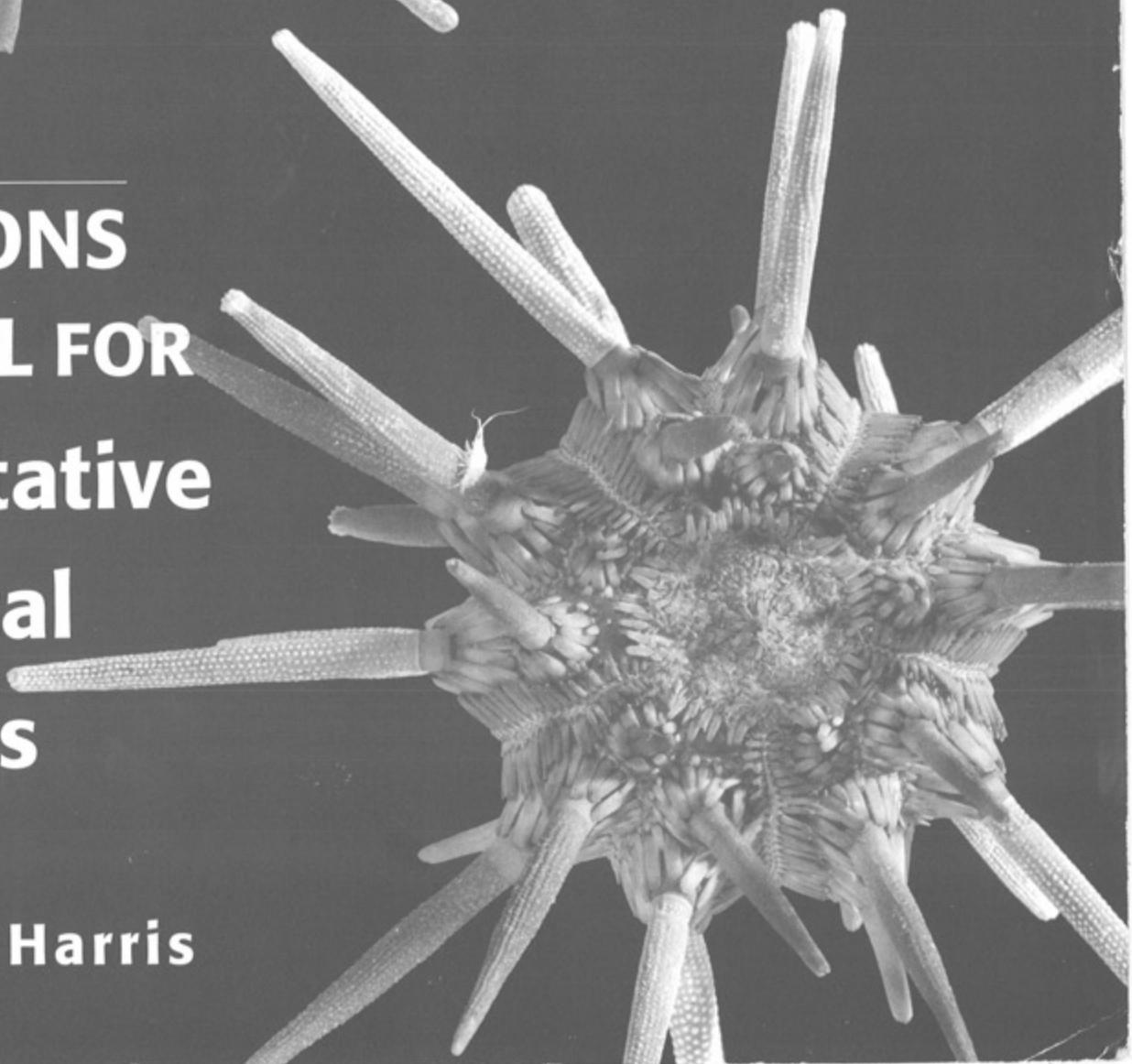


Eighth Edition

**SOLUTIONS
MANUAL FOR
Quantitative
Chemical
Analysis**

Daniel C. Harris



Solutions Manual
for Harris'
Quantitative Chemical Analysis
Eighth Edition

Daniel C. Harris
Michelson Laboratory



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CHAPTER 0

THE ANALYTICAL PROCESS

- 0-1.** Qualitative analysis finds out what is in a sample. Quantitative analysis measures how much is in a sample.
- 0-2.** Steps in a chemical analysis:
- (1) Formulate the question: Convert a general question into a specific one that can be answered by a chemical measurement.
 - (2) Select the appropriate analytical procedure.
 - (3) Obtain a representative sample.
 - (4) Sample preparation: Convert the representative sample into a sample suitable for analysis. If necessary, concentrate the analyte and remove or mask interfering species.
 - (5) Analysis: Measure the unknown concentration in replicate analyses.
 - (6) Produce a clear report of results, including estimates of uncertainty.
 - (7) Draw conclusions: Based on the analytical results, decide what actions to take.
- 0-3.** Masking converts an interfering species to a noninterfering species.
- 0-4.** A calibration curve shows the response of an analytical method as a function of the known concentration of analyte in standard solutions. Once the calibration curve is known, then the concentration of an unknown can be deduced from a measured response.
- 0-5.**
- (a) A homogeneous material has the same composition everywhere. In a heterogeneous material, the composition is not the same everywhere.
 - (b) In a segregated heterogeneous material, the composition varies on a large scale. There could be large patches with one composition and large patches with another composition. The differences are segregated into different regions. In a random heterogeneous material, the differences occur on a fine scale. If we collect a “reasonable-size” portion, we will capture each of the different compositions that are present.
 - (c) To sample a *segregated heterogeneous material*, we take representative amounts from each of the obviously different regions. In panel b in Box 0-1, 66% of the area has composition A, 14% is B, and 20% is C. To construct a

representative bulk sample, we could take 66 randomly selected samples from region A, 14 from region B, and 20 from region C. To sample a *random heterogeneous material*, we divide the material into imaginary segments and collect random segments with the help of a table of random numbers.

- 0-6.** We are apparently observing *interference* by Mn^{2+} in the I^- analysis by method A. The result of the I^- analysis is affected by the presence of Mn^{2+} . The greater the concentration of Mn^{2+} in the mineral water, the greater is the apparent concentration of I^- found by method A. Method B is not subject to the same interference, so the concentration of I^- is low and independent of addition of Mn^{2+} . There must be some Mn^{2+} in the original mineral water, which causes method A to give a higher result than method B even when no Mn^{2+} is deliberately added.

CHAPTER 1

MEASUREMENTS

A note from Dan: Don't worry if your numerical answers are slightly different from those in the *Solutions Manual*. You or I may have rounded intermediate results. In general, retain many extra digits for intermediate answers and save your roundoff until the end. We'll study this process in Chapter 3.

- 1-1.** (a) meter (m), kilogram (kg), second (s), ampere (A), kelvin (K), mole (mol)
(b) hertz (Hz), newton (N), pascal (Pa), joule (J), watt (W)
- 1-2.** Abbreviations above kilo are capitalized: M (mega, 10^6), G (giga, 10^9), T (tera, 10^{12}), P (peta, 10^{15}), E (exa, 10^{18}), Z (zetta, 10^{21}) and Y (yotta, 10^{24}).
- 1-3.**
- | | | | | |
|---------|---|------------|---|------------------|
| (a) mW | = | milliwatt | = | 10^{-3} watt |
| (b) pm | = | picometer | = | 10^{-12} meter |
| (c) kΩ | = | kiloohm | = | 10^3 ohm |
| (d) μF | = | microfarad | = | 10^{-6} farad |
| (e) TJ | = | terajoule | = | 10^{12} joule |
| (f) ns | = | nanosecond | = | 10^{-9} second |
| (g) fg | = | femtogram | = | 10^{-15} gram |
| (h) dPa | = | decipascal | = | 10^{-1} pascal |
- 1-4.** (a) 100 fJ or 0.1 pJ (d) 0.1 nm or 100 pm
(b) 43.172 8 nF (e) 21 TW
(c) 299.79 THz or 0.299 79 PHz (f) 0.483 amol or 483 zmol
- 1-5.** (a) $5.4 \text{ Pg} = 5.4 \times 10^{15} \text{ g}$. $5.4 \times 10^{15} \cancel{\text{g}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} = 5.4 \times 10^{12} \text{ kg of C}$
- (b) The formula mass of CO₂ is $12.010\overline{7} + 2(15.999\overline{4}) = 44.009\overline{5}$
$$5.4 \times 10^{12} \cancel{\text{kg-C}} \times \frac{44.009\overline{5} \text{ kg CO}_2}{12.010\overline{7} \cancel{\text{kg-C}}} = 2.0 \times 10^{13} \text{ kg CO}_2$$
- (c) $2.0 \times 10^{13} \cancel{\text{kg CO}_2} \times \frac{1 \text{ ton}}{1000 \cancel{\text{kg}}} = 2.0 \times 10^{10} \text{ tons of CO}_2$
- $$\frac{2.0 \times 10^{10} \text{ tons}}{5 \times 10^9 \text{ people}} = 4 \text{ tons per person}$$

1-6. Table 1-4 tells us that 1 horsepower = 745.700 W = 745.700 J/s.

$$100.0 \text{ horsepower} = (100.0 \cancel{\text{horsepower}}) \left(\frac{745.700 \text{ J/s}}{\cancel{\text{horsepower}}} \right) = 7.457 \times 10^4 \text{ J/s.}$$

$$\frac{7.457 \times 10^4 \cancel{\text{J}}}{4.184 \frac{\cancel{\text{J}}}{\text{cal}}} \times 3600 \frac{\cancel{\text{s}}}{\text{h}} = 6.416 \times 10^7 \frac{\text{cal}}{\text{h}}.$$

$$\begin{aligned} \text{1-7. (a)} \quad & \frac{\left(2.2 \times 10^6 \frac{\text{cal}}{\text{day}} \right) \left(4.184 \frac{\text{J}}{\text{cal}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right)}{(120 \cancel{\text{pound}}) \left(0.4536 \frac{\text{kg}}{\cancel{\text{pound}}} \right)} = 2.0 \text{ J/(s·kg)} \\ & = 2.0 \text{ W/kg} \end{aligned}$$

Similarly, $3.4 \times 10^3 \frac{\text{kcal}}{\text{day}} \Rightarrow 3.0 \text{ J/(s·kg)} = 3.0 \text{ W/kg.}$

(b) The office worker's power output is

$$\left(2.2 \times 10^6 \frac{\text{cal}}{\text{day}} \right) \left(4.184 \frac{\text{J}}{\text{cal}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) = 1.1 \times 10^2 \frac{\text{J}}{\text{s}} = 1.1 \times 10^2 \text{ W}$$

The person's power output is greater than that of the 100 W light bulb.

$$\text{1-8. } \left(5.00 \times 10^3 \frac{\text{Btu}}{\text{h}} \right) \left(1055.06 \frac{\text{J}}{\text{Btu}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) = 1.47 \times 10^3 \frac{\text{J}}{\text{s}} = 1.47 \times 10^3 \text{ W}$$

$$\text{1-9. (a)} \left(1000 \frac{\text{m}}{\text{km}} \right) \left(\frac{1 \text{ inch}}{0.0254 \text{ m}} \right) \left(\frac{1 \text{ foot}}{12 \text{ inch}} \right) \left(\frac{1 \text{ mile}}{5280 \text{ foot}} \right) = 0.62137 \frac{\text{mile}}{\text{km}}$$

$$\text{(b)} \left(\frac{100 \text{ km}}{4.6 \text{ L}} \right) \left(\frac{0.62137 \text{ miles}}{\text{km}} \right) \left(\frac{3.7854 \text{ L}}{\text{gallon}} \right) = 51 \frac{\text{miles}}{\text{gallon}}$$

(c) The diesel engine produces 223 g CO₂/km, which we will convert into g/mile:

$$\left(223 \frac{\text{g CO}_2}{\text{km}} \right) \left(\frac{1 \text{ km}}{0.62137 \text{ mile}} \right) = 359 \frac{\text{g CO}_2}{\text{mile}}$$

In 15 000 miles, CO₂ = (15 000 miles)(359 g/mile) = 5.38×10^6 g or 5.38×10^3 kg = 5.38 metric tons. The gasoline engine produces 266 g CO₂/km,

which we convert into 428 g/mile or 6.42 metric tons in 15 000 miles.

$$\text{1-10. Newton} = \text{force} = \text{mass} \times \text{acceleration} = \text{kg} \left(\frac{\text{m}}{\text{s}^2} \right)$$

$$\text{Joule} = \text{energy} = \text{force} \times \text{distance} = \text{kg} \left(\frac{\text{m}}{\text{s}^2} \right) \cdot \text{m} = \text{kg} \left(\frac{\text{m}^2}{\text{s}^2} \right)$$

$$\text{Pascal} = \text{pressure} = \text{force / area} = \text{kg} \left(\frac{\text{m}}{\text{s}^2} \right) / \text{m}^2 = \frac{\text{kg}}{\text{m} \cdot \text{s}^2}$$

$$\text{1-11. } \left(0.03 \frac{\cancel{\text{pag}}}{\text{m}^2 \cdot \cancel{\text{day}}} \right) \left(1000 \frac{\cancel{\text{m}}}{\cancel{\text{km}}} \right)^2 (535 \cancel{\text{km}}^2) \left(\frac{1 \cancel{\text{g}}}{1000 \cancel{\text{pag}}} \right) \times \\ \left(\frac{1 \cancel{\text{kg}}}{1000 \cancel{\text{g}}} \right) \left(\frac{1 \text{ton}}{1000 \cancel{\text{kg}}} \right) \left(365 \frac{\cancel{\text{day}}}{\text{year}} \right) = 6 \frac{\text{ton}}{\text{year}}$$

- 1-12.** (a) molarity = moles of solute / liter of solution
 - (b) molality = moles of solute / kilogram of solvent
 - (c) density = grams of substance / milliliter of substance
 - (d) weight percent = $100 \times (\text{mass of substance}/\text{mass of solution or mixture})$
 - (e) volume percent = $100 \times (\text{volume of substance}/\text{volume of solution or mixture})$
 - (f) parts per million = $10^6 \times (\text{grams of substance}/\text{grams of sample})$
 - (g) parts per billion = $10^9 \times (\text{grams of substance}/\text{grams of sample})$
 - (h) formal concentration = moles of formula/liter of solution
- 1-13.** Acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) is a weak electrolyte that is partially dissociated. When we dissolve 0.01 mol in a liter, the concentrations of $\text{CH}_3\text{CO}_2\text{H}$ plus CH_3CO_2^- add to 0.01 M. The concentration of $\text{CH}_3\text{CO}_2\text{H}$ alone is less than 0.01 M.
- 1-14.** $32.0 \text{ g} / [(22.990 + 35.453) \text{ g/mol}] = 0.548 \text{ mol NaCl}$
 $0.548 \text{ mol} / 0.500 \text{ L} = 1.10 \text{ M}$

$$\text{1-15. } \left(1.71 \frac{\text{mol CH}_3\text{OH}}{\text{L solution}} \right) (0.100 \underline{\text{L solution}}) = 0.171 \text{ mol CH}_3\text{OH}$$

$$(0.171 \frac{\text{mol CH}_3\text{OH}}{\text{mol CH}_3\text{OH}}) \left(\frac{32.04 \text{ g}}{\frac{\text{mol CH}_3\text{OH}}{\text{mol CH}_3\text{OH}}} \right) = 5.48 \text{ g}$$

1-16. (a) $19 \text{ mPa} = 19 \times 10^{-3} \text{ Pa}$. $19 \times 10^{-3} \frac{\cancel{\text{Pa}}}{\cancel{\text{Pa}}} \times \frac{1 \text{ bar}}{10^5 \cancel{\text{Pa}}} = 1.9 \times 10^{-7} \text{ bar}$

(b) $T (\text{K}) = 273.15 + {}^\circ\text{C} = 273.15 - 70 = 203 \text{ K}$

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.9 \times 10^{-7} \frac{\cancel{\text{bar}}}{\cancel{\text{L}}} \times 203 \cancel{\text{K}}}{0.08314 \frac{\text{L} \cdot \cancel{\text{bar}}}{\text{mol} \cdot \cancel{\text{K}}}} = 1.1 \times 10^{-8} \text{ M} = 11 \text{ nM}$$

1-17. $1 \text{ ppm} = \frac{1 \text{ g solute}}{10^6 \text{ g solution}}$. Since 1 L of dilute solution $\approx 10^3 \text{ g}$,

$$1 \text{ ppm} = 10^{-3} \text{ g solute/L} (= 10^{-3} \text{ g solute} / 10^3 \text{ g solution}).$$

$$\text{Since } 10^{-3} \text{ g} = 10^3 \mu\text{g}, 1 \text{ ppm} = 10^3 \mu\text{g/L or } 1 \mu\text{g/mL.}$$

$$\text{Since } 10^{-3} \text{ g} = 1 \text{ mg, } 1 \text{ ppm} = 1 \text{ mg/L.}$$

1-18. 0.2 ppb means $0.2 \times 10^{-9} \text{ g}$ of $\text{C}_{20}\text{H}_{42}$ per g of rainwater

$$= 0.2 \times 10^{-6} \frac{\text{g C}_{20}\text{H}_{42}}{1000 \text{ g rainwater}} \approx \frac{0.2 \times 10^{-6} \text{ g C}_{20}\text{H}_{42}}{\text{L rainwater}}.$$

$$\frac{0.2 \times 10^{-6} \cancel{\text{g}} / \text{L}}{282.55 \cancel{\text{g}} / \text{mol}} = 7 \times 10^{-10} \text{ M}$$

1-19. $\left(0.705 \frac{\text{g HClO}_4}{\text{g solution}} \right) (37.6 \cancel{\text{g solution}}) = 26.5 \text{ g HClO}_4$

$$37.6 \text{ g solution} - 26.5 \text{ g HClO}_4 = 11.1 \text{ g H}_2\text{O}$$

1-20. (a) $\left(1.67 \frac{\text{g solution}}{\text{mL}} \right) \left(1000 \frac{\cancel{\text{mL}}}{\text{L}} \right) = 1.67 \times 10^3 \text{ g solution}$

(b) $\left(0.705 \frac{\text{g HClO}_4}{\text{g solution}} \right) (1.67 \times 10^3 \cancel{\text{g solution}}) = 1.18 \times 10^3 \text{ g HClO}_4$

(c) $(1.18 \times 10^3 \cancel{\text{g}}) / (100.46 \cancel{\text{g}} / \text{mol}) = 11.7 \text{ mol}$

1-21. molality = $\frac{\text{mol KI}}{\text{kg solvent}}$

$$20.0 \text{ wt\% KI} = \frac{200 \text{ g KI}}{1000 \text{ g solution}} = \frac{200 \text{ g KI}}{800 \text{ g H}_2\text{O}}$$

To find the grams of KI in 1 kg of H_2O , we set up a proportion:

$$\frac{200 \text{ g KI}}{800 \text{ g H}_2\text{O}} = \frac{x \text{ g KI}}{1000 \text{ g H}_2\text{O}} \Rightarrow x = 250 \text{ g KI}$$

But 250 g KI = 1.51 mol KI, so the molality is 1.51 m.

1-22. (a) $\frac{150 \times 10^{-15} \text{ mol/cell}}{2.5 \times 10^4 \text{ vesicles/cell}} = 6.0 \frac{\text{amol}}{\text{vescicle}}$

(b) $(6.0 \times 10^{-18} \frac{\text{mol}}{\text{cell}}) \left(6.022 \times 10^{23} \frac{\text{molecules}}{\text{mol}} \right) = 3.6 \times 10^6 \text{ molecules}$

(c) Volume = $\frac{4}{3} \pi (200 \times 10^{-9} \text{ m})^3 = 3.35 \times 10^{-20} \text{ m}^3$;

$$\frac{3.35 \times 10^{-20} \text{ m}^3}{10^{-3} \text{ m}^3 / \text{L}} = 3.35 \times 10^{-17} \text{ L}$$

(d) $\frac{10 \times 10^{-18} \text{ mol}}{3.35 \times 10^{-17} \text{ L}} = 0.30 \text{ M}$

1-23. $\frac{80 \times 10^{-3} \text{ g}}{180.2 \text{ g/mol}} = 4.4 \times 10^{-4} \text{ mol}; \quad \frac{4.4 \times 10^{-4} \text{ mol}}{100 \times 10^{-3} \text{ L}} = 4.4 \times 10^{-3} \text{ M};$

Similarly, 120 mg/100 L = $6.7 \times 10^{-3} \text{ M}$.

1-24. (a) Mass of 1.000 L = $1.046 \frac{\text{g}}{\text{mL}} \times 1000 \frac{\text{mL}}{\text{L}} \times 1.000 \text{ L} = 1046 \text{ g}$

$$\text{Grams of C}_2\text{H}_6\text{O}_2 \text{ per liter} = 6.067 \frac{\text{mol}}{\text{L}} \times 62.07 \frac{\text{g}}{\text{mol}} = 376.6 \frac{\text{g}}{\text{L}}$$

(b) 1.000 L contains 376.6 g of C₂H₆O₂ and $1046 - 376.6 = 669 \text{ g of H}_2\text{O}$

$$= 0.669 \text{ kg}$$

$$\text{Molality} = \frac{6.067 \text{ mol C}_2\text{H}_6\text{O}_2}{0.669 \text{ kg H}_2\text{O}} = 9.07 \frac{\text{mol C}_2\text{H}_6\text{O}_2}{\text{kg H}_2\text{O}} = 9.07 \text{ m}$$

1-25. Shredded wheat: 1.000 g contains 0.099 g protein + 0.799 g carbohydrate

$$0.099 \frac{\text{g}}{\text{g}} \times 4.0 \frac{\text{Cal}}{\text{g}} + 0.799 \frac{\text{g}}{\text{g}} \times 4.0 \frac{\text{Cal}}{\text{g}} = 3.6 \text{ Cal}$$

Doughnut: 1.000 g contains 0.046 g protein + 0.514 g carbohydrate + 0.186 g fat

$$0.046 \frac{\text{g}}{\text{g}} \times 4.0 \frac{\text{Cal}}{\text{g}} + 0.514 \frac{\text{g}}{\text{g}} \times 4.0 \frac{\text{Cal}}{\text{g}} + 0.186 \frac{\text{g}}{\text{g}} \times 9.0 \frac{\text{Cal}}{\text{g}} = 3.9 \text{ Cal}$$

In a similar manner, we find 2.8 $\frac{\text{Cal}}{\text{g}}$ for hamburger and 0.48 $\frac{\text{Cal}}{\text{g}}$ for apple.

There are 16 ounces in 1 pound, which Table 1-4 says is equal to 453.59237 g

$$\Rightarrow 28.35 \frac{\text{g}}{\text{ounce}}$$

To convert Cal/g to Cal/ounce, multiply by 28.35:

	Shredded Wheat	Doughnut	Hamburger	Apple
Cal/g	3.6	3.9	2.8	0.48
Cal/ounce	102	111	79	14

1-26. Mass of water = $\pi (225 \text{ m})^2 (10.0 \text{ m}) \left(\frac{1000 \text{ kg}}{\text{m}^3} \right) = 1.59 \times 10^9 \text{ kg}$

$$1.6 \text{ ppm} = \frac{1.6 \times 10^{-3} \text{ g F}^-}{\text{kg H}_2\text{O}}$$

Mass of F⁻ required =

$$\left(1.6 \times 10^{-3} \frac{\text{g F}^-}{\text{kg H}_2\text{O}} \right) (1.59 \times 10^9 \cancel{\text{kg H}_2\text{O}}) = 2.54 \times 10^6 \text{ g F}^-.$$

(If we retain three digits for the next calculation, this last number is 2.54×10^6 .)

The atomic mass of F is 18.998 and the formula mass of H₂SiF₆ is 144.09. One mole of H₂SiF₆ contains 6 moles of F.

$$\frac{\text{mass of F}^-}{\text{mass of H}_2\text{SiF}_6} = \frac{6 \times 18.998}{144.09} = \frac{2.54 \times 10^6 \text{ g F}^-}{x \text{ g H}_2\text{SiF}_6} \Rightarrow x = 3.2 \times 10^6 \text{ g H}_2\text{SiF}_6$$

1-27. (a) $PV = nRT$

$$(1.000 \text{ bar})(5.24 \times 10^{-6} \text{ L}) = n \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \right) (298.15 \text{ K})$$

$$\Rightarrow n = 2.11 \times 10^{-7} \text{ mol} \Rightarrow 2.11 \times 10^{-7} \text{ M}$$

(b) Ar: 0.934% means 0.00934 L of Ar per L of air

$$(1.000 \text{ bar})(0.00934 \text{ L}) = n \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \right) (298.15 \text{ K})$$

$$\Rightarrow n = 3.77 \times 10^{-4} \text{ mol} \Rightarrow 3.77 \times 10^{-4} \text{ M}$$

Kr: 1.14 ppm $\Rightarrow 1.14 \mu\text{L Kr per L of air} \Rightarrow 4.60 \times 10^{-8} \text{ M}$

Xe: 87 ppb $\Rightarrow 87 \text{ nL Xe per L of air} \Rightarrow 3.5 \times 10^{-9} \text{ M}$

1-28. $2.00 \text{ L} \times 0.0500 \frac{\text{mol}}{\text{L}} \times 61.83 \frac{\text{g}}{\text{mol}} = 6.18 \text{ g in a 2 L volumetric flask}$

1-29. Weigh out $2 \times 0.0500 \text{ mol} = 0.100 \text{ mol} = 6.18 \text{ g B(OH)}_3$ and dissolve in 2.00 kg H₂O.

1-30. $M_{\text{con}} \cdot V_{\text{con}} = M_{\text{dil}} \cdot V_{\text{dil}}$

$$\left(0.80 \frac{\text{mol}}{\text{L}}\right)(1.00 \text{ L}) = \left(0.25 \frac{\text{mol}}{\text{L}}\right) V_{\text{dil}} \Rightarrow V_{\text{dil}} = 3.2 \text{ L}$$

1-31. We need $1.00 \text{ L} \times 0.10 \frac{\text{mol}}{\text{L}} = 0.10 \text{ mol NaOH} = 4.0 \text{ g NaOH}$

$$\frac{4.0 \text{ g NaOH}}{0.50 \frac{\text{g NaOH}}{\text{g solution}}} = 8.0 \text{ g solution}$$

1-32. (a) $V_{\text{con}} = V_{\text{dil}} \frac{M_{\text{dil}}}{M_{\text{con}}} = 1000 \text{ mL} \left(\frac{1.00 \text{ M}}{18.0 \text{ M}}\right) = 55.6 \text{ mL}$

(b) One liter of 98.0% H₂SO₄ contains $(18.0 \frac{\text{mol}}{\text{L}})(98.079 \frac{\text{g}}{\text{mol}}) = 1.77 \times 10^3 \text{ g}$ of H₂SO₄. Since the solution contains 98.0 wt% H₂SO₄, and the mass of H₂SO₄ per mL is 1.77 g, the mass of solution per milliliter (the density) is

$$\frac{1.77 \frac{\text{g H}_2\text{SO}_4}{\text{mL}}}{0.980 \frac{\text{g H}_2\text{SO}_4}{\text{g solution}}} = 1.80 \text{ g solution/mL}$$

1-33. 2.00 L of 0.169 M NaOH = 0.338 mol NaOH = 13.5 g NaOH

$$\text{density} = \frac{\text{g solution}}{\text{mL solution}}$$

$$= \frac{13.5 \frac{\text{g NaOH}}{\text{mL}}}{(16.7 \text{ mL solution}) \left(0.534 \frac{\text{g NaOH}}{\text{g solution}}\right)} = 1.52 \frac{\text{g}}{\text{mL}}$$

1-34. FM of Ba(NO₃)₂ = 261.34 4.35 g of solid with 23.2 wt% Ba(NO₃)₂ contains $(0.232)(4.35 \text{ g}) = 1.01 \text{ g Ba(NO}_3)_2$

$$\text{mol Ba}^{2+} = \frac{(1.01 \frac{\text{g Ba(NO}_3)_2}{\text{mol}})}{(261.34 \frac{\text{g Ba(NO}_3)_2}{\text{mol}})} = 3.86 \times 10^{-3} \text{ mol}$$

$$\text{mol H}_2\text{SO}_4 = \text{mol Ba}^{2+} = 3.86 \times 10^{-3} \text{ mol}$$

$$\text{volume of H}_2\text{SO}_4 = \frac{(3.86 \times 10^{-3} \text{ mol})}{(3.00 \text{ mol/L})} = 1.29 \text{ mL}$$

1-35. 25.0 mL of 0.0236 M Th⁴⁺ contains

$$(0.0250 \text{ L})(0.0236 \text{ M}) = 5.90 \times 10^{-4} \text{ mol Th}^{4+}$$

$$\text{mol HF required for stoichiometric reaction} = 4 \times \text{mol Th}^{4+} = 2.36 \times 10^{-3} \text{ mol}$$

$$50\% \text{ excess} = 1.50(2.36 \times 10^{-3} \text{ mol}) = 3.54 \times 10^{-3} \text{ mol HF}$$

Required mass of pure HF = $(3.54 \times 10^{-3} \text{ mol})(20.01 \text{ g/mol}) = 0.0708 \text{ g}$

$$\text{Mass of 0.491 wt\% HF solution} = \frac{(0.0708 \text{ g HF})}{(0.00491 \text{ g HF/g solution})} = 14.4 \text{ g}$$

- 1-36. Concentrations of reagents used in an analysis are determined either by weighing out supposedly pure primary standards or by reaction with such standards. If the standards are not pure, none of the concentrations will be correct.
- 1-37. The equivalence point occurs when the exact stoichiometric quantities of reagents have been mixed. The end point, which comes near the equivalence point, is marked by a sudden change in a physical property brought about by the disappearance of a reactant or appearance of a product.
- 1-38. In a blank titration, the quantity of titrant required to reach the end point in the absence of analyte is measured. By subtracting this quantity from the amount of titrant needed in the presence of analyte, we reduce the systematic error.
- 1-39. In a direct titration, titrant reacts directly with analyte. In a back titration, a known excess of reagent that reacts with analyte is used. The excess is then measured with a second titrant.
- 1-40. Primary standards are purer than reagent-grade chemicals. The assay of a primary standard must be very close to the nominal value (such as 99.95–100.05%), whereas the assay on a reagent chemical might be only 99%. Primary standards must have very long shelf lives.
- 1-41. Since a relatively large amount of acid might be required to dissolve a small amount of sample, we cannot tolerate even modest amounts of impurities in the acid for trace analysis. Otherwise, the quantity of impurity could be greater than quantity of analyte in the sample.
- 1-42. $40.0 \text{ mL of } 0.0400 \text{ M Hg}_2(\text{NO}_3)_2 = 1.60 \text{ mmol of Hg}_2^{2+}$, which will require 3.20 mmol of KI . This is contained in volume $= \frac{3.20 \text{ mmol}}{0.100 \text{ mmol/mL}} = 32.0 \text{ mL}$.
- 1-43. $108.0 \text{ mL of } 0.1650 \text{ M oxalic acid} = 17.82 \text{ mmol}$, which requires $\left(\frac{2 \text{ mol MnO}_4^-}{5 \text{ mol H}_2\text{C}_2\text{O}_4} \right) (17.82 \text{ mol H}_2\text{C}_2\text{O}_4) = 7.128 \text{ mmol of MnO}_4^-$.

$$7.128 \text{ mmol} / (0.1650 \text{ mmol/mL}) = 43.20 \text{ mL of KMnO}_4.$$

Another way to see this is to note that the reagents are both 0.1650 M. Therefore, volume of $\text{MnO}_4^- = \frac{2}{5}$ (volume of oxalic acid).

$$\text{For second question, volume of oxalic acid} = \frac{5}{2}(\text{volume of } \text{MnO}_4^-) = 270.0 \text{ mL.}$$

- 1-44.** 1.69 mg of $\text{NH}_3 = 0.0992 \text{ mmol of } \text{NH}_3$. This will react with $\frac{3}{2}(0.0992) = 0.149 \text{ mmol of OBr}^-$. The molarity of OBr^- is $0.149 \text{ mmol}/1.00 \text{ mL} = 0.149 \text{ M}$.

$$\begin{aligned}\text{1-45. mol sulfamic acid} &= \frac{0.3337 \text{ g}}{97.094 \text{ g/mol}} = 3.4369 \text{ mmol} \\ \text{molarity of NaOH} &= \frac{3.4369 \text{ mmol}}{34.26 \text{ mL}} = 0.1003 \text{ M}\end{aligned}$$

- 1-46.** HCl added to powder = $(10.00 \text{ mL})(1.396 \text{ M}) = 13.96 \text{ mmol}$
 $\text{NaOH required} = (39.96 \text{ mL})(0.1004 \text{ M}) = 4.012 \text{ mmol}$
 $\text{HCl consumed by carbonate} = 13.96 - 4.012 = 9.948 \text{ mmol}$
 $\text{mol CaCO}_3 = \frac{1}{2} \text{ mol HCl consumed} = 4.974 \text{ mmol} = 0.4978 \text{ g CaCO}_3$
 $\text{wt\% CaCO}_3 = \frac{0.4978 \text{ g CaCO}_3}{0.5413 \text{ g limestone}} \times 100 = 92.0 \text{ wt\%}$

CHAPTER 2

TOOLS OF THE TRADE

- 2-1. The primary rule is to familiarize yourself with the hazards of what you are about to do and not to do something you consider to be dangerous.
- 2-3. Dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is soluble in water and contains carcinogenic Cr(VI). Reducing Cr(VI) to Cr(III) decreases the toxicity of the metal. Converting aqueous Cr(III) to solid Cr(OH)_3 decreases the solubility of the metal and therefore decreases its ability to be spread by water. Evaporation produces the minimum volume of waste.
- 2-4. The upper “0” means that the reagent has no fire hazard. The right hand “0” indicates that the reagent is stable. The “3” tells us that the reagent is corrosive or toxic and we should avoid skin contact or inhalation.
- 2-5. The lab notebook must: (1) state what was done; (2) state what was observed; and (3) be understandable to a stranger.
- 2-6. See Section 2.3.
- 2-7. The buoyancy correction is 1 when the substance being weighed has the same density as the weights used to calibrate the balance.

$$2-8. m = \frac{(14.82 \text{ g}) \left(1 - \frac{0.0012 \text{ g/mL}}{8.0 \text{ g/mL}}\right)}{\left(1 - \frac{0.0012 \text{ g/mL}}{0.626 \text{ g/mL}}\right)} = 14.85 \text{ g}$$

- 2-9. The smallest correction will be for PbO_2 , whose density is closest to 8.0 g/mL. The largest correction will be for the least dense substance, lithium.

$$2-10. m = \frac{4.2366 \text{ g} \left(1 - \frac{0.0012 \text{ g/mL}}{8.0 \text{ g/mL}}\right)}{\left(1 - \frac{0.0012 \text{ g/mL}}{1.636 \text{ g/mL}}\right)} = 4.2391 \text{ g}$$

Without correcting for buoyancy, we would think the mass of primary standard is less than the actual mass and we would think the molarity of base reacting with the standard is also less than the actual molarity. The percentage error would be

$$\frac{\text{true mass} - \text{measured mass}}{\text{true mass}} \times 100 = \frac{4.2391 - 4.2366}{4.2391} \times 100 = 0.06\%.$$

- 2-11.** (a) One mol of He (= 4.003 g) occupies a volume of

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol}) \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \right) (293.15 \text{ K})}{1 \text{ bar}} = 24.37 \text{ L}$$

$$\text{Density} = 4.003 \text{ g} / 24.37 \text{ L} = 0.164 \text{ g/L} = 0.000164 \text{ g/mL}$$

$$(b) m = \frac{(0.823 \text{ g}) \left(1 - \frac{0.000164 \text{ g/mL}}{8.0 \text{ g/mL}} \right)}{\left(1 - \frac{0.000164 \text{ g/mL}}{0.97 \text{ g/mL}} \right)} = 0.823 \text{ g}$$

- 2-12.** (a) $(0.42)(2330 \text{ Pa}) = 979 \text{ Pa}$

- (b) Air density =

$$\frac{(0.003485)(94000) - (0.001318)(979)}{293.15} = 1.11 \text{ g/L} = 0.0011 \text{ g/mL}$$

$$(c) \text{ mass} = 1.0000 \text{ g} \left(\frac{1 - \frac{0.0011 \text{ g/mL}}{8.0 \text{ g/mL}}}{1 - \frac{0.0011 \text{ g/mL}}{1.00 \text{ g/mL}}} \right) = 1.0010 \text{ g}$$

$$2-13. m_b = m_a \frac{r_a^2}{r_b^2} = (100.0000 \text{ g}) \frac{(6370000 \text{ m})^2}{(6370030 \text{ m})^2} = 99.9991 \text{ g}$$

- 2-14.** TD means "to deliver" and TC means "to contain."

