The strength of the solvent-adsorbent interaction is independent of solute.
- 24-3.** In hydrophilic interaction chromatography, solute equilibrates between the mobile phase and an aqueous layer on the surface of the polar stationary phase. The more water in the eluent, the better can eluent compete with the stationary aqueous layer to dissolve polar solute and elute it from the column.
- 24-4.** (a) Small particles give increased resistance to flow. High pressure is required to obtain a usable flow rate.
- (b) A bonded stationary phase is covalently attached to the support.
- 24-5.** (a) 
$$L(\text{cm}) \approx \frac{Nd_p(\mu\text{m})}{3000}$$
If  $N = 1.0 \times 10^4$  and  $d_p = 10.0 \mu\text{m}$ ,  $L = 33 \text{ cm}$   
 $d_p = 5.0 \mu\text{m} \Rightarrow L = 17 \text{ cm}; \quad d_p = 3.0 \mu\text{m} \Rightarrow L = 10 \text{ cm}$   
 $d_p = 1.5 \mu\text{m} \Rightarrow L = 5 \text{ cm}$
- (b) Efficiency increases because solute equilibrates between phases more rapidly if the thicknesses of both phases are smaller. This effect decreases the  $C$  term in the van Deemter equation. Also, migration paths between small particles are more uniform, decreasing the multiple path ( $A$ ) term.
- 24-6.** Plates ( $N$ ) =  $(15 \text{ cm})/(5.0 \times 10^{-4} \text{ cm/plate}) = 3.0 \times 10^4$   
$$N = \frac{5.55 t_r^2}{w_{1/2}^2} \Rightarrow w_{1/2} = t_r \sqrt{\frac{5.55}{N}} = (10.0 \text{ min}) \sqrt{\frac{5.55}{3.0 \times 10^4}} = 0.136 \text{ min}$$
If plate height =  $25 \mu\text{m}$ , plates = 6000 and  $w_{1/2} = 0.304 \text{ min}$

- 24-7.** Silica dissolves above pH 8 and the siloxane bond to the stationary phase hydrolyzes below pH 2. Bulky isobutyl groups hinder the approach of  $\text{H}_3\text{O}^+$  to the Si—O—Si bond, so the rate of acid-catalyzed hydrolysis is decreased.
- 24-8.** The high concentration of additive binds to the sites on the stationary phase that would otherwise hold on tightly to solutes and cause tailing.
- 24-9.** (a) Your sketch should look like Figure 22-14, in which the asymmetry factor is  $A/B = 1.8$ , measured at one tenth of the peak height.
- (b) Tailing of amines might be eliminated by adding 30 mM triethylamine to the mobile phase. Tailing of acidic compounds might be eliminated by adding 30 mM ammonium acetate. For unknown mixtures, 30 mM triethylammonium acetate is useful. If tailing persists, 10 mM dimethyloctylamine or dimethyloctylammonium acetate might be effective. Tailing could also be caused by a clogged frit which you might be able to clean by washing with reversed flow.

- 24-10.** (a)



- (b) For 1.8- $\mu\text{m}$  particle size, the experimental van Deemter curve looks almost like the curve with no  $C$  term in (a) (that is, finite equilibration time  $\approx 0$ ). When particle size is small enough, equilibration between the mobile and stationary phases is very rapid and this process contributes little to peak broadening. The experimental curve for 1.8- $\mu\text{m}$  particles levels off at a smaller plate height than the curves for 5- and 3.5- $\mu\text{m}$  particles. This behavior suggests that the  $A$  term (multiple flow paths) is smaller for the smaller particles.

- (c) A superficially porous particle has a thin porous shell on a solid inner core. Solute only needs to diffuse short distances into the thin shell, so equilibration occurs on a time scale similar to that of smaller particles. However, the overall diameter of the superficially porous particle is not small, so its resistance to fluid flow is not as high as that of a small particle.

**24-11.** (a)  $N = \frac{5.55 t_r^2}{w_{1/2}^2} = \frac{5.55 (4.70 \text{ min})^2}{(0.28 \text{ min})^2} = 1\,560$  for *l* enantiomer

$$N = \frac{5.55 (5.37 \text{ min})^2}{(0.35 \text{ min})^2} = 1\,310 \text{ for } d \text{ enantiomer}$$

(b)  $w_{1/2\text{av}} = \frac{1}{2}(0.28 \text{ min} + 0.35 \text{ min}) = 0.315 \text{ min}$

$$\text{Resolution} = \frac{0.589 \Delta t_r}{w_{1/2\text{av}}} = \frac{0.589 (5.37 \text{ min} - 4.70 \text{ min})}{0.315 \text{ min}} = 1.25$$

(c) Unadjusted relative retention:  $\gamma = (5.37 \text{ min})/(4.70 \text{ min}) = 1.14_3$

$$\text{Average } N = \frac{1}{2}(1\,560 + 1\,310) = 1\,435$$

$$\text{Resolution} = \frac{\sqrt{N}}{4} (\gamma - 1) = \frac{\sqrt{1\,435}}{4} (1.14_3 - 1) = 1.35$$

**24-12.** (a)  $P \propto \frac{1}{d_p^2}$  For two difference conditions (1 and 2),

$$\frac{P_2}{P_1} \propto \frac{d_1^2}{d_2^2} = \left(\frac{3 \mu\text{m}}{0.7 \mu\text{m}}\right)^2 = 18. \text{ Pressure must be 18 times greater.}$$

- (b)  $u_x \propto P$ , so if pressure is increased by a factor of 10, then linear velocity should increase by a factor of 10.

- (c) Mass transfer between the mobile and stationary phase is faster for small particles than for large particles. The optimum velocity for maximum efficiency (highest plate number) increases as the rate of mass transfer increases. In the example cited, the high flow rate is closer to the optimum flow rate than is the low flow rate.

- 24-13.** (a) Bonded reversed-phase chromatography  
 (b) Bonded normal-phase chromatography (Dioxane is closer to ethyl acetate than to chloroform in eluent strength.)  
 (c) Ion-exchange or ion chromatography  
 (d) Molecular-exclusion chromatography

- (e) Ion-exchange chromatography
- (f) Molecular-exclusion chromatography

**24-14.** 10-μm-diameter spheres: volume =  $\frac{4}{3} \pi r^3 = \frac{4}{3} \pi (5 \times 10^{-4} \text{ cm})^3 = 5.24 \times 10^{-10} \text{ cm}^3$

Mass of one sphere =  $(5.24 \times 10^{-10} \text{ mL})(2.2 \text{ g/mL}) = 1.15 \times 10^{-9} \text{ g}$

Number of particles in 1 g =  $1 \text{ g} / (1.15 \times 10^{-9} \text{ g/particle}) = 8.68 \times 10^8$

Surface area of one particle =  $4\pi r^2 = 4\pi(5 \times 10^{-6} \text{ m})^2 = 3.14 \times 10^{-10} \text{ m}^2$

Surface area of  $8.68 \times 10^8$  particles =  $0.27 \text{ m}^2$

Since the observed surface area is  $300 \text{ m}^2$ , the particles must have highly irregular shapes or be porous.

- 24-15.** (a) Since the nonpolar compounds should become more soluble in the mobile phase, the retention time will be shorter in 90% methanol.

- (b) At pH 3, the predominant forms are neutral  $\text{RCO}_2\text{H}$  and cationic  $\text{RNH}_3^+$ . The amine will be eluted first, since  $\text{RNH}_3^+$  is insoluble in the nonpolar stationary phase.

- 24-16.** (a) Unretained component travels at the solvent velocity,  $u_x$ .

$$u_x = \frac{\text{column length}}{\text{transit time}} = \frac{4400 \text{ mm}}{(41.7 \text{ min})(60 \text{ s/min})} = 1.76 \text{ mm/s}$$

$$(b) k = \frac{t_r - t_m}{t_m} = \frac{188.1 \text{ min} - 41.7 \text{ min}}{41.7 \text{ min}} = 3.51$$

$$(c) N = \frac{5.55 t_r^2}{w_{1/2}^2} = \frac{5.55 (188.1 \text{ min})^2}{(1.01 \text{ min})^2} = 192000$$

$$H = \frac{4400 \text{ mm}}{192000} = 22.9 \mu\text{m}$$

$$(d) \text{ Resolution} = \frac{0.589 \Delta t_r}{w_{1/2\text{av}}} = \frac{0.589(1.01 \text{ min})}{1.01 \text{ min}} = 0.589$$

$$(e) \alpha = \frac{t_{r2}'}{t_{r1}'} = \frac{194.3 \text{ min} - 41.7 \text{ min}}{193.3 \text{ min} - 41.7 \text{ min}} = 1.006_6$$

$$\gamma = \frac{t_{r2}}{t_{r1}} = \frac{194.3 \text{ min}}{193.3 \text{ min}} = 1.005_2$$

$$(f) \text{ Resolution} = \frac{\sqrt{N}}{4} (\gamma - 1)$$

$$1.000 = \frac{\sqrt{N}}{4} (1.0052 - 1) \Rightarrow N = 5.92 \times 10^5$$

A column length of 440 cm gave  $N = 1.92 \times 10^5$  plates. To obtain  $5.92 \times 10^5$  plates, the column must be longer by a factor of  $\frac{5.92 \times 10^5 \text{ plates}}{1.92 \times 10^5 \text{ plates}} = 3.08$ .

$$\text{Required length} = (3.08)(4.40 \text{ m}) = 13.6 \text{ m}$$

- (g) Slow the flow rate to possibly decrease H and thereby increase N.

Change the solvent to change the relative retention.

$$(h) \text{ Resolution} = \frac{\sqrt{N}}{4} (\gamma - 1) = \frac{\sqrt{192\,000}}{4} (1.008_3 - 1) = 0.91$$

- 24-17.** (a) On  $(R,R)$ -stationary phase,  $(S)$ -gimatecan is eluted at 6.10 min. On  $(S,S)$ -stationary phase,  $(S)$ -gimatecan is retained more strongly and is eluted at 6.96 min.  $(R)$ -gimatecan *must have the exact opposite behavior*. It will be eluted at 6.96 min from  $(R,R)$ -stationary phase and at 6.10 min from  $(S,S)$ -stationary phase.
- (b) With  $(S,S)$ -stationary phase, we observe a small peak at 6.10 min for  $(R)$ -gimatecan. This peak is well separated from the front of the big  $(S)$ -gimatecan peak centered at 6.96 min, so the two areas can be integrated and compared with each other. With  $(R,R)$ -stationary phase, we see the  $(S)$ -gimatecan peak at 6.10 min with no evidence of the minor  $(R)$ -gimatecan peak at 6.96 min. The minor peak is lost beneath the tail of  $(S)$ -gimatecan. Chromatography on each enantiomer of the stationary phase enables us to unambiguously locate where each enantiomer of gimatecan is eluted, even though we do not have a standard sample of  $(R)$ -gimatecan.
- (c) For the  $(S,S)$ -stationary phase, we have the following information:  
 $(S)$ -gimatecan:  $t_r = 6.96 \text{ min} \quad k = 1.50$   
 $(R)$ -gimatecan:  $t_r = 6.10 \text{ min} \quad k = 1.22$
- The definition of retention factor is  $k = (t_r - t_m)/t_m$ . Inserting  $k = 1.50$  and  $t_r = 6.96 \text{ min}$  for  $(S)$ -gimatecan gives  $t_m = 2.78_4 \text{ min}$ . We should get the same value of  $t_m$  for  $(R)$ -gimatecan by inserting  $k = 1.22$  and  $t_r = 6.10 \text{ min}$  into the equation  $k = (t_r - t_m)/t_m$ . In fact, this pair of numbers gives  $t_m = 2.74_8 \text{ min}$ . The difference is from experimental error plus roundoff. Let's take the average value  $t_m = 2.76_6 \text{ min}$ .

The adjusted retention time is  $t'_r = t_r - t_m$ .

$$(S)\text{-gimatecan: } t'_r = t_r - t_m = 6.96 - 2.76_8 = 4.19_2 \text{ min}$$

$$(R)\text{-gimatecan: } t'_r = t_r - t_m = 6.10 - 2.76_8 = 3.33_2 \text{ min}$$

$$\text{Relative retention: } \alpha = \frac{t'_{r2}}{t'_{r1}} = \frac{4.19_2 \text{ min}}{3.33_2 \text{ min}} = 1.25_8$$

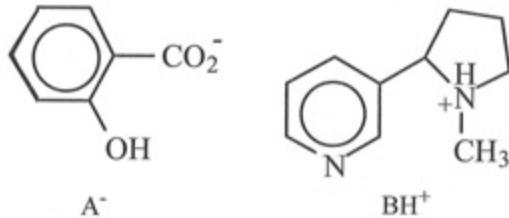
$$\text{Unadjusted relative retention: } \gamma = \frac{t_{r2}}{t_{r1}} = \frac{6.96 \text{ min}}{6.10 \text{ min}} = 1.14_1$$

(d) Resolution =  $\frac{\sqrt{N}}{4} (\gamma - 1) = \frac{\sqrt{6800}}{4} (1.14_1 - 1) = 2.91$  which is more than adequate for “baseline” separation. Tailing of the peaks creates a little overlap, but it should not be very serious for an equal mixture of the enantiomers.

- 24-18.** Peak areas will be proportional to molar absorptivity, since the number of moles of A and B are equal.

$$\begin{aligned} \frac{\text{Area of A}}{\text{Area of B}} &= \frac{2.26 \times 10^4}{1.68 \times 10^4} = \frac{1.064 \times h_{AW1/2}}{1.064 \times h_{BW1/2}} = \frac{(128)(10.1)}{h_B(7.6)} \\ \Rightarrow h_B &= 126 \text{ mm} \end{aligned}$$

- 24-19.** Acetophenone is neutral at all pH values. Its retention is nearly unaffected by pH. For salicylic acid, we expect the neutral molecule, HA, to have some affinity for the C<sub>8</sub> nonpolar stationary phase and the ion, A<sup>-</sup>, to have little affinity for C<sub>8</sub>. Salicylic acid is predominantly HA below pH 2.97 and A<sup>-</sup> above pH 2.97. At pH 3, there is nearly a 1:1 mixture of HA and A<sup>-</sup>, which is moderately retained on the nonpolar column. At pH 5 and 7, more than 99% of the molecules are A<sup>-</sup>, so retention is weak (small retention factor).

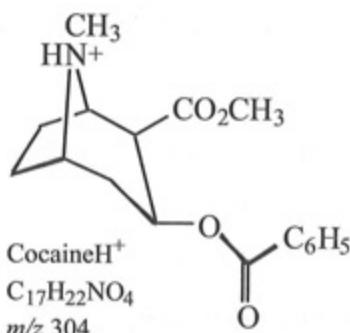


Ionic forms of nicotine ought to have low affinity for the nonpolar stationary phase and the neutral molecule would have some affinity. Abbreviating nicotine as B, the form B is dominant above pH = pK<sub>2</sub> = 7.85. BH<sup>+</sup> is dominant between pH 3.15 and 7.85. BH<sub>2</sub><sup>2+</sup> is dominant below pH 3.15. B does not become

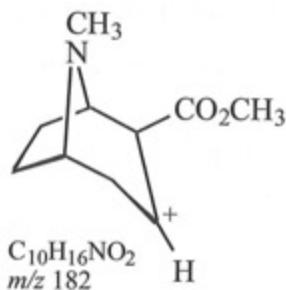
appreciable until  $\text{pH} \approx 7$ , so the retention factor is low below  $\text{pH } 7$  and increases at  $\text{pH } 7$ .

- 24-20.** (a)  $V_m \approx 0.5 L d_c^2 = 0.5(5.0 \text{ cm})(0.46 \text{ cm})^2 = 0.53 \text{ cm}^3 = 0.53 \text{ mL}$   
 $t_m = V_m/F = (0.53 \text{ mL})/(1.4 \text{ mL/min}) = 0.38 \text{ min for column A}$   
 $= (0.53 \text{ mL})/(2.0 \text{ mL/min}) = 0.26 \text{ min for column B}$
- (b) Morphine 3-β-D-glucuronide is more polar than morphine because of the added hydroxyl groups and the carboxylic acid. The more polar compound is less retained by the nonpolar reversed-phase column.
- (c) Bare silica is a polar, hydrophilic surface. Morphine should not be retained as strongly as the more polar morphine 3-β-D-glucuronide. The gradient goes to increasing  $\text{H}_2\text{O}$  for increasing polarity (that is, increasing solvent strength) to remove the more strongly adsorbed, more polar compound.
- (d)  $k = \frac{t_r - t_m}{t_m} = \frac{1.5 - 0.65}{0.65} = 1.3$  for morphine 3-β-D-glucuronide  
 $k = \frac{t_r - t_m}{t_m} = \frac{2.8 - 0.65}{0.65} = 3.3$  for morphine
- (e)  $V_m = F t_m = (2.0 \text{ mL/min})(0.50 \text{ min}) = 1.0 \text{ mL}$   
 $k^* = \frac{t_G F}{\Delta \Phi V_m S} = \frac{(5.0 \text{ min})(2.0 \text{ mL/min})}{(0.4)(1.0 \text{ mL})(4)} = 6.2$
- 24-21.** (a) Electrical power = current  $\times$  voltage. Current is the rate of flow of charge through a circuit. It is analogous to the rate of flow of liquid through a column. Voltage is the potential difference driving charge through the wire. It is analogous to the pressure difference driving liquid through a column.
- (b)  $1 \text{ mL} = 1 \text{ cm}^3 = (10^{-2} \text{ m})^3 = 10^{-6} \text{ m}^3$   
 $1 \text{ mL/min} = 10^{-6} \text{ m}^3/60 \text{ s} = 1.67 \times 10^{-8} \text{ m}^3/\text{s}$ .  
 $3500 \text{ bar} = 3500 \times 10^5 \text{ Pa} = 3.5 \times 10^8 \text{ Pa}$   
power = volume flow rate  $\times$  pressure drop  
 $= (1.67 \times 10^{-8} \text{ m}^3/\text{s})(3.5 \times 10^8 \text{ Pa}) = 5.8 \text{ W}$

24-22. (a)

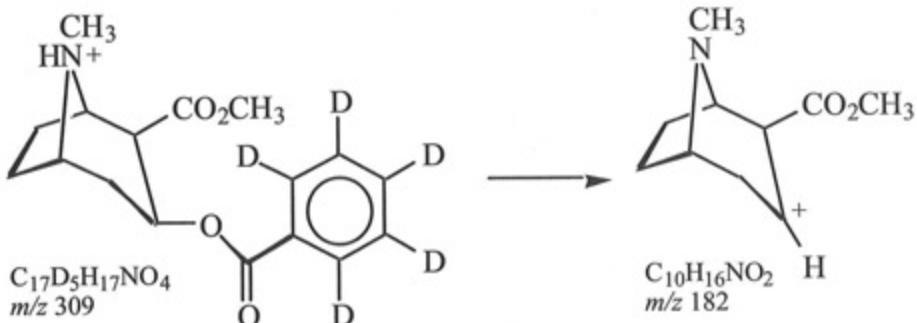


- (b) The  $\text{C}_6\text{H}_5\text{CO}_2$  group has a mass of 121 Da. Subtracting 121 from 304 gives 183 Da. The peak at  $m/z$  182 probably represents cocaine minus  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ . The structure might be the one below or some rearranged form of it.

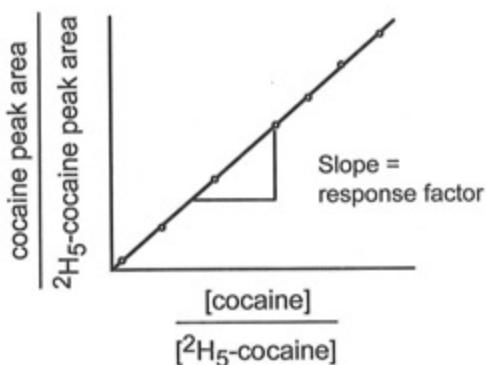


- (c) The ion at  $m/z$  304 was selected by mass filter Q1. Its isotopic partner containing  $^{13}\text{C}$  at  $m/z$  305 was blocked by Q1. Because the species at  $m/z$  304 is isotopically pure, there is no  $^{13}\text{C}$ -containing partner for the collisionally activated dissociation product at  $m/z$  182.
- (d) For selected reaction monitoring, the mass filter Q1 selects just  $m/z$  304, which eliminates components of plasma that do not give a signal at  $m/z$  304. Then this ion is passed to the collision cell, in which it breaks into a major fragment at  $m/z$  182 which passes through Q3. Few other components in the plasma that give a signal at  $m/z$  304 also break into a fragment at  $m/z$  282. The 2-step selection process essentially eliminates everything else in the sample and produces just one clean peak in the chromatogram.

- (e) The phenyl group must be labeled with deuterium because the labeled product gives the same fragment at  $m/z$  182 as unlabeled cocaine.

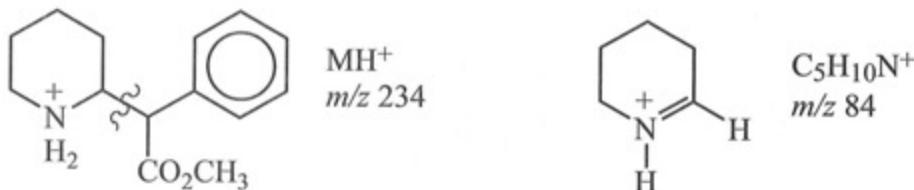


- (f) First, we need to construct a calibration curve to get the response factor for cocaine compared to  $^{2}\text{H}_5$ -cocaine. We expect this response factor to be close to 1.00. We would prepare a series of solutions with known concentration ratios  $[\text{cocaine}]/[^{2}\text{H}_5\text{-cocaine}]$  and measure the area of each chromatographic peak in the chromatography/atmospheric chemical ionization/selected reaction monitoring experiment. A graph would be constructed, in which  $[\text{peak area of cocaine}]/[\text{peak area of }^{2}\text{H}_5\text{-cocaine}]$  is plotted versus  $[\text{cocaine}]/[^{2}\text{H}_5\text{-cocaine}]$ . The slope of this line is the response factor.



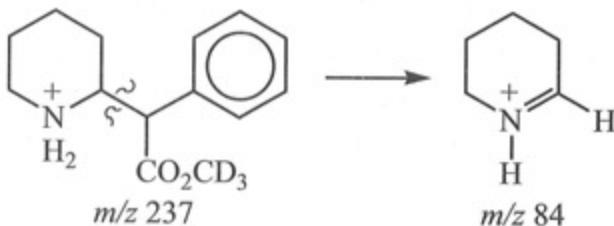
For quantitative analysis, a known amount of the internal standard  $^{2}\text{H}_5$ -cocaine is injected into the plasma. From the calibration curve, the relative peak areas tell us the relative concentrations of cocaine and the internal standard. From the known quantity of internal standard injected into the plasma, we can calculate the quantity of cocaine.

- 24-23. (a) Atmospheric pressure chemical ionization gives a prominent peak at  $m/z$  234, which must be  $\text{MH}^+$ . The peak at  $m/z$  84 is probably the fragment  $\text{C}_5\text{H}_{10}\text{N}^+$ , which might have the structure shown below.



In selected reaction monitoring,  $m/z$  234 is selected by mass filter Q1 and  $m/z$  84 is selected by mass filter Q3 in a triple quadrupole spectrometer.

- (b) Deuterated internal standard has the formula  $\text{C}_{14}\text{H}_{16}\text{D}_3\text{O}_2\text{N}$ , with a nominal mass of 236. The protonated molecule is  $m/z$  237. Cleavage of the C-C bond gives the same  $\text{C}_5\text{H}_{10}\text{N}^+$  fragment as unlabeled Ritalin. The transition to monitor is  $m/z 237 \rightarrow 84$ .



- 24-24. (a) To find  $k$ , measure the retention time for the peak of interest ( $t_r$ ) and the elution time for an unretained solute ( $t_m$ ). Then use the formula  $k = (t_r - t_m)/t_m$ . The resolution between neighboring peaks is the difference in their retention time divided by their average width at the baseline.
- (b) (i)  $t_m$  is usually the time when the first baseline disturbance is observed.  
(ii) Unretained solutes such as uracil or sodium nitrate could be run and observed with an ultraviolet detector. (iii) Alternatively, the formula  $t_m \approx Ld_c^2/(2F)$  can be used, where  $L$  is the length of the column (cm),  $d_c$  is the column diameter (cm), and  $F$  is the flow rate (mL/min).
- (c)  $t_m \approx Ld_c^2/(2F) = (15)(0.46)^2/(2 \cdot 1.5) = 1.06 \text{ min}$   
 $t_m$  does not depend on particle size. The estimate is 1.06 min for both 5.0- and 3.5- $\mu\text{m}$  particles.

- 24-25. *Dead volume* is the volume of the system (not including the chromatography column) from the point of injection to the point of detection. *Dwell volume* is the volume of the system from the point of mixing solvents to the beginning of the

column. Excessive dead volume causes peak broadening by longitudinal diffusion. In gradient elution, dwell volume determines the time from the initiation of a gradient until the gradient reaches the column. The greater the dwell volume, the more the delay between initiating a gradient and the actual increase of solvent strength on the column.

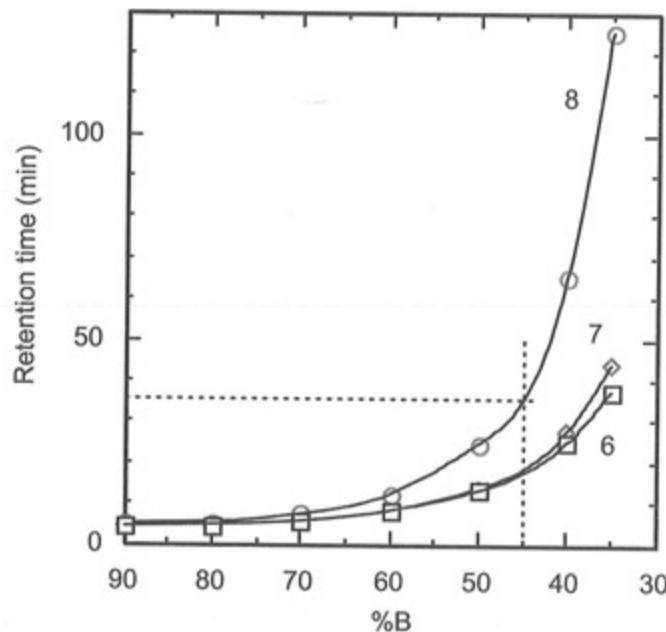
- 24-26.** A rugged procedure should not be seriously affected by gradual deterioration of the column, *small* variations in solvent composition, pH, and temperature, or use of a different batch of the same stationary phase. A procedure should be rugged so that inevitable, small variations in conditions do not substantially affect the outcome of the separation.
- 24-27.**  $0.5 \leq k \leq 20$ ; resolution  $\geq 2$ ; operating pressure  $\leq 15$  MPa;  $0.9 \leq$  asymmetry factor  $\leq 1.5$
- 24-28.** Run a wide gradient (such as 5%B to 100%B) in a gradient time,  $t_G$  selected to produce  $k^* \approx 5$  in Equation 24-10. Measure the difference in retention time ( $\Delta t$ ) between the first and last peaks eluted. Use a gradient if  $\Delta t/t_G > 0.25$  and use isocratic elution if  $\Delta t/t_G < 0.25$ .
- 24-29.** The first steps are to (1) determine the goal of the analysis, (2) select a method of sample preparation, and (3) choose a detector that allows you to observe the desired analytes in the mixture. The next step could be a wide gradient elution to determine whether or not an isocratic or gradient separation is more appropriate. If the isocratic separation is chosen, %B is varied until criteria for a good separation are met. If adequate resolution is not attained, you can try different organic solvents. If adequate resolution is still not attained, you can use a slower flow rate, a longer column, smaller particles, or a different stationary phase.
- 24-30.** To use two organic solvents (A and B), the optimum concentration of A is first found to get the best separation while keeping all retention factors in the range 0.5–20. If adequate separation does not result, then the same procedure is carried out with solvent B. If adequate separation is still not attained, a 1:1 mixture of the best compositions of A and B should be tried. If it looks promising, other mixtures of the optimum concentrations of A and B can be tried.
- 24-31.** Chromatography is conducted with four conditions: (A) high %B, low T, (B) high %B, high T, (C) low %B, high T, and (D) low %B, low T. Based on the

appearance of the chromatograms, combinations between the points A, B, C, and D can be explored for further improvement in the separation.

- 24-32.** Peak 5 has a retention time ( $t_r$ ) of 11.0 min for 50% B. The retention factor is  $k = (t_r - t_m)/t_m = (11.0 - 2.7)/2.7 = 3.1$ . When B is reduced to 40%, the rule of three predicts  $k = 3(3.1) = 9.3$ . Rearranging the definition of retention factor, we find  $t_r = t_m k + t_m = t_m(k + 1)$ . We predict for 40% B  $t_r = t_m(k + 1) = (2.7)(9.3 + 1) = 27.8$  min. The observed retention time at 40% B is 20.2 min.

**24-33.**

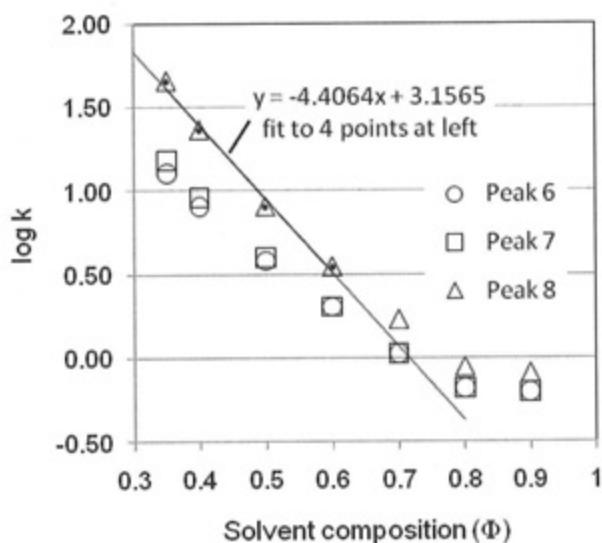
%B	Retention time (min)		
	peak 6	peak 7	peak 8
90	4.4	4.4	4.9
80	4.5	4.5	5.1
70	5.6	5.6	7.3
60	8.2	8.2	12.2
50	13.1	13.6	24.5
40	24.8	27.5	65.1
35	37.6	44.2	125.2



At 45% B, we could estimate that Peak 8 will be eluted halfway between the times for 40% B and 50% B, which is about 45 min. The fit to the curve above suggests that 36 min is a more realistic estimate.

(b) The table shows the calculation of retention factor  $k$  for Peaks 6-8.

$\Phi$	retention time $t_r$ (min)			retention factor $k = (t_r - t_m)/t_m$			$\log k$		
	Peak 6	Peak 7	Peak 8	Peak 6	Peak 7	Peak 8	Peak 6	Peak 7	Peak 8
0.9	4.4	4.4	4.9	0.630	0.630	0.815	-0.201	-0.201	-0.089
0.8	4.5	4.5	5.1	0.667	0.667	0.889	-0.176	-0.176	-0.051
0.7	5.6	5.6	7.3	1.074	1.074	1.704	0.031	0.031	0.231
0.6	8.2	8.2	12.2	2.037	2.037	3.519	0.309	0.309	0.546
0.5	13.1	13.6	24.5	3.852	4.037	8.074	0.586	0.606	0.907
0.4	24.8	27.5	65.1	8.185	9.185	23.111	0.913	0.963	1.364
0.35	37.6	44.2	125.2	12.926	15.370	45.370	1.111	1.187	1.657



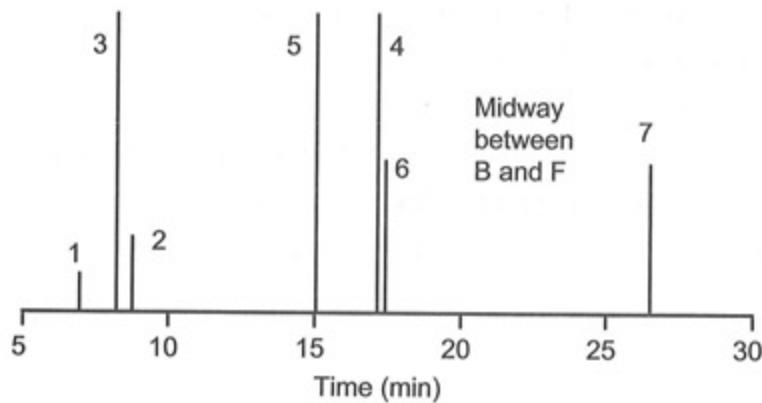
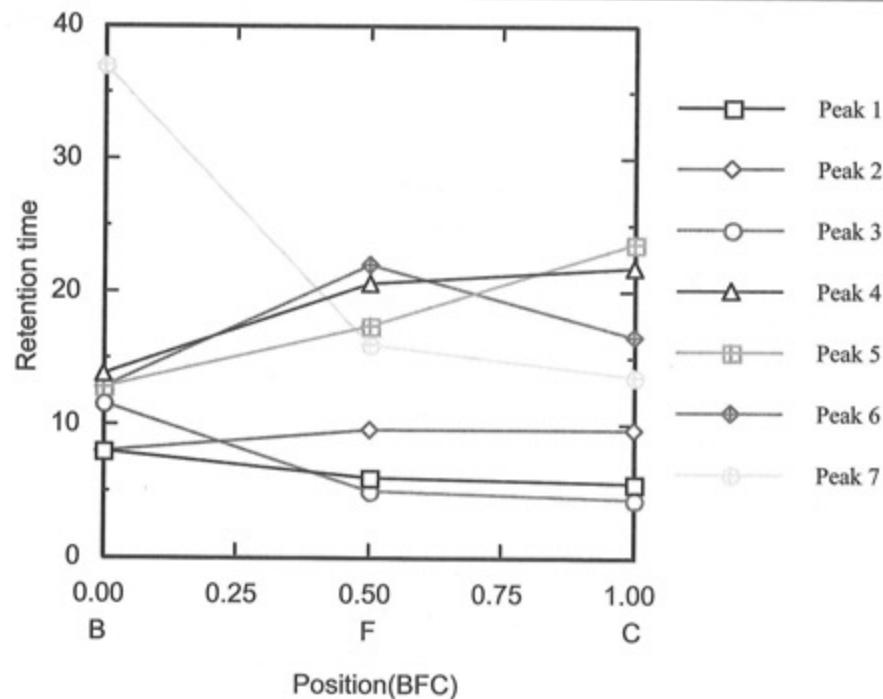
The first obvious point is that  $\log k$  versus  $\Phi$  does not follow a straight line over a wide range of solvent composition. The straight line going through the four points for Peak 8 from  $\Phi = 0.35$  to  $0.6$  is  $\log k = -4.4064\Phi + 3.1565$ . At  $\Phi = 0.45$ , we compute  $\log k = 1.1736$  and  $k = 14.92$ . We compute  $t_r = t_m(k+1) = 43.0$  min. If we had only taken the first three points ( $\Phi = 0.35$  to  $0.5$ ), we would find  $\log k = -4.9364\Phi + 3.3660$ . At  $\Phi = 0.45$ , we compute  $\log k = 1.11447$ ,  $k = 13.95$ , and  $t_r = 40.4$  min.

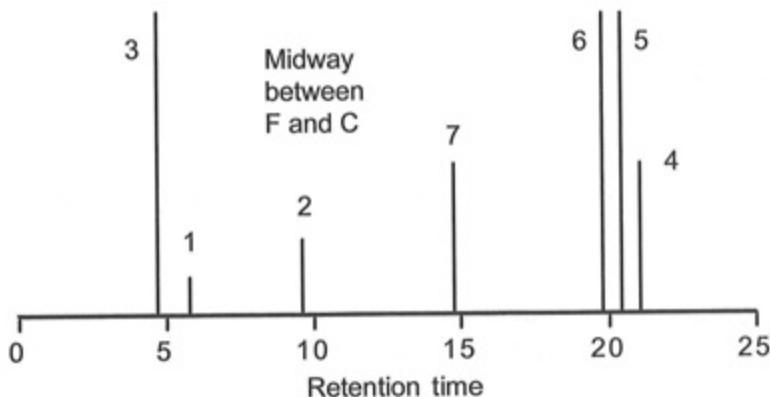
24-34. (a)

Solvent composition	Retention times (min) for Peaks 1-7						
	1	2	3	4	5	6	7
B 0.0	8.0	8.0	11.5	13.8	12.8	12.8	37.0
F 0.5	6.0	9.6	5.0	20.5	17.3	22.0	16.0
C 1.0	5.5	9.6	4.3	21.7	23.6	16.5	13.6

Predicted positions (by linear interpolation):

0.25	7.0	8.80	8.25	17.15	15.05	17.40	26.50
0.75	5.75	9.6	4.65	21.10	20.45	19.75	14.80





- (b) B: 40% methanol/60% buffer  
 C: 32% tetrahydrofuran/68% buffer  
 F: 20% methanol/16% tetrahydrofuran/63% buffer  
 Between B and F: 30% methanol/8% tetrahydrofuran/62% buffer  
 Between F and C: 10% methanol/24% tetrahydrofuran/66% buffer

- 24-35.** D: 25% acetonitrile/30% methanol/45% buffer  
 E: 25% acetonitrile/20% tetrahydrofuran/55% buffer  
 F: 30% methanol/20% tetrahydrofuran/50% buffer  
 G: 16.7% acetonitrile/20% methanol/13.3% tetrahydrofuran/50% buffer
- 24-36.** In the nomograph in Figure 24-26, a vertical line at 48% methanol intersects the acetonitrile line at 38%.
- 24-37.** (a) Lower solvent strength usually increases the difference in retention between different compounds. Use a lower percentage of acetonitrile.  
 (b) In normal-phase chromatography, solvent strength increases as the solvent becomes more polar, which means increasing the methyl *t*-butyl ether concentration. We need a higher concentration of hexane to lower the solvent strength, increase the retention times, and probably improve resolution.
- 24-38.** (a)  $\Delta t/t_G = 19/60 = 0.32$ . Because  $\Delta t/t_G > 0.25$ , gradient elution is suggested.  
 (b) At  $t = 22$  min, the solvent composition entering the column can be calculated by linear interpolation:  $5 + \frac{22}{60}(100 - 5) = 39.8\%$ . At 41 minutes, the composition is  $5 + \frac{41}{60}(100 - 5) = 69.9\%$ . A reasonable gradient for the second experiment is from 40 to 70% acetonitrile in 60 min.

- 24-39.** (a) (1) Change the solvent strength by varying the fraction of each solvent. (2) Change the temperature. (3) Change the pH (in small steps). (4) Use a different solvent. (5) Use a different kind of stationary phase.
- (b) Use a slower flow rate, a different temperature, a longer column, or a smaller particle size.