- 2-15.** Dissolve $(0.2500 \text{ L})(0.1500 \text{ mol/L}) = 0.03750 \text{ mol}$ of K_2SO_4 (= 6.535 g, FM 174.26 g/mol) in less than 250 mL of water in a 250-mL volumetric flask. Add more water and mix. Dilute to the 250.0 mL mark and invert the flask many times for complete mixing.

- 2-16.** The plastic flask is needed for trace analysis of analytes at ppb levels that might be lost by adsorption on the glass surface.

- 2-17.** (a) With a suction device, suck liquid up past the 5.00 mL mark. Discard one or two pipet volumes of liquid to rinse the pipet. Take up a third volume past the calibration mark and quickly replace the bulb with your index finger. (Alternatively, use an automatic suction device that remains attached to the

pipet.) Wipe excess liquid off the outside of the pipet with a clean tissue. Touch the tip of the pipet to the side of a beaker and drain liquid until the bottom of the meniscus reaches the center of the mark. Transfer the pipet to a receiving vessel and drain it by gravity while holding the tip against the wall. After draining stops, hold the pipet to the wall for a few more seconds to complete draining. Do not blow out the last drop. The pipet should be nearly vertical at the end of delivery.

(b) Transfer pipet.

- 2-18. (a) Adjust the knob for 50.0 μL . Place a fresh tip tightly on the barrel. Depress the plunger to the first stop, corresponding to 50.0 μL . Hold the pipet vertically, dip it 3–5 mm into reagent solution, and slowly release the plunger to suck up liquid. Leave the tip in the liquid for a few more seconds. Withdraw the pipet vertically. Take up and discard three squirts of reagent to clean and wet the tip and fill it with vapor. To dispense liquid, touch the tip to the wall of the receiver and gently depress the plunger to the first stop. After a few seconds, depress the plunger further to squirt out the last liquid.

(b) The procedure in (a) is called forward mode. For a foaming liquid, use reverse mode. Depress the plunger beyond the 50.0 μL stop and take in more than 50.0 μL . To deliver 50.0 μL , depress the plunger to the first stop and not beyond.

- 2-19. The trap prevents liquid filtrate from being sucked into the vacuum system. The watchglass keeps dust out of the sample.

- 2-20. Phosphorus pentoxide

- 2-21. $20.214\ 4\ \text{g} - 10.263\ 4\ \text{g} = 9.951\ 0\ \text{g}$. Column 3 of Table 2-7 tells us that the true volume is $(9.951\ 0\ \text{g})(1.002\ 9\ \text{mL/g}) = 9.979\ 9\ \text{mL}$.

- 2-22. Expansion = $\frac{0.999\ 102\ 6}{0.997\ 047\ 9} = 1.002\ 060\ 8 \approx 0.2\%$. Densities were taken from Table 2-7. The 0.500 0 M solution at 25° would be $(0.500\ 0\ \text{M})/(1.002) = 0.499\ 0\ \text{M}$.

- 2-23. Using column 2 of Table 2-7, mass in vacuum = $(50.037\ \text{mL})(0.998\ 207\ 1\ \text{g/mL}) = 49.947\ \text{g}$.

$$\text{Using column 3, mass in air} = \frac{50.037\ \text{mL}}{1.0029\ \text{mL/g}} = 49.892\ \text{g}.$$

- 2-24.** When the solution is cooled to 20°C, the concentration will be higher than the concentration at 24°C by a factor of $\frac{\text{density at } 20^\circ\text{C}}{\text{density at } 24^\circ\text{C}}$. Therefore, the concentration needed at 24° will be lower than the concentration at 20°C.

$$\text{Desired concentration at } 24^\circ\text{C} = (1.000 \text{ M}) \left(\frac{0.997\,299\,5 \text{ g/mL}}{0.998\,207\,1 \text{ g/mL}} \right) = 0.999\,1 \text{ M}$$

(using the quotient of densities from Table 2-7). The true mass of KNO₃

$$\text{needed is } (0.5000 \text{ L}) \left(0.9991 \frac{\text{mol}}{\text{L}} \right) \left(101.103 \frac{\text{g}}{\text{mol}} \right) = 50.506 \text{ g.}$$

$$m' = \frac{(50.506 \text{ g}) \left(1 - \frac{0.001\,2 \text{ g/mL}}{2.109 \text{ g/mL}} \right)}{\left(1 - \frac{0.001\,2 \text{ g/mL}}{8.0 \text{ g/mL}} \right)} = 50.484 \text{ g}$$

- 2-25.** (a) Fraction within specifications = $e^{-t(\ln 2)/t_m}$. If $t_m = 2 \text{ yr}$ and $t = 2 \text{ yr}$, then fraction within specifications = $e^{-2(\ln 2)/2} = e^{-\ln 2} = \frac{1}{2}$.
- (b) Fraction within specifications = 0.95 = $e^{-t(\ln 2)/2} \text{ yr}$
- $$\ln(0.95) = -t(\ln 2)/2 \Rightarrow t = -2 \ln(0.95)/\ln 2 = 0.148 \text{ yr} = 54 \text{ days} \approx 8 \text{ weeks}$$
- To solve for t , take the natural logarithm of both sides:

- 2-26.** Al extracted from glass = $(0.200 \text{ L})(5.2 \times 10^{-6} \text{ M}) = 1.04 \times 10^{-6} \text{ mol}$
mass of Al = $(1.04 \times 10^{-6} \text{ mol})(26.98 \text{ g/mol}) = 28.1 \mu\text{g}$
This much Al was extracted from 0.50 g of glass, so

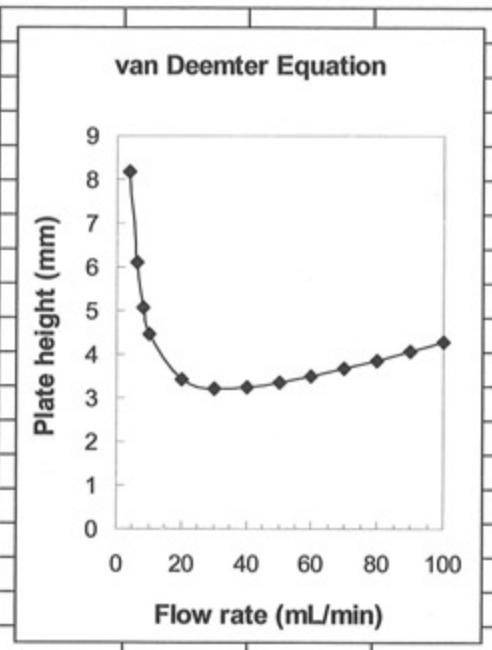
$$\text{wt\% Al extracted} = 100 \times \frac{28.1 \times 10^{-6} \text{ g}}{0.50 \text{ g}} = 0.005\,62 \text{ wt\%}$$

$$\text{Fraction of Al extracted} = \frac{0.005\,62 \text{ wt\%}}{0.80 \text{ wt\%}} = 0.007\,0 \text{ (or } 0.70\% \text{ of the Al)}$$

2-27.

Graph of van Deemter Equation

	Flow rate (mL/min)	Plate height (mm)
Constants		
A =	4	8.194
1.65	6	6.092
B =	8	5.064
25.8	10	4.466
C =	20	3.412
0.0236	30	3.218
	40	3.239
	50	3.346
	60	3.496
	70	3.671
	80	3.861
	90	4.061
	100	4.268
Formula:		
C5 = \$A\$6+\$A\$8/B5+\$A\$10*B5		



CHAPTER 3

EXPERIMENTAL ERROR

- 3-1. (a) 5 (b) 4 (c) 3
- 3-2. (a) 1.237 (b) 1.238 (c) 0.135 (d) 2.1 (e) 2.00
- 3-3. (a) 0.217 (b) 0.216 (c) 0.217
- 3-4. (b) 1.18 (3 significant figures) (c) 0.71 (2 significant figures)
- 3-5. (a) 3.71 (b) 10.7 (c) 4.0×10^1 (d) 2.85×10^{-6}
(e) 12.625 1 (f) 6.0×10^{-4} (g) 242
- 3-6. (a) $\text{BaF}_2 = 137.327 + 2(18.998\ 403\ 2) = 175.324$ because the atomic mass of Ba has only 3 decimal places.
(b) $\text{C}_6\text{H}_4\text{O}_4 = 6(12.010\ 7) + 4(1.007\ 94) + 4(15.999\ 4) = 140.093\ 6$
(The fourth-decimal place in the atomic mass of C has an uncertainty of ± 8 and the fourth-decimal place of O has an uncertainty of ± 3 . These uncertainties are large enough to make the fourth-decimal place in molecular mass of $\text{C}_6\text{H}_4\text{O}_4$ insignificant. Therefore, another good answer is 140.094.)
- 3-7. (a) 12.3 (b) 75.5 (c) 5.520×10^3 (d) 3.04
(e) 3.04×10^{-10} (f) 11.9 (g) 4.600 (h) 4.9×10^{-7}
- 3-9. All measurements have some uncertainty, so there is no way to know the true value.
- 3-10. Systematic error is always above or always below the “true value” if you make replicate measurements. In principle, you can find the source of this error and eliminate it in a better experiment so the measured mean equals the true mean. Random error is equally likely to be positive or negative and cannot be eliminated. Random error can be reduced in a better experiment.
- 3-11. The apparent mass of product is systematically low because the initial mass of the (crucible plus moisture) is higher than the true mass of the crucible. The error is systematic. There is also always some random error superimposed on the systematic error.
- 3-12. (a) 25.031 mL is a systematic error. The pipet always delivers more than it is

rated for. The number ± 0.009 is the random error in the volume delivered.

The volume fluctuates around 25.031 by ± 0.009 mL.

- (b) The numbers 1.98 and 2.03 mL are systematic errors. The buret delivers too little between 0 and 2 mL and too much between 2 and 4 mL. The observed variations ± 0.01 and ± 0.02 are random errors.
- (c) The difference between 1.9839 and 1.9900 g is random error. The mass will probably be different the next time I try the same procedure.
- (d) Differences in peak area are random error based on inconsistent injection volume, inconsistent detector response, and probably other small variations in the condition of the instrument from run to run.

3-13. (a) Carmen (b) Cynthia (c) Chastity (d) Cheryl

3-14. $3.124 (\pm 0.005)$, $3.124 (\pm 0.2\%)$. It would also be reasonable to keep an additional digit: $3.1236 (\pm 0.005_2)$, $3.1236 (\pm 0.17\%)$

3-15. (a) $6.2 (\pm 0.2)$

$$\underline{-4.1 (\pm 0.1)}$$

$$2.1 \pm e \quad e^2 = 0.2^2 + 0.1^2 \Rightarrow e = 0.2_{24} \text{ Answer: } 2.1 \pm 0.2 \text{ (or } 2.1 \pm 11\%)$$

(b) $9.43 (\pm 0.05)$ $9.43 (\pm 0.53\%)$
 $\underline{\times 0.016 (\pm 0.001)} \Rightarrow \underline{\times 0.016 (\pm 6.25\%)}$ $\%e^2 = 0.53^2 + 6.25^2$
 $0.150\ 88 (\pm \%e) \Rightarrow \%e = 6.272$

$$\begin{aligned} \text{Relative uncertainty} &= 6.27\%; \text{ Absolute uncertainty} = 0.150\ 88 \times 0.062\ 7 \\ &= 0.009\ 46; \quad \text{Answer: } 0.151 \pm 0.009 \quad (\text{or } 0.151 \pm 6\%) \end{aligned}$$

(c) The first term in brackets is the same as part (a), so we can rewrite the problem as $2.1 (\pm 0.2_{24}) \div 9.43 (\pm 0.05) = 2.1 (\pm 10.7\%) \div 9.43 (\pm 0.53\%)$
 $\%e = \sqrt{10.7^2 + 0.53^2} = 10.7\%$
 $\text{Absolute uncertainty} = 0.107 \times 0.223 = 0.023\ 9$
 $\text{Answer: } 0.223 \pm 0.024 (\pm 11\%)$

(d) The term in brackets is

$$6.2 (\pm 0.2) \times 10^{-3} \quad e = \sqrt{0.2^2 + 0.1^2} \Rightarrow e = 0.2_{24}$$

$$\underline{+ 4.1 (\pm 0.1) \times 10^{-3}}$$

$$10.3 (\pm 0.2_{24}) \times 10^{-3} = 10.3 \times 10^{-3} (\pm 2.17\%)$$

$$9.43 (\pm 0.53\%) \times 0.010\ 3 (\pm 2.17\%) = 0.097\ 13 \pm 2.23\% = 0.097\ 13 \pm 0.002\ 17$$

$$\text{Answer: } 0.097_1 \pm 0.002_2 (\pm 2.2\%)$$

3-16. (a) $\text{Uncertainty} = \sqrt{0.03^2 + 0.02^2 + 0.06^2} = 0.07$

Answer: $10.18 (\pm 0.07) (\pm 0.7\%)$

(b) $91.3 (\pm 1.0) \times 40.3 (\pm 0.2) / 21.1 (\pm 0.2)$

$$= 91.3 (\pm 1.10\%) \times 40.3 (\pm 0.50\%) / 21.1 (\pm 0.95\%)$$

$$\% \text{ uncertainty} = \sqrt{1.10^2 + 0.50^2 + 0.95^2} = 1.54\%$$

Answer: $174 (\pm 3) (\pm 2\%)$

(c) $[4.97 (\pm 0.05) - 1.86 (\pm 0.01)] / 21.1 (\pm 0.2)$

$$= [3.11 (\pm 0.0510)] / 21.1 (\pm 0.2) = [3.11 (\pm 1.64\%)] / 21.1 (\pm 0.95\%)$$

$$= 0.147 (\pm 1.90\%) = 0.147 (\pm 0.003) (\pm 2\%)$$

(d) $2.0164 (\pm 0.0008)$

$$1.233 (\pm 0.002)$$

$$+ \frac{4.61 (\pm 0.01)}{7.8594 \sqrt{(0.0008)^2 + (0.002)^2 + (0.01)^2}} = 0.0102$$

Answer: $7.86 (\pm 0.01) (\pm 0.1\%)$

(e) $2016.4 (\pm 0.8)$

$$+ 123.3 (\pm 0.2)$$

$$+ \frac{46.1 (\pm 0.1)}{2185.8 \sqrt{(0.8)^2 + (0.2)^2 + (0.1)^2}} = 0.8$$

Answer: $2185.8 (\pm 0.8) (\pm 0.04\%)$

(f) For $y = x^a$, $\% e_y = a\% e_x$

$$x = 3.14 \pm 0.05 \Rightarrow \% e_x = (0.05 / 3.14) \times 100 = 1.592\%$$

$$\% e_y = \frac{1}{3} (1.592\%) = 0.531\%$$

Answer: $1.464_3 \pm 0.007_8 (\pm 0.53\%)$

(g) For $y = \log x$, $e_y = 0.43429 \frac{e_x}{x}$

$$x = 3.14 \pm 0.05 \Rightarrow e_y = 0.43429 \left(\frac{0.05}{3.14} \right) = 0.006915$$

Answer: $0.4969 \pm 0.0069 (\pm 1.39\%)$

3-17. (a) $y = x^{1/2} \Rightarrow \% e_y = \frac{1}{2} \left(100 \times \frac{0.0011}{3.1415} \right) = 0.0175\%$

$$(1.75 \times 10^{-4}) \sqrt{3.1415} = 3.1 \times 10^{-4} \quad \text{Answer: } 1.7724_3 \pm 0.0003_1$$

(b) $y = \log x \Rightarrow e_y = 0.43429 \left(\frac{0.0011}{3.1415} \right) = 1.52 \times 10^{-4}$

Answer: 0.49714 ± 0.00015

$$(c) y = \text{antilog } x = 10^x \Rightarrow e_y = y \times 2.3026 e_x \\ = (10^{3.1415})(2.3026)(0.0011) = 3.51 \quad \text{Answer: } 1.3852 \pm 0.0035 \times 10^3$$

$$(d) y = \ln x \Rightarrow e_y = \frac{0.0011}{3.1415} = 3.5 \times 10^{-4} \quad \text{Answer: } 1.14470 \pm 0.00035$$

$$(e) \text{ Numerator of log term: } y = x^{1/2} \Rightarrow e_y = \frac{1}{2} \left(\frac{0.006}{0.104} \times 100 \right) = 2.88\%$$

$$\frac{0.3225 \pm 2.88\%}{0.0511 \pm 0.0009} = \frac{0.3225 \pm 2.88\%}{0.0511 \pm 1.76\%}$$

$$= 6.311 \pm 3.375\% = 6.311 \pm 0.213$$

$$\text{For } y = \log x, e_y = 0.43429 \frac{e_x}{x} = 0.43429 \left(\frac{0.213}{6.311} \right) = 0.015$$

$$\text{Answer: } 0.80_0 \pm 0.01_5$$

- 3-18.** (a) Standard uncertainty in atomic mass is equal to the uncertainty listed in the periodic table divided by $\sqrt{3}$ because atomic mass has a rectangular distribution of values.

$$\text{Na} = 22.989\ 769\ 28 \pm 0.000\ 000\ 02/\sqrt{3} \text{ g/mol}$$

$$\text{Cl} = 35.453 \pm 0.002/\sqrt{3} \text{ g/mol}$$

$$58.442\ 770 \quad \sqrt{[(2 \times 10^{-8})^2]/3 + [(2 \times 10^{-3})^2]/3} = 1.2 \times 10^{-3}$$

$$58.443 \pm 0.001_2 \text{ g/mol}$$

$$(b) \text{ molarity} = \frac{\text{mol}}{\text{L}} = \frac{[2.634 (\pm 0.002)\text{g}] / [58.443 (\pm 0.001_2)\text{g/mol}]}{0.100\ 00 (\pm 0.000\ 08) \text{ L}}$$

$$= \frac{2.634 (\pm 0.076\%) / [58.443 (\pm 0.002\ 1\%)]}{0.100\ 00 (\pm 0.08\%)}$$

$$\text{relative error} = \sqrt{(0.076\%)^2 + (0.002\ 1\%)^2 + (0.08\%)^2} = 0.11\%$$

$$\text{molarity} = 0.450\ 7 (\pm 0.000\ 5) \text{ M}$$

$$3-19. \quad m = \frac{m' \left(1 - \frac{da}{dw} \right)}{1 - \frac{da}{d}}$$

$$m = \frac{[1.034\ 6 (\pm 0.000\ 2) \text{ g}] \left(1 - \frac{0.001\ 2 (\pm 0.000\ 1) \text{ g/mL}}{8.0 (\pm 0.5) \text{ g/mL}} \right)}{1 - \frac{0.001\ 2 (\pm 0.000\ 1) \text{ g/mL}}{0.997\ 299\ 5 \text{ g/mL}}}$$

$$\begin{aligned}
 m &= \frac{[1.0346 (\pm 0.0193\%)] \left(1 - \frac{0.0012 (\pm 8.33\%)}{8.0 (\pm 6.25\%)}\right)}{1 - \frac{0.0012 (\pm 8.33\%)}{0.9972995 (\pm 0\%)}} \\
 m &= \frac{[1.0346 (\pm 0.0193\%)] [1 - 0.000150 (\pm 10.4\%)]}{[1 - 0.001203 (\pm 8.33\%)]} \\
 m &= \frac{[1.0346 (\pm 0.0193\%)] [1 - 0.000150 (\pm 0.000156\%)]}{[1 - 0.001203 (\pm 0.000100\%)]} \\
 m &= \frac{[1.0346 (\pm 0.0193\%)] [0.9998500 (\pm 0.000156\%)]}{[0.998797 (\pm 0.000100\%)]} \\
 m &= \frac{[1.0346 (\pm 0.0193\%)] [0.9998500 (\pm 0.00156\%)]}{[0.998797 (\pm 0.0100\%)]} \\
 m &= 1.0357 (\pm 0.0218\%) = 1.0357 (\pm 0.0002) \text{ g}
 \end{aligned}$$

3-20. $\text{mol Fe}_2\text{O}_3 = \frac{0.2774 \pm 0.0018 \text{ g}}{159.688 \text{ g/mol}} = \frac{0.2774}{159.688} \pm \frac{0.0018}{159.688}$
 $= 1.7371 \pm 0.0113 \text{ mmol Fe}_2\text{O}_3;$
mass of Fe = $2[1.7371 (\pm 0.0113) \times 10^{-3} \text{ mol}] [55.845 \text{ g/mol}] = 0.19402 \pm 0.00126 \text{ g}$
mass of Fe per tablet = $(0.19402 \pm 0.00126 \text{ g})/12 = 16.168 \pm 0.105 \text{ mg}$
 $= 16.2 \pm 0.1 \text{ mg}$

3-21. $\text{mol H}^+ = 2 \times \text{mol Na}_2\text{CO}_3$

$$\begin{aligned}
 \text{mol Na}_2\text{CO}_3 &= \frac{0.9674 (\pm 0.0009) \text{ g}}{105.9884 (\pm 0.0007) \text{ g/mol}} = \frac{0.9674 (\pm 0.093\%) \text{ g}}{105.988 (\pm 0.00066\%) \text{ g/mol}} \\
 &= 0.0091274 (\pm 0.093\%) \text{ mol}
 \end{aligned}$$

$$\text{mol H}^+ = 2(0.0091274 (\pm 0.093\%)) = 0.018255 (\pm 0.093\%) \text{ mol}$$

(Relative error is not affected by the multiplication by 2 because mol H⁺ and uncertainty in mol H⁺ are both multiplied by 2.)

$$\begin{aligned}
 \text{molarity of HCl} &= \frac{0.018255 (\pm 0.093\%) \text{ mol}}{0.02735 (\pm 0.00004) \text{ L}} = \frac{0.018255 (\pm 0.093\%) \text{ mol}}{0.02735 (\pm 0.146\%) \text{ L}} \\
 &= 0.66746 (\pm 0.173\%) = 0.66746 (\pm 0.001155) \\
 &= 0.667 \pm 0.001 \text{ M}
 \end{aligned}$$

3-22. To find the uncertainty in c_0^3 , we use the function $y = x^a$ in Table 3-1, where $x = c_0$ and $a = 3$. The uncertainty in c_0^3 is

$$\%e_y = a \%e_x = 3 \times \frac{0.00000033}{5.43102036} \times 100 = 1.823 \times 10^{-5}\%$$

So $c_0^3 = (5.43102036 \times 10^{-8} \text{ cm})^3 = 1.6019327960 \times 10^{-22} \text{ cm}^3$ with a

relative uncertainty of $1.823 \times 10^{-5}\%$. We retain extra digits for now and round off at the end of the calculations. (If your calculator cannot hold as many digits as we need for this arithmetic, you can do the math with a spreadsheet set to display 10 decimal places.)

The value of Avogadro's number is computed as follows:

$$N_A = \frac{m_{\text{Si}}}{(\rho c_0^3)/8} = \frac{28.085\ 384\ 2 \text{ g/mol}}{(2.329\ 031\ 9 \text{ g/cm}^3 \times 1.601\ 932\ 79_{60} \times 10^{-22} \text{ cm}^3)/8}$$

$$= 6.022\ 136\ 936\ 1 \times 10^{23} \text{ mol}^{-1}$$

The relative uncertainty in Avogadro's number is found from the relative uncertainties in m_{Si} , ρ , and c_0^3 . (There is no uncertainty in the number 8 atoms/unit cell.)

percent uncertainty in $m_{\text{Si}} = 100 (0.000\ 003\ 5/28.085\ 384\ 2) = 1.246 \times 10^{-5}\%$

percent uncertainty in $\rho = 100 (0.000\ 001\ 8/2.329\ 031\ 9) = 7.729 \times 10^{-5}\%$

percent uncertainty in $c_0^3 = 1.823 \times 10^{-5}\%$ (calculated before)

$$\begin{aligned} \text{percent uncertainty in } N_A &= \sqrt{\%e_{m_{\text{Si}}}^2 + \%e_r^2 + (\%e_{c_0^3})^2} = \\ &= \sqrt{(1.246 \times 10^{-5})^2 + (7.729 \times 10^{-5})^2 + (1.823 \times 10^{-5})^2} = 8.038 \times 10^{-5}\% \end{aligned}$$

The absolute uncertainty in N_A is $(8.038 \times 10^{-5}\%)(6.022\ 136\ 936\ 1 \times 10^{23})/100 = 0.000\ 004\ 841 \times 10^{23}$. Now we will round off N_A to the second digit of its uncertainty to express it in a manner consistent with the other data in this problem:

$$N_A = 6.022\ 136\ 9 (\pm 0.000\ 004\ 8) \times 10^{23} \text{ or } 6.022\ 136\ 9 (48) \times 10^{23}$$

3-23. C: $12.010\ 7 \pm 0.000\ 8/\sqrt{3}$; H: $1.007\ 94 \pm 0.000\ 07/\sqrt{3}$

O: $15.999\ 4 \pm 0.000\ 3/\sqrt{3}$; N: $14.006\ 7 \pm 0.000\ 2/\sqrt{3}$

$$+9C: 9(12.010\ 7 \pm 0.000\ 4_6) = 108.096\ 3 \pm 0.004\ 2$$

$$+9H: 9(1.007\ 94 \pm 0.000\ 04_0) = 9.071\ 46 \pm 0.000\ 36$$

$$+6O: 6(15.999\ 4 \pm 0.000\ 1_7) = 95.996\ 4 \pm 0.001\ 0$$

$$+3N: 3(14.006\ 7 \pm 0.000\ 1_2) = 42.020\ 1 \pm 0.000\ 35$$

$C_9H_9O_6N_3:$	$255.184\ 26 \pm ?$
-----------------	---------------------

Uncertainty = $\sqrt{0.004\ 2^2 + 0.000\ 36^2 + 0.001\ 0^2 + 0.000\ 35^2} = 0.004$

Answer: 255.184 ± 0.004

3-24. Relative uncertainties:

Large volume: $0.000\ 5\ L/5.013\ 8_2\ L = 0.010\%$

Small volume: $0.000\ 9\ mL/3.793\ 0\ mL = 0.024\%$

Pressure: $0.03\ mm/400\ mm = 0.008\%$

Temperature: $0.03\ K/300\ K = 0.01\%$

The largest uncertainty is in the volume of the small vessel = 0.024%.

Uncertainty in $\text{CO}_2 \approx 0.024\%$ of 400 ppm = $0.000\ 24 \times 400\ \text{ppm} = 0.1\ \text{ppm}$.

CHAPTER 4

STATISTICS

- 4-1.** The smaller the standard deviation, the greater the precision. There is no necessary relationship between standard deviation and accuracy. The statistics that we do in this chapter pertains to precision, not accuracy.
- 4-2.** (a) $\mu \pm \sigma$ corresponds to $z = -1$ to $z = +1$. The area from $z = 0$ to $z = +1$ is 0.3413. The area from $z = 0$ to $z = -1$ is also 0.3413.
Total area (= fraction of population) from $z = -1$ to $z = +1$ = 0.6826.
- (b) $z = -2$ to $z = +2 \Rightarrow$ area = $2 \times 0.4773 = 0.9546$
- (c) $z = 0$ to $z = +1 \Rightarrow$ area = 0.3413
- (d) $z = 0$ to $z = 0.5 \Rightarrow$ area = 0.1915
- (e) Area from $z = -1$ to $z = 0$ is 0.3413. Area from $z = -0.5$ to $z = 0$ is 0.1915.
Area from $z = -1$ to $z = -0.5$ is $0.3413 - 0.1915 = 0.1498$.
- 4-3.** (a) Mean = $\frac{1}{8}(1.52660 + 1.52974 + 1.52592 + 1.52731 + 1.52894 + 1.52804 + 1.52685 + 1.52793) = 1.52767$
- (b) Standard deviation = $\sqrt{\frac{(1.52660 - 1.52767)^2 + \dots + (1.52793 - 1.52767)^2}{8-1}} = 0.00126$
- (c) Variance = $(0.00126)^2 = 1.59 \times 10^{-6}$
- (d) Significant figures: $\bar{x} \pm s = 1.5277 \pm 0.0013$ or 1.528 ± 0.001 .
- 4-4.** (a) 1005.3 hours corresponds to $z = (1005.3 - 845.2)/94.2 = 1.700$.
In Table 4-1, the area from the mean to $z = 1.700$ is 0.4554. The area above $z = 1.700$ is therefore $0.5 - 0.4554 = 0.0446$.
- (b) 798.1 corresponds to $z = (798.1 - 845.2)/94.2 = -0.500$.
The area from the mean to $z = -0.500$ is the same as the area from the mean to $z = +0.500$, which is 0.1915 in Table 4-1.
901.7 corresponds to $z = (901.7 - 845.2)/94.2 = 0.600$.
The area from the mean to $z = 0.600$ is 0.2258 in Table 4-1.
The area between 798.1 and 901.7 is the sum of the two areas:
 $0.1915 + 0.2258 = 0.4173$
- (c) The following spreadsheet shows that the area from $-\infty$ to 800 h is 0.3157

and the area from $-\infty$ to 900 h is 0.719 6. Therefore, the area from 800 to 900 h is $0.719\bar{6} - 0.315\bar{7} = 0.404\bar{0}$.

	A	B	C
1	Mean =	Std dev =	
2	845.2	94.2	
3			
4	Area from $-\infty$ to 800 =		0.3157
5	Area from $-\infty$ to 900 =		0.7196
6	Area from 800 to 900		0.4040
7			
8	C4 = NORMDIST(800,\$A\$2,\$B\$2,TRUE)		
9	C5 = NORMDIST(900,\$A\$2,\$B\$2,TRUE)		
10	C6 = C5-C4		

- 4-5. (a) Half the people with tumors have $K < 0.92$ and would not be identified by the test. The false negative rate is 50%.
- (b) The false positive rate is the fraction of healthy people with $K \geq 0.92$. To use Table 4-1, we need to convert $x = 0.92$ to a z value defined as

$$z = \frac{x - \mu}{s} = \frac{0.92 - 0.75}{0.07} = 2.43$$

In Table 4-1, area from mean ($z = 0$) to $z = 2.4$ is 0.491 8. Area from mean to $z = 2.5$ is 0.493 8. We estimate that area from mean to $z = 2.43$ is a little greater than 0.492. Area above $z = 2.43$ is therefore $0.5 - 0.492 = 0.008$.

That is, 0.8% of healthy people will have a false positive indication of cancer.

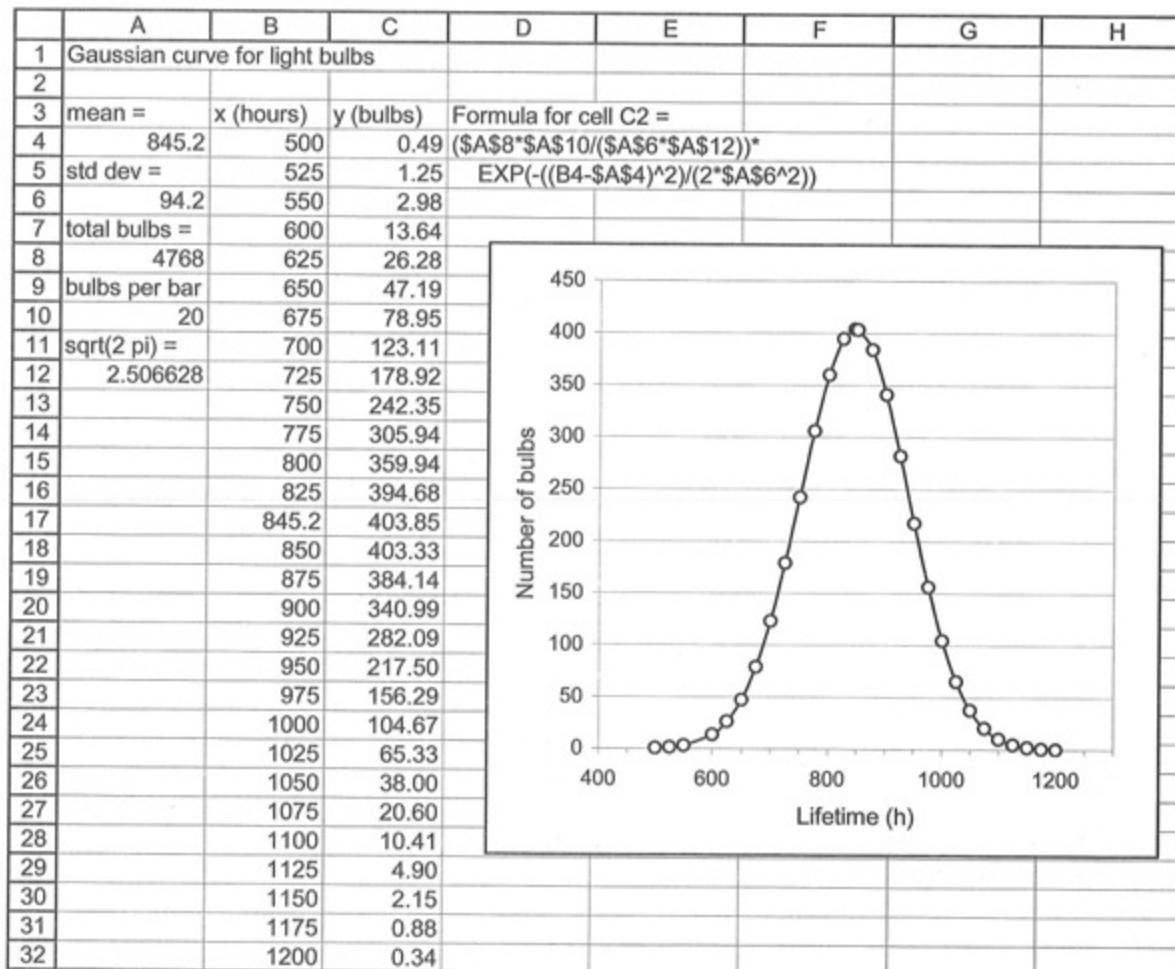
In the following spreadsheet, cell E5 computes the area below $K = 0.92$ with the formula $\text{NORMDIST}(0.92, \$B\$4, \$B\$5, \text{True})$, where B4 contains K and B5 contains the standard deviation. The area below 0.92 is found in cell E5 to be 0.992 4. The area above $K = 0.92$ is therefore $1 - 0.002\bar{4} = 0.007\bar{6}$.