- 24-40.** (a) Start with conditions to give  $k^* = 5$  and assume that  $S = 4$  for molecules in the mixture.  $V_m \approx L d_c^2/2 = (15 \text{ cm})(0.46 \text{ cm})^2/2 = 1.59 \text{ mL}$ . Particle size does not come into the calculation.

$$t_G = \frac{k^* \Delta\Phi V_m S}{F} = \frac{(5)(0.9)(1.59 \text{ mL})(4)}{(1.0 \text{ mL/min})} = 29 \text{ min}$$

$$(b) k^* = \frac{t_G F}{\Delta\Phi V_m S} = \frac{(11.5 \text{ min})(1.0 \text{ mL/min})}{(0.14)(1.59 \text{ mL})(4)} = 12.9$$

The large column has the same length as the small column, but the diameter is increased from 0.46 to 1.0 cm. The volume increases by a factor of  $(1.0/0.46)^2 = 4.7$ . Therefore, we increase the flow rate and the sample loading by a factor of 4.7. Flow rate = 4.7 mL/min and sample load = 4.7 mg. The gradient time is unchanged at 11.5 min. For the large column,  $V_m \approx L d_c^2/2 = (15 \text{ cm})(1.0 \text{ cm})^2/2 = 7.5 \text{ mL}$  and

$$k^* = \frac{t_G F}{\Delta\Phi V_m S} = \frac{(11.5 \text{ min})(4.7 \text{ mL/min})}{(0.14)(7.5 \text{ mL})(4)} = 12.9$$

## CHAPTER 25

### CHROMATOGRAPHIC METHODS AND CAPILLARY ELECTROPHORESIS

- 25-1.** The separator column separates ions by ion exchange, while the suppressor exchanges the counterion to reduce the conductivity of eluent. After separating cations in the cation-exchange column, the suppressor must exchange the anion for  $\text{OH}^-$ , which makes  $\text{H}_2\text{O}$  from the HCl eluent.
- 25-2.** Increased cross-linking gives decreased swelling, increased exchange capacity and selectivity, but longer equilibration time.
- 25-3.** Deionized water has been passed through ion-exchangers to convert cations to  $\text{H}^+$  and anions to  $\text{OH}^-$ , making  $\text{H}_2\text{O}$ . Nonionic impurities (e. g., organic compounds) are not removed by this process, but can be removed by activated carbon.
- 25-4.** One way is to wash extensively with NaOH a column containing a weighed amount of resin to load all ion-exchange sites with  $\text{OH}^-$ . After a thorough washing with water to remove excess NaOH, the column can be eluted with a large quantity of aqueous NaCl to displace  $\text{OH}^-$ . Eluate is then titrated with standard HCl to determine the moles of displaced  $\text{OH}^-$ .
- 25-5.** (a) As pH is lowered the protein becomes protonated, so the magnitude of the negative charge decreases. The protein becomes less strongly retained.  
(b) As the ionic strength of eluent is increased, the protein will be displaced from the gel by solute ions.
- 25-6.** Particles pass through 200 mesh ( $75 \mu\text{m}$ ) sieve and are retained by 400 mesh ( $38 \mu\text{m}$ ) sieve. 200/400 mesh particles are smaller than 100/200 mesh particles.
- 25-7.** The  $pK_a$  values are:  $\text{NH}_4^+$  (9.24),  $\text{CH}_3\text{NH}_3^+$  (10.64),  $(\text{CH}_3)_2\text{NH}_2^+$  (10.77), and  $(\text{CH}_3)_3\text{NH}^+$  (9.80). If the four ammonium ions are adsorbed on a cation exchange resin at, say, pH 7, they might be separated by elution with a gradient of increasing pH. The anticipated order of elution is  $\text{NH}_3 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$ . We should not be surprised if the elution order were different, since steric and hydrogen bonding effects could be significant determinants of the selectivity coefficients. It is also possible that elution with a constant pH (of, say, 8) might separate all four species from each other.

25-8. (a)  $[Cl^-]_i ([Cl^-]_i + [R^-]_i) = [Cl^-]_o^2$

$$[Cl^-]_i ([Cl^-]_i + 3.0) = (0.10)^2 \Rightarrow [Cl^-]_i = 0.00333 \text{ M}$$

$$\Rightarrow [Cl^-]_o/[Cl^-]_i = 0.10/0.0033 = 30$$

(b) Using  $[Cl^-]_o = 1.0$  in (a) gives  $[Cl^-]_o/[Cl^-]_i = 1.0/0.30 = 3.3$

(c) As  $[Cl^-]_o$  increases, the fraction of  $[Cl^-]_i$  increases.

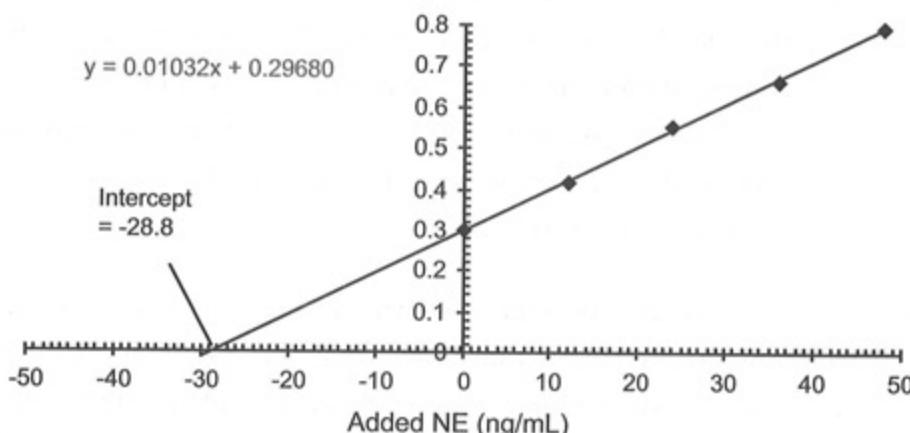
- 25-9. The sum of anion charge in the spreadsheet is  $-0.00159 \text{ M}$ , and the sum of cation charge is  $0.00202 \text{ M}$ . Either some of the ion concentrations are inaccurate, or there are other ions in the pondwater that were not detected. For example, there could be large organic anions derived from living matter (such as humic acid from plants) that are not detected in this experiment.

	A	B	C	D	E	F
1	Ion	Formula mass	Concentration		Ion	Charge
2		(g/mol)	( $\mu\text{g/mL}$ )	(mol/L)	charge	(mol/L)
3	Fluoride	18.998	0.26	1.37E-05	-1	-1.37E-05
4	Chloride	35.453	43.6	1.23E-03	-1	-1.23E-03
5	Nitrate	62.005	5.5	8.87E-05	-1	-8.87E-05
6	Sulfate	96.064	12.6	1.31E-04	-2	-2.62E-04
7						
8			Sum of anion charge =			-0.00159
9						
10	Sodium	22.990	2.8	1.22E-04	1	1.22E-04
11	Ammonium	18.038	0.2	1.11E-05	1	1.11E-05
12	Potassium	39.098	3.5	8.95E-05	1	8.95E-05
13	Magnesium	24.305	7.3	3.00E-04	2	6.01E-04
14	Calcium	40.078	24.0	5.99E-04	2	1.20E-03
15						
16			Sum of cation charge =			0.00202

- 25-10. (a) The hydrophilic stationary phase is a zwitterion with fixed positive and negative charges. Anions are retained by positive charges and cations are retained by negative charges. In hydrophilic interaction chromatography, the stationary phase is polar and there is thought to be a thin layer of aqueous phase on the surface of the stationary phase. Solvent must be made more polar to compete with the stationary phase to elute polar solutes. Eluent strength is increased when the acetonitrile content is decreased.

- (b) Eluent strength increases in hydrophilic interaction chromatography as the fraction of aqueous phase increases. With 20 vol% acetonitrile / 80 vol% aqueous buffer, the eluent strength is high and both ions are eluted rapidly, without an opportunity to be separated. The eluent strength of 40 vol% acetonitrile / 60 vol% aqueous buffer is lower, so the ions are eluted slower and more selectively.
- 25-11.** Hydrophobic regions of the protein are less soluble in water as the salt concentration in the water increases. This decrease in solubility of nonpolar substances in water with increasing salt concentration is known as “salting out.” By decreasing the salt concentration, the protein becomes more soluble in the aqueous phase and can be eluted from the column. Eluent strength increases as the salt concentration decreases.
- 25-12.** At pH 2 (0.01 M HCl), TCA is more dissociated than DCA, which is more dissociated than MCA. The greater the average charge of the compound, the more it is excluded from the ion-exchange resin and the more rapidly it is eluted.
- 25-13.** (a) Sodium octyl sulfate dissolved in the stationary phase forms an ion-pair with NE or DHBA. Other ions in the eluent compete with NE or DHBA, and slowly elute them from the column by ion exchange.
- (b) Construct a graph of (peak height ratio) vs. (added concentration of NE). The  $x$ -intercept gives  $[NE] = 29 \text{ ng/mL}$ .

Added NE	signal
0	0.298
12	0.414
24	0.554
36	0.664
48	0.792



- 25-14.** This is an example of *indirect detection*. Eluent contains naphthalenetrisulfonate, which absorbs at 280 nm. Charge balance dictates that when one of the analyte anions is emerging from the column, there must be less naphthalenetrisulfonate anion emerging. Since analytes do not absorb as strongly at 280 nm, the absorbance is negative with respect to the steady baseline.

**25-15.** (a)  $K^+$  in reservoir =  $(0.75)(1.5\text{ L})(2.0 \frac{\text{mol K}_2\text{PO}_4}{\text{L}})(2 \frac{\text{mol K}^+}{\text{mol K}_2\text{PO}_4}) = 4.5 \text{ mol}$   
 $\text{Flow rate} = (20 \times 10^{-3} \frac{\text{mol KOH}}{\text{L}})(0.0010 \frac{\text{L}}{\text{min}}) = 2.0 \times 10^{-5} \frac{\text{mol KOH}}{\text{min}}$   
 $\text{Time available} = \frac{4.5 \text{ mol K}^+}{2.0 \times 10^{-5} \frac{\text{mol KOH}}{\text{min}}} = 2.25 \times 10^5 \text{ min}$   
 $\frac{2.25 \times 10^5 \text{ min}}{60 \text{ min/h}} = 3.8 \times 10^2 \text{ h}$

- (b) A flow of 5.0 mM KOH at 1.0 mL/min provides

$$(5.0 \times 10^{-3} \text{ mol KOH/L})(0.0010 \text{ L/min}) = 5.0 \times 10^{-6} \text{ mol KOH/min}$$

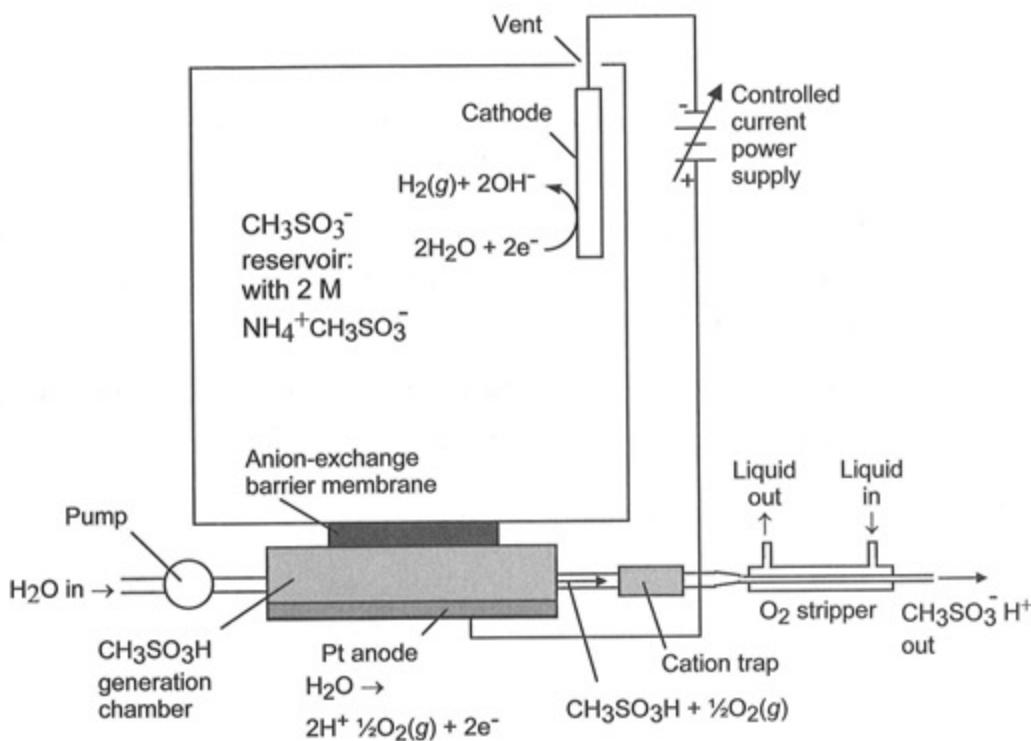
$$\frac{5.0 \times 10^{-6} \text{ mol KOH/min}}{60 \text{ s/min}} = 8.33 \times 10^{-8} \text{ mol KOH/s}$$

One electron provides one  $\text{OH}^-$  at the cathode, so the current must provide  $8.33 \times 10^{-8} \text{ mol e}^-/\text{s}$ . We multiply by the Faraday constant to convert moles of electrons into coulombs:

$$(8.33 \times 10^{-8} \text{ mol e}^-/\text{s})(9.6485 \times 10^4 \text{ C/mol e}^-)$$

$$= 8.0 \times 10^{-3} \text{ C/s} = 8.0 \times 10^{-3} \text{ A} = 8.0 \text{ mA}$$

To produce 0.10 M KOH at 1.0 mL/min requires 20 times as much current, because the concentration of KOH is 20 times higher than 5.0 mM. The current at the end of the gradient will be  $(20)(8.0 \text{ mA}) = 160 \text{ mA} = 0.16 \text{ A}$ .

**25-16.**

- 25-17.** (a) There is a range in which retention volume is logarithmically related to molecular mass. The unknown is compared to a series of standards of known molecular mass.  
 (b) FM 10<sup>5</sup> is near the middle range of the 10 µm pore size column.

**25-18.** (a)  $V_t = \pi(0.80 \text{ cm})^2 (20.0 \text{ cm}) = 40.2 \text{ mL}$

(b)  $K_{av} = \frac{V_r - V_0}{V_m - V_0} = \frac{27.4 - 18.1}{35.8 - 18.1} = 0.53$

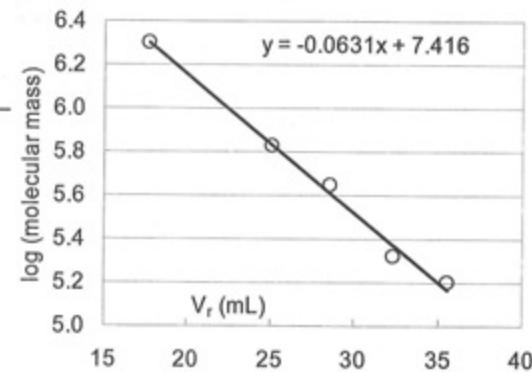
- 25-19.** Ferritin maximum is in tube 22 ( $= 22 \times 0.65 \text{ mL} = 14.3 \text{ mL} = V_0$ )  
 Ferric citrate maximum is in tube 84 ( $= 84 \times 0.65 \text{ mL} = 54.6 \text{ mL} = V_m$ )  
 Does this value of  $V_m$  make sense? The total column volume is  $V_t = \pi r^2 \times \text{length} = \pi(0.75 \text{ cm})^2(37 \text{ cm}) = 65.4 \text{ mL}$ , so  $V_m = 54.6 \text{ mL}$  is plausible.  
 Transferrin maximum = tube 32 = 20.8 mL  $\Rightarrow K_{av} = \frac{20.8 - 14.3}{54.6 - 14.3} = 0.16$

- 25-20.** (a) The vertical line begins at  $\log(\text{molecular mass}) \approx 3.3 \Rightarrow \text{mass} = 10^{3.3} = 2000 \text{ Da.}$   
 (b) A vertical line at 6.5 mL intersects the 10-nm calibration line at  $\log(\text{molecular mass}) \approx 2.5 \Rightarrow \text{mass} = 10^{2.5} = 300 \text{ Da.}$

- 25-21.** (a) The total column volume is  $\pi r^2 \times \text{length} = \pi(0.39)^2 (30) = 14.3 \text{ mL}$ . Totally excluded molecules do not enter the pores and are eluted in the solvent volume (the void volume) outside the particles. Void volume = 40% of 14.3 mL = 5.7 mL.
- (b) The smallest molecules that completely penetrate pores will be eluted in a volume that is the sum of the volumes between particles and within pores = 80% of 14.3 mL = 11.5 mL.
- (c) These solutes must be adsorbed on the polystyrene resin. Otherwise, they would all be eluted between 5.7 and 11.5 mL.

- 25-22.** A graph of  $\log(\text{molecular mass, MM})$  Vs.  $V_r$  should be constructed.

	$\log(\text{MM})$	$V_r(\text{mL})$
aldolase	5.199	35.6
catalase	5.322	32.3
ferritin	5.643	28.6
thyroglobulin	5.825	25.1
Blue Dextran	6.301	17.7
unknown	?	30.3



The equation of the graph of  $K_{av}$  vs.  $\log(\text{MM})$  is  $y = -0.0631x + 7.416$ . Inserting  $x = 30.3$  gives  $y = \log(\text{MM}) = 5.50 \Rightarrow \text{molecular mass} = 320\,000$

- 25-23.** Electroosmosis is the bulk flow of fluid in a capillary caused by migration of the dominant ion in the diffuse part of the double layer toward the anode or cathode.
- 25-24.** At pH 10, the wall of the bare capillary is negatively charged with  $-\text{Si}-\text{O}^-$  groups and there is strong electroosmotic flow toward the cathode. At pH 2.5, the wall is nearly neutral with  $-\text{Si}-\text{OH}$  groups and there is almost no electroosmotic flow. The few  $-\text{Si}-\text{O}^-$  groups left give slight flow toward the cathode. The aminopropyl capillary also has positive flow at pH 10, but the rate is only about half as great as that of the bare capillary. The negative charge might be reduced because there are fewer  $-\text{Si}-\text{O}^-$  groups (because some of them have been converted to  $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) or because some of the aminopropyl groups are protonated ( $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2^+$ ) at pH 10. At pH 2.5, all the aminopropyl groups are protonated. The net charge on the wall is *positive* and the flow is *reversed*.

- 25-25. Arginine is the only amino acid listed with a positively charged side chain. All of the derivatized amino acids have a negative charge because the fluorescent group and the terminal carboxyl group are both negative. Arginine is least negative, so its electrophoretic mobility toward the anode is slowest and its net migration toward the cathode (from electroosmosis) is fastest.
- 25-26. Under ideal conditions, longitudinal diffusion is the principle source of zone broadening. Even under ideal conditions, the finite length of the injected sample and, possibly, the finite length of the detector contribute to zone broadening. In real electrophoresis, adsorption on the capillary wall and irregular flow paths due to imperfections in the capillary could contribute to zone broadening. For an experimental study of zone broadening, see D. Xiao, T. V. Le, and M. J. Wirth, "Surface Modification of the Channels of Poly(dimethylsiloxane) Microfluidic Chips with Polyacrylamide for Fast Electrophoretic Separations of Proteins," *Anal. Chem.* **2004**, 76, 2055.
- 25-27. (a) At pH 2.8, electroosmotic flow will be very small. Anionic analyte will migrate from negative to positive polarity with little effect from the reverse electroosmotic flow.
- (b) The conductivity of the buffer needs to be higher than the conductivity of the sample so that the sample will stack. At lower buffer concentration, analyte bands will be broader and resolution of heparin from its impurities would be diminished.
- (c) High buffer concentration gives high conductivity, high current, and high heat generation. The narrow column reduces the current and the heat generation and makes it easier to cool the entire volume inside the capillary.
- (d)  $\text{Li}^+$  has lower mobility than  $\text{Na}^+$ , so the conductivity of lithium phosphate solution will be lower than the conductivity of sodium phosphate solution at the same pH. The lower the conductivity, the higher the electric field required to generate the same current.  
High field strength reduces the migration time to shorten the analysis. Also, according to Equation 25-14, the number of plates increases in proportion to applied voltage.

- 25-28.** (a) Volume = cross-sectional area  $\times$  length

$$100 \times 10^{-9} \text{ cm}^3 (= 100 \text{ pL}) = (12 \times 10^{-4} \text{ cm})(50 \times 10^{-4} \text{ cm})(\text{length}) \\ \Rightarrow \text{length} = 0.167 \text{ mm}$$

- (b) Time = distance/speed

$$\text{Width of injection band (in seconds)} = \Delta t = \frac{\text{band length}}{\text{speed}} = \frac{0.167 \text{ mm}}{24 \text{ mm / 8 s}} = 0.0557 \text{ s}$$

$$\sigma_{\text{injection}} = \Delta t / \sqrt{12} = 0.016 \text{ s}$$

$$(c) \sigma_{\text{diffusion}} = \sqrt{2Dt} = \sqrt{2(1.0 \times 10^{-8} \text{ m}^2/\text{s})(8 \text{ s})} = 0.00040 \text{ s}$$

$$(d) \sigma_{\text{total}}^2 = \sigma_{\text{diffusion}}^2 + \sigma_{\text{injection}}^2 = (0.004 \text{ s})^2 + (0.016 \text{ s})^2 \\ \Rightarrow \sigma_{\text{total}} = 0.016 \text{ s}$$

$$w = 4\sigma_{\text{total}} = 0.064 \text{ s}$$

- 25-29.** Electroosmotic flow can be reduced by (a) lowering the pH, so the charge on the capillary wall is reduced; (b) adding ions such as  $^{+}\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^{+}$  that adhere to the capillary wall and effectively neutralize its charge; and (c) covalently attaching silanes with neutral, hydrophilic substituents to the Si—O<sup>-</sup> groups on the walls. A cationic surfactant can form a bilayer, such as that shown in Figure 25-24, which effectively reverses the charge on the wall.
- 25-30.** In the absence of micelles, neutral molecules are all swept through the capillary at the electroosmotic velocity. Negatively charged micelles swim upstream with some electrophoretic velocity, so they take longer than neutral molecules to reach the detector. A neutral molecule spends some time free in solution and some time dissolved in the micelles. Therefore, the net velocity of the neutral molecule is reduced from the electroosmotic velocity. Because different neutral molecules have different partition coefficients between the solution and the micelles, each type of neutral molecule has its own net migration speed. We say that micellar electrokinetic chromatography is a form of chromatography because the micelles behave as a “stationary” phase in the capillary because their concentration is uniform throughout the capillary. Analyte partitions between the mobile phase and the micelles as the analyte travels through the capillary.
- 25-31.** (a) Volume of sample = cross-sectional area  $\times$  length  
 $= \pi r^2(\text{length}) = \pi(25 \times 10^{-6} \text{ m})^2(0.0060 \text{ m}) = 1.18 \times 10^{-11} \text{ m}^3$

$$\Delta P = \frac{128\eta L_t(\text{Volume})}{t\pi d^4} = \frac{128(0.0010 \text{ kg/(m}\cdot\text{s)})(0.600 \text{ m})(1.18 \times 10^{-11} \text{ m}^3)}{(4.0 \text{ s})\pi(50 \times 10^{-6} \text{ m})^4}$$

$$= 1.15 \times 10^4 \text{ Pa } (= 1.15 \times 10^4 \text{ kg/(m}\cdot\text{s}^2))$$

$$(b) \Delta P = h\rho g \Rightarrow h = \frac{\Delta P}{\rho g} = \frac{1.15 \times 10^4 \text{ kg/(m}\cdot\text{s}^2)}{(1000 \text{ kg/m}^3)(9.8 \text{ m/s}^2)} = 1.17 \text{ m}$$

Since the column is only 0.6 m long, we cannot raise the inlet to 1.17 m.

Instead, we could use pressure at the inlet ( $1.15 \times 10^4 \text{ Pa} = 0.114 \text{ atm}$ ) or an equivalent vacuum at the outlet.

- 25-32.** (a) Volume =  $\pi r^2(\text{length}) = \pi(12.5 \times 10^{-6} \text{ m})^2(0.0060 \text{ m}) = 2.95 \times 10^{-12} \text{ m}^3 = 2.95 \text{nL}$ . Moles =  $(10.0 \times 10^{-6} \text{ M})(2.95 \times 10^{-9} \text{ L}) = 29.5 \text{ fmol}$ .

$$(b) \text{ Moles injected} = \mu_{\text{app}} \left( E \frac{\kappa_b}{\kappa_s} \right) t \pi r^2 C = \mu_{\text{app}} \left( \frac{V}{L_t \kappa_s} \right) t \pi r^2 C$$

In order for the units to work out, we need to express the concentration,  $C$ , in mol/m<sup>3</sup>:  $(10.0 \times 10^{-6} \text{ mol/L})(1000 \text{ L/m}^3) = 1.00 \times 10^{-2} \text{ mol/m}^3$

$$V = \frac{(\text{moles})L_t(\kappa_s/\kappa_b)}{\mu_{\text{app}} t \pi r^2 C}$$

$$= \frac{(29.5 \times 10^{-15} \text{ mol})(0.600 \text{ m})(1/10)}{(3.0 \times 10^{-8} \text{ m}^2/(\text{V}\cdot\text{s}))(4.0 \text{ s})\pi(12.5 \times 10^{-6} \text{ m})^2(1.00 \times 10^{-2} \text{ mol/m}^3)}$$

$$= 3.00 \times 10^3 \text{ V}$$

- 25-33.** Electrophoretic peak:  $N = \frac{16 t_r^2}{w^2} = \frac{16 (6.08 \text{ min})^2}{(0.080 \text{ min})^2} = 9.2 \times 10^4 \text{ plates}$

$$\text{Chromatographic peak: } N \approx \frac{41.7(t_r/w_{0.1})^2}{(A/B + 1.25)}$$

$$= \frac{41.7(6.03 \text{ min}/0.37 \text{ min})^2}{(1.45 + 1.25)} = 4.1 \times 10^3 \text{ plates}$$

(According to my measurements, both plate counts are about 1/3 lower than the values labeled in the figure from the original source.)

- 25-34.** (a) Fumarate is a longer molecule than maleate, so we guess that fumarate has a greater friction coefficient than maleate. Electrophoretic mobility is (charge)/(friction coefficient). Both ions have the same charge, so we predict that maleate will have the greater electrophoretic mobility.
- (b) Since maleate moves upstream faster than fumarate, fumarate is eluted first.
- (c) Since the anions move faster than the endosmotic flow, the faster anion (maleate) is eluted first.

**25-35.** (a) pH 2:  $u_{\text{neutral}} = \mu_{\text{eo}} E = \left(1.3 \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}}\right) \left(\frac{27 \times 10^3 \text{ V}}{0.62 \text{ m}}\right) = 5.66 \times 10^{-4} \text{ m/s}$

$$\text{Migration time} = (0.52 \text{ m}) / (5.66 \times 10^{-4} \text{ m/s}) = 9.2 \times 10^2 \text{ s}$$

$$\text{pH 12: } u_{\text{neutral}} = \mu_{\text{eo}} E = \left(8.1 \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}}\right) \left(\frac{27 \times 10^3 \text{ V}}{0.62 \text{ m}}\right) = 3.53 \times 10^{-3} \text{ m/s}$$

$$\text{Migration time} = (0.52 \text{ m}) / (3.53 \times 10^{-3} \text{ m/s}) = 1.47 \times 10^2 \text{ s}$$

(b) pH 2:  $\mu_{\text{app}} = \mu_{\text{ep}} + \mu_{\text{eo}} = (-1.6 + 1.3) \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}} = -0.3 \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}}$

The anion will not migrate toward the detector at pH 2.

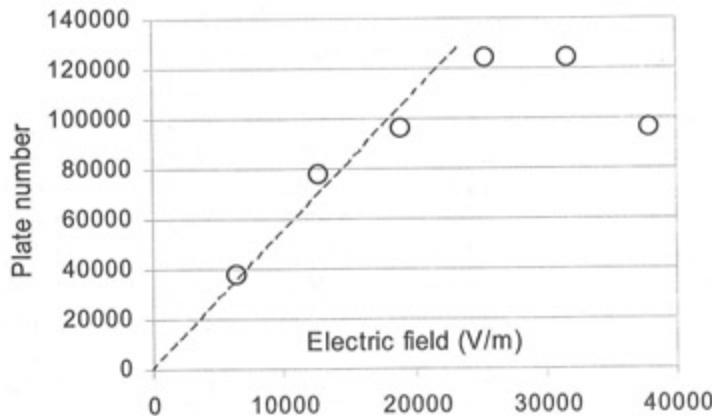
$$\text{pH 12: } \mu_{\text{app}} = \mu_{\text{ep}} + \mu_{\text{eo}} = (-1.6 + 8.1) \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}} = 6.5 \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}}$$

$$u_{\text{anion}} = \mu_{\text{app}} E = \left(6.5 \times 10^{-8} \frac{\text{m}^2}{\text{V}\cdot\text{s}}\right) \left(\frac{27 \times 10^3 \text{ V}}{0.62 \text{ m}}\right) = 2.83 \times 10^{-3} \text{ m/s}$$

$$\text{Migration time} = (0.52 \text{ m}) / (2.83 \times 10^{-3} \text{ m/s}) = 1.84 \times 10^2 \text{ s}$$

- 25-36.** (a) The net speed of an ion moving through the capillary by electroosmosis plus electrophoresis is proportional to electric field ( $u_{\text{net}} = \mu_{\text{app}} E$ ), which, in turn, is proportional to voltage. Increasing voltage by  $120 \text{ kV} / 28 \text{ kV} = 4.3$  should increase the speed by 4.3 and decrease the migration time by 4.3. Peak 1 has a migration time of 211.3 min at 28 kV and 54.36 min at 120 kV. The ratio is  $211.3 \text{ min} / 54.36 \text{ min} = 3.9$ .
- (b) Plate count is proportional to voltage ( $N = \frac{\mu_{\text{app}} V}{2D} \frac{L_d}{L_t}$ ). Increasing voltage by a factor of 4.3 should increase the plate count by 4.3.
- (c) Bandwidth is proportional to the  $1/\sqrt{N}$  ( $N = L_d^2 / \sigma^2 \Rightarrow \sigma = L_d / \sqrt{N}$ ). Increasing voltage by 4.3 should increase  $N$  by 4.3 and decrease bandwidth by  $1/\sqrt{4.3} = 0.48$ . Bandwidth at 120 kV should be 48% as great as bandwidth at 28 kV.
- (d) Increasing voltage makes the ions move faster, which gives them less time to diffuse apart. Therefore, the bandwidth is reduced and resolution is increased.

- 25-37.** At low voltage (low electric field), the number of plates increases in proportion to voltage, as predicted by Equation 25-14. Above  $\sim 25\,000$  V/m, the capillary is probably overheating, which produces band broadening and decreases the number of plates.



$$25-38. \quad N = \frac{5.55 t_r^2}{w_{1/2}^2} = \frac{5.55 (39.9 \text{ min})^2}{(0.81 \text{ min})^2} = 1.35 \times 10^4 \text{ plates}$$

$$\text{Plate height} = 0.400 \text{ m}/(1.35 \times 10^4 \text{ plates}) = 30 \mu\text{m}$$

$$25-39. \quad t = \frac{L}{u_{\text{net}}} = \frac{L}{\mu_{\text{app}} E} \quad (t = \text{migration time}, L = \text{length}, u = \text{speed}, E = \text{field})$$

$$\Rightarrow \mu_{\text{app}} = \frac{L}{tE} = \frac{L/E}{17.12} \text{ for } \text{Cl}^- \text{ and } \mu_{\text{app}} = \frac{L/E}{17.78} \text{ for } \text{I}^-$$

Therefore, we can write that the difference in mobilities is

$$\Delta\mu_{\text{app}}(\text{I}-\text{Cl}) = \frac{L/E}{17.12} - \frac{L/E}{17.78} \quad (L/E \text{ is an unknown constant})$$

$$\text{But we know that } \Delta\mu_{\text{app}}(\text{I}-\text{Cl}) = [\mu_{\text{eo}} + \mu_{\text{ep}}(\text{I}^-)] - [\mu_{\text{eo}} + \mu_{\text{ep}}(\text{Cl}^-)] = \mu_{\text{ep}}(\text{I}^-) - \mu_{\text{ep}}(\text{Cl}^-) = 0.05 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V}) \text{ in Table 14-1.}$$

For the difference between  $\text{Cl}^-$  and  $\text{Br}^-$  we can say

$$\Delta\mu_{\text{app}}(\text{Br}-\text{Cl}) = \frac{L/E}{17.12} - \frac{L/E}{x}$$

$$\text{and we know that } \Delta\mu_{\text{app}}(\text{Br}-\text{Cl}) = 0.22 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V}) \text{ in Table 14-1.}$$

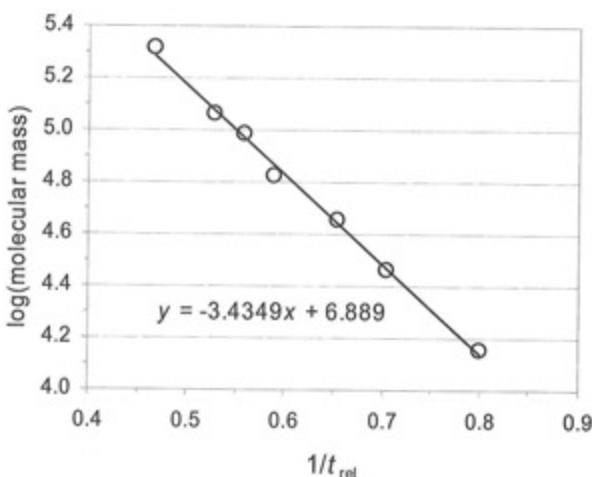
Therefore, we can set up a proportion:

$$\frac{\Delta\mu_{\text{app}}(\text{Br}-\text{Cl})}{\Delta\mu_{\text{app}}(\text{I}-\text{Cl})} = \frac{0.22}{0.05} = \frac{\frac{L/E}{17.12} - \frac{L/E}{x}}{\frac{L/E}{17.12} - \frac{L/E}{17.78}} \Rightarrow x = 20.5 \text{ min}$$

The observed migration time is 19.6 min. Considering the small number of significant digits in the  $\Delta\mu$  values, this is a reasonable discrepancy.

25-40.

	A	B	C	D	E	F
1	Molecular mass by SDS/capillary gel electrophoresis					
2					Relative	
3		Molecular		Migration	migration	
4	Protein	mass (MM)	log(MM)	time (min)	time ( $t_{rel}$ )	$1/t_{rel}$
5	Marker dye	low		13.17		
6	$\alpha$ -Lactalbumin	14200	4.152	16.46	1.250	0.8001
7	Carbonic anhydrase	29000	4.462	18.66	1.417	0.7058
8	Ovalbumin	45000	4.653	20.16	1.531	0.6533
9	Bovine serum albumin	66000	4.820	22.36	1.698	0.5890
10	Phosphorylase B	97000	4.987	23.56	1.789	0.5590
11	$\beta$ -Galactosidase	116000	5.064	24.97	1.896	0.5274
12	Myosin	205000	5.312	28.25	2.145	0.4662
13	Ferritin light chain	?		17.07	1.296	0.7715
14	Ferritin heavy chain	?		17.97	1.364	0.7329



$$\log(\text{MM}) = (-3.4349)/t_{rel} + 6.889$$

$$= 4.239 \text{ for } t_{rel} = 1.296 \text{ (ferritin light chain)}$$

$$= 4.372 \text{ for } t_{rel} = 1.364 \text{ (ferritin heavy chain)}$$

$$\text{Molecular mass} = 10^{\log(\text{MM})}$$

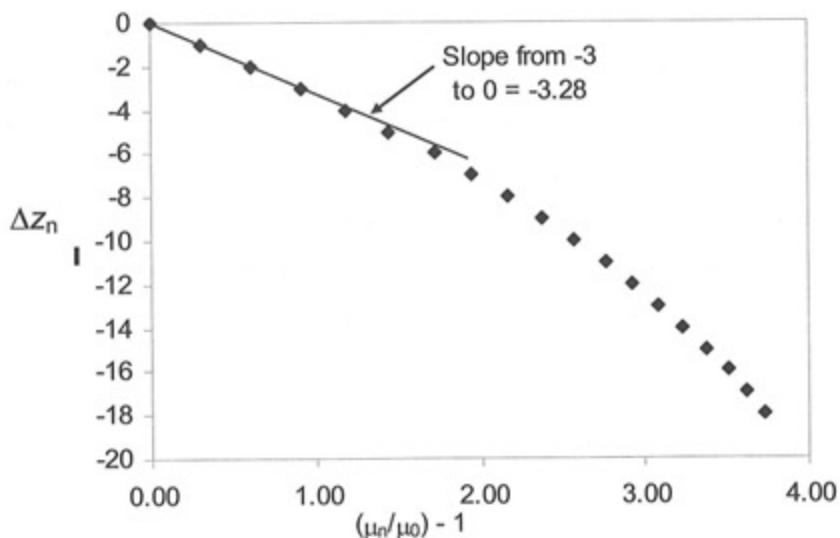
$$= 17\,300 \text{ (ferritin light chain)}$$

$$= 23\,500 \text{ (ferritin heavy chain)}$$

Molecular masses observed from amino acid sequences are 19 766 and 21 099 Da

25-41.

	A	B	C	D	E	F
1	Protein charge ladder	Charge ( $\Delta z$ )	Migration time (s)	Apparent mobility	Electrophoretic mobility	$(\mu n/\mu o)-1$
2		relative to native protein		$m^2/(Vxs)$		
3	Total length of column				$\mu n$	
5	Lt (m) =		0	343.0	6.27E-08	-7.02E-09
6		0.840	-1	355.4	6.05E-08	-9.20E-09
7	Distance to detector		-2	368.2	5.84E-08	-1.13E-08
8			-3	382.2	5.63E-08	-1.34E-08
9	Ld (m) =		-4	395.5	5.44E-08	-1.53E-08
10		0.640	-5	409.1	5.26E-08	-1.71E-08
11	Voltage (V) =		-6	424.9	5.06E-08	-1.91E-08
12		25000	-7	438.5	4.90E-08	-2.07E-08
13	Field (V/Lt) =		-8	453.0	4.75E-08	-2.22E-08
14		2.98E+04	-9	467.0	4.60E-08	-2.37E-08
15	Migration time of neutral marker (s) =		-10	482.0	4.46E-08	-2.51E-08
16		308.5	-11	496.4	4.33E-08	-2.64E-08
17	Electroosmotic mobility ( $m^2/(Vxs)$ ) =		-12	510.1	4.22E-08	-2.75E-08
18		6.97E-08	-13	524.1	4.10E-08	-2.87E-08
19			-14	536.9	4.00E-08	-2.97E-08
20			-15	551.4	3.90E-08	-3.07E-08
21			-16	565.1	3.81E-08	-3.16E-08
22	A20 = (A10/A17)/A14		-17	577.4	3.72E-08	-3.25E-08
23	D5 = (\$A\$10/C5)/\$A\$14		-18	588.5	3.65E-08	-3.32E-08
24	E5 = D5-\$A\$20					
25	F5 = (E5/\$E\$5)-1				slope from points 0 to -2 =	-3.27874
26	F25 = SLOPE(B5:B7,F5:F7)				slope from points 0 to -3 =	-3.28115
27					slope from points 0 to -4 =	-3.36122



The graph is curved, most likely because the shape and friction coefficient of the protein change somewhat as the degree of acetylation increases. The first 4 points (from  $x = 0$  to  $x = -3$ ) lie on a straight line with a slope of  $-3.28$ . This slope is the

charge of the unmodified protein,  $z_0 = -3.28$ . There is no reason why  $z_0$  should be an integer. At any given pH, such as pH 8.3 in this experiment, the native protein is likely to have a fractional average charge because of different amounts of ionization in different species that are all in equilibrium.