	A	B	C	D	E	F	G	H
1	Gaussian distribution for phase partitioning of plasma proteins							
2								
3	Healthy patients			For healthy people, area below 0.92 =			Area below cutoff for people with tumors	
4	Mean K =	0.75					Cutoff (K)	Area
5	s =	0.07			0.992421		0.8	0.137656
6	Malignant tumor			area above 0.92 =			0.81	0.158655
7	Mean K =	0.92			0.007579		0.82	0.181651
8	s =	0.11					0.83	0.206627
9				area below 0.845 =			0.84	0.233529
10					0.912632		0.85	0.26227
11				area above 0.845 =			0.845	0.247677
12					0.087368			
13								
14	E5 = NORMDIST(0.92, \$B\$4, \$B\$5, TRUE)			H6 = NORMDIST(G6, \$B\$7, \$B\$8, TRUE)				
15	E7 = 1 - E5							

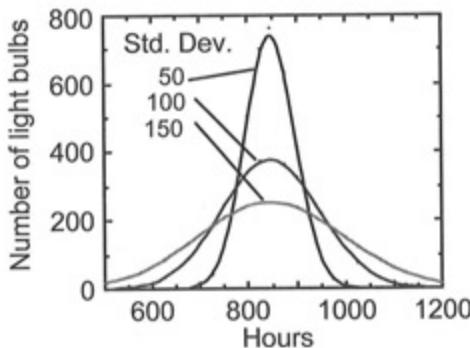
- (c) In column G, we vary the value of K and compute the area above K under the curve for people with malignant tumors in column H. We search for the value of K that gives an area of 0.25, which means that 25% of people with tumors will not be identified. The value 0.84 gives an area of 0.233 5 and the value 0.85 gives an area of 0.262 3. By trial and error, we find that $K = 0.845$ gives an area near 0.25.

In cell E10, we insert $K = 0.845$ into the NORMDIST function for healthy people and find that the area below $K = 0.845$ is 0.912 6. The area above $K = 0.845$ is $1 - 0.912 6 = 0.087 4$. That is, 8.7% of healthy people will produce a false positive result, indicating the presence of a tumor.

4-6.



- 4-7.** Use the same spreadsheet as in the previous problem, but vary the standard deviation. Here are the results:



- 4-8.** A confidence interval is a region around the measured mean in which the true mean is likely to lie: If we were to repeat a set of n measurements many times and compute the mean and standard deviation for each set, the 95% confidence interval would include the true population mean (whose value we do not know) in 95% of the sets of n measurements.
- 4-9.** Since the bars are drawn at a 50% confidence level, 50% of them ought to include the mean value if many experiments are performed. 90% of the 90% confidence bars must reach the mean value if we do enough experiments. The 90% bars must be longer than the 50% bars because more of the 90% bars must reach the mean.
- 4-10.** Case 1: Comparing a measured result to a “known” value. See if the known value is included within the 95% confidence interval computed as in Equation 4-7.
Case 2: Comparing replicate measurements. Use Equations 4-8 and 4-9 if the two standard deviations are not significantly different from each other. Use Equations 4-8a and 4-9a if the standard deviations are significantly different. Use the F test to decide if the two standard deviations are significantly different.
Case 3: Comparing individual differences. (Use Equations 4-10 and 4-11.)

4-11. $\bar{x} = 0.148$, $s = 0.034$

$$90\% \text{ confidence interval} = 0.148 \pm \frac{(2.015)(0.034)}{\sqrt{6}} = 0.148 \pm 0.028$$

$$99\% \text{ confidence interval} = 0.148 \pm \frac{(4.032)(0.034)}{\sqrt{6}} = 0.148 \pm 0.056$$

4-12. 99% confidence interval = $\bar{x} \pm \frac{(3.707)(0.000\ 07)}{\sqrt{7}} = \bar{x} \pm 0.000\ 10$
 $(1.527\ 83 \text{ to } 1.528\ 03)$

- 4-13.** (a) dL = deciliter = 0.1 L = 100 mL
(b) $F_{\text{calculated}} = (0.05_3/0.04_2)^2 = 1.59 < F_{\text{table}} = 6.26$ (for 5 degrees of freedom in the numerator and 4 degrees of freedom in the denominator). Since $F_{\text{calculated}} < F_{\text{table}}$, we can use the following equations:

$$s_{\text{pooled}} = \sqrt{\frac{0.53^2(5) + 0.42^2(4)}{6+5-2}} = 0.484$$

$$t = \frac{|14.57 - 13.95|}{0.484} \sqrt{\frac{6 \cdot 5}{6+5}} = 2.12 < 2.262 \text{ (listed for 95% confidence and 9 degrees of freedom). The results agree and the trainee should be released.}$$

4-14.

	A	B	C	D	E	F
1	Comparison of two methods					
2						
3	Sample	Method 1	Method 2	d_i		
4	A	0.88	0.83	0.05	= B4-C4	
5	B	1.15	1.04	0.11		
6	C	1.22	1.39	-0.17		
7	D	0.93	0.91	0.02		
8	E	1.17	1.08	0.09		
9	F	1.51	1.31	0.20		
10			mean =	0.050	= AVERAGE(D4:D9)	
11			stdev =	0.124	= STDEV(D4:D9)	
12			$t_{\text{calculated}} =$	0.987	= D10/D11*SQRT(6)	
13			$t_{\text{table}} =$	2.571	= TINV(0.05,5)	

$t_{\text{calculated}} = 0.987 < 2.571$ (Student's t for 95% confidence and 5 deg of freedom)

The difference is not significant.

- 4-15.** In the following spreadsheet, we find $t_{\text{calculated}}$ (which is labeled t Stat in cell F10) is less than t_{table} (t Critical two-tail in cell F14). Therefore, the difference between the methods is *not* significant.
The probability P(T<=t) two-tail in cell F13 is 0.37. There is a 37% chance of finding the observed difference between equivalent methods by random variations in results. The probability would have to be ≤ 0.05 for us to conclude that the methods differ.

	A	B	C	D	E	F	G
1	Paired t test				t-Test: Paired Two Sample for Means		
2							
3	Sample	Method 1	Method 2			Variable 1	Variable 2
4	A	0.88	0.83		Mean	1.14333333	1.09333333
5	B	1.15	1.04		Variance	0.05118667	0.04818667
6	C	1.22	1.39		Observations	6	6
7	D	0.93	0.91		Pearson Correlation	0.84541418	
8	E	1.17	1.08		Hypothesized Mean Difference	0	
9	F	1.51	1.31		df	5	
10					t Stat	0.98692754	
11	Calculated t Statistic in cell F10 is				P(T<=t) one-tail	0.18449929	
12	less than critical t in cell F14.				t Critical one-tail	2.01504918	
13	Therefore, the difference between the				P(T<=t) two-tail	0.36899857	
14	methods is <i>not significant</i> .				t Critical two-tail	2.57057764	

4-16. $F_{\text{calculated}} = s_2^2/s_1^2 = (0.039)^2/(0.025)^2 = 2.43$

$F_{\text{table}} = 9.28$ for 3 degrees of freedom in the numerator and denominator

Since $F_{\text{calculated}} < F_{\text{table}}$, the difference in standard deviation is not significant and

we use Equations 4-8 and 4-9.

$$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}} = \sqrt{\frac{0.025^2(4 - 1) + 0.039^2(4 - 1)}{4 + 4 - 2}} = 0.0328$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} = \frac{|1.382 - 1.346|}{0.0328} \sqrt{\frac{4 \cdot 4}{4 + 4}} = 1.55$$

$$t_{\text{table}} (4 + 4 - 2 = 6 \text{ degrees of freedom}) = 2.447$$

Since $t_{\text{calculated}} < t_{\text{table}}$, the difference is not significant.

4-17. For Method 1, we compute $\bar{x}_1 = 0.082605_2$, $s_1 = 0.0000134$.

For Method 2, $\bar{x}_2 = 0.082005$, $s_2 = 0.000129$.

The two standard deviations differ by approximately a factor of 10. We should use the F test to compare the two standard deviations:

$$F_{\text{calculated}} = s_2^2/s_1^2 = (0.000129)^2/(0.0000134)^2 = 92.7$$

$F_{\text{table}} = 6.26$. Since $F_{\text{calculated}} > F_{\text{table}}$, we use Equations 4-8a and 4-9a.

The following spreadsheet shows that $t_{\text{calculated}} = 11.3$ and $t_{\text{table}} = 2.57$.

$t_{\text{calculated}} > t_{\text{table}}$, so the difference is significant at the 95% confidence level.

Paired t test		t-Test: Two-Sample Assuming Unequal Variances		
Method 1	Method 2		Variable 1	Variable 2
0.082601	0.08183	Mean	0.082605	0.082005
0.082621	0.08186	Variance	1.8E-10	1.67E-08
0.082589	0.08205	Observations	5	6
0.082617	0.08206	Hypothesized Mean Difference	0	
0.082598	0.08215	df	5	
	0.08208	t Stat	11.31371	$\leftarrow t_{\text{calculated}} = 11.3$
		P(T<=t) one-tail	4.72E-05	
		t Critical one-tail	2.015049	
		P(T<=t) two-tail	9.43E-05	
		t Critical two-tail	2.570578	$\leftarrow t_{\text{table}} = 2.57$

4-18. 90% confidence interval = $\bar{x} \pm \frac{(2.353)(1\%)}{\sqrt{4}} = \bar{x} \pm 1.18\% < 1.2\%$.

The answer is yes.

- 4-19. For indicators 1 and 2: $F_{\text{calculated}} = (0.00225/0.00098)^2 = 5.27 > F_{\text{table}} \approx 2.2$ (for 27 degrees of freedom in the numerator and 17 degrees of freedom in the denominator). Since $F_{\text{calculated}} > F_{\text{table}}$, we use the following equations:

$$\begin{aligned}\text{Degrees of freedom} &= \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\frac{(s_1^2/n_1)^2}{n_1 - 1} + \frac{(s_2^2/n_2)^2}{n_2 - 1}} \\ &= \frac{(0.00225^2/28 + 0.00098^2/18)^2}{\frac{(0.00225^2/28)^2}{28 - 1} + \frac{(0.00098^2/18)^2}{18 - 1}} = 39.8 \approx 40\end{aligned}$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} = \frac{|0.09565 - 0.08686|}{\sqrt{0.00225^2/28 + 0.00098^2/18}} = 18.2$$

This is much greater than t for 40 degrees of freedom, which is 2.02.

The difference is significant.

- For indicators 2 and 3: $F_{\text{calculated}} = (0.00113/0.00098)^2 = 1.33 < F_{\text{table}} \approx 2.2$ (for 28 degrees of freedom in the numerator and 17 degrees of freedom in the denominator). Since $F_{\text{calculated}} < F_{\text{table}}$, we use the following equations:

$$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}} = 0.0010758$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} = 1.39 < 2.02 \Rightarrow \text{difference is } \underline{\text{not}} \text{ significant.}$$

4-20. $s_{\text{pooled}} = \sqrt{\frac{30.0^2(31) + 29.8^2(31)}{32 + 32 - 2}} = 29.9$

$t = \frac{52.9 - 31.4}{29.9} \sqrt{\frac{32 \cdot 32}{32 + 32}} = 2.88$. The table gives t for 60 degrees of freedom, which is close to 62. The difference is significant at the 95 and 99% levels.

4-21. $\bar{x} = 97.0_0, s = 1.6_6$

$$95\% \text{ confidence interval} = \bar{x} \pm \frac{ts}{\sqrt{n}} = 97.0_0 \pm \frac{(2.776)(1.6_6)}{\sqrt{5}} = 97.0_0 \pm 2.0_6$$

Range = 94.94 to 99.06

The 95% confidence interval does not include the certified value of 94.6 ppm, so the difference is significant at the 95% confidence level.

If we make one more measurement, the results are $\bar{x} = 96.5_8, s = 1.8_0$

$$95\% \text{ confidence interval} = 96.5_8 \pm \frac{(2.571)(1.8_0)}{\sqrt{6}} = 96.5_8 \pm 1.8_9$$

Range = 94.69 to 98.47

The 95% confidence interval still does not include the certified value of 94.6 ppm, so the difference is still significant at the 95% confidence level.

4-22. (a) Rainwater:

$F_{\text{calculated}} = (0.008/0.005)^2 = 2.56 < F_{\text{table}} = 4.53$ (for 4 degrees of freedom in the numerator and 6 degrees of freedom in the denominator). Since $F_{\text{calculated}} < F_{\text{table}}$, we use the following equations:

$$s_{\text{pooled}} = \sqrt{\frac{0.005^2(6) + 0.008^2(4)}{7 + 5 - 2}} = 0.00637$$

$$t_{\text{calculated}} = \frac{0.069 - 0.063}{0.00637} \sqrt{\frac{7 \cdot 5}{7 + 5}} = 1.61 < t_{\text{table}} = 2.228$$

The difference is not significant.

Drinking water:

$F_{\text{calculated}} = (0.008/0.007)^2 = 1.31 < F_{\text{table}} = 6.39$ (for 4 degrees of freedom in the numerator and 4 degrees of freedom in the denominator).

Since $F_{\text{calculated}} < F_{\text{table}}$, we use the following equations:

$$s_{\text{pooled}} = \sqrt{\frac{0.007^2(4) + 0.008^2(4)}{5 + 5 - 2}} = 0.00752$$

$$t = \frac{0.087 - 0.078}{0.00752} \sqrt{\frac{5 \cdot 5}{5 + 5}} = 1.89 < 2.306. \text{ The difference is } \underline{\text{not}} \text{ significant.}$$

(b) Gas chromatography:

$$s_{\text{pooled}} = \sqrt{\frac{0.005^2(6) + 0.007^2(4)}{7+5-2}} = 0.00588$$

$$t = \frac{0.078 - 0.069}{0.00588} \sqrt{\frac{7 \cdot 5}{7+5}} = 2.61 > 2.228. \text{ The difference is significant.}$$

Spectrophotometry:

$$s_{\text{pooled}} = \sqrt{\frac{0.008^2(4) + 0.008^2(4)}{5+5-2}} = 0.00800$$

$$t = \frac{0.087 - 0.063}{0.00800} \sqrt{\frac{5 \cdot 5}{5+5}} = 4.74 > 2.306. \text{ The difference is significant.}$$

4-23. $\bar{x} = 201.8$; $s = 9.34$

$$G_{\text{calculated}} = |216 - 201.8| / 9.34 = 1.52$$

$G_{\text{table}} = 1.672$ for five measurements

Because $G_{\text{calculated}} < G_{\text{table}}$, we should retain 216.

4-24. Slope $= -1.29872 \times 10^4 (\pm 0.0013190 \times 10^4)$

$$= -1.299 (\pm 0.001) \times 10^4 \text{ or } -1.2987 (\pm 0.001_3) \times 10^4$$

$$\text{Intercept} = 256.695 (\pm 323.57) = 3 (\pm 3) \times 10^2$$

4-25.

x_i	y_i	$x_i y_i$	x_i^2	d_i	d_i^2
0	1	0	0	0.07143	0.00510
2	2	4	4	-0.21429	0.04592
3	3	9	9	0.14286	0.02041
sums: 5	6	13	13	0	0.07143

$$m = \frac{n \sum(x_i y_i) - \sum x_i \sum y_i}{n \sum(x_i^2) - (\sum x_i)^2} = \frac{3 \times 13 - 5 \times 6}{3 \times 13 - 5^2} = \frac{9}{14} = 0.64286$$

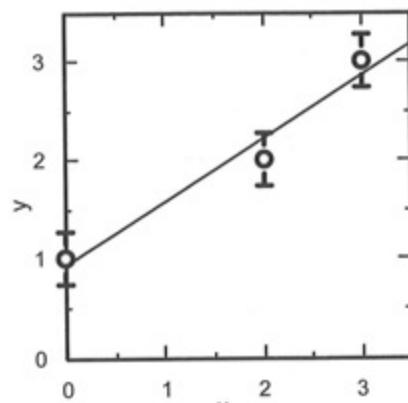
$$b = \frac{\sum(x_i^2) \sum y_i - \sum(x_i y_i) \sum x_i}{n \sum(x_i^2) - (\sum x_i)^2} = \frac{13 \times 6 - 13 \times 5}{3 \times 13 - 5^2} = \frac{13}{14} = 0.92857$$

$$s_y = \sqrt{\frac{\sum(d_i^2)}{n-2}} = \sqrt{\frac{0.07143}{3-2}} = 0.26726$$

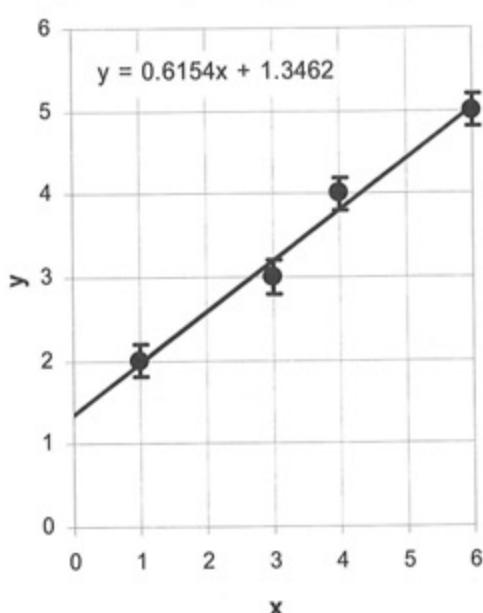
$$s_m = s_y \sqrt{\frac{n}{D}} = (0.26726) \sqrt{\frac{3}{14}} = 0.12371$$

$$s_b = s_y \sqrt{\frac{\sum(x_i^2)}{D}} = (0.26726) \sqrt{\frac{13}{14}} \\ = 0.25754$$

$$\text{slope} = 0.64 \pm 0.12 \quad \text{intercept} = 0.93 \pm 0.26$$

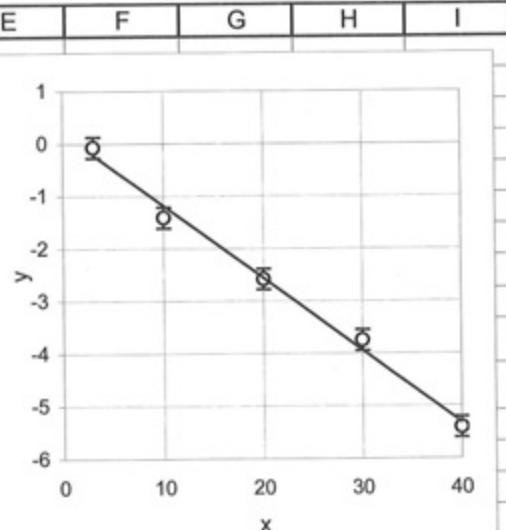


4-26.



4-27.

	A	B	C	D	E	F	G	H	I
1	x	y							
2	3.0	-0.074							
3	10.0	-1.411							
4	20.0	-2.584							
5	30.0	-3.750							
6	40.0	-5.407							
7									
8		LINEST output							
9	m	-0.13789	0.195343	b					
10	s _m	0.006635	0.162763	s _b					
11	R ²	0.993102	0.197625	s _y					
12									
13	Highlight cells B9:C11								
14	Type								
15	"=LINEST(B2:B6,A2:A6,TRUE,TRUE)"								
16	Press CTRL+SHIFT+ENTER (on PC)								
17	Press COMMAND+RETURN (on Mac)								



- 4-28.** We must measure how an analytical procedure responds to a known quantity of analyte (or a known quantity of a related compound) before the procedure can be used for an unknown. Therefore, we must be able to measure out the analyte (or a related compound) in pure form to use as a calibration standard.
- 4-29.** Hopefully, the negative value is within experimental error of 0. If so, no detectable analyte is present. If the negative concentration is beyond experimental error, there is something wrong with your analysis. The same is true for a value above 100% of the theoretical maximum concentration of an analyte. Another possible way to get values below 0 or above 100% is if you extrapolated the calibration curve past the range covered by standards, and the curve is not linear.

4-30. Corrected absorbance = $0.264 - 0.095 = 0.169$

Equation of line: $0.169 = 0.01630x + 0.0047 \Rightarrow x = 10.1 \mu\text{g}$

4-31. (a) $x = \frac{y-b}{m} = \frac{2.58 - 1.35}{0.615} = 2.00$

$$\bar{y} = (2 + 3 + 4 + 5)/4 = 3.5 \quad \bar{x} = (1 + 3 + 4 + 6)/4 = 3.5$$

$$\Sigma(x_i - \bar{x})^2 = (1 - 3.5)^2 + (3 - 3.5)^2 + (4 - 3.5)^2 + (6 - 3.5)^2 = 13.0$$

$$s_x = \frac{s_y}{|m|} \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y - \bar{y})^2}{m^2 \sum(x_i - \bar{x})^2}}$$

$$= \frac{0.19612}{|0.61538|} \sqrt{\frac{1}{4} + \frac{1}{4} + \frac{(2.58 - 3.5)^2}{(0.61538)^2 (13.0)}} = 0.38$$

Answer: 2.00 ± 0.38

(b) For $k = 4$ replicate measurements,

$$s_x = \frac{s_y}{|m|} \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y - \bar{y})^2}{m^2 \sum(x_i - \bar{x})^2}}$$

$$= \frac{0.19612}{|0.61538|} \sqrt{\frac{1}{4} + \frac{1}{4} + \frac{(2.58 - 3.5)^2}{(0.61538)^2 (13.0)}} = 0.26$$

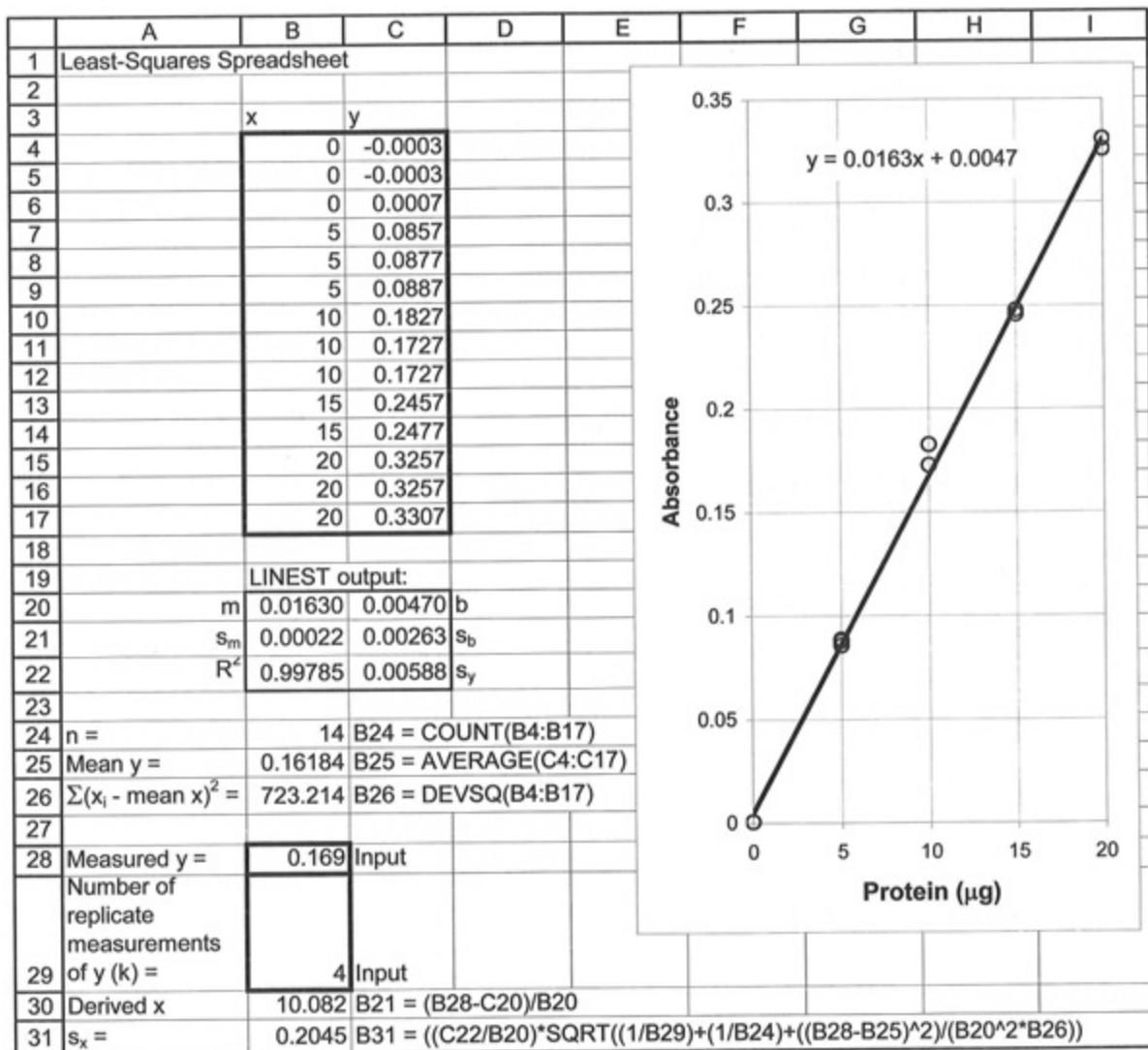
Answer: 2.00 ± 0.26

$$4-32. \text{ Mean absorbance} = (0.265 + 0.269 + 0.272 + 0.258)/4 = 0.266_0$$

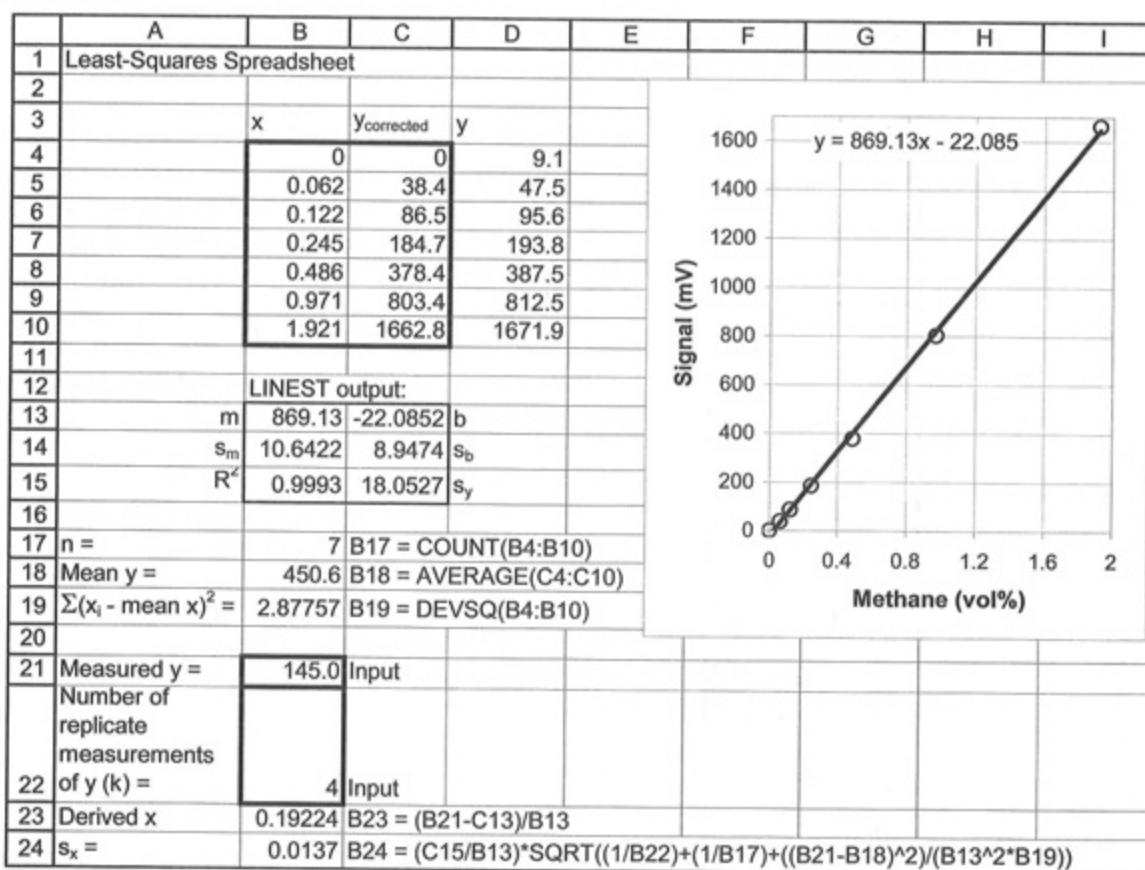
$$\text{Mean blank: } (0.099 + 0.091 + 0.101 + 0.097)/4 = 0.097_0$$

$$\Rightarrow \text{Corrected absorbance} = 0.266_0 - 0.097_0 = 0.169_0$$

Cells B30 and B31 of the spreadsheet show that there are $10.1 \pm 0.2 \mu\text{g}$ protein.



4-33. (a)



(b) Corrected signal = 154.0 - 9.0 = 145.0 mV

(c) Cells B23 and B24 give [CH₄] = 0.19₂ (± 0.014) vol%

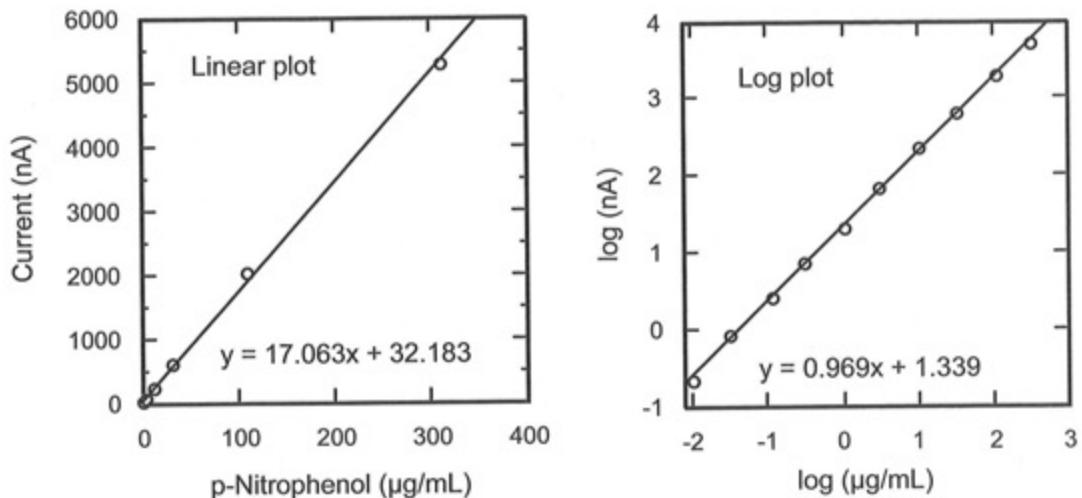
4-34. $0.350 = -1.17 \times 10^{-4} x^2 + 0.01858 x - 0.0007$

$1.17 \times 10^{-4} x^2 - 0.01858 x + 0.3507 = 0$

$x = \frac{+0.01858 \pm \sqrt{0.01858^2 - 4(1.17 \times 10^{-4})(0.3507)}}{2(1.17 \times 10^{-4})} = 137 \text{ or } 21.9 \mu\text{g}$

Correct answer is 21.9 μg .

4-35. (a) The logarithmic graph spreads out the data and is linear over the entire range.



(b) $\log(\text{current, nA}) = 0.969 \cdot 2 \log(\text{concentration, } \mu\text{g/mL}) + 1.339$

(c) $\log(99.9) = 0.969 \cdot 2 \log[X] + 1.339$

$$\Rightarrow \log[X] = 0.6816 \Rightarrow [X] = 4.80 \mu\text{g/mL}$$

4-36. For 8 degrees of freedom, $t_{90\%} = 1.860$ and $t_{99\%} = 3.355$.

$$90\% \text{ confidence interval: } 15.2_2 (\pm 1.860 \times 0.4_6) = 15.2_2 \pm 0.86 \mu\text{g}$$

$$99\% \text{ confidence interval: } 15.2_2 (\pm 3.355 \times 0.4_6) = 15.2 \pm 1.5 \mu\text{g}$$

CHAPTER 5

QUALITY ASSURANCE AND CALIBRATION METHODS

- 5-1. Get the right data: Measure what is relevant to the question at hand.
Get the data right: Sampling and analytical procedures must be satisfactory to measure what we intend to measure.
Keep the data right: Record keeping should document that samples were collected properly and data has demonstrated reliability.
- 5-2. The three parts of quality assurance are defining use objectives, setting specifications, and assessing results.
- Use objectives:*
- Question: Why do I want the data and results and how will I use them?
- Actions: Write use objectives.
- Specifications:*
- Question: How good do the numbers have to be?
- Actions: Write specifications and pick an analytical method to meet the specifications. Consider requirements for sampling, precision, accuracy, selectivity, sensitivity, detection limit, robustness, and allowed rate of false results. Plan to employ blanks, fortification, calibration checks, quality control samples, and control charts. Write and follow standard operating procedures.
- Assessment:*
- Question: Did I meet the specifications?
- Actions: Compare data and results with specifications. Document procedures and keep records suitable for meeting use objectives. Verify that the use objectives were met.
- 5-3. *Precision* is demonstrated by the repeatability of analyses of replicate samples and replicate portions of the same sample. Accuracy is demonstrated by analyzing certified reference materials, by comparing results from different analytical methods, by fortification (spike) recovery, by standard additions, by calibration checks, blanks, and quality control samples (blind samples).
- 5-4. *Raw data* are directly measured quantities, such as peak area in a chromatogram or volume from a buret. *Treated data* are concentrations or amounts found by applying a calibration method to the raw data. *Results*, such as the mean and standard deviation, are what we ultimately report after applying statistics to treated data.