- 25-42.**  $\text{SO}_4^{2-}$ :  $\mu_{\text{ep}} = -8.27 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})$  in Table 14-1

$$\mu_{\text{app}} = \mu_{\text{eo}} + \mu_{\text{ep}} = 16.1 \times 10^{-8} - 8.27 \times 10^{-8} = 7.83 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})$$

- $\text{Br}^-$ :  $\mu_{\text{ep}} = -8.13 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})$  in Table 14-1

$$\mu_{\text{app}} = \mu_{\text{eo}} + \mu_{\text{ep}} = 16.1 \times 10^{-8} - 8.13 \times 10^{-8} = 7.97 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})$$

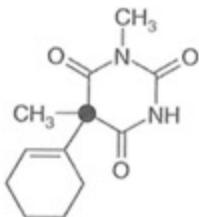
$$\mu_{\text{av}} = \frac{1}{2} (7.83 + 7.97 \times 10^{-8}) = 7.90 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})$$

$$\Delta\mu = (8.27 - 8.13) \times 10^{-8} = 0.14 \times 10^{-8} \text{ m}^2/(\text{s}\cdot\text{V})$$

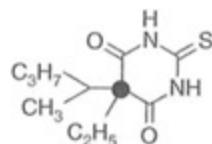
$$N = \left( 4 \text{ (Resolution)} \frac{\mu_{\text{av}}}{\Delta\mu} \right)^2 = \left( 4 (2.0) \frac{7.90}{0.14} \right)^2 = 2.0 \times 10^5 \text{ plates}$$

- 25-43.** In the absence of micelles, the expected order of elution is cations before neutrals before anions: thiamine < (niacinamide + riboflavin) < niacin. Since thiamine is eluted last, it must be most soluble in the micelles.

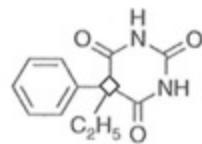
- 25-44.** Carbon atoms labeled with black circles in cyclobarbital and thiopental are chiral, with four different substituents. These compounds are not superimposable on their mirror images. The carbon atom indicated by the diamond in phenobarbital is not chiral because two of its substituents are identical. Cyclodextrin has a chiral pocket, in which these compounds can bind. The equilibrium constant for association of each of the enantiomers of cyclobarbital and thiopental with cyclodextrin will not be the same. Each enantiomer spends a different fraction of time associated with cyclodextrin as it migrates through the capillary. Therefore, cyclobarbital and thiopental will each separate into two peaks. Phenobarbital will only give one peak because it does not have enantiomers.



Cyclobarbital



Thiopental



Phenobarbital

- 25-45.** (a) Plate height rises sharply at low velocity because bands broaden by diffusion when they spend more time in the capillary. This is the effect of the  $B$  term in the van Deemter equation, and it always operates in capillary electrophoresis. Plate height rises gradually at high velocity because solutes require a finite time to equilibrate with the micelles on the column. This is the effect of the  $C$  term in the van Deemter equation, and it is absent in capillary electrophoresis but present to a small extent in micellar electrokinetic capillary chromatography.
- (b) There should be no irregular flow paths because the micelles are nanosized structures in solution. The large  $A$  term most likely arises from extra-column effects, such as the finite size of the injection plug and the finite width of the detector zone.
- 25-46.** For the acid  $H_2A$ , the average charge is  $\alpha_{HA^-} + 2\alpha_{A^{2-}}$ , where  $\alpha$  is the fraction in each form. From our study of acids and bases, we know that

$$\alpha_{HA^-} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \text{ and } \alpha_{A^{2-}} = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

where  $K_1$  and  $K_2$  are acid dissociation constants of  $H_2A$ . The following spreadsheet finds the average charge of malonic acid ( $H_2M$ ) and phthalic acid ( $H_2P$ ) and finds that the maximum difference between them occurs at pH 5.55.

Charge Difference Between Malonic and Phthalic Acids

	A	B	C	D	E	F	G	H	I	J
1	Malonic:			Alpha	Alpha	Alpha	Alpha	Average charges		Charge
2	K1 =	pH	[H <sup>+</sup> ]	HM-	M2-	HP-	P2-	Malonate	Phthalate	Difference
3	1.42E-03	5.52	3.0E-06	0.600	0.399	0.436	0.563	-1.398	-1.562	-0.16392
4	K2 =	5.53	3.0E-06	0.594	0.405	0.430	0.569	-1.403	-1.567	-0.16405
5	2.01E-06	5.54	2.9E-06	0.589	0.410	0.425	0.574	-1.409	-1.573	-0.16413
6	Phthalic:	5.55	2.8E-06	0.583	0.416	0.419	0.580	-1.415	-1.579	-0.16418
7	K1 =	5.56	2.8E-06	0.577	0.421	0.413	0.585	-1.420	-1.584	-0.16417
8	1.12E-03	5.57	2.7E-06	0.572	0.427	0.408	0.591	-1.426	-1.590	-0.16413
9	K2 =	5.58	2.6E-06	0.566	0.433	0.402	0.597	-1.432	-1.596	-0.16404
10	3.90E-06	5.59	2.6E-06	0.561	0.438	0.397	0.602	-1.437	-1.601	-0.16391
11										
12	$D3 = \$A\$3*C3/(C3^2+\$A\$3*C3+\$A\$3*\$A\$5)$						$C3 = 10^{-B3}$			
13	$E3 = \$A\$3*\$A\$5/(C3^2+\$A\$3*C3+\$A\$3*\$A\$5)$						$H3 = -D3-2*E3$			
14	$F3 = \$A\$8*C3/(C3^2+\$A\$8*C3+\$A\$8*\$A\$10)$						$I3 = -F3-2*G3$			
15	$G3 = \$A\$8*\$A\$10/(C3^2+\$A\$8*C3+\$A\$8*\$A\$10)$						$J3 = I3-H3$			

$$25-47. \quad (a) \quad {}^{18}\alpha = \frac{K/R}{(K/R) + [H^+]} = \frac{K}{K + R[H^+]}$$

Approximating  $\bar{\alpha}$  as  ${}^{16}\alpha$ , we can write

$$\begin{aligned} \frac{\Delta\alpha}{\sqrt{\bar{\alpha}}} &\approx \frac{\frac{K}{K+[H^+]} - \frac{K}{K+R[H^+]}}{\sqrt{\frac{K}{K+[H^+]}}} \\ \frac{\Delta\alpha}{\sqrt{\bar{\alpha}}} &\approx \frac{(R-1)K[H^+]}{(K+[H^+])(K+R[H^+])} \cdot \frac{\sqrt{K+[H^+]}}{\sqrt{K}} = \frac{(R-1)\sqrt{K}[H^+]}{\sqrt{K+[H^+]}(K+R[H^+])} \end{aligned}$$

- (b) The function  $\frac{\Delta\alpha}{\sqrt{\bar{\alpha}}}$  has the form  $\frac{u}{v}$ , where  $u$  and  $v$  are functions of  $[H^+]$ :

$$u = (R-1)\sqrt{K}[H^+] \quad v = \sqrt{K+[H^+]}(K+R[H^+])$$

$$\frac{d\left(\frac{u}{v}\right)}{d[H^+]} = \frac{-v\frac{du}{d[H^+]} + u\frac{dv}{d[H^+]}}{v^2}$$

The derivative of  $u/v$  is  $\frac{d\left(\frac{u}{v}\right)}{d[H^+]} = \frac{-v\frac{du}{d[H^+]} + u\frac{dv}{d[H^+]}}{v^2}$ .

Setting the derivative equal to zero gives

$$-v\frac{du}{d[H^+]} + u\frac{dv}{d[H^+]} = 0 \Rightarrow v\frac{du}{d[H^+]} = u\frac{dv}{d[H^+]} \quad (\text{A})$$

The derivatives are

$$\begin{aligned} \frac{du}{d[H^+]} &= (R-1)\sqrt{K} \\ \frac{dv}{d[H^+]} &= (K+R[H^+])\frac{1}{2}(K+[H^+])^{-1/2} + \sqrt{K+[H^+]}(R) \end{aligned}$$

Inserting  $u$  and  $v$  and the two derivatives into Equation A gives an equation that can be solved for  $[H^+]$ .

$$\begin{aligned} v\left(\frac{du}{d[H^+]}\right) &= u\left(\frac{dv}{d[H^+]}\right) \\ \sqrt{K+[H^+]}(K+R[H^+])\{(R-1)\sqrt{K}\} &= (R-1)\sqrt{K}[H^+]\{(K+R[H^+])\frac{1}{2}(K+[H^+])^{-1/2} + \sqrt{K+[H^+]}(R)\} \end{aligned}$$

Solving for  $[H^+]$  gives — after many lines of algebra —

$$[H^+] = \frac{K + K\sqrt{1 + 8R}}{2R}$$

$$(c) \quad \text{Setting } R = 1 \text{ gives } [H^+] = \frac{K + K\sqrt{9}}{2} = 2K$$

$$-\log [H^+] = -\log K - \log 2$$

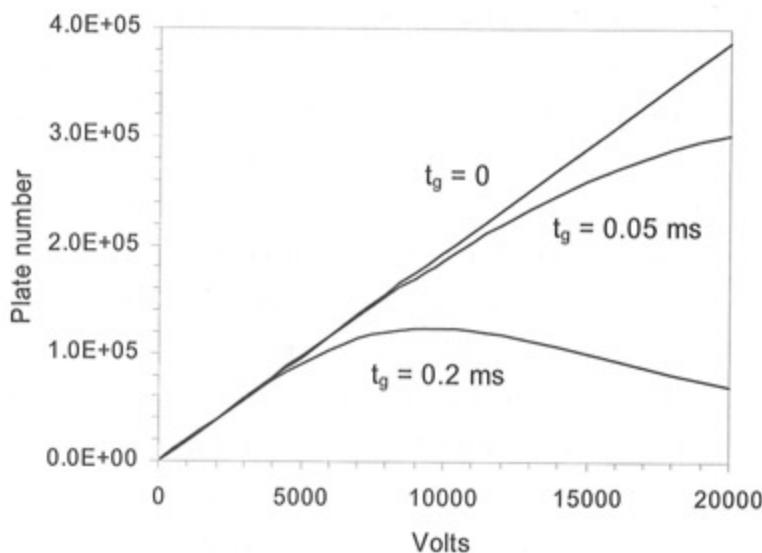
$$\text{pH} = \text{p}K - 0.30$$

- 25-48.** (a) In ion mobility spectrometry, gaseous ions are generated by irradiating analyte plus reagent gas (such as acetone in air) with high energy electrons ( $\beta$  emission) from radioactive  $^{63}\text{Ni}$ . Periodically, ions are admitted into a drift tube by a short voltage pulse applied to an electronic gate (a grid). In the drift tube, ions experience a constant electric field that causes either cations or anions to migrate from the gate to a detector at the other end of the tube. The time to reach the detector is the drift time. Ions drift at a constant speed governed by the driving force of the electric field and the retarding force of friction (drag) by the atmosphere of gas (usually dry air) in the drift tube. Also, gas in the drift tube flows from the detector to the source, further decreasing the migration speed of an ion.

The electric field in ion mobility spectrometry causes ions to migrate from the source to the detector, just as the electric field in electrophoresis causes ions to migrate. Drift time in ion mobility spectrometry is the same quantity as migration time in electrophoresis. The mobility of an ion in liquid or in gas is governed by the charge-to-size ratio. The greater the charge and the smaller the size, the greater the mobility. In liquid or gas, the retarding force is caused by collisions with solvent or gas molecules.

(b)

	A	B	C	D	E	F
1	Ion Mobility Spectrometry					
2						
3	$k =$	Volts	$t_d$ (s)	$w_{1/2}$ (s)	N	
4	1.38065E-23	J/K	100	5.0000	2.68E-01	1.94E+03
5	e =		1000	0.5000	8.47E-03	1.94E+04
6	1.60218E-19	C	2000	0.2500	2.99E-03	3.87E+04
7	T =		3000	0.1667	1.63E-03	5.80E+04
8	300	K	4000	0.1250	1.06E-03	7.73E+04
9	$\mu =$		5000	0.1000	7.59E-04	9.64E+04
10	0.00008	$\text{m}^2/(\text{sV})$	6000	0.0833	5.78E-04	1.15E+05
11	$z =$		7000	0.0714	4.60E-04	1.34E+05
12	1		8000	0.0625	3.77E-04	1.52E+05
13	L =		9000	0.0556	3.18E-04	1.70E+05
14	0.2	m	10000	0.0500	2.72E-04	1.87E+05
15	$t_g =$		12000	0.0417	2.10E-04	2.19E+05
16	5.00E-05	s	14000	0.0357	1.69E-04	2.47E+05
17	$16kT(\ln 2)/ez =$		16000	0.0313	1.41E-04	2.71E+05
18	2.86707E-01		18000	0.0278	1.22E-04	2.90E+05
19			20000	0.0250	1.07E-04	3.03E+05
20	$D_4 = \$A\$14^2/(\$A\$10*C4)$					
21	$E_4 = \text{SQRT}(\$A\$16^2 + (\$A\$18/C4)*D_4^2)$					
22	$F_4 = 5.55*(D_4/E_4)^2$					



Increasing  $V$  increases  $N$  by decreasing the drift time, and therefore decreasing the time for diffusion to broaden the peak. Increasing the time that the ion gate is open increases the initial width of the peak, and therefore decreases the plate number. The peak can never be narrower than the pulse that is admitted by the gate. At high voltage, the effect of  $t_g$  on plate number overwhelms the effect of  $t_d$ . The disadvantage of using a short gate opening time is that fewer ions are admitted to the drift cell and the signal will be weaker.

- (c) Decreasing  $T$  increases  $N$  because diffusional broadening decreases with decreasing temperature.
- (d) 
$$N = 5.55 (t_d/w_{1/2})^2 = 5.55 (0.024\ 925 \text{ s}/0.000\ 154 \text{ s})^2 = 1.45 \times 10^5 \text{ plates}$$

$$\begin{aligned} \text{Theoretical } w_{1/2}^2 &= t_g^2 + \left( \frac{16kT \ln 2}{Vez} \right) t_d^2 \\ &= (5.0 \times 10^{-5} \text{ s})^2 + \left( \frac{16(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K}) \ln 2}{(12\ 500 \text{ V})(1.602 \times 10^{-19} \text{ C})(1)} \right) (0.0249\ 25 \text{ s})^2 \\ &= 1.674 \times 10^{-8} \text{ s}^2 \end{aligned}$$

$$\begin{aligned} \text{Theoretical } N &= 5.55 (t_d^2/w_{1/2}^2) = 5.55 (0.024\ 925 \text{ s})^2/(1.674 \times 10^{-8} \text{ s}^2) \\ &= 2.06 \times 10^5 \text{ plates} \end{aligned}$$
- (e) 
$$R = (\sqrt{N}/4)(\gamma - 1) = \frac{\sqrt{80\ 000}}{4} \left( \frac{22.5}{22.0} - 1 \right) = 1.6$$

**CHAPTER 26**  
**GRAVIMETRIC ANALYSIS, PRECIPITATION TITRATIONS, AND**  
**COMBUSTION ANALYSIS**

- 26-1.** (a) In adsorption, a substance becomes bound to the surface of another substance. In absorption, a substance is taken up inside another substance.  
(b) An inclusion is an impurity that occupies lattice sites in a crystal. An occlusion is an impurity trapped inside a pocket in a growing crystal.
- 26-2.** An ideal gravimetric precipitate should be insoluble, easily filterable, pure, and possess a known, constant composition.
- 26-3.** High relative supersaturation often leads to formation of colloidal product with a large amount of impurities.
- 26-4.** Relative supersaturation can be decreased by increasing temperature (for most solutions), mixing well during addition of precipitant, and using dilute reagents. Homogeneous precipitation is also an excellent way to control relative supersaturation.
- 26-5.** Washing with electrolyte preserves the electric double layer and prevents peptization.
- 26-6.**  $\text{HNO}_3$  evaporates during drying.  $\text{NaNO}_3$  is nonvolatile and will lead to a high mass for the precipitate.
- 26-7.** During the first precipitation, the concentration of unwanted species in the solution is high, giving a relatively high concentration of impurities in the precipitate. In the reprecipitation, the level of solution impurities is reduced, giving a purer precipitate.
- 26-8.** In thermogravimetric analysis, the mass of a sample is measured as the sample is heated. The mass lost during decomposition provides some information about the composition of the sample.
- 26-9.** A quartz crystal microbalance consists of a specially cut, thin, disk-shape slice of quartz with gold electrodes on each of the two faces. Application of an oscillating electric field causes the crystal to oscillate at a characteristic frequency. Binding of small masses to the gold electrodes increases the mass of

the system and lowers the oscillation frequency. From the change in frequency, we can deduce how much mass was bound.

**26-10.**  $\frac{0.2146 \text{ g AgBr}}{187.772 \text{ g AgBr/mol}} = 1.1429 \times 10^{-3} \text{ mol AgBr}$

$$[\text{NaBr}] = \frac{1.1429 \times 10^{-3} \text{ mol}}{50.00 \times 10^{-3} \text{ L}} = 0.02286 \text{ M}$$

**26-11.**  $\frac{0.104 \text{ g CeO}_2}{172.114 \text{ g CeO}_2/\text{mol}} = 6.043 \times 10^{-4} \text{ mol CeO}_2 = 6.043 \times 10^{-4} \text{ mol Ce}$   
 $= 0.08466 \text{ g Ce}$

$$\text{weight \% Ce} = \frac{0.08466 \text{ g}}{4.37 \text{ g}} \times 100 = 1.94 \text{ wt\%}$$

**26-12.** Formula mass of AgCl =  $107.8 + 35.4 = 143.2$

$$\text{mol AgCl} = \frac{0.08890 \text{ g AgCl}}{143.2 \text{ g AgCl/mol AgCl}} = 6.2081 \times 10^{-4} \text{ mol}$$

$$\text{mol radium} = \frac{6.2081 \times 10^{-4} \text{ mol Cl}^-}{2 \text{ mol Cl}^-/\text{mol Ra}} = 3.1040 \times 10^{-4} \text{ mol}$$

$$3.1040 \times 10^{-4} \text{ mol RaCl}_2 = \frac{0.09192 \text{ g RaCl}}{x \text{ g RaCl}_2/\text{mol RaCl}_2}$$

$$x = \frac{0.09192 \text{ g RaCl}}{3.1040 \times 10^{-4} \text{ mol RaCl}_2} = 296.13 \text{ g RaCl}_2/\text{mol RaCl}_2$$

$$\text{formula mass of RaCl}_2 = \text{atomic mass of Ra} + 2(35.4 \text{ g/mol}) = 296.13 \text{ g/mol}$$

$$\Rightarrow \text{atomic mass of Ra} = 225.3 \text{ g/mol}$$

**26-13.** One mole of product (206.240 g) comes from one mole of piperazine (86.136 g).

$$\text{Grams of piperazine in sample} =$$

$$(0.7129 \text{ g of piperazine / g of sample}) \times (0.05002 \text{ g of sample}) = 0.03566.$$

$$\text{Mass of product} = \left(\frac{206.240}{86.136}\right)(0.03566) = 0.08538 \text{ g.}$$

**26-14.** 2.500 g bis(dimethylglyoximate) nickel (II) =  $8.6532 \times 10^{-3} \text{ mol Ni} = 0.50785 \text{ g Ni} = 50.79\% \text{ Ni.}$

**26-15.** Formula masses:  $\text{CaC}_{14}\text{H}_{10}\text{O}_6\cdot\text{H}_2\text{O}$  (332.32),  $\text{CaCO}_3$  (100.09),  $\text{CaO}$  (56.08). At  $550^\circ$ ,  $\text{CaC}_{14}\text{H}_{10}\text{O}_6\cdot\text{H}_2\text{O}$  is converted to  $\text{CaCO}_3$  (calcium carbonate). 332.32 g of starting material will produce 100.09 g of  $\text{CaO}$ .