- 5-5. A calibration check is an analysis of a solution *formulated by the analyst* to contain a known concentration of analyte. It is the analyst's own check that procedures and instruments are functioning correctly. A performance test sample is an analysis of a solution *formulated by someone other than the analyst* to contain a known concentration of analyte. It is a test to see if the analyst gets the right answer when he or she does not know the right answer.
- 5-6. A blank is a sample intended to contain no analyte. Positive response to the blank arises from analyte impurities in reagents and equipment and from interference by other species. A method blank is taken through all steps in a chemical analysis. A reagent blank is the same as a method blank, but it has not been subjected to all sample preparation procedures. A field blank is similar to a method blank, but it has been taken into the field and exposed to the same environment as samples collected in the field and transported to the lab.
- 5-7. Linear range is the analyte concentration interval over which the analytical signal is proportional to analyte concentration. Dynamic range is the concentration range over which there is a useable response to analyte, even if it is not linear. Range is the analyte concentration interval over which an analytical method has specified linearity, accuracy, and precision.
- 5-8. A false positive is a conclusion that analyte exceeds a certain limit when, in fact, it is below the limit. A false negative is a conclusion that analyte is below a certain limit when, in fact, it is above the limit.
- 5-9. ~1% of the area under the curve for blanks lies to the right of the detection limit. Therefore, ~1% of samples containing no analyte will give a signal above the detection limit. 50% of the area under the curve for samples containing analyte at the detection limit lies below the detection limit. Therefore, 50% of samples containing analyte at the detection limit will be reported as not containing analyte at a level above the detection limit.
- 5-10. A control chart tracks the performance of a process to see if it remains within expected bounds. Six indications that a process might be out of control are (1) a reading outside the action lines, (2) 2 out of 3 consecutive readings between the warning and action lines, (3) 7 consecutive measurements all above or all below the center line, (4) six consecutive measurements, all steadily increasing or all

steadily decreasing, wherever they are located, (5) 14 consecutive points alternating up and down, regardless of where they are located, and (6) an obvious nonrandom pattern.

- 5-11.** Statement (c) is correct. The purpose of the analysis is to see if concentrations are in compliance with (in other words, do not exceed) levels set by a certain rule.
- 5-12.** The *instrument detection limit* is obtained by replicate measurements of aliquots from one sample. The *method detection limit* is obtained by preparing and analyzing many independent samples. There is more variability in the latter procedure, so the method detection limit should be higher than the instrument detection limit.

Robustness is the ability of an analytical method to be unaffected by small, deliberate changes in operating parameters. *Intermediate precision* is the variation observed when an assay is performed by different people on different instruments on different days in the same lab. Each analysis might incorporate independently prepared reagents and different lots of the same chromatography column from one manufacturer. When demonstrating intermediate precision, experimental conditions are intended to be the same in each analysis. When measuring robustness, conditions are intentionally varied by small amounts.

- 5-13.** *Instrument precision*, also called *injection precision*, is the reproducibility observed when the same quantity of one sample is repeatedly introduced into an instrument.

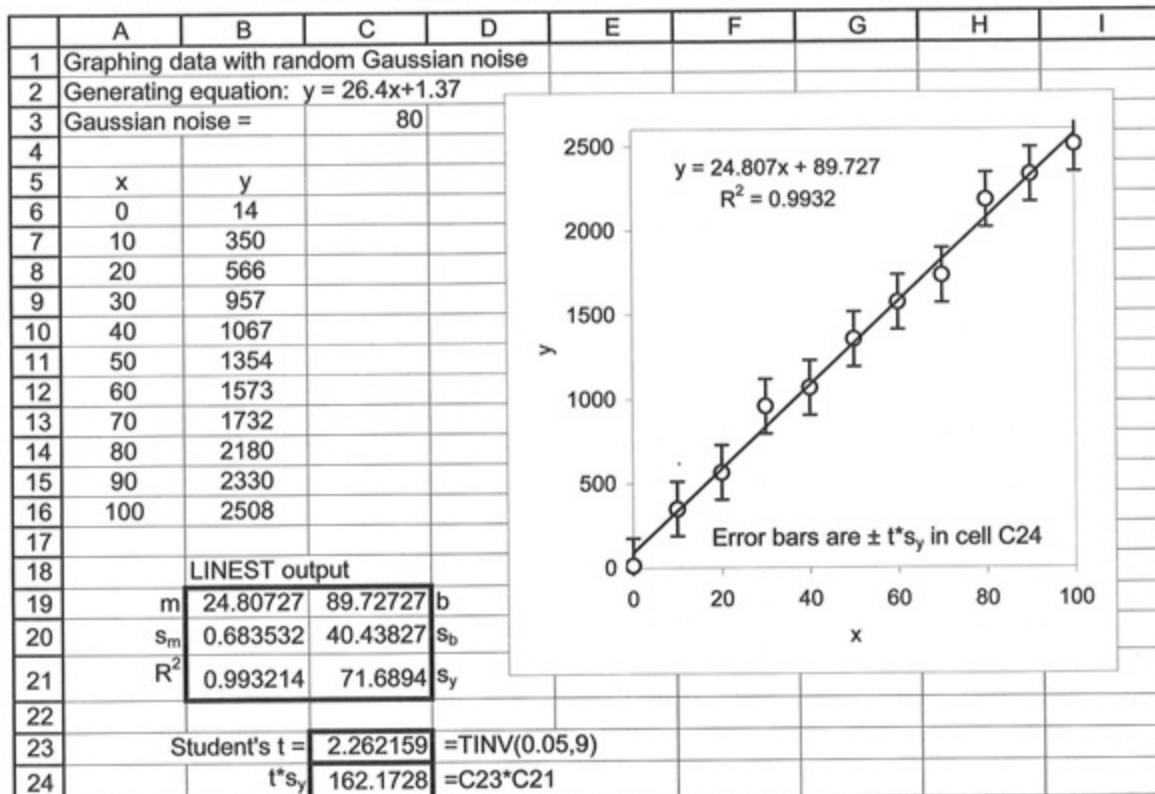
Intra-assay precision is evaluated by analyzing aliquots of a homogeneous material several times by one person on one day with the same equipment.

Intermediate precision is the variation observed when an assay is performed by different people on different instruments on different days in the same lab.

Interlaboratory precision is the reproducibility observed when aliquots of the same sample are analyzed by different people in different laboratories at different times using equipment and reagents belonging to each lab.

- 5-14.** Criteria:
- Observations outside action lines — no
 - 2 out of 3 consecutive measurements between warning and action lines — no

- 7 consecutive measurements all above or all below the center line — YES:
observations 2-10 (starting from the left side) are all below the center line
 - 6 consecutive measurements steadily increasing or steadily decreasing — no
 - 14 consecutive points alternating up and down — no
 - Obvious nonrandom pattern — no
- 5-15.** LINEST gives m , b , s_m , s_b , R^2 , and s_y in cells B19:C21. TRENDLINE produces the same value of m , b , and R^2 , which are printed inside the graph. The 95% confidence interval for y is computed in cell C24.



- 5-16.** (a) For the fortification level of 22.2 ng/mL, the mean of the 5 values is 23.66 ng/mL and the standard deviation is 5.63 ng/mL.

$$\text{Precision} = 100 \times \frac{5.63}{23.66} = 23.8\%.$$

$$\text{Accuracy} = 100 \times \frac{23.66 - 22.2}{22.2} = 6.6\%$$

For the fortification level of 88.2 ng/mL, the mean of the 5 values is 82.48 ng/mL and the standard deviation is 11.49 ng/mL.

$$\text{Precision} = 100 \times \frac{11.49}{82.48} = 13.9\%.$$

$$\text{Accuracy} = 100 \times \frac{82.48 - 88.2}{88.2} = -6.5\%$$

For the fortification level of 314 ng/mL, the mean of the 5 values is 302.8 ng/mL and the standard deviation is 23.51 ng/mL.

$$\text{Precision} = 100 \times \frac{23.51}{302.8} = 7.8\%.$$

$$\text{Accuracy} = 100 \times \frac{302.8 - 314}{314} = -3.6\%$$

- (b) Standard deviation of 10 samples: $s = 28.2$; mean blank: $y_{\text{blank}} = 45.0$
 Signal detection limit = $y_{\text{blank}} + 3s = 45.0 + (3)(28.2) = 129.6$

$$\text{Concentration detection limit} = \frac{3s}{m} = \frac{(3)(28.2)}{1.75 \times 10^9 \text{ M}^{-1}} = 4.8 \times 10^{-8} \text{ M}$$

$$\text{Lower limit of quantitation} = \frac{10s}{m} = \frac{(10)(28.2)}{1.75 \times 10^9 \text{ M}^{-1}} = 1.6 \times 10^{-7} \text{ M}$$

- 5-17.** (a) $1 \text{ wt\%} \Rightarrow C = 0.01$: $\text{CV}(\%) \approx 2^{(1-0.5 \log 0.01)} = 2^2 = 4\%$
 If $C = 10^{-12}$, $\text{CV}(\%) \approx 2^7 = 128\%$.
 (b) If class CV is 50% of the value given by the Horwitz curve, it would be $0.5 \times 2^{(1-0.5 \log 0.1)} = 1.4\%$.

- 5-18.** Mean = 0.383 $\mu\text{g/L}$ and standard deviation = 0.0214 $\mu\text{g/L}$

$$\% \text{ recovery} = \frac{0.383 \mu\text{g/L}}{0.40 \mu\text{g/L}} \times 100 = 96\%$$

The measurements are already expressed in concentration units. The concentration detection limit is 3 times the standard deviation = $3(0.0214 \mu\text{g/L}) = 0.064 \mu\text{g/L}$.

- 5-19.** The low concentration of Ni-EDTA has a standard deviation of 28.2 counts for 10 measurements. The detection limit is estimated to be

$$y_{\text{dl}} = y_{\text{blank}} + 3s = 45 + 3(28.2) = 129.6 \text{ counts}$$

To convert counts to molarity, we note that a 1.00 μM solution gave a net signal of $1797 - 45 = 1752$ counts. The slope of the calibration curve is therefore estimated to be

$$m = \frac{y_{\text{sample}} - y_{\text{blank}}}{\text{sample concentration}} = \frac{1797 - 45}{1.00 \mu\text{M}} = 1.752 \times 10^9 \frac{\text{counts}}{\text{M}}$$

The minimum detectable concentration is

$$\frac{3s}{m} = \frac{(3)(28.2) \text{ counts}}{1.75_2 \times 10^9 \text{ counts/M}} = 4.8 \times 10^{-8} \text{ M}$$

- 5-20.** For a concentration of 0.2 µg/L, the relative standard deviation of 14.4% corresponds to $(0.144)(0.2 \text{ } \mu\text{g/L}) = 0.0288 \text{ } \mu\text{g/L}$. The detection limit is $3(0.0288 \text{ } \mu\text{g/L}) = 0.086 \text{ } \mu\text{g/L}$. Here are the results for the other concentrations:

Concentration (µg/L)	Relative standard deviation (%)	Concentration standard deviation (µg/L)	Detection limit (µg/L)
0.2	14.4	0.0288	0.086
0.5	6.8	0.0340	0.102
1.0	3.2	0.0320	0.096
2.0	1.9	0.0380	<u>0.114</u>
mean detection limit: 0.10			

- 5-21.** If an athlete tests positive for drugs, the test should be repeated with a second sample that was drawn at the same time as the first sample and preserved in an appropriate manner. If there is a 1% chance of a false positive in each test, the chances of observing a false positive twice in a row are 1% of 1% or 0.01%. Instead of falsely accusing 1% of innocent athletes, we would be falsely accusing 0.01% of innocent athletes.

- 5-22.** *Comparison of Lab C with Lab A:*

First, use the *F* test to see if the standard deviations are significantly different:

$F_{\text{calculated}} = s_C^2/s_A^2 = 0.78^2/0.14^2 = 31.0 > F_{\text{table}} = 3.88$ (with 2 degrees of freedom for s_C and 12 degrees of freedom for s_A)

Standard deviations are not equivalent, so use the following *t* test:

$$\text{Degrees of freedom} = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\frac{(s_1^2/n_1)^2}{n_1 - 1} + \frac{(s_2^2/n_2)^2}{n_2 - 1}} = \frac{(0.14^2/13 + 0.78^2/3)^2}{\frac{(0.14^2/13)^2}{13 - 1} + \frac{(0.78^2/3)^2}{3 - 1}} = 2.03 \approx 2$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} = \frac{|1.59 - 2.68|}{\sqrt{0.14^2/13 + 0.78^2/3}} = 2.41$$

For 2 degrees of freedom, $t_{\text{table}} = 4.303$ for 95% confidence. Since $t_{\text{calculated}} < t_{\text{table}}$, we conclude that the difference between Lab C and Lab A is not significant.

Comparison of Lab C with Lab B:

$F_{\text{calculated}} = s_C^2/s_B^2 = 0.78^2/0.56^2 = 1.94 < F_{\text{table}} = 4.74$ (with 2 degrees of freedom for s_C and 7 degrees of freedom for s_A). The standard deviations are not significantly different, so we use the following t test:

$$s_{\text{pooled}} = \sqrt{\frac{0.56^2(8-1) + 0.78^2(3-1)}{8+3-2}} = 0.616$$

$$t_{\text{calculated}} = \frac{|1.65 - 2.68|}{0.616} \sqrt{\frac{8 \cdot 3}{8+3}} = 2.47$$

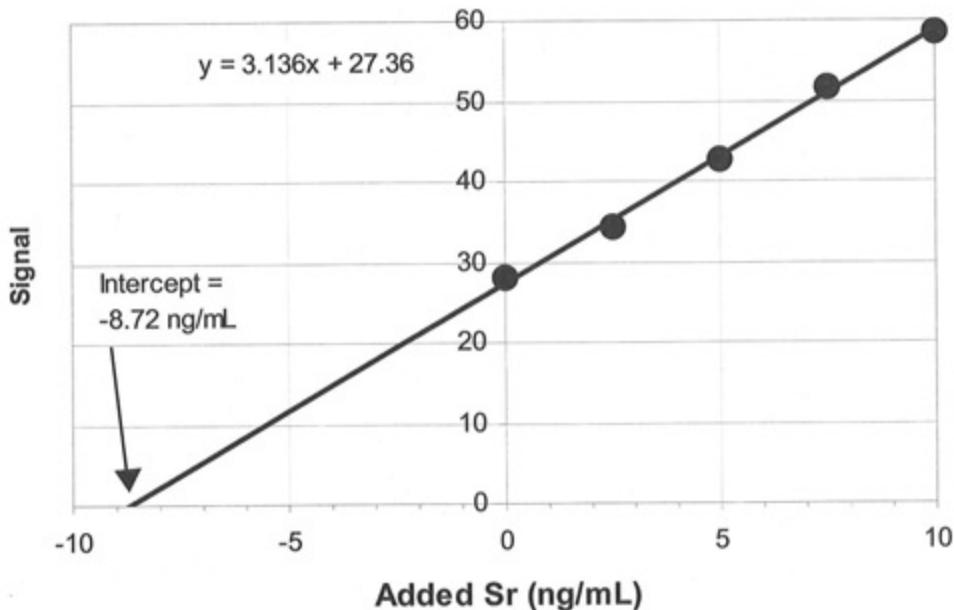
$t_{\text{table}} = 2.262$ for 95% confidence and $8+3-2 = 9$ degrees of freedom.

$t_{\text{calculated}} > t_{\text{table}}$, so the difference is significant at the 95% confidence level.

It makes no sense to conclude that Lab C [2.68 ± 0.78 (3)] > Lab B [1.65 ± 0.56 (8)], but Lab C = Lab A [1.59 ± 0.14 (13)]. The problem with the comparison of Labs C and A is that the standard deviation of C is much greater than the standard deviation of A and the number of replicates for C is much less than the number of replicates for A. The result is that we used a large composite standard deviation and a small composite number of degrees of freedom. The conclusion is biased by a large standard deviation and a small number of degrees of freedom. I would tentatively conclude that results from Lab C are greater than results from Labs B and A. I would also ask for more replicate results from Lab C. With just 3 replications, it is hard to reach any statistically significant conclusions.

- 5-23. A small volume of standard will not change the sample matrix very much, so matrix effects remain nearly constant. If large, variable volumes of standard are used, the matrix is different in every mixture and the matrix effects will be different in every sample.
- 5-24. (a) $[\text{Cu}^{2+}]_f = [\text{Cu}^{2+}]_i \frac{V_i}{V_f} = 0.950 [\text{Cu}^{2+}]_i$
- (b) $[\text{S}]_f = [\text{S}]_i \frac{V_i}{V_f} = (100.0 \text{ ppm}) \left(\frac{1.00 \text{ mL}}{100.0 \text{ mL}} \right) = 1.00 \text{ ppm}$
- (c) $\frac{[\text{Cu}^{2+}]_i}{1.00 \text{ ppm} + 0.950[\text{Cu}^{2+}]_i} = \frac{0.262}{0.500} \Rightarrow [\text{Cu}^{2+}]_i = 1.04 \text{ ppm}$

- 5-25.** (a) All solutions were made up to the same final volume. Therefore, we prepare a graph of signal versus concentration of added standard. The line in the graph was drawn by the method of least squares with the following spreadsheet. The x -intercept, 8.72 ppb, is the concentration of unknown in the 10-mL solution. In cell B27 of the spreadsheet (on the next page), we find the standard deviation of the x -intercept to be 0.427 ppm. A reasonable answer is 8.72 ± 0.43 ppb.



- (b) Unknown solution volume = 10.0 mL with Sr = 8.72 ppb = 8.72 ng/mL. In 10.0 mL, there are $(10 \text{ mL})(8.72 \text{ ng/mL}) = 87.2 \text{ ng}$. Solution was made from 0.750 mg of tooth enamel. Sr (ppm) in tooth enamel is

$$\begin{aligned} \text{Concentration (ppm)} &= \frac{\text{mass of Sr}}{\text{mass of enamel}} \times 10^6 \\ &= \frac{87.2 \times 10^{-9} \text{ g}}{0.750 \times 10^{-3} \text{ g}} \times 10^6 = 116 \text{ ppm} \end{aligned}$$

- (c) Relative uncertainty of intercept is $100 \times 0.43/8.72 = 4.9\%$, which leads to a 4.9% uncertainty in the concentration of Sr in the tooth enamel. $0.049 \times 116 \text{ ppm} = 5.7 \text{ ppm}$. Final answer: $116 \pm 6 \text{ ppm}$.
- (d) Student's t for $n - 2 = 5 - 2 = 3$ degrees of freedom and 95% confidence is 3.182. We found standard deviation = 5.7 ppm. 95% confidence interval is $\pm ts = (3.182)(5.7 \text{ ppm}) = 18.1 \text{ ppm}$. Answer: $116 \pm 18 \text{ ppm}$.

Spreadsheet for 5-25 (a). To execute LINEST, highlight cells B16-C18, enter “=LINEST(B7:B11,A7:A11,TRUE,TRUE”, and press CONTROL + SHIFT + ENTER on a PC or COMMAND(⌘) + RETURN on a Mac.

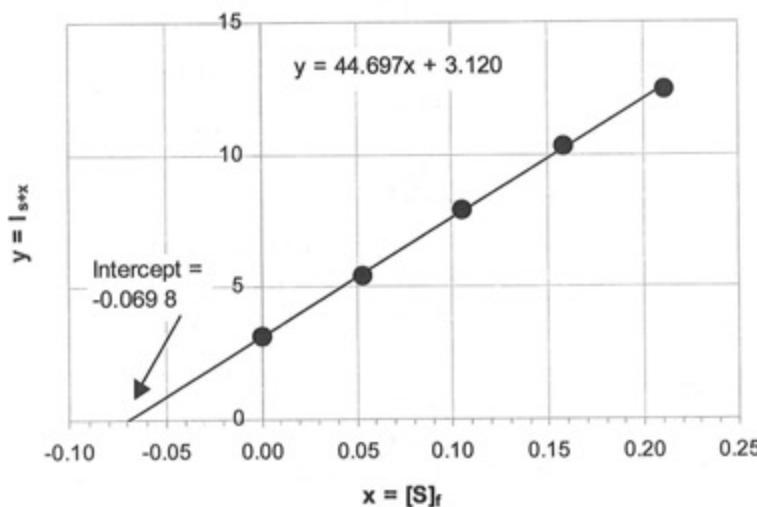
	A	B	C	D	E
1	Standard Addition Constant Volume Least-Squares Spreadsheet				
2					
3					
4	x	y			
5	Added Sr				
6	(ng/mL)	Signal			
7	0.00	28.000			
8	2.50	34.300			
9	5.00	42.800			
10	7.50	51.500			
11	10.00	58.600			
12					
13	B16:C18 = LINEST(B7:B11,A7:A11,TRUE,TRUE)				
14					
15		LINEST output:			
16	m	3.1360	27.3600	b	
17	s _m	0.0945	0.5790	s _b	
18	R ²	0.9973	0.7474	s _y	
19					
20	x-intercept = -b/m =	-8.724			
21					
22	n =	5	B22 = COUNT(A7:A11)		
23	Mean y =	43.040	B23 = AVERAGE(B7:B11)		
24	$\sum(x_i - \text{mean } x)^2 =$	62.5	B24 = DEVSQ(A7:A11)		
25					
26	Std deviation of				
27	x-intercept =	0.427			
28	B27 = (C18/ABS(B16))*SQRT((1/B22) + B23^2/(B16^2*B24))				

- 5-26. (a) The intercept for tap water is -6.0 mL , corresponding to an addition of $(6.0 \text{ mL})(0.152 \text{ ng/mL}) = 0.912 \text{ ng Eu(III)}$. This much Eu(III) is in 10.00 mL of tap water, so the concentration is $0.912 \text{ ng}/10.00 \text{ mL} = 0.091 \text{ ng/mL}$. For pond water, the intercept of -14.6 mL corresponds to an addition of $(14.6 \text{ mL})(15.2 \text{ ng/mL}) = 2.22 \times 10^2 \text{ ng}/10.00 \text{ mL pond water} = 22.2 \text{ ng/mL}$.
- (b) Added standard Eu(III) gives a response of 3.03 units/ng for tap water and 0.0822 units/ng for pond water. The relative response is $3.03/0.0822 = 36.9$ times greater in tap water than in pond water. There is probably a *matrix effect* in which something in pond water decreases the Eu(III) emission. By using standard addition, we measure the response in the actual sample matrix. Even though Eu(III) in pond water and tap water do not give equal

signals, we measure the actual signal in each matrix and can therefore carry out accurate analyses.

5-27.

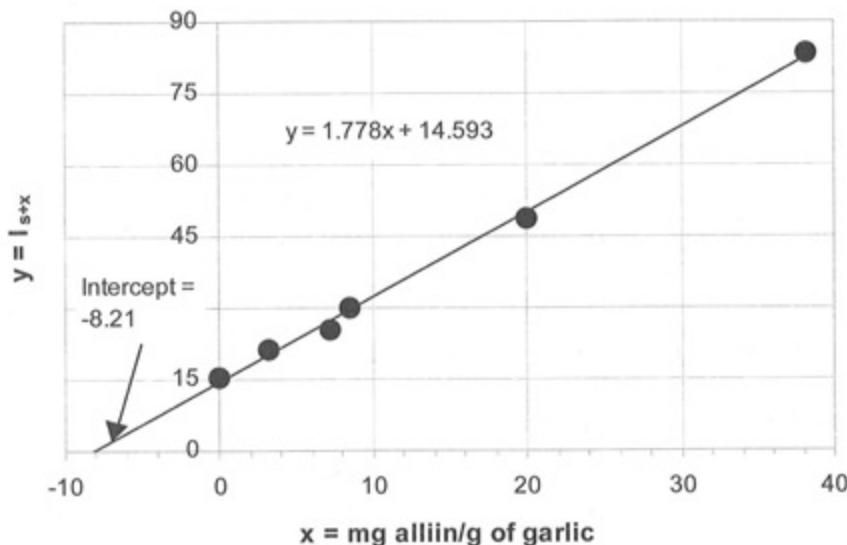
	A	B	C	D
1	Standard Addition Constant Volume Least-Squares Spreadsheet			
2				
3	$V_{\text{total}} =$	$V_s \text{ (mL)} =$	x	y
4	50	NaCl	Concentration of	
5	[S] _i (M) =	standard	added NaCl	$I(s+x) =$
6	2.64	added	[S] _r	signal
7	$V_0 =$	0.000	0	3.13
8	25.00	1.000	0.0528	5.40
9		2.000	0.1056	7.89
10		3.000	0.1584	10.30
11		4.000	0.2112	12.48
12	$C7 = \$A\$6*B7/\$A\4			
13	$B16:D18 = \text{LINEST}(E7:E11,C7:C11,TRUE,TRUE)$			
14				
15		LINEST output:		
16	m	44.6970	3.1200	b
17	s_m	0.5511	0.0713	s_b
18	R^2	0.9995	0.0920	s_y
19				
20	x-intercept = $-b/m =$	-0.06980		
21				
22	n =	5	$B22 = \text{COUNT}(B7:B11)$	
23	Mean y =	7.84	$B23 = \text{AVERAGE}(E7:E11)$	
24	$\sum(x_i - \text{mean } x)^2 =$	0.0278784	$B24 = \text{DEVSQ}(C7:C11)$	
25				
26	Std deviation of			
27	x-intercept =	0.00235		
28	$B27 = (C18/ABS(B16)) * \text{SQRT}((1/B22) + B23^2/(B16^2 * B24))$			



- (a) All solutions are made to constant volume, so we plot I_{S+x} vs. $[S]_f$. The negative intercept is $[X]_f = 0.069\text{8 M}$. The initial concentration of NaCl is larger by the dilution factor of 2 ($50.00\text{ mL}/25.00\text{ mL}$). The initial concentration of NaCl in serum was $2.000 \times 0.069\text{8 M} = 0.013\text{96 M}$.
- (b) The x -intercept is computed in cell B20 and its uncertainty in cell B27. The relative uncertainty is $(0.002\text{35})/(0.069\text{8}) = 3.37\%$. This uncertainty is much larger than the relative uncertainties in volume measurement, so the uncertainty in the original concentration of Na^+ should be 3.37%. A reasonable expression of $[\text{Na}^+]$ in the original serum is $0.140 (\pm 3.37\%) \text{ M} = 0.140 (\pm 0.004_7) \text{ M}$.
- 95% confidence interval = $\pm ts = \pm (3.182)(0.004_7 \text{ M}) = \pm 0.015 \text{ M}$, where t is taken for $5 - 2 = 3$ degrees of freedom.

5-28.

	A	B	C	D
1	Standard Addition Constant Volume Least-Squares Spreadsheet			
2				
3		x	y	
4		Spike (mg/g)	$I(s+x) =$	
5		$[S]_f$	signal	
6		0.00	15.6	
7		3.12	21.1	
8		7.18	25.5	
9		8.48	30.0	
10		20.0	48.8	
11		38.2	83.4	
12				
13	B16:D18 = LINEST(C6:C11,B6:B11,TRUE,TRUE)			
14				
15		LINEST output:		
16	m	1.7776	14.5928	b
17	s_m	0.0449	0.8190	s_b
18	R^2	0.9974	1.4246	s_y
19				
20	$x\text{-intercept} = -b/m =$	-8.20906		
21				
22	n =		6	B22 = COUNT(B6:B11)
23	Mean y =		37.40	B23 = AVERAGE(C6:C11)
24	$\sum(x_i - \text{mean } x)^2 =$	1004.7838	B24 = DEVSQ(B6:B11)	
25				
26	Std deviation of			
27	$x\text{-intercept} =$	0.62445		
28	B27 = (C18/ABS(B16))*SQRT((1/B22) + B23^2/(B16^2*B24))			



- (a) In cells B20 and B27 of the spreadsheet, the negative x -intercept of the standard addition graph is $8.21 \pm 0.62 \text{ mg alliin/g garlic}$.
- (b) Two moles of alliin (FM 177.2) produce one mole of allicin (FM 162.3) in the assay. Therefore, the quantity of allicin in garlic is $\frac{1}{2}(162.3/177.2)(8.21 \pm 0.62 \text{ mg/g}) = 3.76 \pm 0.28 \text{ mg allicin/g garlic or } 3.8 \pm 0.3 \text{ mg allicin/g garlic}$.
- 5-29. Standard addition is appropriate when the sample matrix is unknown or complex and hard to duplicate, and unknown matrix effects are anticipated. An internal standard can be added to an unknown at the start of a procedure in which uncontrolled losses of sample will occur. The relative amounts of unknown and standard remain constant. The internal standard is excellent if instrument conditions vary from run to run. Variations affect the analyte and standard equally, so the relative signal remains constant. In chromatography the amount of sample injected into the instrument is very small and not very reproducible. However, the relative quantities of standard and analyte remain constant regardless of the sample size.
- 5-30. (a) $\frac{A_X}{[X]} = F \left(\frac{A_S}{[S]} \right) \Rightarrow \frac{3.473}{[3.47 \text{ mM}]} = F \left(\frac{10.222}{[1.72 \text{ mM}]} \right) \Rightarrow F = 0.1684$
- (b) $[S] = (8.47 \text{ mM}) \left(\frac{1.00 \text{ mL}}{10.0 \text{ mL}} \right) = 0.847 \text{ mM}$
- (c) $\frac{A_X}{[X]} = F \left(\frac{A_S}{[S]} \right) \Rightarrow \frac{5.428}{[X]} = 0.1684 \left(\frac{4.431}{[0.847 \text{ mM}]} \right) \Rightarrow [X] = 6.16 \text{ mM}$

- (d) The original concentration of [X] was twice as great as the diluted concentration, so $[X] = 12.3 \text{ mM}$.

- 5-31.** For the standard mixture:

$$\frac{A_X}{[X]} = F \left(\frac{A_S}{[S]} \right) \Rightarrow \frac{10.1 \mu\text{A}}{[0.800 \text{ mM}]} = F \left(\frac{15.3 \mu\text{A}}{[0.500 \text{ mM}]} \right) \Rightarrow F = 0.4126$$

Chloroform added to unknown = $(10.2 \times 10^{-6} \text{ L})(1484 \text{ g/L}) = 0.01514 \text{ g} = 0.1268 \text{ mmol}$ in $0.100 \text{ L} = 1.268 \text{ mM}$

For the unknown mixture:

$$\frac{A_X}{[X]} = F \left(\frac{A_S}{[S]} \right) \Rightarrow \frac{8.7 \mu\text{A}}{[X]} = 0.4126 \left(\frac{29.4 \mu\text{A}}{[1.268 \text{ mM}]} \right) \Rightarrow [X] = 0.909 \text{ mM}$$

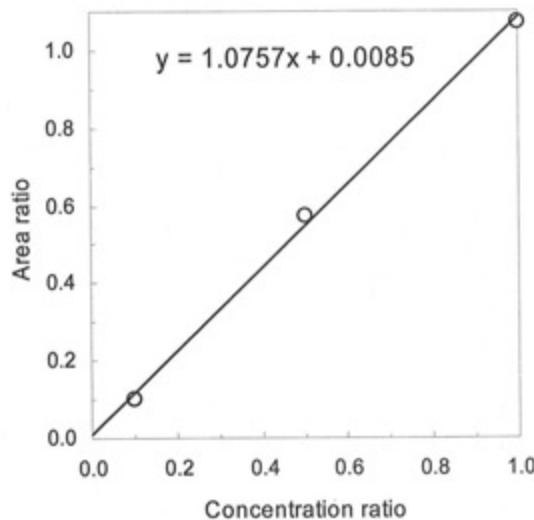
$$[\text{DDT}] \text{ in unknown} = (0.909 \text{ mM}) \left(\frac{100 \text{ mL}}{10.0 \text{ mL}} \right) = 9.09 \text{ mM}$$

- 5-32.** Data in the following table are plotted in the accompanying graph. If the equation

$$\frac{\text{area of analyte signal}}{\text{area of standard signal}} = F \left(\frac{\text{concentration of analyte}}{\text{concentration of standard}} \right)$$

is obeyed, the graph should be a straight line going through the origin, which it is. The slope, 1.0757 , is the response factor. Over the concentration ratio analyte/standard = 0.10 to 1.00, the standard deviation of the response factor in the table is $0.0668 = 6.2\%$.

Sample	Concentration ratio $C_{10}\text{H}_8/C_{10}\text{D}_8$	Area ratio $C_{10}\text{H}_8/C_{10}\text{D}_8$	$F =$ area ratio/conc. ratio
1	0.10	0.101	1.01 ₂₇
2	0.50	0.573	1.14 ₆₁
3	1.00	1.072	1.07 ₂₄
mean = 1.07 ₅₇			
standard deviation 0.0668			
relative standard deviation 6. ₂ %			



- 5-33. To use the internal standard, a known quantity of internal standard is added to a sample of sewage. Analyte signal is measured relative to the signal from internal standard. Since the internal standard is so similar to analyte (differing only by the substitution of D for H), matrix effects are likely to be essentially identical for both compounds. If matrix enhances the response to analyte, it enhances the response to internal standard to the same extent. By measuring unknown relative to the known injection of standard, an accurate measurement of unknown can be made. The key is to use a standard that is almost identical to the analyte in physical properties.