Mass at 550° =  $(100.09/332.32)(0.635\text{ g}) = 0.191\text{ g}$ . At 1 000°C, the product is CaO (calcium oxide) and the mass is  $(56.08/332.32)(0.635\text{ g}) = 0.107\text{ g}$ .

**26-16.**  $2.378\text{ mg CO}_2 / (44.010\text{ g/mol}) = 5.403\text{ }3 \times 10^{-5}\text{ mol CO}_2 = 5.403\text{ }3 \times 10^{-5}\text{ mol C}$   
 $= 6.490\text{ }0 \times 10^{-4}\text{ g C}$   
 $\text{ppm C} = 10^6 (6.490\text{ }0 \times 10^{-4} / 6.234) = 104.1\text{ ppm}$

**26-17.**  $2.07\% \text{ of } 0.998\text{ g} = 0.020\text{ }67\text{ g of Ni} = 3.521 \times 10^{-4}\text{ mol of Ni}$ .  
This requires  $(2)(3.521 \times 10^{-4})\text{ mol of DMG} = 0.081\text{ }77\text{ g}$ .  
A 50.0% excess is  $(1.5)(0.081\text{ }77\text{ g}) = 0.122\text{ }7\text{ g}$ . The mass of solution containing  $0.122\text{ }7\text{ g}$  is  $0.122\text{ }7\text{ g DMG} / (0.021\text{ }5\text{ g DMG/g solution}) = 5.705\text{ g of solution}$ .  
The volume of solution is  $5.705\text{ g}/(0.790\text{ g/mL}) = 7.22\text{ mL}$ .

**26-18.** Moles of Fe in product ( $\text{Fe}_2\text{O}_3$ ) = moles of Fe in sample.

Because 1 mole of ( $\text{Fe}_2\text{O}_3$ ) contains 2 moles of Fe, we can write the equation

$$\frac{2 (0.264\text{ g})}{159.69\text{ g/mol}} = 3.306 \times 10^{-3}\text{ mol of Fe.}$$

This many moles of Fe equals  $0.919\text{ g of FeSO}_4 \cdot 7\text{ H}_2\text{O}$ . Because we analyzed just  $2.998\text{ g}$  out of  $22.131\text{ g}$  of tablets, the  $\text{FeSO}_4 \cdot 7\text{ H}_2\text{O}$  in the  $22.131\text{ g}$  sample is  $\frac{22.131\text{ g}}{2.998\text{ g}} (0.919\text{ g}) = 6.786\text{ g}$ . This is the  $\text{FeSO}_4 \cdot 7\text{ H}_2\text{O}$  content of 20 tablets.

The content in one tablet is  $(6.786\text{ g})/20 = 0.339\text{ g}$ .

**26-19.** (a) Mass of product ( $\text{CaCO}_3$ ) =  $18.546\text{ g} - 18.231\text{ g} = 0.315\text{ g}$

$$\text{mol CaCO}_3 = \left( \frac{0.315\text{ g}}{100.087\text{ g/mol}} \right) = 3.153 \times 10^{-3}\text{ mol}$$

The product contains  $3.153\text{ mmol Ca} = (3.153 \times 10^{-3}\text{ mol})(40.078\text{ g/mol}) = 0.1264\text{ g Ca}$ .

$$\text{wt\% Ca} = \frac{0.1264\text{ g Ca}}{0.632\text{ g mineral}} \times 100 = 19.98\%$$

- (b) The solutions are heated before mixing to increase the solubility of the product that will precipitate. If the solution is less supersaturated during the precipitation, crystals form more slowly and grow to be larger and purer than if they precipitate rapidly. The larger crystals are easier to filter.
- (c)  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  provides oxalate ion to prevent  $\text{CaC}_2\text{O}_4$  from redissolving. Also, the ammonium and oxalate ions provide an ionic atmosphere that prevents the precipitate from peptizing (breaking into colloidal particles).

(d)  $\text{AgNO}_3$  solution is added to the filtrate to test for  $\text{Cl}^-$  in the filtrate. If  $\text{Cl}^-$  is present,  $\text{AgCl}(s)$  will precipitate when  $\text{Ag}^+$  is added. The source of  $\text{Cl}^-$  is the HCl used to dissolve the mineral. All the original solution needs to be washed away, so no extra material is present that would increase the mass of final product, which should be pure  $\text{CaCO}_3(s)$ .

**26-20.** (a)  $70 \text{ kg} \left( \frac{6.3 \text{ g P}}{\text{kg}} \right) = 441 \text{ g P}$  in  $8.00 \times 10^3 \text{ L}$ . This corresponds to  $\frac{441 \text{ g P}}{8.00 \times 10^3 \text{ L}} = 0.0551 \text{ g/L}$  or  $5.51 \text{ mg}/100 \text{ mL}$ .

(b) Fraction of P in one formula mass is  $\frac{2(30.974)}{3596.46} = 1.722\%$ .

$$\text{P in } 0.3387 \text{ g of } \text{P}_2\text{O}_5 \cdot 24 \text{ MoO}_3 = (0.01722)(0.3387) = 5.834 \text{ mg}$$

This is near the amount expected from a dissolved man.

**26-21.** Let  $x$  = mass of  $\text{NH}_4\text{Cl}$  and  $y$  = mass of  $\text{K}_2\text{CO}_3$ .

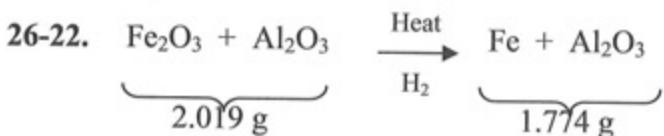
For the first part, 1/4 of the sample (25 mL) gave 0.617 g of precipitate containing both products:

$$\begin{array}{c} \text{mol NH}_4\text{Cl} \\ \underbrace{\frac{1}{4} \left[ \underbrace{\left( \frac{x}{53.492} \right) (337.27)}_{\text{g } \phi_4\text{BNH}_4} + \underbrace{\left( \frac{2y}{138.21} \right) (358.33)}_{\text{g } \phi_4\text{BK}} \right] \times 2 } \\ = 0.617 \text{ g} \end{array}$$

We multiplied moles of  $\text{K}_2\text{CO}_3$  by 2 because one mole of  $\text{K}_2\text{CO}_3$  gives 2 moles of  $\phi_4\text{BK}$ . In the second part, half of the sample (50 mL) gave 0.554 g of  $\phi_4\text{BK}$ :

$$\begin{array}{c} \text{mol K}_2\text{CO}_3 \times 2 \\ \underbrace{\frac{1}{2} \left( \frac{2y}{138.21} \right) (358.33) = 0.554 \text{ g}}_{\text{g } \phi_4\text{BK}} \Rightarrow y = 0.2137 \text{ g} = 14.5 \text{ wt\% K}_2\text{CO}_3 \end{array}$$

Putting this value of  $y$  into the first equation gives  $x = 0.2157 \text{ g} = 14.6 \text{ wt\% NH}_4\text{Cl}$



The mass of oxygen lost is  $2.019 - 1.774 = 0.245$  g, which equals 0.01531 moles of oxygen atoms. For every 3 moles of oxygen there is 1 mole of  $\text{Fe}_2\text{O}_3$ , so moles of  $\text{Fe}_2\text{O}_3 = \frac{1}{3}(0.01531) = 0.005105$  mol of  $\text{Fe}_2\text{O}_3$ . This much  $\text{Fe}_2\text{O}_3$  equals 0.815 g, which is 40.4 wt% of the original sample.

- 26-23.** Let  $x = \text{g}$  of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  and  $y = \text{g}$  of  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ . We can say that  $x + y = 0.5485$  g. The moles of Fe in the final product ( $\text{Fe}_2\text{O}_3$ ) must equal the moles of Fe in the sample.

$$\text{The moles of Fe in } \text{Fe}_2\text{O}_3 = 2 \left( \text{moles of } \text{Fe}_2\text{O}_3 \right) = 2 \left( \frac{0.1678}{159.69} \right) = 0.0021016 \text{ mol.}$$

$$\text{Mol Fe in } \text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O} = x / 392.13 \text{ and}$$

$$\text{mol Fe in } \text{FeCl}_2 \cdot 6\text{H}_2\text{O} = y / 234.84.$$

$$0.0021016 = \frac{x}{392.13} + \frac{y}{234.84} \quad (1)$$

Substituting  $x = 0.5485 - y$  into Eq. (1) gives  $y = 0.41146$  g of  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ .

$$\text{Mass of Cl} = 2 \left( \frac{35.453}{234.84} \right) (0.41146) = 0.12423 \text{ g} = 22.65 \text{ wt\%}$$

- 26-24.** (a) Let  $x = \text{mass of } \text{AgNO}_3$  and  $(0.4321 - x) = \text{mass of } \text{Hg}_2(\text{NO}_3)_2$  in unknown. Each mol of  $\text{AgNO}_3$  gives  $1/3$  mol  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  and each mol of  $\text{Hg}_2(\text{NO}_3)_2$  gives  $1/3$  mol  $(\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2$ . Mass of both products must equal 0.4515 g:

$$\underbrace{\frac{\text{mol } \text{Ag}_3[\text{Co}(\text{CN})_6]}{\frac{1}{3}\left(\frac{x}{169.873}\right)} (538.643)}_{\text{mass of } \text{Ag}_3[\text{Co}(\text{CN})_6]} + \underbrace{\frac{\text{mol } (\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2}{\frac{1}{3}\left(\frac{0.4321-x}{525.19}\right)} (1633.62)}_{\text{mass of } (\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2} = 0.4515$$

$$\Rightarrow x = 0.1731 \text{ g} = 40.05 \text{ wt\%}$$

- (b) 0.30% error in 0.4515 g =  $\pm 0.00135$  g. This changes the equation of (a) to:

$$\frac{1}{3}\left(\frac{x}{169.873}\right)(538.643) + \frac{1}{3}\left(\frac{0.4321-x}{525.19}\right)(1633.62) = 0.4515 (\pm 0.00135)$$

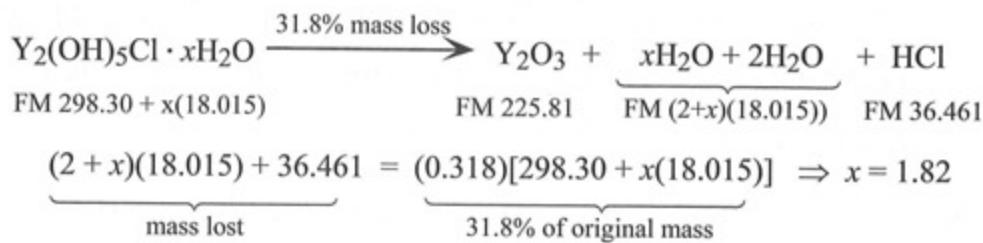
$$1.056952x + 0.448020 - 1.036844x = 0.4515 (\pm 0.00135)$$

$$0.020109x = 0.4515 (\pm 0.00135) - 0.448020$$

$$0.020109x = 0.003480 (\pm 0.00135)$$

$$x = \frac{0.003480 (\pm 0.00135)}{0.020109} = \frac{0.003480 (\pm 38.8\%)}{0.020109} = 0.17 \text{ g} \pm 39\%$$

- 26-25.** (a) Balanced equation for overall (31.8%) mass loss:



- (b) Logical molecular units that could be lost are  $\text{H}_2\text{O}$  and  $\text{HCl}$ . At ~8.1% mass loss, the product is  $\text{Y}_2(\text{OH})_5\text{Cl}$ . Loss of 2 more  $\text{H}_2\text{O}$  would give a total mass loss of

$$\frac{1.82\text{H}_2\text{O} + 2\text{H}_2\text{O}}{\text{Y}_2(\text{OH})_5\text{Cl} \cdot 1.82\text{H}_2\text{O}} = \frac{68.82}{331.09} = 20.8\%$$

Loss of  $\text{HCl}$  from  $\text{Y}_2(\text{OH})_5\text{Cl}$  would give a total mass loss of

$$\frac{1.82\text{H}_2\text{O} + \text{HCl}}{\text{Y}_2(\text{OH})_5\text{Cl} \cdot 1.82\text{H}_2\text{O}} = \frac{69.25}{331.09} = 20.9\%$$

The composition at the ~19.2% plateau could be either  $\text{Y}_2\text{O}_2(\text{OH})\text{Cl}$  (from loss of  $2\text{H}_2\text{O}$ ) or  $\text{Y}_2\text{O}(\text{OH})_4$  (from loss of  $\text{HCl}$ ).

- 26-26.** (a)  $\alpha = \frac{\text{mass of KPO}_3}{\text{mass of K(D}_x\text{H}_{1-x}\text{)}_2\text{PO}_4} = \frac{118.070 \ 3}{136.085 \ 3 + 2.012 \ 55x}$

$$\text{Cross-multiply: } (136.085 \ 3)\alpha + (2.012 \ 55)\alpha x = 118.070 \ 3$$

$$(2.012 \ 55)\alpha x = 118.070 \ 3 - (136.085 \ 3)\alpha$$

Divide by  $(2.012 \ 55)\alpha$ :

$$x = \frac{118.070 \ 3}{(2.012 \ 55)\alpha} - \frac{(136.085 \ 3)\alpha}{(2.012 \ 55)\alpha} \qquad x = \frac{58.667 \ 0}{\alpha} - 67.618 \ 3$$

$$\text{For fully deuterated material, } x = 1 \text{ and } \alpha = \frac{58.667 \ 0}{x + 67.618 \ 3} = 0.854 \ 976$$

$$(b) x = \frac{58.667 \ 0}{0.856 \ 77} - 67.618 \ 3 = 0.856 \ 3_2$$

- (c) For the function  $x = f(\alpha)$ , we can write

$$e_x = \sqrt{\left(\frac{\partial F}{\partial \alpha}\right)^2 e_\alpha^2}$$

$$\text{For } x = \frac{58.667 \ 0}{\alpha} - 67.618 \ 3, \frac{\partial F}{\partial \alpha} = -\frac{58.667 \ 0}{\alpha^2} \text{ giving}$$

$$e_x = \sqrt{\left(-\frac{58.667 \ 0}{\alpha^2}\right)^2 e_\alpha^2} = \frac{58.667 \ 0 e_\alpha}{\alpha^2}$$

$$(d) \text{ For } e_x = 0.0001, e_x = \frac{(58.6670)(0.0001)}{(0.85677)^2} = 0.008$$

$$\text{D:H stoichiometry} = x \pm e_x = 0.856 \pm 0.008$$

$$\text{If } e_x \text{ were } 0.001, \text{ then } e_x = \frac{(58.6670)(0.001)}{(0.85677)^2} = 0.08 \text{ and}$$

$$\text{D:H stoichiometry} = 0.86 \pm 0.08$$

- 26-27.** (a) Formula mass of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x} = 666.19 - (16.00)x$

$$\text{mmol of } \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \text{ in experiment} = \frac{34.397 \text{ mg}}{[666.19 - (16.00)x] \text{ mg/mmol}}$$

$$\text{mmol of oxygen atoms lost in experiment} = \frac{(34.397 - 31.661) \text{ mg}}{16.00 \text{ mg/mmol}}$$

$$= 0.17100 \text{ mmol}$$

From the stoichiometry of the reaction, we can write

$$\frac{\text{mmol oxygen atoms lost}}{\text{mmol } \text{YBa}_2\text{Cu}_3\text{O}_{7-x}} = \frac{3.5 - x}{1}$$

$$\frac{0.17100}{34.397 / [666.19 - (16.00)x]} = 3.5 - x \Rightarrow x = 0.2042$$

(without regard to significant figures)

- (b) Now let the uncertainty in each mass be 0.002 mg and let all atomic and molecular masses have negligible uncertainty.

The mmol of oxygen atoms lost are:

$$\frac{[34.397(\pm 0.002) - 31.661(\pm 0.002)] \text{ mg}}{16.00 \text{ mg / mmol}} = \frac{2.736(\pm 0.0028)}{16.00} \\ = 0.17100 (\pm 0.102\%)$$

$$\text{The relative error in the mass of starting material is } \frac{0.002}{34.397} = 0.0058\%$$

The master equation becomes

$$\frac{0.17100 (\pm 0.102\%)}{34.397 (\pm 0.0058\%) / [666.19 - (16.00)x]} = 3.5 - x$$

$$0.17100 (\pm 0.102\%) [666.19 - (16.00)x] = (3.5 - x) [34.397 (\pm 0.0058\%)]$$

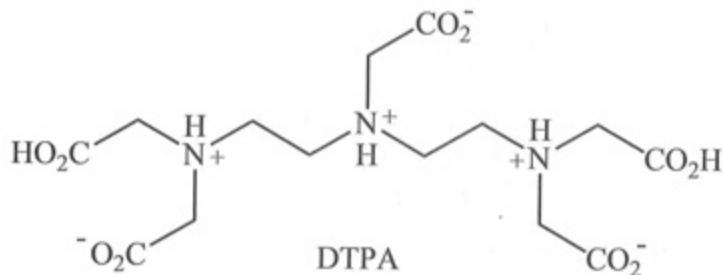
$$113.918 (\pm 0.116) - [2.736 (\pm 0.00279)] x$$

$$= 120.3895 (\pm 0.00698) - [34.397 (\pm 0.002)] x$$

$$[31.66 (\pm 0.00346)] x = 6.4715 (\pm 0.116)$$

$$= 0.2044 (\pm 1.79\%) = 0.204 \pm 0.004$$

26-28.

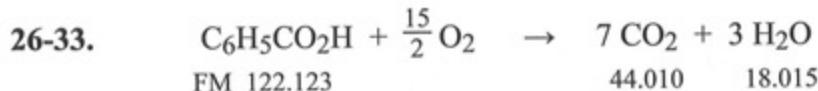


Neutral DTPA has 2 carboxylic acid protons and 3 ammonium protons. We are not given the  $pK_a$  values, but, by analogy with EDTA, we expect carboxyl  $pK_a$  values to be below  $\sim 3$  and ammonium  $pK_a$  values to be above  $\sim 6$ . At pH 14, we expect all the acidic protons of DTPA to be dissociated, so the predominant species will be  $\text{DTPA}^{5-}$ . At pH 3-4, the nitrogen atoms should all be protonated, but the carboxyl groups should be all (or mostly) deprotonated. The predominant species is probably  $\text{DTPA}^{2-}$ .