- 5-34. Molarities are given in row 12 of the following spreadsheet and uncertainties are given in row 13:

	A	B	C	D	E
1	Experimental Design				
2					
3	Volumes of unknown acids (mL)		mmol		
4	A	B	C	NaOH	
5	2	2	2	3.015	
6	0	2	2	1.385	
7	2	0	2	2.180	
8	2	2	0	2.548	
9	2	2	2	3.140	
10					
11		[C]	[B]	[A]	
12	Molarity	0.25635	0.44035	0.83785	
13	Std. dev.	0.026729	0.026729	0.026729	
14		0.995942	0.063896	#N/A	
15		R ²	s _y		
16	Highlight cells C12:E14				
17	Type "=LINEST(D5:D9,A5:C9, FALSE, TRUE)"				
18	Press CTRL+SHIFT+ENTER (on PC)				
19	Press COMMAND+RETURN (on Mac)				

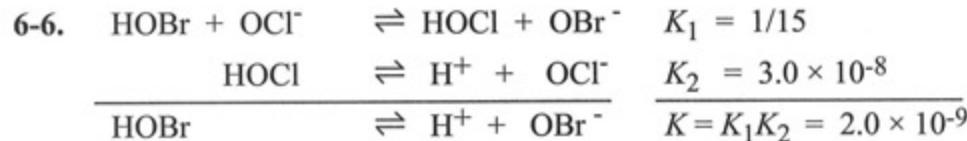
CHAPTER 6

CHEMICAL EQUILIBRIUM

- 6-1.** Concentrations in an equilibrium constant are really dimensionless ratios of actual concentrations divided by standard state concentrations. Since standard states are 1 M for solutes, 1 bar for gases, and pure substances for solids and liquids, these are the units we must use. A solvent is approximated as a pure liquid.
- 6-2.** All concentrations in equilibrium constants are expressed as dimensionless ratios of actual concentrations divided by standard-state concentrations.
- 6-3.** Predictions based on free energy or Le Châtelier's principle tell us which way a reaction will go (thermodynamics), but not how long it will take (kinetics). A reaction could be over instantly or it could take forever.

6-4. (a) $K = 1/[\text{Ag}^+]^3 [\text{PO}_4^{3-}]$ (b) $K = P_{\text{CO}_2}^6 / P_{\text{O}_2}^{15/2}$

6-5.
$$K = \frac{P_E^3}{P_A^2 [\text{B}]} = \frac{\left(\frac{3.6 \times 10^4 \text{ Torr}}{760 \text{ Torr/atm}} \times 1.013 \frac{\text{bar}}{\text{atm}}\right)^3}{\left(\frac{2.8 \times 10^3 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)^2 (1.2 \times 10^{-2} \text{ M})} = 1.2 \times 10^{10}$$



- 6-7.** (a) Decrease (b) give off (c) negative

6-8. $K = e^{-(59.0 \times 10^3 \text{ J/mol})/(8.314472 \text{ J/(K}\cdot\text{mol)})(298.15 \text{ K})} = 5 \times 10^{-11}$

- 6-9.** (a) Right because reactant is added
 (b) Right because product is removed
 (c) Neither because solid graphite does not appear in the reaction quotient
 (d) Right. The pressure of reactant and product both increase by a factor of 8. However, reactant appears to the second power in the reaction quotient and product only appears to the first power. Increasing each pressure by the same factor decreases the reaction quotient.
 (e) Smaller. An exothermic reaction liberates heat. Adding heat is like adding a product.

6-10. (a) $K = P_{\text{H}_2\text{O}} = e^{-\Delta G^\circ/RT} = e^{-(\Delta H^\circ - T\Delta S^\circ)/RT}$
 $= e^{-\{(63.11 \times 10^3 \text{ J/mol}) - (298.15 \text{ K})(148 \text{ J K}^{-1} \text{ mol}^{-1})\}/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$
 $= 4.7 \times 10^{-4} \text{ bar}$

(b) $P_{\text{H}_2\text{O}} = 1 = e^{-(\Delta H^\circ - T\Delta S^\circ)/RT} \Rightarrow \Delta H^\circ - T\Delta S^\circ \text{ must be zero.}$

$$\Delta H^\circ - T\Delta S^\circ = 0 \Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = 426 \text{ K} = 153^\circ\text{C}$$

6-11. (a) Let's designate the equilibrium constant at temperature T_1 as K_1 and the equilibrium constant at temperature T_2 as K_2 .

$$K_1 = e^{-\Delta G^\circ/RT_1} = e^{-(\Delta H^\circ - T_1\Delta S^\circ)/RT_1} = e^{-\Delta H^\circ/RT_1} \cdot e^{\Delta S^\circ/R}$$

$$\text{Similarly, } K_2 = e^{-\Delta H^\circ/RT_2} \cdot e^{\Delta S^\circ/R}$$

$$\text{Dividing } K_1 \text{ by } K_2 \text{ gives } \frac{K_1}{K_2} = e^{-(\Delta H^\circ/R)(1/T_1 - 1/T_2)}$$

$$\Rightarrow \Delta H^\circ = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} R \ln \frac{K_1}{K_2}$$

Putting in $K_1 = 1.479 \times 10^{-5}$ at $T_1 = 278.15 \text{ K}$ and

$K_2 = 1.570 \times 10^{-5}$ at $T_2 = 283.15 \text{ K}$ gives $\Delta H^\circ = +7.82 \text{ kJ/mol}$.

(b) $K = e^{-\Delta H^\circ/RT} \cdot e^{\Delta S^\circ/R}$

$$\ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

$$y \quad m \quad x \quad b$$

A graph of $\ln K$ vs. $1/T$ will have a slope of $-\Delta H^\circ/R$

6-12. (a) $Q = \left(\frac{48.0 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)^2 / \left(\frac{1370 \text{ Pa}}{10^5 \text{ Pa/bar}}\right) \left(\frac{3310 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)$
 $= 5.08 \times 10^{-4} < K \quad \text{The reaction will go to the right.}$

It was not really necessary to convert Pa to bar, since the units cancel.



Initial pressure: 1370 3310 48.0

Final pressure: $1370 - x$ $3310 - x$ $48.0 + 2x$

Note that $2x \text{ Pa}$ of HBr are formed when $x \text{ Pa}$ of H_2 are consumed.

$$\frac{(48.0 + 2x)^2}{(1370 - x)(3310 - x)} = 7.2 \times 10^{-4} \Rightarrow x = 4.50 \text{ Pa}$$

$$P_{\text{H}_2} = 1366 \text{ Pa}, \quad P_{\text{Br}_2} = 3306 \text{ Pa}, \quad P_{\text{HBr}} = 57.0 \text{ Pa}$$

- (c) Neither, since Q is unchanged.
 (d) HBr will be formed, since ΔH° is positive.

6-13. The concentration of MTBE in solution is $100 \text{ }\mu\text{g/mL} = 100 \text{ mg/L}$. The molarity is $[\text{MTBE}] = \frac{0.100 \text{ g/L}}{88.15 \text{ g/mol}} = 1.134 \times 10^{-3} \text{ M}$. The pressure in the gas phase is $P = [\text{MTBE}]/K_h = (1.134 \times 10^{-3} \text{ M})/(1.71 \text{ M/bar}) = 0.663 \text{ mbar}$.

6-14. $[\text{Cu}^+][\text{Br}^-] = K_{\text{sp}}$
 $[\text{Cu}^+][0.10] = 5 \times 10^{-9} \Rightarrow [\text{Cu}^+] = 5 \times 10^{-8} \text{ M}$

6-15. $[\text{Ag}^+]^4[\text{Fe}(\text{CN})_6^{4-}] = K_{\text{sp}}$
 $[1.0 \times 10^{-6}]^4[\text{Fe}(\text{CN})_6^{4-}] = 8.5 \times 10^{-45} \Rightarrow [\text{Fe}(\text{CN})_6^{4-}] = 8.5 \times 10^{-21} \text{ M} = 8.5 \text{ zM}$

6-16. If we let $x = [\text{Cu}^{2+}]$, then $[\text{SO}_4^{2-}] = \frac{1}{4}x$.
 $K = [\text{Cu}^{2+}]^4 [\text{OH}^-]^6 [\text{SO}_4^{2-}] = (x)^4 (1.0 \times 10^{-6})^6 (\frac{1}{4}x) = 2.3 \times 10^{-69}$
 $\Rightarrow x = [\text{Cu}^{2+}] = \left(\frac{(4)(2.3 \times 10^{-69})}{(1.0 \times 10^{-6})^6} \right)^{1/5} = 3.9 \times 10^{-7} \text{ M}$

6-17. (a) $[\text{Zn}^{2+}]^2[\text{Fe}(\text{CN})_6^{4-}] = (0.00010)^2[\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-16}$
 $\Rightarrow [\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-8} \text{ M}$

(b) $[\text{Zn}^{2+}]^2[\text{Fe}(\text{CN})_6^{4-}] = (5.0 \times 10^{-7})^2[\text{Fe}(\text{CN})_6^{4-}] = 2.1 \times 10^{-16}$
 $\Rightarrow [\text{Fe}(\text{CN})_6^{4-}] = 8.4 \times 10^{-4} \text{ M}$

6-18. BX_2 coprecipitates with AX_3 . This means that some BX_2 is trapped in the AX_3 during precipitation of AX_3 .

6-19. For CaSO_4 , $K_{\text{sp}} = 2.4 \times 10^{-5}$. For Ag_2SO_4 , $K_{\text{sp}} = 1.5 \times 10^{-5}$. Removing 99% of the Ca^{2+} reduces $[\text{Ca}^{2+}]$ to 0.000500 M. The concentration of SO_4^{2-} in equilibrium with 0.000500 M Ca^{2+} is $2.4 \times 10^{-5}/0.000500 = 0.048 \text{ M}$. This much SO_4^{2-} will precipitate Ag_2SO_4 , because $Q = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (0.0300)^2 (0.048) = 4.3 \times 10^{-5} > K_{\text{sp}}$. The separation is not feasible. When Ag^+ first precipitates, $[\text{SO}_4^{2-}] = 1.5 \times 10^{-5}/(0.0300)^2 = 1.67 \times 10^{-2} \text{ M}$. $[\text{Ca}^{2+}] = 2.4 \times 10^{-5}/1.67 \times 10^{-2} = 0.0014 \text{ M}$. 97% of the Ca^{2+} has precipitated.

6-20. $\text{BaCrO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{CrO}_4^{2-} \quad K_{\text{sp}} = 2.1 \times 10^{-10}$
 $\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} \quad K_{\text{sp}} = 1.2 \times 10^{-12}$

The stoichiometries are not identical, so it is not clear that the salt with lower K_{sp} will precipitate first. Let's try each possibility. Suppose that BaCrO_4 precipitates first. The concentration of CrO_4^{2-} that will reduce Ba^{2+} to 0.1% of its initial concentration is

$$[\text{Ba}^{2+}][\text{CrO}_4^{2-}] = [1.0 \times 10^{-5}][\text{CrO}_4^{2-}] = 2.1 \times 10^{-10} \Rightarrow [\text{CrO}_4^{2-}] = 2.1 \times 10^{-5} \text{ M.}$$

Will this much chromate precipitate 0.010 M Ag^+ ? We test by evaluating the reaction quotient for Ag_2CrO_4 :

$$Q = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (0.010)^2(2.1 \times 10^{-5}) = 2.1 \times 10^{-9} > K_{\text{sp}} \text{ for } \text{Ag}_2\text{CrO}_4$$

Since $Q > K_{\text{sp}}$ for Ag_2CrO_4 , Ag^+ will precipitate.

Let's try the reverse calculation. If Ag_2CrO_4 precipitates first, the concentration of CrO_4^{2-} that will reduce Ag^+ to $1.0 \times 10^{-5} \text{ M}$ is

$$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = [1.0 \times 10^{-5}]^2[\text{CrO}_4^{2-}] = 1.2 \times 10^{-12} \Rightarrow [\text{CrO}_4^{2-}] = 0.012 \text{ M.}$$

This concentration of CrO_4^{2-} exceeds the concentration required to precipitate 99.90% of Ba^{2+} . Neither Ag^+ nor Ba^{2+} can be 99.90% precipitated without precipitating the other ion.

6-21.	Salt	K_{sp}	$[\text{Ag}^+]$	
			(M, in equilibrium with 0.1 M anion)	
	AgCl	1.8×10^{-10}	$K_{\text{sp}} / 0.10$	$= 1.8 \times 10^{-9}$
	AgBr	5.0×10^{-13}	$K_{\text{sp}} / 0.10$	$= 5.0 \times 10^{-12}$
	AgI	8.3×10^{-17}	$K_{\text{sp}} / 0.10$	$= 8.3 \times 10^{-16}$
	Ag_2CrO_4	1.2×10^{-12}	$\sqrt{K_{\text{sp}} / 0.10}$	$= 3.5 \times 10^{-6}$

I^- requires the lowest concentration of Ag^+ to begin precipitating, so I^- precipitates first. The order of precipitation is: I^- before Br^- before Cl^- before CrO_4^{2-} .

- 6-22. At low I^- concentration, $[\text{Pb}^{2+}]$ decreases with increasing $[\text{I}^-]$ because of the reaction $\text{Pb}^{2+} + 2\text{I}^{2-} \rightarrow \text{PbI}_2(s)$. Concentrations of other $\text{Pb}^{2+}-\text{I}^-$ species are negligible. At high I^- concentration, complex ions form by reactions such as $\text{PbI}_2(s) + \text{I}^- \rightarrow \text{PbI}_3^-$.

- 6-23. (a) BF_3 (b) AsF_5

- 6-24.
$$\frac{[\text{SnCl}_2(aq)]}{[\text{Sn}^{2+}][\text{Cl}^-]^2} = \beta_2 \Rightarrow [\text{SnCl}_2(aq)] = \beta_2[\text{Sn}^{2+}][\text{Cl}^-]^2 = (12)(0.20)(0.20)^2 = 0.096 \text{ M}$$

6-25. $[Zn^{2+}] = K_{sp}/[OH^-]^2 = 2.93 \times 10^{-3} M$

$$[ZnOH^+] = \beta_1[Zn^{2+}][OH^-] = \beta_1 K_{sp}/[OH^-] = 9 \times 10^{-6} M$$

$$[Zn(OH)_2(aq)] = \beta_2[Zn^{2+}][OH^-]^2 = \beta_2 K_{sp}[OH^-] = 6 \times 10^{-6} M$$

$$[Zn(OH)_3] = \beta_3[Zn^{2+}][OH^-]^3 = \beta_3 K_{sp}[OH^-] = 8 \times 10^{-9} M$$

$$[Zn(OH)_4^2] = \beta_4[Zn^{2+}][OH^-]^4 = \beta_4 K_{sp}[OH^-]^2 = 9 \times 10^{-14} M$$



Initial concentration:	1	1	0
Final concentration:	$1-x$	$1-x$	x

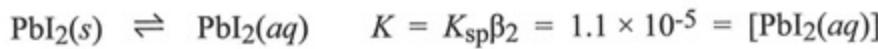
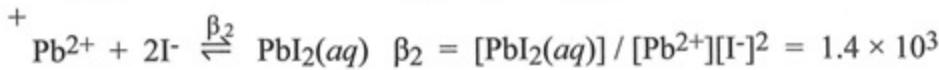
$$\frac{x}{(1-x)^2} = 0.2 \Rightarrow x = 0.15 M$$

$$x = 0.2 - 0.4x + 0.2x^2$$

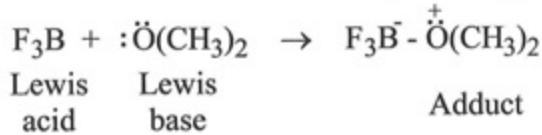
$$\begin{matrix} 0.2x^2 - 1.4x + 0.2 \\ a \quad \quad \quad b \quad \quad \quad c \end{matrix} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{1.4 \pm \sqrt{1.4^2 - 4(0.2)(0.2)}}{2(0.2)} = 6.85 \text{ or } 0.15$$

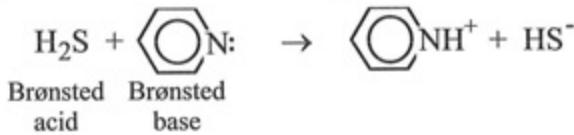
x cannot be greater than 1 (the initial or formal concentration of NaOH), so the correct answer must be 0.15. That is, 15% of the sodium is in the form $\text{NaOH}(aq)$.



6-28. Lewis acids and bases are electron pair acceptors and donors, respectively:



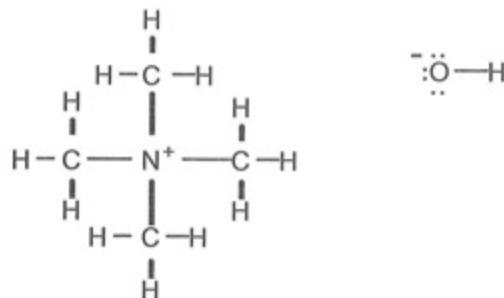
Brønsted acids and bases are proton donors and acceptors, respectively:



6-29. (a) An adduct (b) dative or coordinate covalent

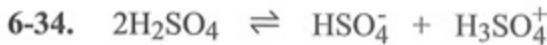
(c) conjugate (d) $[\text{H}^+] > [\text{OH}^-]$; $[\text{OH}^-] > [\text{H}^+]$

- 6-30.** Dissolved CO₂ from the atmosphere lowers the pH by reacting with water to form carbonic acid. Water can be distilled under an inert atmosphere to exclude CO₂, or most CO₂ can be removed by boiling the distilled water.
- 6-31.** SO₂ in the atmosphere reacts with moisture to make H₂SO₃, which is a weak acid. H₂SO₃ can be oxidized to H₂SO₄, which is a strong acid.

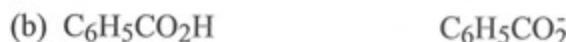
6-32.

There is no place for OH⁻ to bond to (CH₃)₄N⁺.

- 6-33.** (a) HI (b) H₂O



6-35. acid base



- 6-36.** (a) [H⁺] = 0.010 M ⇒ pH = -log [H⁺] = 2.00
 (b) [OH⁻] = 0.035 M ⇒ [H⁺] = K_w / [OH⁻] = 2.86 × 10⁻¹³ M ⇒ pH = 12.54
 (c) [H⁺] = 0.030 M ⇒ pH = 1.52
 (d) [H⁺] = 3.0 M ⇒ pH = -0.48
 (e) [OH⁻] = 0.010 M ⇒ [H⁺] = 1.0 × 10⁻¹² M ⇒ pH = 12.00

- 6-37.** (a) K_w = [H⁺][OH⁻] = 1.01 × 10⁻¹⁴ at 25°C

$$x \quad x$$

$$x^2 = 1.01 \times 10^{-14} \Rightarrow x = [H^+] = 1.005 \times 10^{-7} M \Rightarrow pH = -\log [H^+] = 6.998$$

- (b) At 100°C, pH = 6.132

- 6-38.** Since [H⁺][OH⁻] = 1.0 × 10⁻¹⁴, K = [H⁺]⁴[OH⁻]⁴ = 1.0 × 10⁻⁵⁶

6-39. $[\text{La}^{3+}] [\text{OH}^-]^3 = K_{\text{sp}} = 2 \times 10^{-21}$

$$[\text{OH}^-]^3 = K_{\text{sp}} / (0.010) \Rightarrow [\text{OH}^-] = 5.8 \times 10^{-7} \text{ M} \Rightarrow \text{pH} = 7.8$$

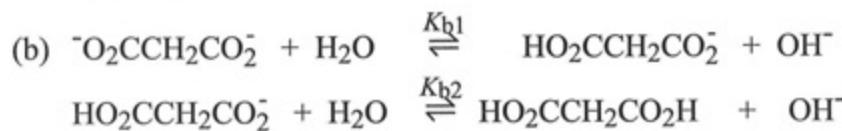
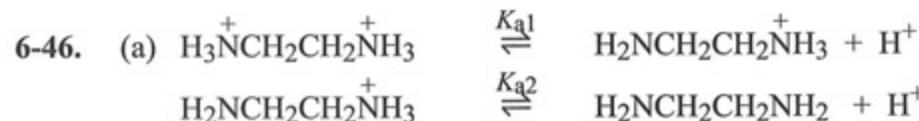
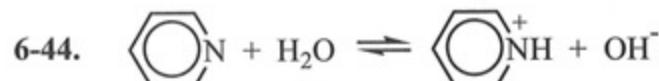
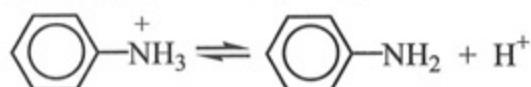
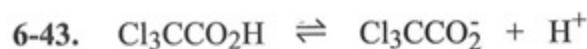
6-40. (a) At 25°C , K_w increases as temperature increases \Rightarrow endothermic

(b) At 100°C , K_w increases as temperature increases \Rightarrow endothermic

(c) At 300°C , K_w decreases as temperature increases \Rightarrow exothermic

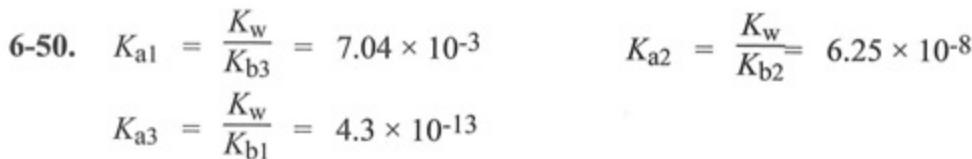
6-41. See Table 6-2.

6-42. Weak acids:	RCO_2H Carboxylic acids	$\text{R}_3\text{NH}^+\text{X}^-$ Ammonium ions	M^{n+} Metal ions
Weak bases:	R_3N : Amines	RCO_2M^+ Carboxylate ions	

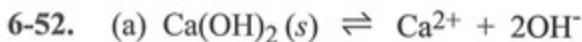


6-47. (a), (c)





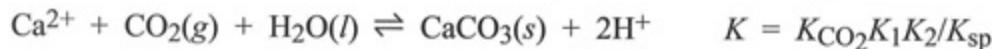
6-51. Add the two reactions and multiply their equilibrium constants to get $K = 2.9 \times 10^{-6}$.



$$x(2x)^2 = K_{\text{sp}} = 10^{-5.19} \Rightarrow x = 1.2 \times 10^{-2} \text{ M}$$

(b) Since some Ca^{2+} reacts with OH^- to form CaOH^+ , the K_{sp} reaction will be drawn to the right, and the solubility of $\text{Ca}(\text{OH})_2$ will be greater than we would expect just on the basis of K_{sp} .

6-53. Reversing the first reaction and then adding the four reactions gives



$$K = (3.4 \times 10^{-2})(4.5 \times 10^{-7})(4.7 \times 10^{-11})/(6.0 \times 10^{-9}) = 1.2 \times 10^{-10}$$

$$\frac{[\text{H}^+]^2}{[\text{Ca}^{2+}]P_{\text{CO}_2}} = \frac{(1.8 \times 10^{-7})^2}{[\text{Ca}^{2+}][0.10]} = K = 1.2 \times 10^{-10}$$

$$[\text{Ca}^{2+}] = 2.7 \times 10^{-3} \text{ M} = 0.22 \text{ g}/2.00 \text{ L}$$

CHAPTER 7

ACTIVITY AND SYSTEMATIC TREATMENT OF EQUILIBRIUM

7-1. As ionic strength increases, the charges of the ionic atmospheres increase and the net ionic attractions decrease. There is less tendency for ions to bind to each other.

7-2. (a) true (b) true (c) true

7-3. (a) $\frac{1}{2}[0.0087 \cdot 1^2 + 0.0087 \cdot (-1)^2] = 0.0087 \text{ M}$

(b) $\frac{1}{2}[0.0002 \cdot 3^2 + 0.0006 \cdot (-1)^2] = 0.0012 \text{ M}$

7-4. (a) 0.660 (b) 0.54 (c) 0.18 (Eu³⁺ is a lanthanide ion) (d) 0.83

7-5. The ionic strength 0.030 M is halfway between the values 0.01 and 0.05 M. Therefore, the activity coefficient will be halfway between the tabulated values:
 $\gamma = \frac{1}{2}(0.914 + 0.86) = 0.887$.

7-6. (a) $\log \gamma = \frac{-0.51 \cdot 2^2 \cdot \sqrt{0.083}}{1 + (600\sqrt{0.083} / 305)} = -0.375 \Rightarrow \gamma = 10^{-0.375} = 0.42_2$

(b) $\gamma = \left(\frac{0.083 - 0.05}{0.1 - 0.05} \right) (0.405 - 0.485) + 0.485 = 0.43_2$

7-7. $\gamma = \left(\frac{0.083 - 0.05}{0.1 - 0.05} \right) (0.18 - 0.245) + 0.245 = 0.20_2$

7-8. If [ether(*aq*)] becomes smaller, γ_{ether} must become larger, since $K (= [\text{ether}(\text{aq})] \gamma_{\text{ether}})$ is a constant.

7-9. The solubility of Hg₂Br₂ is small, so we assume that Hg₂Br₂ contributes negligible Br⁻ to 0.001 00 M KBr.

$$\mu = 0.001 00 \text{ M}, [\text{Br}^-] = 0.001 00 \text{ M}, \gamma_{\text{Hg}_2^{2+}} = 0.867, \gamma_{\text{Br}^-} = 0.964$$

$$\begin{aligned} K_{\text{sp}} &= 5.6 \times 10^{-23} = [\text{Hg}_2^{2+}] \gamma_{\text{Hg}_2^{2+}} [\text{Br}^-]^2 \gamma_{\text{Br}^-}^2 \\ &= [\text{Hg}_2^{2+}] (0.867) (0.001 00)^2 (0.964)^2 \quad \Rightarrow \quad [\text{Hg}_2^{2+}] = 7.0 \times 10^{-17} \text{ M} \end{aligned}$$

Check our assumption: Yes, Br⁻ from Hg₂Br₂ is negligible.

7-10. The solubility of Ba(IO₃)₂ is small, so we assume that Ba(IO₃)₂ contributes negligible IO₃⁻ to 0.100 M (CH₃)₄NIO₃.

$$\mu = 0.100 \text{ M}, [\text{IO}_3^-] = 0.100 \text{ M}, \gamma_{\text{Ba}^{2+}} = 0.38, \gamma_{\text{IO}_3^-} = 0.775$$

$$\begin{aligned} K_{\text{sp}} &= 1.5 \times 10^{-9} = [\text{Ba}^{2+}] \gamma_{\text{Ba}^{2+}} [\text{IO}_3^-]^2 \gamma_{\text{IO}_3^-}^2 \\ &= [\text{Ba}^{2+}] (0.38) (0.100)^2 (0.775)^2 \Rightarrow [\text{Ba}^{2+}] = 6.6 \times 10^{-7} \text{ M} \end{aligned}$$

- 7-11.** Ionic strength = 0.010 M (from HCl) + 0.040 M (from KClO₄) that gives $\text{K}^+ + \text{ClO}_4^- = 0.050 \text{ M}$. Using Table 7-1, $\gamma_{\text{H}^+} = 0.86$.
- $$\text{pH} = -\log [\text{H}^+] \gamma_{\text{H}^+} = -\log[(0.010)(0.86)] = 2.07.$$

- 7-12.** Ionic strength = 0.010 M from NaOH + 0.012 M from LiNO₃ = 0.022 M. Interpolating in Table 7-1 gives $\gamma_{\text{OH}^-} = 0.873$.

$$[\text{H}^+] \gamma_{\text{H}^+} = \frac{K_w}{[\text{OH}^-] \gamma_{\text{OH}^-}} = \frac{1.0 \times 10^{-14}}{(0.010)(0.873)} = 1.15 \times 10^{-12}$$

$$\text{pH} = -\log(1.15 \times 10^{-12}) = 11.94$$

If we had neglected activities, $\text{pH} \approx -\log[\text{H}^+] = -\log \frac{K_w}{[\text{OH}^-]} = 12.00$

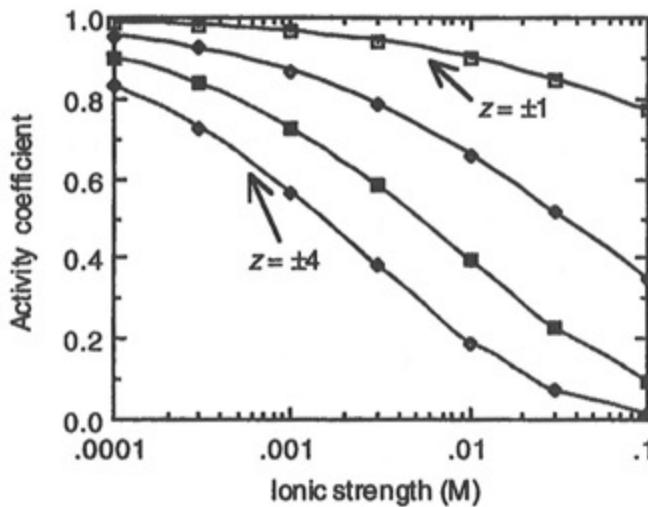
- 7-13.** $\varepsilon = 79.755 e^{-4.6 \times 10^{-3} (323.15 - 293.15)} = 69.474$

$$\log \gamma = \frac{(-1.825 \times 10^6)[(69.474)(323.15)]^{-3/2}(-2)^2 \sqrt{0.100}}{1 + \frac{400 \sqrt{0.100}}{2.00 \sqrt{(69.474)(323.15)}}}$$

$$= -0.4826 \Rightarrow \gamma = 0.329 \quad (\text{In the table, } \gamma = 0.355 \text{ at } 25^\circ\text{C}.)$$

- 7-14.** Spreadsheet for Debye-Hückel calculations

	A	B	C	D	E
1	Ionic strength	Gamma ($z = \pm 1$)	Gamma ($z = \pm 2$)	Gamma ($z = \pm 3$)	Gamma ($z = \pm 4$)
2	0.0001	0.988	0.955	0.901	0.831
3	0.0003	0.980	0.924	0.836	0.727
4	0.001	0.965	0.867	0.725	0.565
5	0.003	0.942	0.787	0.583	0.383
6	0.01	0.901	0.660	0.393	0.190
7	0.03	0.847	0.515	0.225	0.071
8	0.1	0.769	0.350	0.094	0.015
9					
10	$B2 = 10^{(-0.51 * \text{Sqrt}(A2)/(1+400 * \text{Sqrt}(A2)/305))}$				
11	$C2 = 10^{(-0.51 * 4 * \text{Sqrt}(A2)/(1+400 * \text{Sqrt}(A2)/305))}$				
12	$D2 = 10^{(-0.51 * 9 * \text{Sqrt}(A2)/(1+400 * \text{Sqrt}(A2)/305))}$				
13	$E2 = 10^{(-0.51 * 16 * \text{Sqrt}(A2)/(1+400 * \text{Sqrt}(A2)/305))}$				



7-15. The equilibrium constant is

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{A}^-] \gamma_{\text{A}^-}}{[\text{HA}] \gamma_{\text{HA}}}.$$

From the table of activity coefficients, $\gamma_{\text{H}^+} = 0.83$ and $\gamma_{\text{A}^-} = 0.80$ at $\mu = 0.1 \text{ M}$.

For HA, we estimate

$$\log \gamma_{\text{HA}} = k\mu = (0.2)(0.1) = 0.02, \text{ or } \gamma_{\text{HA}} = 10^{0.02} = 1.05.$$

Putting activity coefficients for $\mu = 0.1 \text{ M}$ into the equilibrium expression gives

$$K_a = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{A}^-] \gamma_{\text{A}^-}}{[\text{HA}] \gamma_{\text{HA}}} = \frac{[\text{H}^+](0.83)[\text{A}^-](0.80)}{[\text{HA}](1.05)} = 0.63 \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{or } \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} (\mu = 0.1 \text{ M}) = K_a/0.63.$$

The activity coefficients at $\mu = 0$ are all 1, so the equilibrium expression is

$$K_a = \frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{A}^-] \gamma_{\text{A}^-}}{[\text{HA}] \gamma_{\text{HA}}} = \frac{[\text{H}^+](1)[\text{A}^-](1)}{[\text{HA}](1)} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} (\mu = 0).$$

The concentration quotient at the two different ionic strengths is

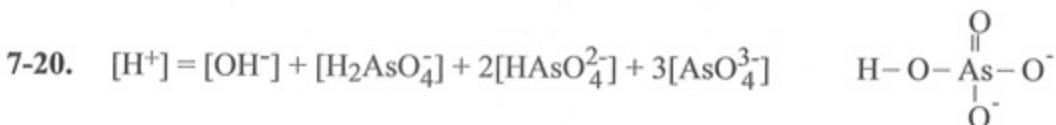
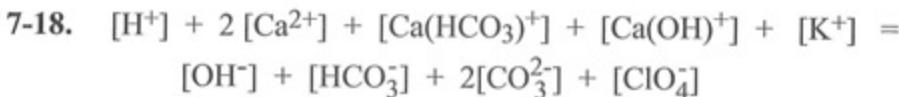
$$\text{Concentration quotient} = \frac{\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} (\mu = 0)}{\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} (\mu = 0.1 \text{ M})} = \frac{K_a}{K_a/0.63} = 0.63$$

in agreement with the observed value of 0.63 ± 0.03 .

7-16. The charge balance states the magnitude of positive charge equals the magnitude of negative charge in a solution. That is, the solution must be neutral. The mass balance states that atoms are conserved. If we deliver a certain number of atom A into a solution, then the sum of atom A in all species must equal the atoms of A

delivered to the solution. If we deliver a certain ratio of atoms A and B into the solution, then the sum of atoms of A and B in all species must be in that same ratio.

7-17. Charge and mass are proportional to molarity, not to activity.



7-21. (a) Charge balance: $2[Mg^{2+}] + [H^+] + [MgBr^+] + [MgOH^+] = [Br^-] + [OH^-]$
Mass balance: total Br = 2(total Mg)

$$[MgBr^+] + [Br^-] = 2\{[Mg^{2+}] + [MgBr^+] + [MgOH^+]\}$$

(b) $[Mg^{2+}] + [MgBr^+] + [MgOH^+] = 0.2 \text{ M}$
 $[MgBr^+] + [Br^-] = 0.4 \text{ M}$

7-22. 250 mL of $1.0 \times 10^{-6} \text{ M}$ charge = 0.25×10^{-6} moles of charge.

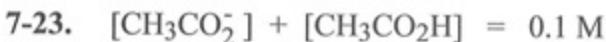
$$(0.25 \times 10^{-6} \text{ moles of charge}) \left(9.648 \times 10^4 \frac{\text{coulombs}}{\text{mole of charge}} \right) = 0.02412 \text{ C.}$$

The dielectric constant of air is $\epsilon = 1$ and the separation is 1.5 m.

$$\text{Force} = -(8.988 \times 10^9) \frac{(0.02412)(-0.02412)}{(1)(1.5^2)} = 2.3 \times 10^6 \text{ N.}$$

$$(2.3 \times 10^6 \text{ N})(0.2248 \text{ pounds/N}) = 5.2 \times 10^5 \text{ pounds.}$$

Two elephants do not weigh enough to keep the beakers apart.



7-24. $Y_{\text{total}} = \frac{3}{2} X_{\text{total}}$

$$2[X_2Y_2^{2+}] + [X_2Y_4^+] + 3[X_2Y_3] + [Y^{2-}] = \frac{3}{2} \{2[X_2Y_2^{2+}] + 2[X_2Y_4^+] + 2[X_2Y_3]\}$$

$$[Y^{2-}] = [X_2Y_2^{2+}] + 2[X_2Y_4^+]$$

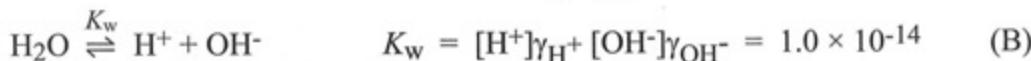
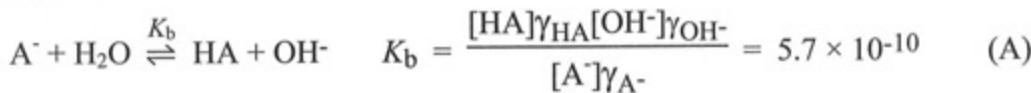
7-25. 3 (total Fe) = 2 (total sulfur)

$$3\{[Fe^{3+}] + [Fe(OH)^{2+}] + [Fe(OH)_2^+] + 2[Fe_2(OH)_2^{4+}] + [FeSO_4^+]\}$$

$$= 2\{[FeSO_4^+] + [SO_4^{2-}] + [HSO_4^-]\}$$

We write 2 in front of $[Fe_2(OH)_2^{4+}]$ because $Fe_2(OH)_2^{4+}$ contains 2 Fe.

7-26. (a) Pertinent reactions:



$$\text{Charge balance: } [H^+] + [Na^+] = [OH^-] + [A^-] \quad (C)$$

$$\text{Mass balance: } [Na^+] = 0.01 \text{ M} \equiv F \quad (D)$$

$$\text{Mass balance: } [HA] + [A^-] = 0.01 \text{ M} \equiv F \quad (E)$$

- (b) Now we neglect activity coefficients. We will make the following substitutions in the charge balance:

$$[OH^-] = K_w/[H^+]$$

$$\text{From Equation A: } [HA] = \frac{K_b[A^-]}{[OH^-]} \quad (F)$$

$$\text{From Equation E: } [HA] = F - [A^-] \quad (G)$$

Now equate the expressions for [HA] from Equations F and G to solve for [A⁻]

$$\frac{K_b[A^-]}{[OH^-]} = F - [A^-]$$

$$[A^-] \left(\frac{K_b}{[OH^-]} + 1 \right) = F \Rightarrow [A^-] = \frac{F[OH^-]}{K_b + [OH^-]}$$

Now substitute $K_w/[H^+]$ for each $[OH^-]$ in the equation above to get

$$[A^-] = \frac{FK_w/[H^+]}{K_b + FK_w/[H^+]} = \frac{FK_w}{K_b[H^+] + K_w} \quad (H)$$

We can now substitute for all terms in the charge balance using $[A^-]$ from Equation H, $[OH^-] = K_w/[H^+]$, and $[Na^+] = F$:

$$\text{Charge balance: } [H^+] + [Na^+] = [OH^-] + [A^-]$$

$$[H^+] + F = \frac{K_w}{[H^+]} + \frac{FK_w}{K_b[H^+] + K_w} \quad (I)$$

Equation I has the form we were looking for. The only unknown is $[H^+]$. For convenience in finding a numerical solution, I will rearrange as follows:

$$0 = \frac{K_w}{[H^+]} + \frac{FK_w}{K_b[H^+] + K_w} - [H^+] - F \quad (J)$$

The following spreadsheet evaluates the right side of Equation J in cell D9.

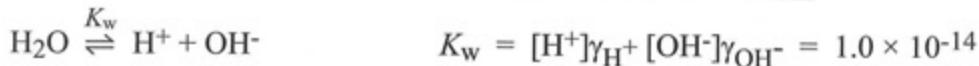
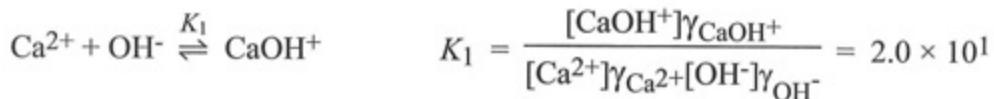
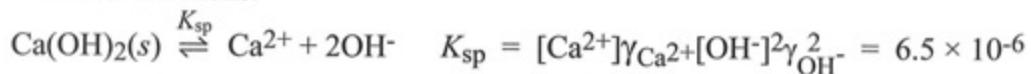
Guess a value for $[H^+]$ in cell B7. Before using Goal Seek in Excel 2007, click the Microsoft Office button at the top left of the spreadsheet, click on Excel Options, and then on Formulas. Set Maximum Change to 1e-14. In earlier versions of Excel, go to Tools and Options and select the Calculations tab and set Maximum change to 1e-14. Then execute Goal Seek to vary $[H^+]$ in cell B7 until the sum in cell D9 is close to 0 (within 1e-14). The answer in cell B7 is $[H^+] = 4.19 \times 10^{-9} \text{ M}$ or $\text{pH} = 8.38$.

Cells C15:C17 compute other concentrations from the relations

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad [\text{A}^-] = \frac{FK_w}{K_b[\text{H}^+] + K_w} \quad [\text{HA}] = \frac{K_b[\text{A}^-]}{[\text{OH}^-]}$$

	A	B	C	D	E
1	Finding the species in NaOAc solution				
2	Using GOAL SEEK to Solve for $[\text{H}^+]$				
3	$K_w = 1.00E-14$				
4	$K_b = 5.70E-10$				
5	$F = 0.01$				
6					
7	Guess for $[\text{H}^+] = 4.19E-09$			$\text{pH} = -\log[\text{H}^+] =$	8.38
8					
9	$K_w/[\text{H}^+] + FK_w/(K_b[\text{H}^+] + K_w) - [\text{H}^+] - F =$			1.41E-16	
10					
11	Tools --> Options --> Calculation --> Maximum change = 1e-14				
12	Use GOAL SEEK to vary $[\text{H}^+]$ in cell B7 until the sum in				
13	cell D9 is equal to zero				
14					
15	$[\text{OH}^-] = K_w/[\text{H}^+] = 2.39E-06$				
16	$[\text{A}^-] = FK_w/(K_b[\text{H}^+] + K_w) = 1.00E-02$				
17	$[\text{HA}] = K_b[\text{A}^-]/[\text{OH}^-] = 2.39E-06$				

7-27. (a) Pertinent reactions:



$$\text{Charge balance: } 2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{H}^+] = [\text{OH}^-]$$

$$\text{Mass balance: } \underbrace{[\text{OH}^-] + [\text{CaOH}^+]}_{\text{species containing OH}^-} = 2\{\underbrace{[\text{Ca}^{2+}] + [\text{CaOH}^+]}\}_{\text{species containing Ca}^{2+}} + [\text{H}^+]$$

(Mass balance gives the same result as charge balance.)

There are 4 equations (3 equilibria and charge balance) and 4 unknowns:

$[\text{Ca}^{2+}]$, $[\text{CaOH}^+]$, $[\text{H}^+]$, and $[\text{OH}^-]$.

(b) The approximations we make are to disregard the activity coefficients and to neglect $[\text{H}^+]$ in the charge balance because $[\text{H}^+] \ll [\text{OH}^-]$ in basic solution.

The charge balance becomes



Substituting $[\text{CaOH}^+] = K_1[\text{Ca}^{2+}][\text{OH}^-]$ into (A) gives

$$2[\text{Ca}^{2+}] + K_1[\text{Ca}^{2+}][\text{OH}^-] = [\text{OH}^-] \Rightarrow [\text{Ca}^{2+}] = \frac{[\text{OH}^-]}{2 + K_1[\text{OH}^-]}$$

Substitute this expression for $[\text{Ca}^{2+}]$ into the solubility product:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = \frac{[\text{OH}^-]^3}{2 + K_1[\text{OH}^-]} \quad (\text{B})$$

We solve Equation B in the spreadsheet by guessing $[\text{OH}^-]$ in cell C4 until the expression in cell D4 is equal to K_{sp} . We used Goal Seek for this purpose.

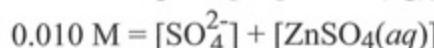
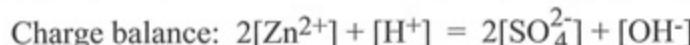
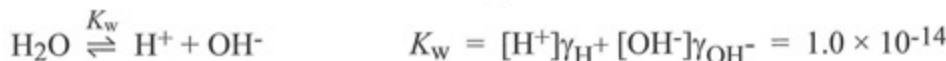
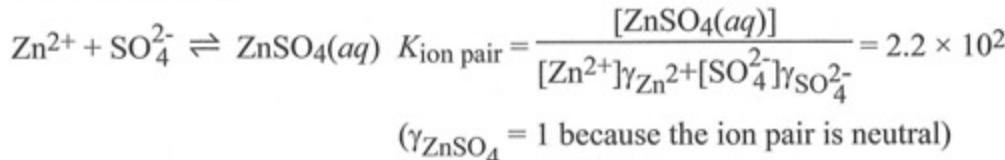
	A	B	C	D
1	Ca(OH) ₂ solubility			
2				
3	$K_{\text{sp}} =$	$[\text{OH}^-]_{\text{guess}} =$	$[\text{OH}^-]^3/(2 + K_1[\text{OH}^-]) =$	
4	6.5E-06	0.0253528	6.5000E-06	
5	$K_1 =$			
6	2.0E+01	$[\text{Ca}^{2+}] =$	$[\text{CaOH}^+] =$	
7		0.0101126	0.0051276	
8				
9	$D4 = C4^3/(2 + A6*C4)$	$[\text{H}^+] = K_w/[\text{OH}^-] =$		
10	$C7 = A4/C4^2$		3.94E-13	
11	$D7 = A6*C7*C4$			

Results: $[\text{Ca}^{2+}] = 0.0101 \text{ M}$ $[\text{CaOH}^+] = 0.0051 \text{ M}$
 $[\text{OH}^-] = 0.0254 \text{ M}$ $[\text{H}^+] = K_w/[\text{OH}^-] = 3.9 \times 10^{-13} \text{ M}$

Total dissolved Ca = 0.0101 + 0.0051 = 0.0152 M

The formula mass of Ca(OH)₂ is 74.09 g/mol, so 0.0152 M is 1.13 g/L. The *Handbook of Chemistry and Physics* lists the solubility of Ca(OH)₂ as 1.85 g/L at 0°C and 0.77 g/L at 100°C.

7-28. (a) Pertinent reactions:



5 equations and 5 unknowns: $[\text{Zn}^{2+}]$, $[\text{SO}_4^{2-}]$, $[\text{ZnSO}_4(aq)]$, $[\text{H}^+]$, $[\text{OH}^-]$

Since there is no coupling of the zinc sulfate and water equilibria, $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$ and we can disregard H^+ and OH^- in this problem.

Substituting $[ZnSO_4(aq)] = 0.010 - [Zn^{2+}]$ and $[SO_4^{2-}] = [Zn^{2+}]$ into the ion pair equilibrium expression gives

$$K_{\text{ion pair}} = \frac{[ZnSO_4(aq)]}{[Zn^{2+}]\gamma_{Zn^{2+}}[SO_4^{2-}]\gamma_{SO_4^{2-}}} = 2.2 \times 10^2$$

$$K_{\text{ion pair}} = \frac{0.010 - [Zn^{2+}]}{[Zn^{2+}]\gamma_{Zn^{2+}}[Zn^{2+}]\gamma_{SO_4^{2-}}} = 2.2 \times 10^2$$

Rearranging gives

$$(220)[Zn^{2+}]^2\gamma_{Zn^{2+}}\gamma_{SO_4^{2-}} + [Zn^{2+}] - 0.010 = 0. \quad (\text{A})$$

Setting $\gamma_{Zn^{2+}} = \gamma_{SO_4^{2-}} = 1$ allows us to solve quadratic Equation (A) to find $[Zn^{2+}] = 4.84 \times 10^{-3} M$.

(b) Ionic strength = $\frac{1}{2}([Zn^{2+}] \cdot 4 + [SO_4^{2-}] \cdot 4) = 0.0194 M$

Interpolation in Table 7-1 gives $\gamma_{Zn^{2+}} = 0.630$ and $\gamma_{SO_4^{2-}} = 0.609$.

Putting these values of γ into Equation (A) gives $[Zn^{2+}] = 6.47 \times 10^{-3} M$

3rd iteration: $\mu = 4(6.47 \times 10^{-3}) = 0.0259 M$

$$\gamma_{Zn^{2+}} = 0.599 \quad \gamma_{SO_4^{2-}} = 0.574 \quad [Zn^{2+}] = 6.65 \times 10^{-3} M$$

4th iteration: $\mu = 0.0266 M$

$$\gamma_{Zn^{2+}} = 0.596 \quad \gamma_{SO_4^{2-}} = 0.571 \quad [Zn^{2+}] = 6.67 \times 10^{-3} M$$

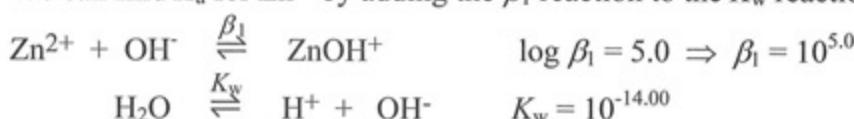
$$\text{Ion-paired percent} = \frac{0.010 - 6.67 \times 10^{-3}}{0.010} \times 100 = 33\%$$

$$\text{Ionic strength} = 4(6.67 \times 10^{-3}) = 0.027 M$$

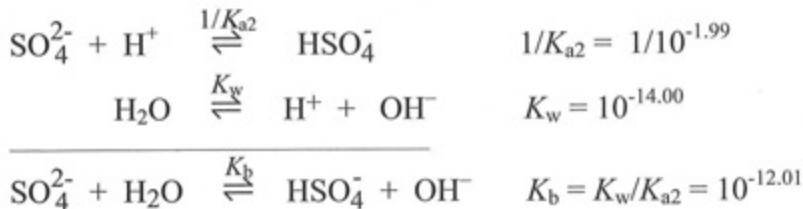


Appendix I gives the formation constant (β_l) for $ZnOH^+$.

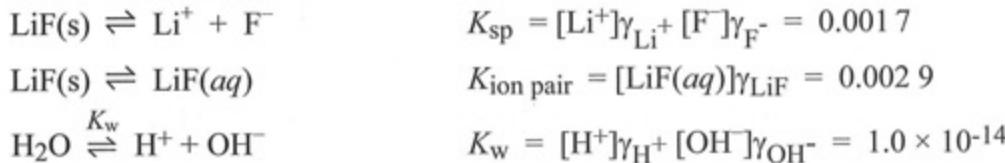
We can find K_a for Zn^{2+} by adding the β_l reaction to the K_w reaction:



The base hydrolysis constant for SO_4^{2-} is K_w/K_{a2} for H_2SO_4 :



7-29. Pertinent reactions:



$$\text{Charge balance: } [\text{Li}^+] + [\text{H}^+] = [\text{F}^-] + [\text{OH}^-]$$

$$\text{Mass balance: } [\text{Li}^+] + [\text{LiF}(aq)] = [\text{F}^-] + [\text{LiF}(aq)]$$

There are five equations and five unknowns: $[\text{Li}^+]$, $[\text{F}^-]$, $[\text{LiF}(aq)]$, $[\text{H}^+]$, and $[\text{OH}^-]$. There is no coupling between the LiF reactions and the dissociation of water, so $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$. $[\text{H}^+]$ and $[\text{OH}^-]$ cancel in the charge balance, leaving $[\text{Li}^+] = [\text{F}^-]$. Also, the ion-pairing equilibrium constant tells us that $[\text{LiF}(aq)] = 0.0029 \text{ M}$ with the good approximation that $\gamma_{\text{LiF}} = 1$. All that is left is to find $[\text{Li}^+]$ and $[\text{F}^-]$ from the solubility product with the condition $[\text{Li}^+] = [\text{F}^-]$.

$$[\text{Li}^+] \gamma_{\text{Li}^+} [\text{F}^-] \gamma_{\text{F}^-} = K_{sp}$$

$$[\text{Li}^+]^2 \gamma_{\text{Li}^+} \gamma_{\text{F}^-} = K_{sp} \Rightarrow [\text{Li}^+] = [\text{F}^-] = \sqrt{K_{sp}/\gamma_{\text{Li}^+} \gamma_{\text{F}^-}}$$

$$1^{\text{st}} \text{ iteration: Let } \gamma_{\text{Li}^+} = \gamma_{\text{F}^-} = 1 \Rightarrow [\text{Li}^+] = [\text{F}^-] = \sqrt{K_{sp}} = 0.041 \text{ M}$$

$$2^{\text{nd}} \text{ iteration: } \mu = 0.041 \text{ M} \Rightarrow \gamma_{\text{Li}^+} = 0.843 \text{ and } \gamma_{\text{F}^-} = 0.824$$

$$\Rightarrow [\text{Li}^+] = [\text{F}^-] = \sqrt{K_{sp}/\gamma_{\text{Li}^+} \gamma_{\text{F}^-}} = 0.049 \text{ M}$$

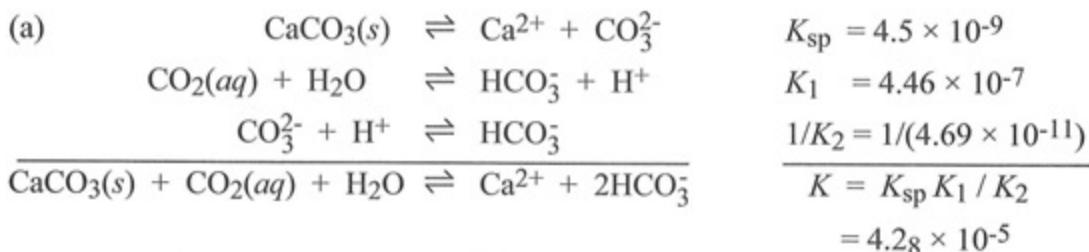
$$3^{\text{rd}} \text{ iteration: } \mu = 0.049 \text{ M} \Rightarrow \gamma_{\text{Li}^+} = 0.834 \text{ and } \gamma_{\text{F}^-} = 0.812$$

$$\Rightarrow [\text{Li}^+] = [\text{F}^-] = \sqrt{K_{sp}/\gamma_{\text{Li}^+} \gamma_{\text{F}^-}} = 0.050 \text{ M}$$

$$4^{\text{th}} \text{ iteration: } \mu = 0.049 \text{ M} \Rightarrow \gamma_{\text{Li}^+} = 0.833 \text{ and } \gamma_{\text{F}^-} = 0.811$$

$$\Rightarrow [\text{Li}^+] = [\text{F}^-] = \sqrt{K_{sp}/\gamma_{\text{Li}^+} \gamma_{\text{F}^-}} = 0.050 \text{ M}$$

7-30. (a)



(b) The equilibrium constant for the net reaction is

$$\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2(aq)]} = K = 4.28 \times 10^{-5}$$

We can substitute into this equation $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$ and $[\text{CO}_2(aq)] = K_{\text{CO}_2} P_{\text{CO}_2}$ (where $K_{\text{CO}_2} = 0.032$ and $P_{\text{CO}_2} = 3.8 \times 10^{-4}$ bar) to get

$$\frac{[\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2}{K_{\text{CO}_2} P_{\text{CO}_2}} = K \Rightarrow [\text{Ca}^{2+}] = 5.07 \times 10^{-4} \text{ M} = 20 \text{ mg/L}$$

(c) If $[\text{Ca}^{2+}] = 80 \text{ mg/L} = 2.0 \times 10^{-3} \text{ M}$, then

$$P_{\text{CO}_2} = \frac{[\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2}{K_{\text{CO}_2} K} = 0.023 \text{ bar}$$

The partial pressure of CO_2 in the river is about $(0.023 \text{ bar})/(3.8 \times 10^{-4} \text{ bar}) = 60$ times higher than the atmospheric pressure of CO_2 . There must be a source of extra CO_2 such as respiration in the river or inflow of ground water that is very rich in CO_2 and not in equilibrium with the atmosphere.

CHAPTER 8

MONOPROTIC ACID-BASE EQUILIBRIA

8-1. HBr (or any other acid or base) drives the reaction $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ to the left, according to Le Châtelier's principle. If, for example, the solution contains 10^{-4} M HBr, the concentration of OH^- from H_2O is $K_w/[\text{H}^+] = 10^{-10}$ M. The concentration of H^+ from H_2O must also be 10^{-10} M, since H^+ and OH^- are created in equimolar quantities.

- 8-2.** (a) $\text{pH} = -\log [\text{H}^+] = -\log (1.0 \times 10^{-3}) = 3.00$
 (b) $[\text{H}^+] = K_w/[\text{OH}^-] = (1.0 \times 10^{-14})/(1.0 \times 10^{-2}) = 1.0 \times 10^{-12}$ M
 $\text{pH} = -\log [\text{H}^+] = 12.00$

- 8-3.** Charge balance: $[\text{H}^+] = [\text{OH}^-] + [\text{ClO}_4^-] \Rightarrow [\text{OH}^-] = [\text{H}^+] - 5.0 \times 10^{-8}$

Mass balance is the same as charge balance.

Equilibrium: $[\text{H}^+] [\text{OH}^-] = K_w$
 $[\text{H}^+] ([\text{H}^+] - 5.0 \times 10^{-8}) = 1.0 \times 10^{-14} \Rightarrow [\text{H}^+] = 1.28 \times 10^{-7}$ M
 $\text{pH} = -\log [\text{H}^+] = 6.89$
 $[\text{OH}^-] = K_w/[\text{H}^+] = 7.8 \times 10^{-8}$ M $\Rightarrow [\text{H}^+]$ from $\text{H}_2\text{O} = 7.8 \times 10^{-8}$ M
 Fraction of total $[\text{H}^+]$ from $\text{H}_2\text{O} = \frac{7.8 \times 10^{-8} \text{ M}}{1.28 \times 10^{-7} \text{ M}} = 0.61$

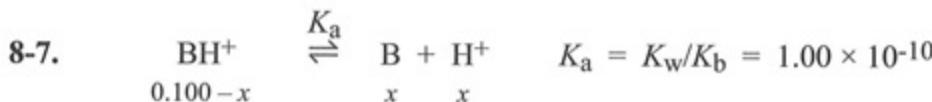
- 8-4.** (a) $\text{pH} = -\log [\text{H}^+] \gamma_{\text{H}^+}$
 $1.092 = -\log (0.100) \gamma_{\text{H}^+} \Rightarrow \gamma_{\text{H}^+} = 0.809$
 The tabulated activity coefficient is 0.83.
 (b) $2.102 = -\log (0.0100) \gamma_{\text{H}^+} \Rightarrow \gamma_{\text{H}^+} = 0.791$
 (c) The activity coefficient depends somewhat on the identity of the counterions in solution.

- 8-5.** (a) \rightleftharpoons K_a
 (b) \rightleftharpoons K_b
 (c) \rightleftharpoons K_b
 (d) \rightleftharpoons K_a

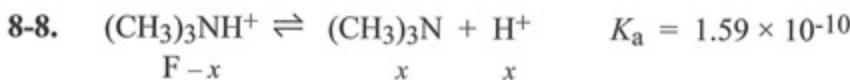
8-6. Let $x = [\text{H}^+] = [\text{A}^-]$ and $0.100 - x = [\text{HA}]$.

$$\frac{x^2}{0.100 - x} = 1.00 \times 10^{-5} \Rightarrow x = 9.95 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = -\log x = 3.00$$

$$\alpha = \frac{[\text{A}^-]}{[\text{A}^-] + [\text{HA}]} = \frac{9.95 \times 10^{-4}}{0.100} = 9.95 \times 10^{-3}$$

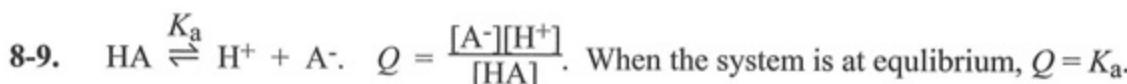


$$\frac{x^2}{0.100 - x} = 1.00 \times 10^{-10} \Rightarrow x = [\text{B}] = [\text{H}^+] = 3.16 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.50$$



$$\frac{x^2}{0.060 - x} = K_a \Rightarrow x = 3.09 \times 10^{-6} \Rightarrow \text{pH} = 5.51$$

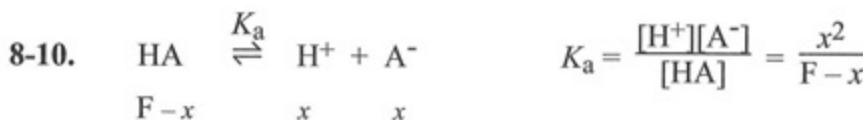
$$[(\text{CH}_3)_3\text{N}] = x = 3.1 \times 10^{-6} \text{ M}, \quad [(\text{CH}_3)_3\text{NH}^+] = F - x = 0.060 \text{ M}$$



Let's call the concentrations at equilibrium $[\text{A}^-]_e$, $[\text{H}^+]_e$, and $[\text{HA}]_e$. If the solution is diluted by a factor of 2, the concentrations become $\frac{1}{2}[\text{A}^-]_e$, $\frac{1}{2}[\text{H}^+]_e$, and $\frac{1}{2}[\text{HA}]_e$.

$$\text{The reaction quotient becomes } Q = \frac{\frac{1}{2}[\text{A}^-]_e \frac{1}{2}[\text{H}^+]_e}{\frac{1}{2}[\text{HA}]_e} = \frac{\frac{1}{2}[\text{A}^-]_e [\text{H}^+]_e}{\frac{1}{2}[\text{HA}]_e} = \frac{1}{2}K_a.$$

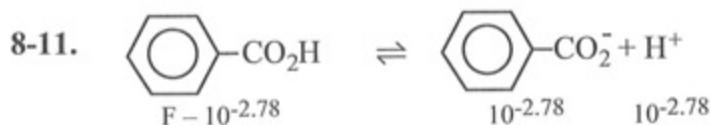
Since $Q < K_a$, the concentrations of products must increase and the concentration of reactant must decrease to attain equilibrium. That means that the weak acid dissociates further as it is diluted in order to stay in equilibrium.



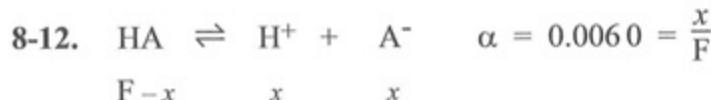
$$\text{For } F = \frac{K_a}{10}, \quad \frac{x^2}{\frac{K_a}{10} - x} = K_a \Rightarrow x = 0.092 K_a; \quad \alpha = \frac{x}{F} = \frac{0.092 K_a}{0.100 K_a} = 92\%$$

$$\text{For } F = 10 K_a, \quad \frac{x^2}{10 K_a - x} = K_a \Rightarrow x = 2.7 K_a; \quad \alpha = \frac{x}{F} = \frac{2.7 K_a}{10 K_a} = 27\%$$

$$\text{For 99\% dissociation, } x = 0.99 F \Rightarrow K_a = \frac{(0.99 F)^2}{F - 0.99 F} \Rightarrow F = (0.0102)K_a$$

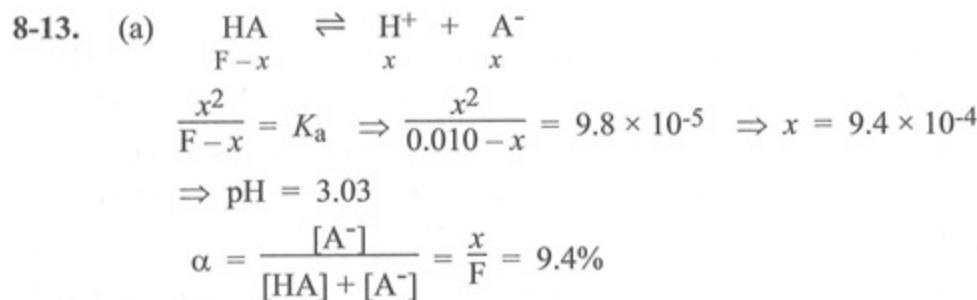


$$K_a = \frac{(10^{-2.78})^2}{0.0450 - 10^{-2.78}} = 6.35 \times 10^{-5} = pK_a = 4.20$$



$$F = 0.0450 \text{ M and } x = (0.0060)(0.0450 \text{ M}) = 2.7 \times 10^{-4} \text{ M}$$

$$\Rightarrow K_a = \frac{x^2}{F - x} = 1.6 \times 10^{-6} \Rightarrow pK_a = 5.79$$



(b) pH = 7.00 because the acid is so dilute. From the K_a equilibrium we write

$$[\text{A}^-] = \frac{K_a}{[\text{H}^+]} [\text{HA}] = \frac{9.8 \times 10^{-5}}{1.0 \times 10^{-7}} [\text{HA}] = 980 [\text{HA}]$$

$$\alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} = \frac{980 [\text{HA}]}{[\text{HA}] + 980 [\text{HA}]} = \frac{980}{981} = 99.9\%$$

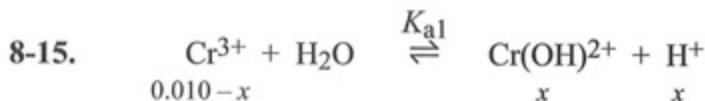
8-14. Phenol is a weak acid, so it will contribute negligible ionic strength. The ionic strength of the solution is 0.050 M.



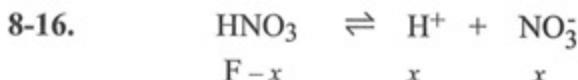
$$\frac{[\text{H}^+] \gamma_{\text{H}^+} [\text{A}^-] \gamma_{\text{A}^-}}{[\text{HA}] \gamma_{\text{HA}}} = K_a \Rightarrow \frac{(x)(0.86)(x)(0.835)}{(0.0500 - x)(1.00)} = 1.01 \times 10^{-10} \Rightarrow x = 2.65 \times 10^{-6}$$

$$\text{pH} = -\log[\text{H}^+] \gamma_{\text{H}^+} = -\log[2.65 \times 10^{-6}](0.86) = 5.64$$

$$\alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} = \frac{2.65 \times 10^{-6}}{0.0500} = 5.30 \times 10^{-5} = 0.0053\%$$



$$\text{pH} = -\log x = 2.86 \quad \alpha = \frac{x}{0.010} = 0.14$$



$$\Rightarrow x = 0.965 \text{ M when } F = 1.00 \text{ M} \Rightarrow \alpha = \frac{x}{F} = 96.5\%$$

- 8-17. The initial spreadsheet follows (on the left). Guess a value for x in cell A4. The formula in cell B4 is “=A4^2/(A6-A4)”. In Excel 2007, click the Microsoft Office button at the top left of the spreadsheet, click on Excel Options, and then on Formulas. Set Maximum Change to a small number such as 1e-20 to find an answer with high precision. In earlier versions of Excel, in the Tools menu, go to Options and then Calculation. Check Iteration and set Maximum change to 1e-20. Highlight cell B4 and select Goal Seek. Set cell B4 To value 1e-5 By changing cell A4. Click OK and Goal Seek finds the solution in the second spreadsheet (on the right). The value $x = 9.95 \times 10^{-5}$ makes the quotient $x^2/(F-x)$ equal to 1.00×10^{-5} .

	A	B
1	Using Excel GOAL SEEK	
2		
3	$x =$	$x^2/(F-x) =$
4	0.01	1.1111E-03
5	F =	
6	0.1	

Before executing Goal Seek

	A	B
1	Using Excel GOAL SEEK	
2		
3	$x =$	$x^2/(F-x) =$
4	0.00099501	1.0000E-05
5	F =	
6	0.1	

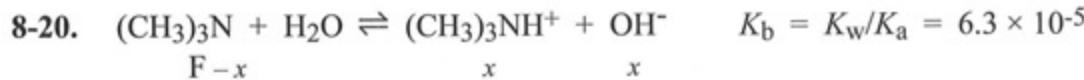
After executing Goal Seek

- 8-18. The “fishy” smell comes from volatile amines (RNH_2). Lemon juice protonates the amines, giving much less volatile ammonium ions (RNH_3^+).