For  $\text{HSO}_4^-$ ,  $pK_a = 2.0$ . At pH 14 and at pH 3, sulfate should mainly be in the form  $\text{SO}_4^{2-}$ .

At pH 14,  $\text{DTPA}^{5-}$  is apparently a strong enough ligand to chelate  $\text{Ba}^{2+}$  and dissolve  $\text{BaSO}_4(s)$ . At pH 3-4,  $\text{DTPA}^{2-}$  is not a strong enough ligand to dissolve  $\text{BaSO}_4(s)$ . Another way to say the same thing is that  $\text{H}^+$  at a concentration of  $10^{-3}\text{-}10^{-4} \text{ M}$  competes with  $\text{Ba}^{2+}$  for binding sites on DTPA, but  $\text{H}^+$  at a concentration of  $10^{-14} \text{ M}$  does not compete with  $\text{Ba}^{2+}$  for binding sites on DTPA.

- 26-29. In *combustion*, a substance is heated in the presence of excess  $\text{O}_2$  to convert carbon to  $\text{CO}_2$  and hydrogen to  $\text{H}_2\text{O}$ . In *pyrolysis*, the substance is decomposed by heating in the absence of added  $\text{O}_2$ . All oxygen in the sample is converted to  $\text{CO}$  by passage through a suitable catalyst.
- 26-30.  $\text{WO}_3$  catalyzes the complete combustion of C to  $\text{CO}_2$  in the presence of excess  $\text{O}_2$ . Cu converts  $\text{SO}_3$  to  $\text{SO}_2$  and removes excess  $\text{O}_2$ .
- 26-31. The tin capsule melts and is oxidized to  $\text{SnO}_2$  to liberate heat and crack the sample. Tin uses the available oxygen immediately, ensures that sample oxidation occurs in the gas phase, and acts as an oxidation catalyst.
- 26-32. By dropping the sample in before very much  $\text{O}_2$  is present, pyrolysis of the sample to give gaseous products occurs prior to oxidation. This minimizes the formation of nitrogen oxides.



One mole of  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  gives 7 moles of  $\text{CO}_2$  and 3 moles of  $\text{H}_2\text{O}$ .

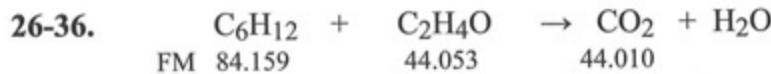
4.635 mg of benzoic acid = 0.03795 mmol, which gives 0.2657 mmol  $\text{CO}_2$  (= 11.69 mg  $\text{CO}_2$ ) and 0.1139 mmol  $\text{H}_2\text{O}$  (= 2.051 mg  $\text{H}_2\text{O}$ ).



- 26-35.** 100 g of compound contains 46.21 g C, 9.02 g H, 13.74 g N, and 31.03 g O. The atomic ratios are C : H : N : O =

$$\begin{aligned} \frac{46.21 \text{ g}}{12.0107 \text{ g/mol}} : \frac{9.02 \text{ g}}{1.00794 \text{ g/mol}} : \frac{13.74 \text{ g}}{14.00674 \text{ g/mol}} : \frac{31.03 \text{ g}}{15.9994 \text{ g/mol}} \\ = 3.847 : 8.949 : 0.9810 : 1.940 \end{aligned}$$

Dividing by the smallest factor (0.9810) gives the ratios C : H : N : O = 3.922 : 9.12 : 1 : 1.978. The empirical formula is probably  $\text{C}_4\text{H}_9\text{NO}_2$ .



Let  $x$  = mg of  $\text{C}_6\text{H}_{12}$  and  $y$  = mg of  $\text{C}_2\text{H}_4\text{O}$

$$x + y = 7.290.$$

We also know that moles of  $\text{CO}_2$  = 6 (moles of  $\text{C}_6\text{H}_{12}$ ) + 2 (moles of  $\text{C}_2\text{H}_4\text{O}$ ), by conservation of carbon atoms.

$$6\left(\frac{x}{84.159}\right) + 2\left(\frac{y}{44.053}\right) = \frac{21.999}{44.010}$$

Making the substitution  $x = 7.290 - y$  allows us to solve for  $y$ .

$$y = 0.767 \text{ mg} = 10.5 \text{ wt\%}.$$

- 26-37.** The atomic ratio H : C is

$$\frac{\left(\frac{6.76 \pm 0.12 \text{ g}}{1.00794 \text{ g/mol}}\right)}{\left(\frac{71.17 \pm 0.41 \text{ g}}{12.0107 \text{ g/mol}}\right)} = \frac{6.707 \pm 0.119}{5.926 \pm 0.0341} = \frac{6.707 \pm 1.78\%}{5.926 \pm 0.576\%} = 1.132 \pm 0.021$$

If we define the stoichiometry coefficient for C to be 8, then the stoichiometry coefficient for H is  $8(1.132 \pm 0.021) = 9.06 \pm 0.17$ .

The atomic ratio N:C is

$$\begin{aligned} \frac{\left(\frac{10.34 \pm 0.08 \text{ g}}{14.00674 \text{ g/mol}}\right)}{\left(\frac{71.17 \pm 0.41 \text{ g}}{12.0107 \text{ g/mol}}\right)} &= \frac{0.7382 \pm 0.0057}{5.926 \pm 0.0341} = \frac{0.7382 \pm 0.774\%}{5.925 \pm 0.576\%} \\ &= 0.1246 \pm 0.0012 \end{aligned}$$

If we define the stoichiometry coefficient for C to be 8, then the stoichiometry coefficient for N is  $8(0.1246 \pm 0.0012) = 0.9968 \pm 0.0096$ .

The empirical formula is reasonably expressed as  $\text{C}_8\text{H}_{9.06 \pm 0.17}\text{N}_{0.997 \pm 0.010}$ .

- 26-38.** The reaction between  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  can be written



One mole of  $\text{H}_2\text{SO}_4$  requires two moles of  $\text{NaOH}$ . In 3.01 mL of 0.01576 M  $\text{NaOH}$  there are  $(0.00301 \text{ L})(0.01576 \text{ mol/L}) = 4.744 \times 10^{-5} \text{ mol}$  of  $\text{NaOH}$ . The moles of  $\text{H}_2\text{SO}_4$  must have been  $(\frac{1}{2})(4.744 \times 10^{-5}) = 2.372 \times 10^{-5} \text{ mol}$ . Because one mole of  $\text{H}_2\text{SO}_4$  contains one mole of S, there must have been  $2.372 \times 10^{-5} \text{ mol}$  of S ( $= 0.7606 \text{ mg}$ ). The percentage of S in the sample is

$$\frac{0.7606 \text{ mg S}}{6.123 \text{ mg sample}} \times 100 = 12.4 \text{ wt\%}.$$

- 26-39.** (a) Experiment 1:  $\bar{x} = 10.16_0 \mu\text{mol Cl}^-$   $s = 2.70_7 \mu\text{mol Cl}^-$

$$\begin{aligned} 95\% \text{ confidence interval} &= \bar{x} \pm \frac{ts}{\sqrt{n}} \\ &= 10.16_0 \pm \frac{(2.262)(2.70_7)}{\sqrt{10}} = 10.16_0 \pm 1.93_6 \mu\text{mol Cl}^- \end{aligned}$$

Experiment 2:  $\bar{x} = 10.77_0 \mu\text{mol Cl}^-$   $s = 3.20_5 \mu\text{mol Cl}^-$

$$\begin{aligned} 95\% \text{ confidence interval} &= \bar{x} \pm \frac{ts}{\sqrt{n}} \\ &= 10.77_0 \pm \frac{(2.262)(3.20_5)}{\sqrt{10}} = 10.77_0 \pm 2.29_3 \mu\text{mol Cl}^- \end{aligned}$$

$$(b) s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}} = \sqrt{\frac{2.70_7^2(10 - 1) + 3.20_5^2(10 - 1)}{10 + 10 - 2}} = 2.96_6$$

$$\begin{aligned} t_{\text{calculated}} &= \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} = \frac{|10.16_0 - 10.77_0|}{2.96_6} \sqrt{\frac{(10)(10)}{10 + 10}} \\ &= 0.46_0 < t_{\text{tabulated}} \text{ for 18 degrees of freedom for } 95\% \text{ confidence level (or even for 50\% confidence level)} \end{aligned}$$

Therefore, the difference is not significant. The result means that addition of

excess Cl<sup>-</sup> prior to precipitation does not lead to additional coprecipitation of Cl<sup>-</sup> under the conditions of these experiments. (In general, under other conditions we would expect extra Cl<sup>-</sup> to lead to extra coprecipitation.)

- (c) 10.0 mg of SO<sub>4</sub><sup>2-</sup> = 0.104<sub>10</sub> mmol = 24.295 mg BaSO<sub>4</sub>
- (d) In Experiment 1, the precipitate includes an additional 10.160 μmol Cl<sup>-</sup> = 5.08 μmol BaCl<sub>2</sub> = 1.05 g mg BaCl<sub>2</sub>. The increase in mass is (1.05)/(24.295) = 4.35%. This represents a large error in the analysis.

- 26-40.** (i) I<sup>-</sup>(excess) + Ag<sup>+</sup> → AgI(s) [Ag<sup>+</sup>] = K<sub>sp</sub> (for AgI) / [I<sup>-</sup>]
- (ii) A stoichiometric quantity of Ag<sup>+</sup> has been added that would be just equivalent to I<sup>-</sup>, if no Cl<sup>-</sup> were present. Instead, a tiny amount of AgCl precipitates and a slight amount of I<sup>-</sup> remains in solution.
- (iii) Cl<sup>-</sup>(excess) + Ag<sup>+</sup> → AgCl(s) [Ag<sup>+</sup>] = K<sub>sp</sub> (for AgCl) / [Cl<sup>-</sup>]
- (iv) Virtually all I<sup>-</sup> and Cl<sup>-</sup> have precipitated.  

$$[Ag^+] \approx [Cl^-] \Rightarrow [Ag^+] = \sqrt{K_{sp} \text{ (for AgCl)}}$$
- (v) There is excess Ag<sup>+</sup> delivered from the buret.  

$$[Ag^+] = [Ag^+]_{\text{titrant}} \cdot \left( \frac{\text{volume added past 2nd equivalence point}}{\text{total volume}} \right)$$

- 26-41.** At V<sub>e</sub>, moles of Ag<sup>+</sup> = moles of I<sup>-</sup>  

$$(V_e \text{ mL})(0.0511 \text{ M}) = (25.0 \text{ mL})(0.0823 \text{ M}) \Rightarrow V_e = 40.26 \text{ mL}$$
  
When V<sub>Ag<sup>+</sup></sub> = 39.00 mL, [I<sup>-</sup>] =  $\frac{40.26 - 39.00}{40.26} (0.08230) \left( \frac{25.00}{25.00 + 39.00} \right)$   
=  $1.006 \times 10^{-3} \text{ M}$ . [Ag<sup>+</sup>] = K<sub>sp</sub>/[I<sup>-</sup>] =  $8.3 \times 10^{-14} \text{ M} \Rightarrow pAg^+ = 13.08$ .  
When V<sub>Ag<sup>+</sup></sub> = V<sub>e</sub>, [Ag<sup>+</sup>][I<sup>-</sup>] = x<sup>2</sup> = K<sub>sp</sub> ⇒ x = [Ag<sup>+</sup>] =  $9.1 \times 10^{-9} \text{ M}$   
⇒ pAg<sup>+</sup> = 8.04.  
When V<sub>Ag<sup>+</sup></sub> = 44.30 mL, there is an excess of  $(44.30 - 40.26) = 4.04 \text{ mL}$  of Ag<sup>+</sup>. [Ag<sup>+</sup>] =  $\left( \frac{4.04}{25.00 + 44.30} \right) (0.05110) = 2.98 \times 10^{-3} \text{ M} \Rightarrow pAg^+ = 2.53$ .

- 26-42.** At the equivalence point, [Ag<sup>+</sup>][I<sup>-</sup>] = K<sub>sp</sub> ⇒ (x)(x) =  $8.3 \times 10^{-17}$   
⇒ [Ag<sup>+</sup>] =  $9.1 \times 10^{-9} \text{ M}$ . The concentration of Cl<sup>-</sup> in the titration solution is the initial concentration (0.0500 M) corrected for dilution from an initial volume of 40.00 mL up to ~63.85 mL at the equivalence point:

$$[Cl^-] = (0.0500 \text{ M}) \left( \frac{40.00}{63.85} \right) = 0.0313 \text{ M}$$

Is AgCl solubility exceeded? The reaction quotient is  $Q = [\text{Ag}^+][\text{Cl}^-] = (9.1 \times 10^{-9})(0.0313) = 2.8 \times 10^{-10}$ , which is greater than  $K_{\text{sp}}$  for AgCl ( $= 1.8 \times 10^{-10}$ ).

Therefore, AgCl begins to precipitate before AgI finishes precipitating. If  $[\text{Cl}^-]$  were  $\sim 2$  times lower, AgCl would not precipitate prematurely.

**26-43.** Moles of  $\text{Ca}^{2+}$  = moles of  $\text{C}_2\text{O}_4^{2-}$

$$(V_e)(0.0257 \text{ M}) = (25.00 \text{ mL})(0.0311 \text{ M}) \Rightarrow V_e = 30.25 \text{ mL}$$

(a) The fraction of  $\text{C}_2\text{O}_4^{2-}$  remaining when 10.00 mL of  $\text{Ca}^{2+}$  have been added is

$$(30.25 - 10.00)/(30.25) = 0.6694$$

$$[\text{C}_2\text{O}_4^{2-}] = (0.6694)(0.03110 \text{ M}) \left( \frac{25.00}{35.00} \right) = 0.01487 \text{ M}$$

$$[\text{Ca}^{2+}] = K_{\text{sp}}/[\text{C}_2\text{O}_4^{2-}] = (1.3 \times 10^{-8})/(0.01487) = 8.7 \times 10^{-7}$$

$$\Rightarrow \text{pCa}^{2+} = -\log(8.7 \times 10^{-7}) = 6.06$$

(b) At the equivalence point, there are equal numbers of moles of  $\text{Ca}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  dissolved. Call each concentration  $x$ :

$$[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (x)(x) = K_{\text{sp}} \Rightarrow x = \sqrt{K_{\text{sp}}} = 1.14 \times 10^{-4} \text{ M}$$

$$\text{pCa}^{2+} = -\log(1.14 \times 10^{-4}) = 3.94$$

(c)  $[\text{Ca}^{2+}] = (0.02570 \text{ M}) \left( \frac{35.00 - 30.25}{60.00} \right) = 0.002035 \text{ M} \quad \text{pCa}^{2+} = 2.69$

**26-44.** Equilibrium constants for ion pair formation:

$$\frac{[\text{AgX}(aq)]}{[\text{Ag}^+][\text{X}^-]} = \begin{cases} 10^{3.31} & (\text{X} = \text{Cl}) \\ 10^{4.6} & (\text{X} = \text{Br}) \\ 10^{6.6} & (\text{X} = \text{I}) \end{cases}$$

Calling the ion pair formation constant  $K_f$ , we can write

$$[\text{AgX}(aq)] = K_f[\text{Ag}^+][\text{X}^-]. \text{ But the product } [\text{Ag}^+][\text{X}^-] \text{ is just } K_{\text{sp}}. \text{ So,}$$

$$[\text{AgX}(aq)] = K_f K_{\text{sp}}. \text{ Putting in the values } K_{\text{sp}} = 10^{-9.74} \text{ for AgCl, } 10^{-12.30} \text{ for AgBr, and } 10^{-16.08} \text{ for AgI gives}$$

$$[\text{AgCl}(aq)] = 10^{3.31} 10^{-9.74} = 10^{-6.43} \text{ M} = 370 \text{ nM}$$

$$[\text{AgBr}(aq)] = 10^{4.6} 10^{-12.30} = 10^{-7.70} \text{ M} = 20 \text{ nM}$$

$$[\text{AgI}(aq)] = 10^{6.6} 10^{-16.08} = 10^{-9.48} \text{ M} = 0.33 \text{ nM}$$

**26-45.** FM of NaCl = 58.443. FM of KBr = 119.002. 48.40 mL of 0.04837 M

$\text{Ag}^+ = 2.3411 \text{ mmol}$ . This must equal the mmol of  $(\text{Cl}^- + \text{Br}^-)$ . Let  $x$  = mass of NaCl and  $y$  = mass of KBr.  $x + y = 0.2386 \text{ g}$ .

$$\underbrace{\frac{x}{58.443}}_{\text{mol Cl}^-} + \underbrace{\frac{y}{119.002}}_{\text{mol Br}^-} = 2.3411 \times 10^{-3} \text{ mol}$$

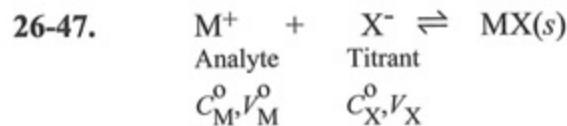
Substituting  $x = 0.2386 - y$  gives  $y = 0.2000 \text{ g of KBr} = 1.681 \text{ mmol of KBr} = 1.681 \text{ mmol of Br} = 0.1343 \text{ g of Br} = 56.28\% \text{ of the sample.}$

**26-46.** mmol of  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} = \frac{82.67 \text{ mg}}{171.46 \text{ mg/mmol}} = 0.4822 \text{ mmol}$

There will be 0.4822 mmol of  $\text{Cl}^-$  and 0.4822 mmol of  $\text{Br}^-$  liberated by reaction with  $\text{CH}_3\text{O}^-\text{Na}^+$ .

$$\text{Ag}^+ \text{ required for Br}^- = \frac{0.4822 \text{ mmol}}{0.02570 \text{ mmol/mL}} = 18.76 \text{ mL}$$

The same amount of  $\text{Ag}^+$  is required to react with  $\text{Cl}^-$ , so the second equivalence point is at  $18.76 + 18.76 = 37.52 \text{ mL}$ .



$$\text{Mass balance for M: } C_M^0 V_M^0 = [\text{M}^+](V_M^0 + V_X) + \text{mol MX}(s)$$

$$\text{Mass balance for X: } C_X^0 V_X^0 = [\text{X}^-](V_M^0 + V_X) + \text{mol MX}(s)$$

Equating mol  $\text{MX}(s)$  from both mass balances gives

$$C_M^0 V_M^0 - [\text{M}^+](V_M^0 + V_X) = C_X^0 V_X^0 - [\text{X}^-](V_M^0 + V_X)$$

$$\text{which can be rearranged to } V_X = V_M^0 \left( \frac{C_M^0 - [\text{M}^+] + [\text{X}^-]}{C_X^0 + [\text{M}^+] - [\text{X}^-]} \right)$$

**26-48.** Your graph should look like the figure in the text.

**26-49.** Mass balance for M:  $C_M^0 V_M^0 = [\text{M}^{m+}](V_M^0 + V_X^0) + x\{\text{mol M}_x\text{X}_m(s)\}$

$$\text{Mass balance for X: } C_X^0 V_X^0 = [\text{X}^{x-}](V_M^0 + V_X^0) + m\{\text{mol M}_x\text{X}_m(s)\}$$

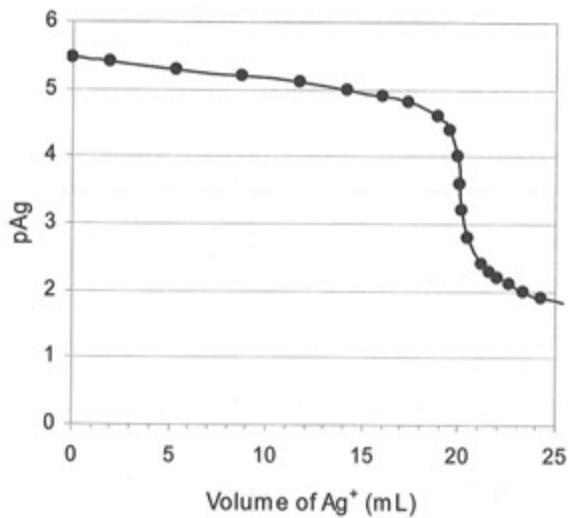
Equating mol  $\text{M}_x\text{X}_m$  from the two equations gives

$$\frac{1}{x} \{C_M^0 V_M^0 - [\text{M}^{m+}](V_M^0 + V_X^0)\} = \frac{1}{m} \{C_X^0 V_X^0 - [\text{X}^{x-}](V_M^0 + V_X^0)\}$$

which can be rearranged to the required form.