- 8-19. Let $x = [\text{OH}^-] = [\text{BH}^+]$ and $0.100 - x = [\text{B}]$. $\frac{x^2}{0.100 - x} = 1.00 \times 10^{-5}$

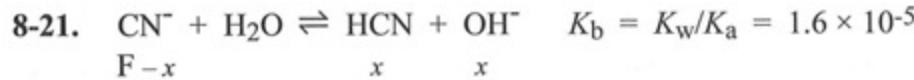
$$\Rightarrow x = 9.95 \times 10^{-4} \text{ M} \Rightarrow [\text{H}^+] = \frac{K_w}{x} = 1.005 \times 10^{-11} \Rightarrow \text{pH} = 11.00$$

$$\alpha = \frac{[\text{BH}^+]}{[\text{B}] + [\text{BH}^+]} = \frac{9.95 \times 10^{-4}}{0.100} = 9.95 \times 10^{-3}$$

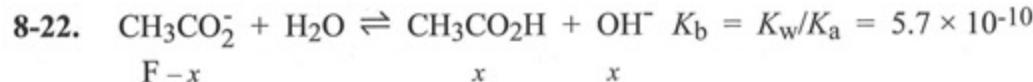


$$\frac{x^2}{0.060 - x} = K_b \Rightarrow x = 1.91 \times 10^{-3} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 11.28$$

$$[(\text{CH}_3)_3\text{NH}^+] = x = 1.91 \times 10^{-3} \text{ M}, \quad [(\text{CH}_3)_3\text{N}] = F - x = 0.058 \text{ M}$$



$$\frac{x^2}{0.050 - x} = K_b \Rightarrow x = 8.9 \times 10^{-4} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 10.95$$



$$\frac{x^2}{(1.00 \times 10^{-1}) - x} = K_b \Rightarrow x = 7.6 \times 10^{-6} \Rightarrow \alpha = \frac{x}{F} = 0.0076\%$$

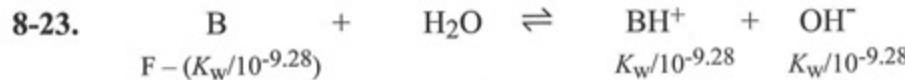
$$\frac{x^2}{(1.00 \times 10^{-2}) - x} = K_b \Rightarrow x = 2.4 \times 10^{-6} \Rightarrow \alpha = \frac{x}{F} = 0.024\%$$

For $1.00 \times 10^{-12} \text{ M}$ sodium acetate, $\text{pH} = 7.00$ and we can say

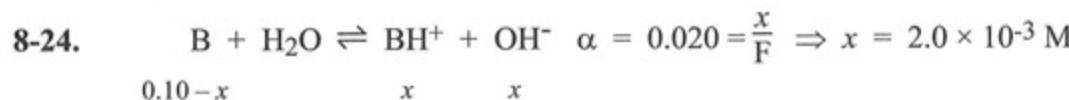
$$[\text{HA}] = \frac{K_b[\text{A}^-]}{[\text{OH}^-]} = (5.7 \times 10^{-3})[\text{A}^-]$$

$$\alpha = \frac{[\text{HA}]}{[\text{HA}] + [\text{A}^-]} = \frac{(5.7 \times 10^{-3})[\text{A}^-]}{(5.7 \times 10^{-3})[\text{A}^-] + [\text{A}^-]} = 0.57\%$$

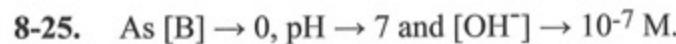
The more dilute the solution, the greater is α .



$$K_b = \frac{(K_w/10^{-9.28})^2}{F - (K_w/10^{-9.28})} = \frac{(K_w/10^{-9.28})^2}{0.10 - (K_w/10^{-9.28})} = 3.6 \times 10^{-9}$$



$$K_b = \frac{x^2}{0.10 - x} = \frac{(2.0 \times 10^{-3})^2}{0.10 - (2.0 \times 10^{-3})} = 4.1 \times 10^{-5}$$



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = 10^{-7} \frac{[\text{BH}^+]}{[\text{B}]} \Rightarrow [\text{BH}^+] = 10^7 K_b [\text{B}]$$

$$\alpha = \frac{[\text{BH}^+]}{[\text{B}] + [\text{BH}^+]} = \frac{10^7 K_b [\text{B}]}{[\text{B}] + 10^7 K_b [\text{B}]} = \frac{10^7 K_b}{1 + 10^7 K_b}$$

$$\text{For } K_b = 10^{-4}, \text{ we have } \alpha = \frac{10^7 K_b}{1 + 10^7 K_b} = \frac{10^7 10^{-4}}{1 + 10^7 10^{-4}} = 0.999$$

$$\text{For } K_b = 10^{-10}, \text{ we have } \alpha = \frac{10^7 K_b}{1 + 10^7 K_b} = \frac{10^7 10^{-10}}{1 + 10^7 10^{-10}} = 0.000\ 999$$

- 8-26.** I would weigh out 0.0200 mol of acetic acid (= 1.201 g) and place it in a beaker with ~75 mL of water. While monitoring the pH with a pH electrode, I would add 3 M NaOH (~4 mL is required) until the pH is exactly 5.00. I would then pour the solution into a 100 mL volumetric flask and wash the beaker several times with a few milliliters of distilled water. Each washing would be added to the volumetric flask, to ensure quantitative transfer from the beaker to the flask. After swirling the volumetric flask to mix the solution, I would carefully add water up to the 100 mL mark, insert the cap, and invert 20 times to ensure complete mixing.
- 8-27.** The pH of a buffer depends on the ratio of the concentrations of HA and A⁻ ($\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}]$). When the volume of solution is changed, both concentrations are affected equally and their ratio does not change.
- 8-28.** Buffer capacity measures the ability to maintain the original [A⁻]/[HA] ratio when acid or base is added. A more concentrated buffer has more A⁻ and HA, so a smaller fraction of A⁻ or HA is consumed by added acid or base. Therefore, there is a smaller change in the ratio [A⁻]/[HA].
- 8-29.** At very low or very high pH, there is so much acid or base in the solution already that small additions of acid or base will hardly have any effect. At low pH, the buffer is H₃O⁺/H₂O; and at high pH, the buffer is H₂O/OH⁻.
- 8-30.** When $\text{pH} = \text{p}K_a$, the ratio of concentrations [A⁻]/[HA] is unity. A given increment of added acid or base has the least effect on the ratio [A⁻]/[HA] when the concentrations of A⁻ and HA are initially equal.
- 8-31.** The Henderson-Hasselbalch is just a rearranged form of the K_a equilibrium expression, which is always true. When we make the approximation that [HA] and [A⁻] are unchanged from what we added, we are neglecting acid dissociation and base hydrolysis, which can change the concentrations in dilute solutions of moderately strong acids or bases.

8-32.	<u>acid</u>	<u>pK_a</u>
	hydrogen peroxide	11.65
	propanoic acid	4.87
	cyanoacetic acid	2.47
	4-aminobenzenesulfonic acid	3.23 ← most suitable because pK_a is closest to desired pH

8-33. $\text{pH} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 5.00 + \log \frac{0.050}{0.100} = 4.70$

8-34.	$\text{pH} = 3.744 + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$
	pH: 3.000 3.744 4.000
	[HCO_2^-]/[HCO_2H]: 0.180 1.00 1.80

8-35. $\text{pH} = 3.57 + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$ where 3.57 is pK_a at $\mu = 0.1 \text{ M}$

Substituting $\text{pH} = 3.744$ gives [HCO_2^-]/[HCO_2H] = 1.5

8-36. $\text{pH} = pK_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$, where $pK_a = 14.00 - pK_b = 3.15$

(a) If $\text{pH} = 2.00$, [HNO_2]/[NO_2^-] = 14

(b) If $\text{pH} = 10.00$, [HNO_2]/[NO_2^-] = 1.4×10^{-7}

8-37. (a) HEPES is an acid with $pK_a = 7.56$. When it is dissolved in water, the solution will be acidic and will require NaOH to raise the pH to 7.45.

- (b)
1. Weigh out $(0.250 \text{ L})(0.0500 \text{ M}) = 0.0125 \text{ mol}$ of HEPES and dissolve in $\sim 200 \text{ mL}$.
 2. Adjust the pH to 7.45 with NaOH.
 3. Dilute to 250 mL.

8-38. 213 mL of 0.00666 M 2,2'-bipyridine = 1.419 mmol base. We will add x mol H^+ to get a pH of 4.19.

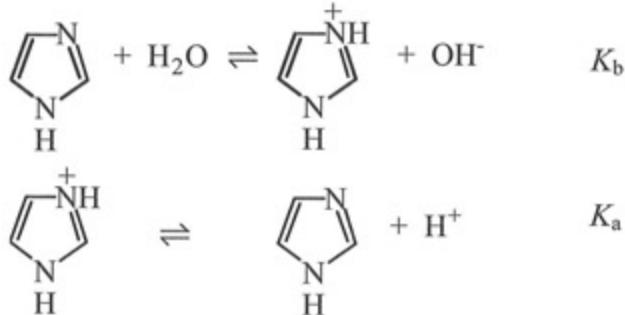
2,2'-bipyridine		+	H^+	→	2,2'-bipyridine H^+
Initial mmol:	1.419		x		—
Final mmol:	1.419 - x		—		x

$$\text{pH} = \text{p}K_a + \log \frac{[\text{bipyridine}]}{[\text{bipyridineH}^+]}$$

$$4.19 = 4.34 + \log \frac{1.419-x}{x} \Rightarrow x = 0.831 \text{ mmol}$$

$$\text{volume} = \frac{0.831 \text{ mmol}}{0.246 \text{ mmol/mL}} = 3.38 \text{ mL}$$

8-39. (a)



(b) FM of imidazole = 68.08. FM of imidazole hydrochloride = 104.54.

$$\text{pH} = 6.993 + \log \frac{1.00/68.08}{1.00/104.54} = 7.18$$

(c)

	B	+	H ⁺	→	BH ⁺
Initial mmol:	14.69		2.46		9.57
Final mmol:	12.23		—		12.03

$$\text{pH} = 6.993 + \log \frac{12.23}{12.03} = 7.00$$

(d) The imidazole must be half neutralized to obtain pH = pK_a. Since there are 14.69 mmol of imidazole, this will require $\frac{1}{2}(14.69) = 7.34$ mmol of HClO₄ = 6.86 mL.

8-40. (a) pH = 2.865 + log $\frac{0.0400}{0.0800} = 2.56$

(b) Using Eqns. (8-20) and (8-21), and neglecting [OH⁻], we can write

$$K_a = 1.36 \times 10^{-3} = \frac{[\text{H}^+](0.0400 + [\text{H}^+])}{0.0800 - [\text{H}^+]} \Rightarrow [\text{H}^+] = 2.48 \times 10^{-3} \text{ M}$$

$$\Rightarrow \text{pH} = 2.61$$

(c) 0.080 mol of HNO₃ + 0.080 mol of Ca(OH)₂ react completely, leaving an excess of 0.080 mol of OH⁻. This much OH⁻ converts 0.080 mol of ClCH₂CO₂H into 0.080 mol of ClCH₂CO₂⁻. The final concentrations are [ClCH₂CO₂⁻] = 0.020 + 0.080 = 0.100 M and [ClCH₂CO₂H] = 0.180 - 0.080 = 0.100 M. So pH = pK_a = 2.86.

8-41.



$$\text{Initial moles: } 0.0224 \quad x \quad -$$

$$\text{Final moles: } 0.0224 - x \quad - \quad x$$

$$\text{pH} = 7.40 = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 7.48 + \log \frac{x}{0.0224 - x} \Rightarrow x = 0.01017 \text{ mol.}$$

$$\text{volume} = \frac{0.01017 \text{ mol}}{0.626 \text{ M}} = 16.2 \text{ mL}$$

- 8-42. (a) Since $\text{p}K_a$ for acetic acid is 4.756, we expect the solution to be acidic and will ignore $[\text{OH}^-]$ in comparison to $[\text{H}^+]$.

$$[\text{HA}] = 0.0020 - [\text{H}^+] \quad [\text{A}^-] = 0.00400 + [\text{H}^+]$$

$$K_a = 1.75 \times 10^{-5} = \frac{[\text{H}^+](0.00400 + [\text{H}^+])}{0.00200 - [\text{H}^+]} \Rightarrow [\text{H}^+] = 8.69 \times 10^{-6} \text{ M}$$

$$\Rightarrow \text{pH} = 5.06 \quad [\text{HA}] = 0.00199 \text{ M} \quad [\text{A}^-] = 0.00401 \text{ M}$$

If you used $K_a = 10^{-4.756}$ instead of rounding to 1.75×10^{-5} , then $[\text{H}^+] = 8.71 \times 10^{-6} \text{ M}$.

- (b) We use Goal Seek to vary cell B5 until cell D4 is equal to K_a .

	A	B	C	D	E
1	$\text{Ka} = 10^{-\text{p}K_a} =$	1.75E-05	Reaction quotient		
2	$\text{Kw} =$	1.00E-14	for $\text{Ka} =$		
3	$\text{FHA} =$	0.002000	$[\text{H}^+][\text{A}^-]/[\text{HA}] =$		
4	$\text{FA} =$	0.004000	1.75E-05		
5	$\text{H} =$	8.693E-06	<-Goal Seek solution		
6	$\text{OH} = \text{Kw}/\text{H} =$	1.15E-09	$\text{D4} = \text{H}^*(\text{FA} + \text{H-OH})/(\text{FHA} - \text{H} + \text{OH})$		
7	$\text{pH} = -\log \text{H} =$	5.0608262			
8	$[\text{HA}] =$	0.0019913	$\text{B8} = \text{FHA} - \text{H} + \text{OH}$		
9	$[\text{A}^-] =$	0.0040087	$\text{B9} = \text{FA} + \text{H} - \text{OH}$		

- 8-43. (a) If we dissolve B and BH^+Br^- (where Br^- is an inert anion), the mass balance is $\text{FBH}^+ + \text{F}_B = [\text{BH}^+] + [\text{B}]$ and the charge balance is $[\text{Br}^-] + [\text{OH}^-] = [\text{BH}^+] + [\text{H}^+]$. Noting that $[\text{Br}^-] = \text{FBH}^+$, the charge balance can be rewritten as

$$[\text{BH}^+] = \text{FBH}^+ + [\text{OH}^-] - [\text{H}^+] \quad (\text{A})$$

Substituting this expression into the mass balance gives

$$[\text{B}] = \text{F}_B - [\text{OH}^-] + [\text{H}^+] \quad (\text{B})$$

If we assume that $[\text{B}] = 0.0100 \text{ M}$ and $[\text{BH}^+] = 0.0200 \text{ M}$, we calculate

$$\text{pH} = \text{p}K_a + \log \frac{[\text{B}]}{[\text{BH}^+]} = 12.00 + \log \frac{0.0100}{0.0200} = 11.70$$

If we do not assume that $[\text{B}] = 0.0100 \text{ M}$ and $[\text{BH}^+] = 0.0200 \text{ M}$, we use Equations A and B. Since the solution is basic, we neglect $[\text{H}^+]$ relative to $[\text{OH}^-]$ and write $[\text{B}] = 0.0100 - x$ and $[\text{BH}^+] = 0.0200 + x$, where $x = [\text{OH}^-]$.

Then we can say $K_b = 10^{-2.00} = \frac{[BH^+][OH^-]}{[B]} = \frac{(0.0200 + x)(x)}{(0.0100 - x)} \Rightarrow$
 $x = 0.00303 \text{ M}$ $pH = -\log \frac{K_w}{x} = 11.48.$

(b) We use Goal Seek to vary cell B5 until cell D4 is equal to K_b .

	A	B	C	D	E
1	$K_b =$	1.00E-02	Reaction quotient		
2	$K_w =$	1.00E-14	for $K_b =$		
3	$FBH =$	0.02	$[OH^-][BH^+]/[B] =$		
4	$FB =$	0.01	0.01		
5	$OH =$	3.028E-03	<-Goal Seek solution		
6	$H = Kw/OH =$	3.303E-12	$D4 = OH^*(FBH-H+OH)/(FB+H-OH)$		
7	$pH = -\log H =$	11.481121			
8	$BH =$	0.0230278	$C8 = FBH-H+OH$		
9	$B =$	0.0069722	$C9 = FB+H-OH$		

$$8-44. K_a = \frac{[HPO_4^{2-}][H^+]\gamma_{HPO_4^{2-}}\gamma_{H^+}}{[H_2PO_4^-]\gamma_{H_2PO_4^-}} = 10^{-7.20}$$

To find pH, rearrange the K_a expression to solve for the activity of H^+ , which is $[H^+]\gamma_{H^+}$:

$$[H^+]\gamma_{H^+} = \frac{K_a[H_2PO_4^-]\gamma_{H_2PO_4^-}}{[HPO_4^{2-}]\gamma_{HPO_4^{2-}}}$$

At $\mu = 0.1 \text{ M}$, the activity coefficients are $\gamma_{H^+} = 0.83$, $\gamma_{H_2PO_4^-} = 0.775$, and

$$\gamma_{HPO_4^{2-}} = 0.355, \text{ so}$$

$$[H^+]\gamma_{H^+} = \frac{10^{-7.20}[H_2PO_4^-](0.775)}{[HPO_4^{2-}](0.355)} = 1.38 \times 10^{-7} \text{ when } [H_2PO_4^-] = [HPO_4^{2-}]$$

$$pH = -\log A_{H^+} = -\log[H^+]\gamma_{H^+} = -\log(1.38 \times 10^{-7}) = 6.86$$

$$8-45. \text{ Equilibria: } \beta_1 = \frac{[AlOH_2^{2+}][H^+]}{[Al^{3+}]} \quad (\text{a})$$

$$\beta_2 = \frac{[Al(OH)_2^+][H^+]^2}{[Al^{3+}]} \quad (\text{b})$$

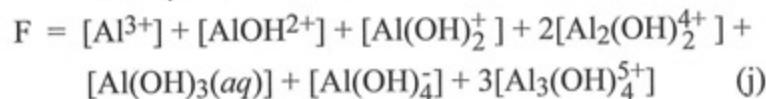
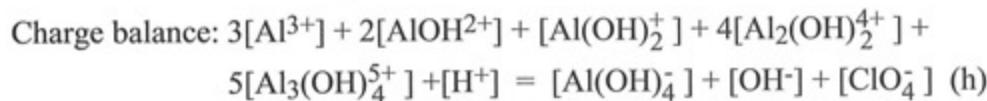
$$\beta_3 = \frac{[Al(OH)_3(aq)][H^+]^3}{[Al^{3+}]} \quad (\text{c})$$

$$\beta_4 = \frac{[Al(OH)_4^-][H^+]^4}{[Al^{3+}]} \quad (\text{d})$$

$$K_{22} = \frac{[Al_2(OH)_2^{4+}][H^+]^2}{[Al^{3+}]^2} \quad (\text{e})$$

$$K_{43} = \frac{[\text{Al}_3(\text{OH})_4^{5+}][\text{H}^+]^4}{[\text{Al}^{3+}]^3} \quad (\text{f})$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (\text{g})$$



We have 10 equations and 10 unknowns, so the problem can, in principle, be solved.

CHAPTER 9
POLYPROTIC ACID-BASE EQUILIBRIA

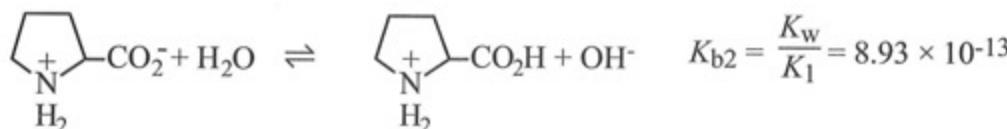
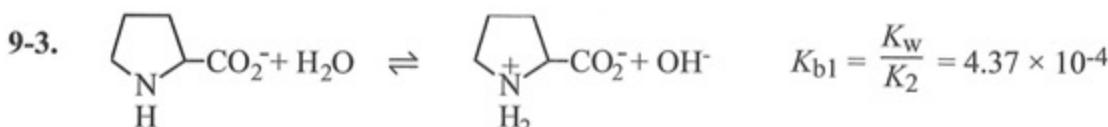
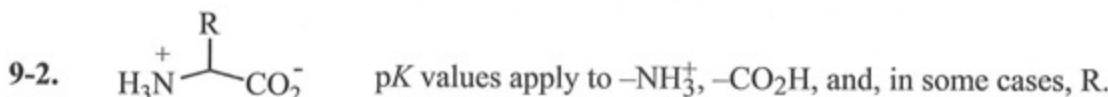
- 9-1. The K_a reaction, with a much greater equilibrium constant than K_b , releases H^+ :



Each mole of H^+ reacts with one mole of OH^- from the K_b reaction:



The net result is that the K_b reaction is driven almost as far toward completion as the K_a reaction.



9-4. (a) $\frac{x^2}{0.100-x} = K_1 \Rightarrow x = 3.11 \times 10^{-3} = [H^+] = [HA^-] \Rightarrow pH = 2.51$

$$[H_2A] = 0.100 - x = 0.0969 \text{ M} \quad [A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = 1.00 \times 10^{-8} \text{ M}$$

(b) $[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} = 1.00 \times 10^{-6} \Rightarrow pH = 6.00$

$$[HA^-] \approx 0.100 \text{ M}$$

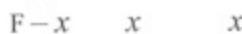
$$[H_2A] = \frac{[H^+][HA^-]}{K_1} = 1.00 \times 10^{-3} \text{ M} \quad [A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = 1.00 \times 10^{-3} \text{ M}$$

(c) $\frac{x^2}{0.100-x} = \frac{K_w}{K_2} \Rightarrow x = [OH^-] = [HA^-] = 3.16 \times 10^{-4} \text{ M} \Rightarrow pH = 10.50$

$$[A^{2-}] = 0.100 - x = 9.97 \times 10^{-2} \text{ M} \quad [H_2A] = \frac{[H^+][HA^-]}{K_1} = 1.00 \times 10^{-10} \text{ M}$$

	pH	$[H_2A]$	$[HA^-]$	$[A^{2-}]$
0.100 M H_2A	2.51	9.69×10^{-2}	3.11×10^{-3}	1.00×10^{-8}
0.100 M $NaHA$	6.00	1.00×10^{-3}	1.00×10^{-1}	1.00×10^{-3}
0.100 M Na_2A	10.50	1.00×10^{-10}	3.16×10^{-4}	9.97×10^{-2}

9-5. (a) $\text{H}_2\text{M} = \text{H}^+ + \text{HM}^- \quad K_1 = 1.42 \times 10^{-3}$



$$\frac{x^2}{0.100 - x} = K_1 \Rightarrow x = 1.12 \times 10^{-2} \Rightarrow \text{pH} = -\log x = 1.95$$

$$[\text{H}_2\text{M}] = 0.100 - x = 0.089 \text{ M}$$

$$[\text{HM}^-] = x = 1.12 \times 10^{-2} \text{ M} \quad [\text{M}^{2-}] = \frac{[\text{HM}^-] K_2}{[\text{H}^+]} = 2.01 \times 10^{-6} \text{ M}$$

(b) $[\text{H}^+] = \sqrt{\frac{K_1 K_2 (0.100) + K_1 K_w}{K_1 + 0.100}} = 5.30 \times 10^{-5} \Rightarrow \text{pH} = 4.28$

$$[\text{HM}^-] \approx 0.100 \text{ M} \quad [\text{H}_2\text{M}] = \frac{[\text{HM}^-][\text{H}^+]}{K_1} = 3.7 \times 10^{-3} \text{ M}$$

$$[\text{M}^{2-}] = \frac{K_2 [\text{HM}^-]}{[\text{H}^+]} = 3.8 \times 10^{-3} \text{ M}$$

The method of Box 9-2 would give more accurate answers, since $[\text{HM}^-]$ is not that much greater than $[\text{H}_2\text{M}]$ or $[\text{M}^{2-}]$ in this case.

(c) $\text{M}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HM}^- + \text{OH}^- \quad K_{b1} = K_w / K_{a2} = 4.98 \times 10^{-9}$



$$\frac{x^2}{0.100 - x} = K_{b1} \Rightarrow x = 2.23 \times 10^{-5} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 9.35$$

$$[\text{M}^{2-}] = 0.100 - x = 0.100 \text{ M} \quad [\text{HM}^-] = x = 2.23 \times 10^{-5} \text{ M}$$

$$[\text{H}_2\text{M}] = \frac{[\text{H}^+][\text{HM}^-]}{K_1} = 7.04 \times 10^{-12} \text{ M}$$



$$\frac{x^2}{0.300 - x} = K_{b1} \Rightarrow x = 3.99 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = -\log K_w/x = 11.60$$

$$[\text{B}] = 0.300 - x = 0.296 \text{ M} \quad [\text{BH}^+] = x = 3.99 \times 10^{-3} \text{ M}$$

$$[\text{BH}_2^{2+}] = \frac{[\text{BH}^+][\text{H}^+]}{K_1} = 2.15 \times 10^{-9} \text{ M}$$

9-7. For H_2A , $K_1 = 5.62 \times 10^{-2}$ and $K_2 = 5.42 \times 10^{-5}$

First approximation ($[\text{HA}^-]_1 \approx 0.00100 \text{ M}$):

$$[\text{H}^+]_1 = \sqrt{\frac{K_1 K_2 (0.00100) + K_1 K_w}{K_1 + 0.00100}} = 2.31 \times 10^{-4} \text{ M} \Rightarrow \text{pH}_1 = 3.64$$

$$[\text{H}_2\text{A}]_1 = \frac{[\text{H}^+]_1 [\text{HA}^-]_1}{K_1} = 4.10 \times 10^{-6} \text{ M}$$

$$[A^{2-}]_1 = \frac{K_2 [HA^-]_1}{[H^+]} = 2.35 \times 10^{-4} \text{ M}$$

Second approximation:

$$[HA^-]_2 \approx 0.00100 - [H_2A]_1 - [A^{2-}]_1 = 0.000761 \text{ M}$$

$$[H^+]_2 = \sqrt{\frac{K_1 K_2 (0.000761) + K_1 K_w}{K_1 + 0.000761}} = 2.02 \times 10^{-4} \text{ M} \Rightarrow pH_2 = 3.70$$

$$[H_2A]_2 = \frac{[H^+]_2 [HA^-]_2}{K_1} = 2.73 \times 10^{-6} \text{ M}$$

$$[A^{2-}]_2 = \frac{K_2 [HA^-]_2}{[H^+]_2} = 2.04 \times 10^{-4} \text{ M}$$

Third approximation:

$$[HA^-]_3 \approx 0.00100 - [H_2A]_2 - [A^{2-}]_2 = 0.000793 \text{ M}$$

$$[H^+]_3 = \sqrt{\frac{K_1 K_2 (0.000793) + K_1 K_w}{K_1 + 0.000793}} = 2.06 \times 10^{-4} \text{ M} \Rightarrow pH_3 = 3.69$$

$$[H_2A]_3 = \frac{[H^+]_3 [HA^-]_3}{K_1} = 2.90 \times 10^{-6} \text{ M}$$

$$[A^{2-}]_3 = \frac{K_2 [HA^-]_3}{[H^+]_3} = 2.09 \times 10^{-4} \text{ M}$$

9-8. (a) Charge balance: $[K^+] + [H^+] = [OH^-] + [HP^-] + 2[P^{2-}] \quad (1)$

Mass balance: $[K^+] = [H_2P] + [HP^-] + [P^{2-}] \quad (2)$

Equilibria: $K_1 = \frac{[H^+] \gamma_{H^+} [HP^-] \gamma_{HP^-}}{[H_2P] \gamma_{H_2P}} \quad (3)$

$$K_2 = \frac{[H^+] \gamma_{H^+} [P^{2-}] \gamma_{P^{2-}}}{[HP^-] \gamma_{HP^-}} \quad (4)$$

$$K_w = [H^+] \gamma_{H^+} [OH^-] \gamma_{OH^-} \quad (5)$$

Solving for $[K^+]$ in Eqns. (1) and (2) and equating the results gives

$$[H_2P] + [H^+] - [P^{2-}] - [OH^-] = 0$$

Making substitutions from Eqns. (3), (4), and (5), we can write

$$\frac{[H^+] \gamma_{H^+} [HP^-] \gamma_{HP^-}}{K_1 \gamma_{H_2P}} + [H^+] - \frac{K_2 [HP^-] \gamma_{HP^-}}{[H^+] \gamma_{H^+} \gamma_{P^{2-}}} - \frac{K_w}{[H^+] \gamma_{H^+} \gamma_{OH^-}} = 0$$

which can be rearranged to

$$[\text{H}^+] = \sqrt{\frac{\frac{K_1 K_2 [\text{HP}^-] \gamma_{\text{HP}} \gamma_{\text{H}_2\text{P}}}{\gamma_{\text{H}} \gamma_{\text{P}^{2-}}} + \frac{K_1 K_w \gamma_{\text{H}_2\text{P}}}{\gamma_{\text{H}} \gamma_{\text{OH}^-}}}{K_1 \gamma_{\text{H}_2\text{P}} + [\text{HP}^-] \gamma_{\text{H}} \gamma_{\text{HP}^-}}}$$

- (b) The ionic strength of 0.050 M KHP is 0.050 M, since the only major ions are K^+ and HP^- .

$$[\text{HP}^-] \approx 0.050 \text{ M}, \gamma_{\text{HP}^-} = 0.835, \gamma_{\text{P}^{2-}} = 0.485, \gamma_{\text{H}_2\text{P}} \approx 1.00,$$

$\gamma_{\text{H}^+} = 0.86, \gamma_{\text{OH}^-} = 0.81$. Using these values in the previous equation gives $[\text{H}^+] = 1.09 \times 10^{-4} \Rightarrow \text{pH} = -\log [\text{H}^+] \gamma_{\text{H}^+} = 4.03$.

- 9-9. Case (a): $\text{pH} = 6.002$, $[\text{HM}^-] = 9.80 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{M}] = 9.76 \times 10^{-5} \text{ M}$, $[\text{M}^{2-}] = 9.85 \times 10^{-5} \text{ M}$

Case (b):

	A	B	C	D	E	F	G	H	I	J
1	Box 9-1 Successive Approximations									
2										
3	$pK_{a1} =$	4	1st approx.	2nd approx.	3rd approx.	4th approx.	5th approx.		15th approx.	
4	$pK_{a2} =$	5	$[\text{HA}] =$	0.01000	0.003675	0.007675	0.005146	0.006745	0.00613201	
5	$K_{a1} =$	0.0001	$[\text{H}^+] =$	3.15E-05	3.12E-05	3.14E-05	3.13E-05	3.14E-05	3.14E-05	
6	$K_{a2} =$	0.00001	$[\text{H}_2\text{A}] =$	3.15E-03	1.15E-03	2.41E-03	1.61E-03	2.12E-03	1.92E-03	
7	$F =$	0.01	$[\text{A}^{2-}] =$	3.18E-03	1.18E-03	2.44E-03	1.64E-03	2.15E-03	1.95E-03	
8	$K_w =$	1.00E-14	$\text{pH} =$	4.50	4.51	4.50	4.50	4.50	4.50	
9										
10	Cell D4: $[\text{HA}] = F$									
11	Cell D5: $[\text{H}^+] = \text{SQRT}((\text{Ka1} * \text{Ka2} * \text{D4} + \text{Ka1} * \text{Kw}) / (\text{Ka1} + \text{D4}))$									
12	Cell D6: $[\text{H}_2\text{A}] = \text{D4} * \text{D5} / \text{Ka1}$									
13	Cell D7: $[\text{A}^{2-}] = \text{Ka2} * \text{D4} / \text{D5}$									
14	Cell D8: $\text{pH} = -\log_{10}(\text{D5})$									
15	Cell E4: $[\text{HA}] = \text{F} - \text{D6} - \text{D7}$									
16	After computing E4, then highlight cells D5:E8 and FILL RIGHT									
17	After completing column E, highlight cells E4:F8 and FILL RIGHT									
18	Continue to highlight each column and FILL RIGHT									

$$9-10. \text{ Mass balance: } F = [\text{Na}^+] = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] \quad (\text{A})$$

$$\text{Charge balance: } [\text{Na}^+] + [\text{H}^+] = [\text{HA}^-] + 2[\text{A}^{2-}] + [\text{OH}^-] \quad (\text{B})$$

$$\text{Equilibria: } [\text{H}_2\text{A}] = [\text{H}^+] [\text{HA}^-] / K_1 \quad (\text{C})$$

$$[\text{A}^{2-}] = K_2 [\text{HA}^-] / [\text{H}^+] \quad (\text{D})$$

$$[\text{OH}^-] = K_w / [\text{H}^+] \quad (\text{E})$$

Substitute $[\text{Na}^+] = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]$ from Equation A for $[\text{Na}^+]$ in

Equation B:

$$\begin{aligned} [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] + [\text{H}^+] &= [\text{HA}^-] + 2[\text{A}^{2-}] + [\text{OH}^-] \\ [\text{H}_2\text{A}] + [\text{H}^+] &= [\text{A}^{2-}] + [\text{OH}^-] \end{aligned} \quad (\text{F})$$

Substitute expressions for $[H_2A]$ from Equation C, $[A^{2-}]$ from Equation D, and $[OH^-]$ from Equation (E) into Equation F:

$$[H^+][HA^-]/K_1 + [H^+] = K_2[HA^-]/[H^+] + K_w/[H^+]$$

Multiply all terms by $[H^+]$ and factor $[H^+]^2$ out on the left side of the equation:

$$[H^+]^2[HA^-]/K_1 + [H^+]^2 = K_2[HA^-] + K_w$$

$$[H^+]^2\{[HA^-]/K_1 + 1\} = K_2[HA^-] + K_w$$

Solve for $[H^+]$:

$$[H^+] = \sqrt{\frac{K_2[HA^-] + K_w}{[HA^-]/K_1 + 1}} = \sqrt{\frac{K_1K_2[HA^-] + K_1K_w}{[HA^-] + K_1}}$$

The last expression is equivalent to Equation 9-10. Substituting $[HA^-] \approx F$ gives Equation 9-11.

9-11. $["H_2CO_3"] = [CO_2(aq)] = KP_{CO_2} = 10^{-1.5} \cdot 10^{-3.4} = 10^{-4.9} M$



$$10^{-4.9} - x \quad x \quad x$$

$$\frac{x^2}{10^{-4.9} - x} = K_{a1} \Rightarrow x = 2.16 \times 10^{-6} M \Rightarrow pH = 5.67$$

9-12. (a) From Equation C, $[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]}$ (F)

$$\text{From Equation B, } [HCO_3^-] = \frac{K_{a1}[CO_2(aq)]}{[H^+]} \quad (G)$$

Substituting $[HCO_3^-]$ from Equation G into Equation F gives

$$[CO_3^{2-}] = \frac{K_{a2}K_{a1}[CO_2(aq)]}{[H^+]^2} \quad (H)$$

Substituting for $[CO_2(aq)]$ from Equation A into Equation H gives

$$[CO_3^{2-}] = \frac{K_{a2}K_{a1}K_H P_{CO_2}}{[H^+]^2} \quad (I)$$

(b) For $P_{CO_2} = 800 \mu\text{bar}$, $pH = 7.8$, 0°C , we find

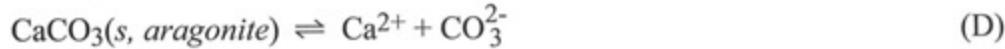
$$\begin{aligned} [CO_3^{2-}] &= \frac{K_{a2}K_{a1}K_H P_{CO_2}}{[H^+]^2} = \\ &\frac{10^{-9.3762} \text{ mol kg}^{-1} 10^{-6.1004} \text{ mol kg}^{-1} 10^{-1.2073} \text{ mol kg}^{-1} \text{ bar}^{-1} (800 \times 10^{-6} \text{ bar})}{[10^{-7.8} \text{ mol kg}^{-1}]^2} \\ &= 6.6 \times 10^{-5} \text{ mol kg}^{-1} \end{aligned}$$

For $P_{CO_2} = 800 \mu\text{bar}$, $pH = 7.8$, 30°C , we find

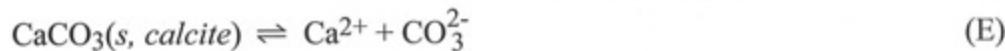
$$[CO_3^{2-}] = \frac{K_{a2}K_{a1}K_H P_{CO_2}}{[H^+]^2} =$$

$$\frac{10^{-8.8324} \text{ mol kg}^{-1} 10^{-5.8008} \text{ mol kg}^{-1} 10^{-1.6048} \text{ mol kg}^{-1} \text{ bar}^{-1} (800 \times 10^6 \text{ bar})}{[10^{-7.8} \text{ mol kg}^{-1}]^2} \\ = 1.8 \times 10^{-4} \text{ mol kg}^{-1}$$

- (c) The equilibrium expressions for aragonite and calcite are



$$K_{\text{sp}}^{\text{arg}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-6.1113} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 0^\circ\text{C} \\ = 10^{-6.1391} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 30^\circ\text{C}$$



$$K_{\text{sp}}^{\text{cal}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-6.3652} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 0^\circ\text{C} \\ = 10^{-6.3713} \text{ mol}^2 \text{ kg}^{-2} \text{ at } 30^\circ\text{C}$$

The reaction quotient at 0°C is

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = [0.010 \text{ mol kg}^{-1}][6.6 \times 10^{-5} \text{ mol kg}^{-1}] \\ = 6.6 \times 10^{-7} \text{ mol}^2 \text{ kg}^{-2} = 10^{-6.18} \text{ mol}^2 \text{ kg}^{-2} < 10^{-6.1113} \text{ mol}^2 \text{ kg}^{-2},$$

so aragonite will dissolve.