**26-50.** Titration of chromate with  $\text{Ag}^+$ :

	A	B	C	D	E	F	G	H	I
1	$K_{\text{sp}} =$	pM	[M]	[X]	$V_M$				
2	1.2E-12	5.46	3.47E-06	9.98E-02	0.013	C2 = 10^-B2			
3	$C_M =$	5.4	3.98E-06	7.57E-02	1.932	D2 = \$A\$2/C2^2			
4	0.1	5.3	5.01E-06	4.78E-02	5.342	E2 = \$A\$8*(2*\$A\$6+C2-2*D2)			
5	$C_X =$	5.2	6.31E-06	3.01E-02	8.717				/(\$A\$4-C2+2*D2)
6	0.1	5.1	7.94E-06	1.90E-02	11.734				
7	$V_X =$	5	1.00E-05	1.20E-02	14.195				
8	10	4.9	1.26E-05	7.57E-03	16.057				
9		4.8	1.58E-05	4.78E-03	17.388				
10		4.6	2.51E-05	1.90E-03	18.908				
11		4.4	3.98E-05	7.57E-04	19.564				
12		4	1.00E-04	1.20E-04	19.958				
13		3.6	2.51E-04	1.90E-05	20.064				
14		3.2	6.31E-04	3.01E-06	20.189				
15		2.8	1.58E-03	4.78E-07	20.483				
16		2.4	3.98E-03	7.57E-08	21.244				
17		2.3	5.01E-03	4.78E-08	21.583				
18		2.2	6.31E-03	3.01E-08	22.020				
19		2.1	7.94E-03	1.90E-08	22.589				
20		2	1.00E-02	1.20E-08	23.333				
21		1.9	1.26E-02	7.57E-09	24.321				
22		1.8	1.58E-02	4.78E-09	25.650				



- 26-51.** Consider the titration of  $\text{C}^+$  (in a flask) by  $\text{A}^-$  (from a buret). Before the equivalence point, there is excess  $\text{C}^+$  in solution. Selective adsorption of  $\text{C}^+$  on the CA crystal surface gives the crystal a positive charge. After the equivalence point, there is excess  $\text{A}^-$  in solution. Selective adsorption of  $\text{A}^-$  on the CA crystal surface gives it a negative charge.

- 26-52. Beyond the equivalence point, there is excess  $\text{Fe}(\text{CN})_6^{4-}$  in solution. Selective adsorption of this ion by the precipitate will give the particles a negative charge.
- 26-53. A known excess of  $\text{Ag}^+$  is added to form  $\text{AgI}(s)$ . In the presence of  $\text{Fe}^{3+}$ , the excess  $\text{Ag}^+$  is titrated with standard  $\text{SCN}^-$  to precipitate  $\text{AgSCN}(s)$ . When  $\text{Ag}^+$  is consumed,  $\text{SCN}^-$  reacts with  $\text{Fe}^{3+}$  to form the red complex,  $\text{FeSCN}^{2+}$ .
- 26-54.  $50.00 \text{ mL of } 0.3650 \text{ M AgNO}_3 = 18.25 \text{ mmol of Ag}^+$   
 $37.60 \text{ mL of } 0.2870 \text{ M KSCN} = 10.79 \text{ mmol of SCN}^-$   
Difference =  $18.25 - 10.79 = 7.46 \text{ mmol of I}^- = 947 \text{ mg of I}^-$

**CHAPTER 27**  
**SAMPLE PREPARATION**

- 27-1.** There is no point analyzing a sample if you do not know that it was selected in a sensible way and stored so that its composition did not change after it was taken.
- 27-2.** “Analytical quality” refers to the accuracy and precision of the method applied to the sample that was analyzed. High quality means that the analysis is accurate and precise. “Data quality” means that the sample that was analyzed is representative and appropriate for the question being asked and that the analytical quality is adequate for the intended purpose. If an accurate and precise analysis is performed on an unrepresentative or contaminated or decomposed sample, the results are meaningless.
- 27-3.** (a)  $s_o^2 = s_a^2 + s_s^2 = 3^2 + 4^2 \Rightarrow s_o = 5\%$ .  
(b)  $s_s^2 = s_o^2 - s_a^2 = 4^2 - 3^2 \Rightarrow s_s = 2.6\%$ .
- 27-4.**  $mR^2 = K_s$ .  $m(6^2) = 36 \text{ g} \Rightarrow m = 1.0 \text{ g}$
- 27-5.** Pass the powder through a 120 mesh sieve and then through a 170 mesh sieve. Sample retained by 170 mesh sieve has a size between 90 and 125  $\mu\text{m}$ . It would be called 120/170 mesh.
- 27-6.**  $11.0 \times 10^2 \text{ g}$  will contain  $10^6$  total particles, since  $11.0 \text{ g}$  contains  $10^4$  particles.  
 $n_{\text{KCl}} = np = (10^6)(0.01) = 10^4$ .  
Relative standard deviation =  $\sqrt{npq}/n_{\text{KCl}} = \sqrt{(10^6)(0.01)(0.99)}/10^4 = 0.99\%$ .
- 27-7.** (a)  $\sqrt{(10^3)(0.5)(0.5)} = 15.8$ .  
(b) We are looking for the value of  $z$ , whose area is 0.45 (since the area from  $-z$  to  $+z$  is 0.90). The value lies between  $z = 1.6$  and  $1.7$ , whose areas are 0.445 2 and 0.455 4, respectively. Linear interpolation:  
$$\frac{z - 1.6}{1.7 - 1.6} = \frac{0.45 - 0.4452}{0.4554 - 0.4452} \Rightarrow z = 1.647$$
.  
(c) Since  $z = (x - \bar{x})/s$ ,  $x = \bar{x} \pm zs = 500 \pm (1.647)(15.8) = 500 \pm 26$ .  
The range 474–526 will be observed 90% of the time.

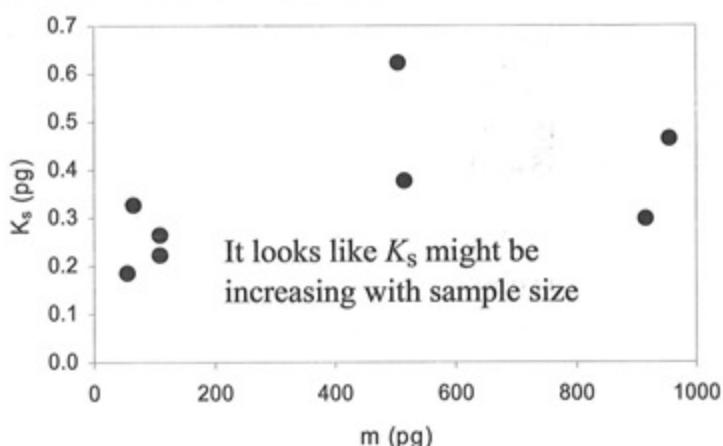
**27-8.** Use Equation 27-7, with  $s_s = 0.05$  and  $e = 0.04$ . The initial value of  $t$  for 95% confidence in Table 4-2 is 1.960.  $n = t^2 s_s^2 / e^2 = 6.0$  For  $n = 6$ , there are 5 degrees of freedom, so  $t = 2.571$ , which gives  $n = 10.3$ . For 9 degrees of freedom,  $t = 2.262$ , which gives  $n = 8.0$ . Continuing, we find  $t = 2.365 \Rightarrow n = 8.74$ . This gives  $t = 2.306 \Rightarrow n = 8.30$ . Use 8 samples. For 90% confidence, the initial  $t$  is 1.645 in Table 4-2 and the same series of calculations gives  $n = 6$  samples.

- 27-9.** (a)  $mR^2 = K_s$ . For  $R = 2$  and  $K_s = 20$  g, we find  $m = 5.0$  g.  
 (b) Use Equation 27-7 with  $s_s = 0.02$  and  $e = 0.015$ . The initial value of  $t$  for 90% confidence in Table 4-2 is 1.645.  $n = t^2 s_s^2 / e^2 = 4.8$   
 For  $n = 5$ , there are 4 degrees of freedom, so  $t = 2.132$ , which gives  $n = 8.1$ .  
 For 7 degrees of freedom,  $t = 1.895$ , which gives  $n = 6.4$ .  
 Continuing, we find  $t = 2.015 \Rightarrow n = 7.2$ . This gives  $t = 1.943 \Rightarrow n = 6.7$ .  
 Use 7 samples.

**27-10.**

	A	B	C	D
1	Evaluation of the relation $mR^2 = K_s$			
2				
3	$m$ (pg)	$R\%$	$R^2$	$K_s = mR^2$
4	57	0.057	0.00325	0.185
5	68	0.069	0.00476	0.324
6	110	0.049	0.00240	0.264
7	110	0.045	0.00203	0.223
8	506	0.035	0.00123	0.620
9	515	0.027	0.00073	0.375
10	916	0.018	0.00032	0.297
11	955	0.022	0.00048	0.462
12			average	0.344
13			std dev	0.141

Average value of  $K_s = 0.34 \pm 0.14$  pg



The confidence interval is  $\pm ts/\sqrt{n}$ , where  $t$  is Student's  $t$ ,  $s$  is the standard deviation, and  $n$  is the number of replicate measurements. If  $n$  is the same for all points, then  $t$  is the same for all points and the confidence interval is proportional to  $s$ . The equation in the text is expressed in terms of  $s$ . If the confidence interval is proportional to  $s$ , then the same equation should hold for the confidence interval.

- 27-11.** (a) Volume =  $(4/3)\pi r^3$ , where  $r = 0.075 \text{ mm} = 7.5 \times 10^{-3} \text{ cm}$ .  
 Volume =  $1.767 \times 10^{-6} \text{ mL}$ .  
 $\text{Na}_2\text{CO}_3$  mass =  $(1.767 \times 10^{-6} \text{ mL})(2.532 \text{ g/mL}) = 4.474 \times 10^{-6} \text{ g}$ .  
 $\text{K}_2\text{CO}_3$  mass =  $(1.767 \times 10^{-6} \text{ mL})(2.428 \text{ g/mL}) = 4.291 \times 10^{-6} \text{ g}$ .  
 Number of particles of  $\text{Na}_2\text{CO}_3$  =  $(4.00 \text{ g})/(4.474 \times 10^{-6} \text{ g/particle})$   
 $= 8.941 \times 10^5$ .  
 Number of particles of  $\text{K}_2\text{CO}_3$  =  $(96.00 \text{ g})/(4.291 \times 10^{-6} \text{ g/particle})$   
 $= 2.237 \times 10^7$ .

The fraction of each type (which we will need for part c) is  
 $p_{\text{Na}_2\text{CO}_3} = (8.941 \times 10^5)/(8.941 \times 10^5 + 2.237 \times 10^7) = 0.0384$   
 $q_{\text{K}_2\text{CO}_3} = (2.237 \times 10^7)/(8.941 \times 10^5 + 2.237 \times 10^7) = 0.962$ .

- (b) Total number of particles in 0.100 g is  $n = 2.326 \times 10^4$ .  
 (c) Expected number of  $\text{Na}_2\text{CO}_3$  particles in 0.100 g is 1/1000 of number in 100 grams =  $8.94 \times 10^2$ .

Expected number of  $\text{K}_2\text{CO}_3$  particles in 0.100 g is 1/1 000 of number in 100 grams =  $2.24 \times 10^4$ .

Sampling standard deviation =  $\sqrt{npq} = \sqrt{(2.326 \times 10^4)(0.0384)(0.962)}$   
 $= 29.3$ .

Relative sampling standard deviation for  $\text{Na}_2\text{CO}_3 = \frac{29.3}{8.94 \times 10^2} = 3.28\%$ .

Relative sampling standard deviation for  $\text{K}_2\text{CO}_3 = \frac{29.3}{2.24 \times 10^4} = 0.131\%$ .

- 27-12.** Metals with reduction potentials below zero [for the reaction  $\text{M}^{n+} + ne^- \rightarrow \text{M}(s)$ ] are expected to dissolve in acid. These are Zn, Fe, Co, and Al.  
**27-13.**  $\text{HNO}_3$  was used first to oxidize any material that could be easily oxidized. This helps prevent the possibility that an explosion will occur when  $\text{HClO}_4$  is added.

27-14. Barbital has a higher affinity for the octadecyl phase than for water, so it is retained by the column. The drug dissolves readily in acetone/chloroform, which elutes it from the column.

27-15. Cocaine is an amine base. It will be a cation at low pH and neutral in ammonia. The cation at pH 2 is retained by the cation-exchange resin. The neutral molecule is easily eluted by methanol. Benzoylecgonine has an amine and carboxylate functionality. At pH 2, the amine will be protonated and the carboxylic acid should be neutral, so the molecule will be retained by the cation exchange column. At elevated pH, the amine will be neutral and the carboxylate will be negative. The anion is not retained by the cation-exchanger and is eluted with methanol.

27-16. The product gas stream is passed through an anion-exchange column, on which  $\text{SO}_2$  is absorbed by the following reactions:



The sulfite is eluted with  $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}_2$ , which oxidizes it to sulfate that can be measured by ion chromatography.

27-17. Large particle size allows sample to drain through the solid-phase extraction column without applying high pressure. In chromatography, small particle size increases the efficiency of separation, but high pressure is necessary to force solvent through the column.

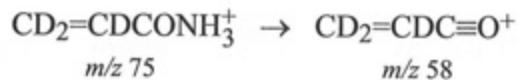
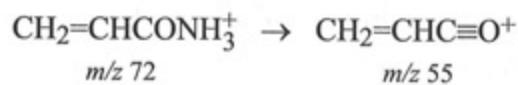
27-18. (a) Solid-phase extraction retains acrylamide while passing many other components in the aqueous extract of the french fries. We want to remove as many other components as possible to simplify the chromatographic analysis. The strong acid of the ion-exchange resin protonates acrylamide and retains it by ionic attraction:



(b) There are many ultraviolet-absorbing components in addition to acrylamide in the acrylamide fraction obtained from the ion-exchange column. Ultraviolet absorbance is not specific for acrylamide.

(c) For acrylamide,  $m/z$  72 is selected by the mass filter Q1 of the mass spectrometer. This ion dissociates by collisions in Q2. The product  $m/z$  55

is selected in Q3 for passage to the detector.



- (d) Even though many compounds are applied to the chromatography column, acrylamide is the only one with *m/z* 72 that gives a significant reaction product at *m/z* 55.
- (e) Acrylamide gives one peak by selected reaction monitoring of the transition *m/z* 72→55. The internal standard gives just one peak for <sup>2</sup>H<sub>3</sub>-acrylamide monitored by the transition *m/z* 75→58 with the same retention time as acrylamide. The transition *m/z* 72→55 does not respond to the internal standard, and the transition *m/z* 75→58 does not respond to unlabeled acrylamide. We know the concentration of internal standard added to the aqueous extract of the french fries, and we measure the integrated area of the *m/z* 75→58 peak for the internal standard. We also measure the integrated area of the *m/z* 72→55 peak for acrylamide. The concentration of acrylamide in the aqueous extract is found by the proportion

$$\frac{[\text{acrylamide}]}{[\text{internal standard}]} = \frac{[\text{area of } m/z 72 \rightarrow 55 \text{ peak}]}{[\text{area of } m/z 75 \rightarrow 58 \text{ peak}]}$$

- (f) With ultraviolet absorption, the internal standard appears at the same elution time as acrylamide. The molar absorptivity of deuterated internal standard is probably very similar to that of acrylamide, so equal concentrations of internal standard and acrylamide contribute approximately the same integrated area in the chromatogram. With selected reaction monitoring by mass spectrometry, the detector sees either acrylamide or the internal standard, with no interference from the other, even though they are eluted at the same time.
- (g) The internal standard is mixed with the aqueous extract from the french fries prior to solid-phase extraction. We expect little isotope effect on the binding of acrylamide to the solid-phase sorbent or the HPLC stationary phase. Therefore, the fraction of acrylamide and the fraction of internal standard that bind to and are recovered from the solid-phase extraction column are equal. Even though neither one is bound or eluted quantitatively, equal

fractions of each are bound and eluted. The ratio of acrylamide and internal standard should remain constant throughout the entire procedure.

- 27-19. (a) Highest concentration of Ni  $\approx$  80 ng/mL. A 10 mL sample contains 800 ng Ni =  $1.36 \times 10^{-8}$  mol Ni. To this is added 50  $\mu$ g Ga =  $7.17 \times 10^{-7}$  mol Ga. Atomic ratio Ga/Ni =  $(7.17 \times 10^{-7})/(1.36 \times 10^{-8}) = 53$ .
- (b) Apparently all the Ni is in solution because filtration does not decrease its total concentration. Since filtration removes most of the Fe, it must be present as a suspension of solid particles.
- 27-20. One-fourth of the sample (25 mL out of 100 mL) required  $(0.011\ 44\ M)(0.032\ 49\ L) = 3.717 \times 10^{-4}$  mol EDTA  $\Rightarrow (3.717 \times 10^{-4})(4) = 1.487 \times 10^{-3}$  mol Ba<sup>2+</sup> in sample = 0.2042 g Ba = 64.90 wt%.
- 27-21. (a) From the acid dissociation constants of Cr(III), we see that the dominant forms at pH 8 are Cr(OH)<sub>2</sub><sup>+</sup> and Cr(OH)<sub>3</sub>(aq). The dominant form of Cr(VI) is CrO<sub>4</sub><sup>2-</sup>.
- (b) The anion exchanger retains the anion, CrO<sub>4</sub><sup>2-</sup>, but permits the Cr(OH)<sub>2</sub><sup>+</sup> cation and neutral Cr(OH)<sub>3</sub>(aq) to pass through, thereby separating Cr(VI) from Cr(III).
- (c) A “weakly basic” anion exchanger contains a protonated amine ( $-^+NHR_2$ ) that might lose its positive charge in basic solution. A “strongly basic” anion exchanger ( $-^+NR_3$ ) is a stable cation in basic solution.
- (d) CrO<sub>4</sub><sup>2-</sup> is eluted from the anion exchanger when the concentration of sulfate in the buffer is increased from 0.05 M in step 3 to 0.5 M in step 4.
- 27-22. One possible cost-saving scheme is to monitor wells 8, 11, 12, and 13 individually, but to pool samples from the other sites. For example, a composite sample could be made with equal volumes from wells 1, 2, 3, and 4. Other composites could be constructed from (5, 6, 7), (9, 10), (14, 15, 16, 17), and (18, 19, 20, 21). If no warning level of analyte is found in a composite sample, we would assume that each well in that composite is free of the analyte. If analyte is found in a composite sample, then each contributor to the composite would be separately analyzed. The disadvantage of pooling samples from  $n$  wells is that the sensitivity of the analysis for analyte in any one well is reduced by  $1/n$ .



































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