But $10^{-6.18} \text{ mol}^2 \text{ kg}^{-2} > 10^{-6.3652} \text{ mol}^2 \text{ kg}^{-2}$, so calcite will not dissolve.

The reaction quotient at 30°C is

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = [0.010 \text{ mol kg}^{-1}][1.84 \times 10^{-4} \text{ mol kg}^{-1}] \\ = 1.84 \times 10^{-6} \text{ mol}^2 \text{ kg}^{-2} = 10^{-5.74} \text{ mol}^2 \text{ kg}^{-2} > 10^{-6.1113} \text{ mol}^2 \text{ kg}^{-2},$$

so neither aragonite nor calcite dissolve.

9-13. $\text{pH} = \text{p}K_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$

$$10.00 = 10.329 + \log \frac{(x \text{ g})/(105.99 \text{ g/mol})}{(5.00 \text{ g})/(84.01 \text{ g/mol})} \Rightarrow x = 2.96 \text{ g}$$

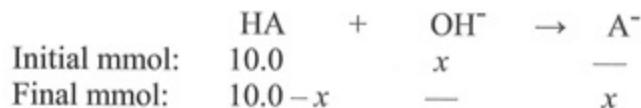
- 9-14. We begin with $(25.0 \text{ mL})(0.0233 \text{ M}) = 0.582_5 \text{ mmol}$ salicylic acid (H_2A , $\text{p}K_1 = 2.972$, $\text{p}K_2 = 13.7$). At pH 3.50, there will be a mixture of H_2A and HA^- .

H_2A	+	OH^-	\rightarrow	HA^-	+	H_2O
Initial mmol:	0.582 ₅	x		—		
Final mmol:	0.582 ₅ - x	—		x		

$$3.50 = 2.972 + \log \frac{x}{0.582_5 - x} \Rightarrow x = 0.449_3 \text{ mmol}$$

$$(0.449_3 \text{ mmol})/(0.202 \text{ M}) = 2.223 \text{ mL NaOH}$$

- 9-15.** Picolinic acid is HA, the intermediate form of a diprotic system with $pK_1 = 1.01$ and $pK_2 = 5.39$. To achieve pH 5.50, we need a mixture of HA + A⁻.



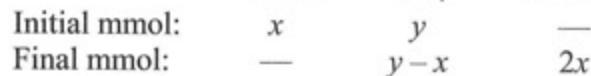
$$5.50 = 5.39 + \log \frac{x}{10.0 - x} \Rightarrow x = 5.63 \text{ mmol} \approx 5.63 \text{ mL NaOH}$$

Procedure: Dissolve 10.0 mmol (1.23 g) picolinic acid in ≈ 75 mL H₂O in a beaker. Add NaOH (≈ 5.63 mL) until the measured pH is 5.50. Transfer to a 100 mL volumetric flask and use small portions of H₂O to rinse the contents of the beaker into the flask. Dilute to 100.0 mL and mix well.

- 9-16.** At pH 2.80, we have a mixture of SO₄²⁻ and HSO₄⁻, since pK_a for HSO₄⁻ is 1.99.

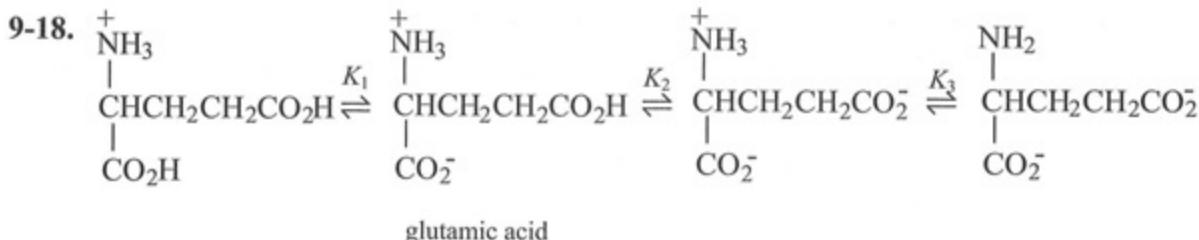
$$2.80 = 1.987 + \log \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \Rightarrow \text{HSO}_4^- = 0.1538 [\text{SO}_4^{2-}]$$

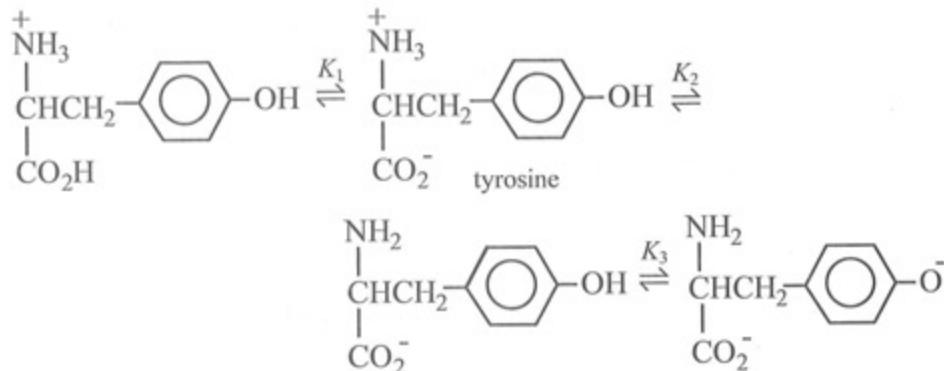
The reaction between H₂SO₄ and SO₄²⁻ produces 2 moles of HSO₄⁻:



The Henderson-Hasselbalch equation told us that $[\text{HSO}_4^-] = 0.1538 [\text{SO}_4^{2-}]$
 $\Rightarrow 2x = 0.1538(y - x)$. Since the total sulfur is 0.200 M, $x + y = 0.200$ mol.
 Substituting $x = 0.200 - y$ into the equation $2x = 0.1538(y - x)$ gives
 $\text{Na}_2\text{SO}_4 = y = 0.1867 \text{ mol} = 26.52 \text{ g}$ and $\text{H}_2\text{SO}_4 = x = 0.0133 \text{ mol} = 1.31 \text{ g}$.

- 9-17.** pK_2 for phosphoric acid is 7.20, so it has a high buffer capacity at pH 7.45 (from the buffer pair H₂PO₄⁻/HPO₄²⁻). At pH 8.5, the buffer capacity of phosphate would be low and it would not be very useful.





9-19. (a) For 0.0500 M KH_2PO_4 , $[\text{H}^+] = \sqrt{\frac{K_1 K_2 (0.0500) + K_1 K_w}{K_1 + 0.0500}} = 1.99 \times 10^{-5}$
 $\Rightarrow \text{pH} = 4.70$

$$4.70 = 2.148 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]} = 2.8 \times 10^{-3}$$

(b) For 0.0500 M K_2HPO_4 , $[\text{H}^+] = \sqrt{\frac{K_2 K_3 (0.0500) + K_2 K_w}{K_2 + 0.0500}} = 1.99 \times 10^{-10}$
 $\Rightarrow \text{pH} = 9.70$

$$9.70 = 2.148 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]} = 2.8 \times 10^{-8}$$

9-20. (a) $\text{H}_3\text{PO}_4 \xrightarrow{\text{p}K_1 = 2.148} \text{H}_2\text{PO}_4^- \xrightarrow{\text{p}K_2 = 7.198} \text{HPO}_4^{2-} \xrightarrow{\text{p}K_3 = 12.375} \text{PO}_4^{3-}$

$$\begin{array}{ccc} \uparrow & & \uparrow \\ \text{pH} \approx (2.148 + 7.198)/2 & & \text{pH} \approx (7.198 + 12.375)/2 \\ = 4.67 & & = 9.79 \end{array}$$

pH 7.45 corresponds to a mixture of NaH_2PO_4 and Na_2HPO_4 . (You could get the same result by mixing other combinations such as H_3PO_4 and Na_3PO_4 or H_3PO_4 and Na_2HPO_4 .)

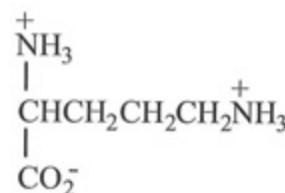
(b) $\text{pH} = \text{p}K_2 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$

$$7.45 = 7.198 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \Rightarrow \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 1.786$$

Combining this last result with $[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] = 0.0500 \text{ M}$ gives $[\text{HPO}_4^{2-}] = 0.03205 \text{ M}$ and $[\text{H}_2\text{PO}_4^-] = 0.01795 \text{ M}$. Use 4.55 g of Na_2HPO_4 and 2.15 g of NaH_2PO_4 .

- (c) Here is one of several ways: Weigh out 0.0500 mol Na₂HPO₄ and dissolve it in 900 mL of water. Add HCl while monitoring the pH with a pH electrode. When the pH is 7.45, stop adding HCl and dilute up to exactly 1 L with H₂O.

- 9-21. Lysine hydrochloride (H₂L⁺) is

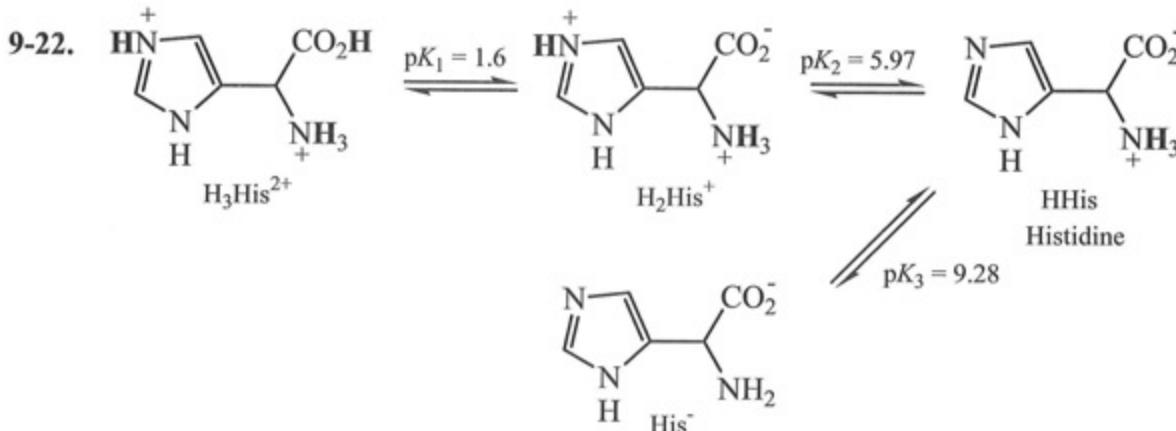


$$\text{for which } [\text{H}^+] = \sqrt{\frac{K_1 K_2 (0.0100) + K_1 K_w}{K_1 + 0.0100}} = 2.32 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.64$$

$$[\text{H}_2\text{L}^+] = 0.0100 \text{ M}$$

$$[\text{H}_3\text{L}^{2+}] = \frac{[\text{H}^+][\text{H}_2\text{L}^+]}{K_1} = 1.36 \times 10^{-6} \text{ M}$$

$$[\text{HL}] = \frac{K_2[\text{H}_2\text{L}^+]}{[\text{H}^+]} = 3.68 \times 10^{-6} \text{ M} \quad [\text{L}^-] = \frac{K_3[\text{HL}]}{[\text{H}^+]} = 2.40 \times 10^{-11} \text{ M}$$



Histidine hydrochloride (FM 191.62) is H₂His⁺Cl⁻, the intermediate form between pK₁ and pK₂. A pH of 9.30 requires neutralizing all of the H₂His⁺ to HHis and then adding more KOH to create a mixture of HHIs and His⁻. Therefore, we must add 1 mol KOH for each mol of His-HCl to get to HHIs and then add some more KOH to obtain the mixture of HHIs and His⁻. Initial mol of His-HCl = 10.0 g/(191.62 g/mol) = 0.05219 mol. We require 0.05219 mol of KOH plus the amount *x* in the following table to obtain the correct mixture:

	HHis	+	OH ⁻	\rightarrow	His ⁻
Initial mol:	0.05219		<i>x</i>		—
Final mol:	0.05219 - <i>x</i>		—		<i>x</i>

$$\text{pH} = \text{p}K_3 + \log \frac{[\text{His}^{2-}]}{[\text{HHis}^-]} \Rightarrow 9.30 = 9.28 + \log \frac{x}{0.05219 - x}$$

$$\Rightarrow x = 0.02670$$

$$\begin{aligned}\text{Total mol KOH required} &= 0.05219 + 0.02670 = 0.0789 \text{ mol} \\ &= 78.9 \text{ mL of } 1.00 \text{ M KOH}\end{aligned}$$

9-23. (a) $\text{pH} = \text{p}K_3 (\text{citric acid}) + \log \frac{[\text{C}^{3-}] \gamma_{\text{C}^{3-}}}{[\text{HC}^{2-}] \gamma_{\text{HC}^{2-}}}$

$$\text{pH} = 6.396 + \log \frac{(1.00)(0.405)}{(2.00)(0.665)} = 5.88$$

(b) If the ionic strength is raised to 0.10 M,

$$\text{pH} = 6.396 + \log \frac{(1.00)(0.115)}{(2.00)(0.37)} = 5.59$$

9-24. (a) HA (b) A⁻

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

$$7.00 = 7.00 + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{A}^-]/[\text{HA}] = 1.0$$

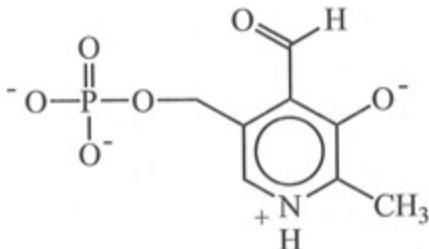
$$6.00 = 7.00 + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{A}^-]/[\text{HA}] = 0.10$$

9-25. (a) 4.00 (b) 8.00 (c) H₂A (d) HA⁻ (e) A²⁻

9-26. (a) 9.00 (b) 9.00 (c) BH⁺

(d) $12.00 = 9.00 + \log \frac{[\text{B}]}{[\text{BH}^+]} \Rightarrow [\text{B}]/[\text{BH}^+] = 1.0 \times 10^3$

9-27.



9-28. Fraction in form HA = $\alpha_{\text{HA}} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a} = \frac{10^{-5}}{10^{-5} + 10^{-4}} = 0.091$.

Fraction in form A⁻ = $\alpha_{\text{A}^-} = \frac{K_a}{[\text{H}^+] + K_a} = 0.909$.

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{\alpha_{\text{A}^-}}{\alpha_{\text{HA}}} = 10, \text{ which makes sense.}$$

9-29. $\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$, where $[\text{H}^+] = 10^{-7.00}$, $K_1 = 10^{-8.00}$, and $K_2 = 10^{-10.00} \Rightarrow \alpha_{\text{H}_2\text{A}} = 0.91$

	<u>pH 8.00</u>	<u>pH 10.00</u>
$\alpha_{\text{H}_2\text{A}}$	0.877	0.0496
α_{HA^-}	0.123	0.694
$\alpha_{\text{A}^{2-}}$	4.54×10^{-4}	0.257

	1.00	1.92	6.00	6.27	10.00
$\alpha_{\text{H}_2\text{A}}$	0.893	0.500	5.41×10^{-5}	2.23×10^{-5}	1.55×10^{-12}
α_{HA^-}	0.107	0.500	0.651	0.500	1.86×10^{-4}
$\alpha_{\text{A}^{2-}}$	5.76×10^{-7}	2.23×10^{-5}	0.349	0.500	0.9998

- 9-32. (a) The derivation follows the outline of Equations 9-19 through 9-21. The results are

$$\alpha_{\text{H}_3\text{A}} = \frac{[\text{H}_3\text{A}]}{F} = \frac{[\text{H}^+]^3}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

$$\alpha_{\text{H}_2\text{A}^-} = \frac{[\text{H}_2\text{A}^-]}{F} = \frac{[\text{H}^+]^2 K_1}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

$$\alpha_{\text{HA}^{2-}} = \frac{[\text{HA}^{2-}]}{F} = \frac{[\text{H}^+] K_1 K_2}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

$$\alpha_{\text{A}^{3-}} = \frac{[\text{A}^{3-}]}{F} = \frac{K_1 K_2 K_3}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

- (b) For phosphoric acid, $\text{p}K_1 = 2.148$, $\text{p}K_2 = 7.198$, and $\text{p}K_3 = 12.375$. At pH = 7.00, the previous expressions give $\alpha_{\text{H}_3\text{A}} = 8.6 \times 10^{-6}$, $\alpha_{\text{H}_2\text{A}^-} = 0.61$, $\alpha_{\text{HA}^{2-}} = 0.39$, and $\alpha_{\text{A}^{3-}} = 1.6 \times 10^{-6}$.

9-33. $\text{pH} = \text{p}K_{\text{NH}_4^+} + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \Rightarrow 9.00 = 9.245 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \Rightarrow \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 0.569$

$$\text{Fraction unprotonated} = \frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]} = \frac{0.569}{0.569 + 1} = 0.36$$

- 9-34. The quantity of morphine in the solution is negligible compared to the quantity of cacodylic acid. The pH is determined by the reaction of cacodylic acid (HA) with NaOH:

	HA	+	OH ⁻	→	A ⁻	+	H ₂ O
Initial mmol:	1.000		0.800		—		—
Final mmol:	0.200		—		0.800		—

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 6.19 + \log \frac{0.800}{0.200} = 6.79$$

For morphine (B), $K_a = K_w/K_b = 1.0 \times 10^{-14}/1.6 \times 10^{-6} = 6.25 \times 10^{-9}$

$$\Rightarrow \text{p}K_a = 8.20$$

At pH 6.79, we can write $\text{pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} \Rightarrow$

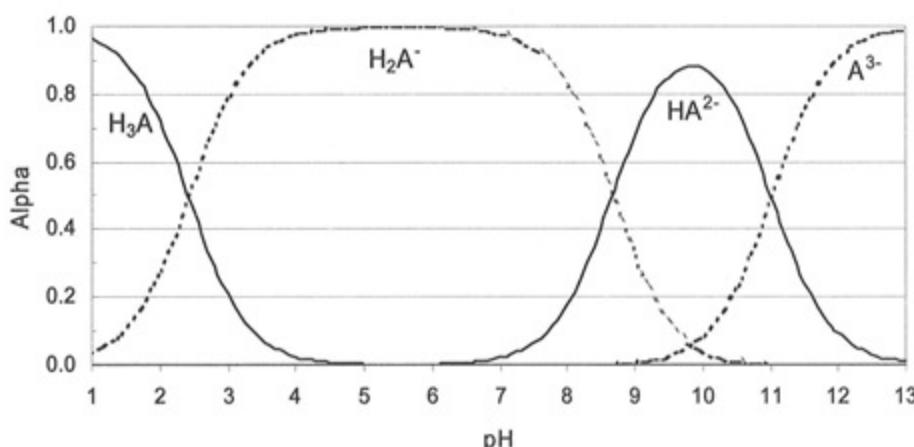
$$6.79 = 8.20 + \log \frac{[\text{B}]}{[\text{BH}^+]} \Rightarrow \frac{[\text{B}]}{[\text{BH}^+]} = 0.039 \Rightarrow [\text{B}] = 0.039 [\text{BH}^+]$$

$$\text{Fraction in form BH}^+ = \frac{[\text{BH}^+]}{[\text{B}] + [\text{BH}^+]} = \frac{[\text{BH}^+]}{0.039 [\text{BH}^+] + [\text{BH}^+]} = 96\%$$

- 9-35.

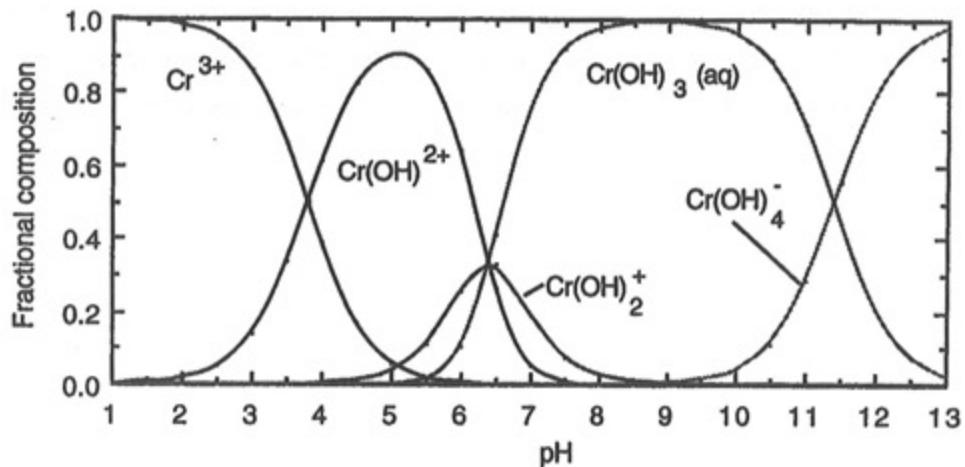
	A	B	C	D	E	F
1	Fractional composition for diprotic acid					
2						
3	K1 =	pH	[H ⁺]	$\alpha(\text{H}_2\text{A})$	$\alpha(\text{HA}^-)$	$\alpha(\text{A}^{2-})$
4	9.55E-04		1	0.1	9.91E-01	0.00946
5	K2 =		2	0.01	0.912562	0.087149
6	3.31E-05		3	0.001	0.503369	0.480713
7	pK1 =		4	0.0001	0.072928	0.696455
8	3.02		5	0.00001	0.002423	0.231386
9	pK2 =		6	0.000001	3.07E-05	0.029313
10	4.48		7	1E-07	3.15E-07	0.003011
11						
12	A4 = 10 ^{-A8}	$D4 = \$C4^2/(\$C4^2+\$C4*\$A\$4+\$A\$4*\$A\$6)$				
13	A6 = 10 ^{-A10}	$E4 = \$C4*\$A\$4/(\$C4^2+\$C4*\$A\$4+\$A\$4*\$A\$6)$				
14	C4 = 10 ^{-B4}	$F4 = \$A\$4*\$A\$6/(\$C4^2+\$C4*\$A\$4+\$A\$4*\$A\$6)$				

- 9-36.



9-37. (a) Fractional composition in tetraprotic system

	A	B	C	D	E	F	G	H	I
1	Fractional composition in tetraprotic system								
2									
3	Ka1 =	pH	[H ⁺]	Denom.	Alph(H4A)	Alph(H3A)	Alph(H2A)	Alph(HA)	Alph(A)
4	1.58E-04	1	1E-01	1.0E-04	1.0E+00	1.6E-03	6.3E-09	2.5E-14	9.9E-25
5	Ka2 =	2	1E-02	1.0E-08	9.8E-01	1.6E-02	6.2E-07	2.5E-11	9.8E-21
6	3.98E-07	3	1E-03	1.2E-12	8.6E-01	1.4E-01	5.4E-05	2.2E-08	8.6E-17
7	Ka3 =	4	1E-04	2.6E-16	3.9E-01	6.1E-01	2.4E-03	9.7E-06	3.9E-13
8	3.98E-07	5	1E-05	1.7E-19	5.7E-02	9.1E-01	3.6E-02	1.4E-03	5.7E-10
9	Ka4 =	6	1E-06	2.5E-22	4.1E-03	6.4E-01	2.5E-01	1.0E-01	4.0E-07
10	3.98E-12	7	1E-07	3.3E-24	3.0E-05	4.8E-02	1.9E-01	7.6E-01	3.0E-05
11		8	1E-08	2.6E-25	3.9E-08	6.2E-04	2.4E-02	9.7E-01	3.9E-04
12		9	1E-09	2.5E-26	4.0E-11	6.3E-06	2.5E-03	9.9E-01	4.0E-03
13		10	1E-10	2.6E-27	3.8E-14	6.1E-08	2.4E-04	9.6E-01	3.8E-02
14		11	1E-11	3.5E-28	2.9E-17	4.5E-10	1.8E-05	7.2E-01	2.8E-01
15		12	1E-12	1.2E-28	8.0E-21	1.3E-12	5.0E-07	2.0E-01	8.0E-01
16		13	1E-13	1.0E-28	9.8E-25	1.5E-15	6.2E-09	2.5E-02	9.8E-01
17									
18	C4 = 10^-B4								
19	$D4 = C4^4 + A4 * C4^3 + A4 * A6 * C4^2 + A4 * A6 * A8 * C4$								
20	$+ A4 * A6 * A8 * A10$								
21	E4 = C4^4 / D4								
22	F4 = \$A\$4 * C4^3 / D4			$H4 = \$A\$4 * \$A\$6 * \$A\$8 * C4 / D4$					
23	G4 = \$A\$4 * \$A\$6 * C4^2 / D4			$I4 = \$A\$4 * \$A\$6 * \$A\$8 * \$A\$10 / D4$					



(b) $K = 10^{-6.84} = [\text{Cr(OH)}_3(\text{aq})]$, so $[\text{Cr(OH)}_3(\text{aq})] = 10^{-6.84} \text{ M} = 1.45 \times 10^{-7} \text{ M}$

(c) $K_{a3} = 10^{-6.40} = \frac{[\text{Cr(OH)}_3(\text{aq})][\text{H}^+]}{[\text{Cr(OH)}_2^+]^2} = \frac{[10^{-6.84}][10^{-4.00}]}{[\text{Cr(OH)}_2^+]^2}$

$$\Rightarrow [\text{Cr(OH)}_2^+] = \frac{[10^{-6.84}][10^{-4.00}]}{10^{-6.40}} = 10^{-4.44} \text{ M}$$

$$K_{a2} = 10^{-6.40} = \frac{[\text{Cr(OH)}_2^+][\text{H}^+]}{[\text{Cr(OH})^{2+}]} = \frac{[10^{-4.44}][10^{-4.00}]}{[\text{Cr(OH})^{2+}]}$$

$$\Rightarrow [\text{Cr(OH})^{2+}] = \frac{[10^{-4.44}][10^{-4.00}]}{10^{-6.40}} = 10^{-2.04} \text{ M}$$

- 9-38. The isoelectric pH is the pH at which the protein has no net charge, even though it has many positive and negative sites. The isoionic pH is the pH of a solution containing only protein, H⁺, and OH⁻.
- 9-39. The average charge is zero. There is no pH at which all molecules have zero charge.
- 9-40. Isoionic [H⁺] = $\sqrt{\frac{K_1 K_2 (0.010) + K_1 K_w}{K_1 + (0.010)}}$ ⇒ pH = 5.72
 Isoelectric pH = $\frac{pK_1 + pK_2}{2} = 5.59$
- 9-41. A mixture of proteins is exposed to a strong electric field in a medium with a pH gradient. Positively charged molecules move toward the negative pole and negatively charged molecules move toward the positive pole. Each protein migrates until it reaches the point where the pH is the same as its isoelectric pH. At this point, the protein has no net charge and no longer moves. Each protein is therefore focused in one region at its isoelectric pH. If a protein diffuses out of its isoelectric zone, it becomes charged and migrates back into the zone.

CHAPTER 10

ACID-BASE TITRATIONS

- 10-1.** The equivalence point occurs when the quantity of titrant is exactly the stoichiometric amount needed for complete reaction with analyte. The end point occurs when there is an abrupt change in a physical property, such as pH or indicator color. Ideally, the end point is chosen to occur at the equivalence point.

10-2.	V_a	0	1	5	9	9.9	10	10.1	12
	pH	13.00	12.95	12.68	11.96	10.96	7.00	3.04	1.75

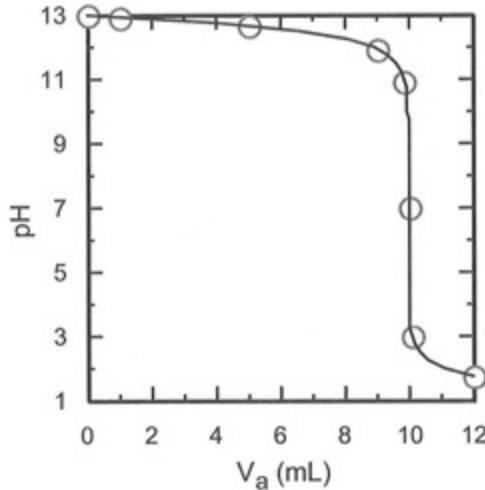
Representative calculations:

$$\underline{0 \text{ mL}}: \quad \text{pH} = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{10^{-14}}{0.100} = 13.00$$

$$\underline{1 \text{ mL}}: \quad [\text{OH}^-] = \frac{9}{10} (0.100) \frac{100}{101} = 0.0891 \text{ M} \Rightarrow \text{pH} = 12.95$$

$$\underline{10 \text{ mL}}: \quad [\text{OH}^-] = [\text{H}^+] = 10^{-7} \text{ M}$$

$$\underline{10.1 \text{ mL}}: \quad [\text{H}^+] = \left(\frac{0.1}{110.1} \right) (1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.04$$



- 10-3.** Consider the titration curve near the equivalence point. If we titrate strong acid with strong base, the concentration of H^+ is close to 1% of its initial value when we are 99% of the way to the equivalence point (i.e., when $V_b = 0.99V_e$). (This statement would be exactly true if there were no dilution occurring. We will neglect dilution.) If the initial acid concentration were, say, 0.1 M, then $[\text{H}^+] = 1\% \text{ of } 0.1 \text{ M} = 0.001 \text{ M}$ at $V_b = 0.99 V_e$. The pH is $-\log(0.001) = 3$. At 99.9% completion, $[\text{H}^+] = 0.1\% \text{ of } 0.1 \text{ M} = 0.0001 \text{ M}$ and the pH is 4. When the titration is 0.1% past the equivalence point, $[\text{OH}^-] = 0.0001 \text{ M}$ and the pH is $-\log(K_w/0.0001) = 10$. The pH jumps from 4 to 10 in the interval from $V_b =$

$0.999V_e$ to $1.001V_e$. Even though the concentration of H^+ hardly changes, its logarithm changes rapidly around the equivalence point because $[H^+]$ decreases by orders of magnitude with tiny additions of OH^- when there is hardly any H^+ present.

- 10-4.** The sketch should look like Figure 10-2. Before base is added, the pH is determined by the acid dissociation reaction of HA. Between the initial point and the equivalence point, each mole of OH^- converts an equivalent quantity of HA into A^- . The resulting buffer containing HA and A^- determines the pH. At the equivalence point, all HA has been converted to A^- . The pH is controlled by the base hydrolysis reaction of A^- with H_2O . After the equivalence point, excess OH^- is being added to the solution. To a good approximation, the pH is determined just by the concentration of excess OH^- .
- 10-5.** If the analyte is too weak or too dilute, there is very little change in pH at the equivalence point.

10-6.	V_b	0	1	5	9	9.9	10	10.1	12
	pH	3.00	4.05	5.00	5.95	7.00	8.98	10.96	12.25

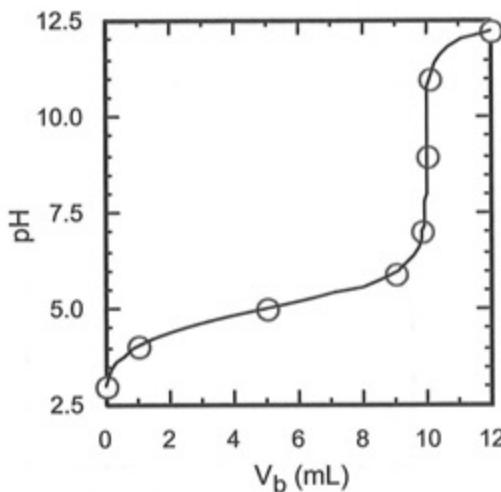
Representative calculations:

$$\underline{0 \text{ mL}}: \frac{0 \text{ mL}}{0.100 - x} = \frac{H^+}{x} + \frac{A^-}{x} \quad \frac{x^2}{0.100 - x} = 10^{-5.00} \Rightarrow x = 9.95 \times 10^{-4} \text{ M} \\ \Rightarrow \text{pH} = 3.00$$

$$\underline{1 \text{ mL}}: \text{pH} = pK_a + \log \frac{[A^-]}{[HA]} = 5.00 + \log \frac{1}{9} = 4.05$$

$$\underline{10 \text{ mL}}: \frac{10 \text{ mL}}{(100/110)(0.100) - x} = \frac{A^-}{x} + \frac{H_2O}{x} \quad \frac{x^2}{0.0909 - x} = \frac{K_w}{K_a} \\ \Rightarrow x = 9.53 \times 10^{-6} \\ \Rightarrow [H^+] = \frac{K_w}{x} \Rightarrow \text{pH} = 8.96$$

$$\underline{10.1 \text{ mL}}: [OH^-] = \left(\frac{0.1}{110.1} \right) (1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 10.96$$



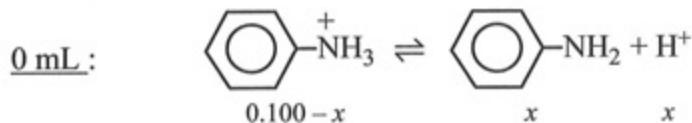
10-7. $\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{A}^-]}{[\text{HA}]}$ $\text{p}K_{\text{a}} - 1 = \text{p}K_{\text{a}} + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow \frac{[\text{A}^-]}{[\text{HA}]} = \frac{1}{10}$

If the ratio $\frac{[\text{A}^-]}{[\text{HA}]}$ is to be $\frac{1}{10}$, then $\frac{1}{11}$ of the initial HA must remain as HA.

At this point, $[\text{A}^-]/[\text{HA}] = (1/11)/(10/11) = 1/10$. So $\text{pH} = \text{p}K_{\text{a}} - 1$ when $V_{\text{b}} = V_{\text{e}}/11$.

In a similar manner, $\text{pH} = \text{p}K_{\text{a}} + 1$ when $V_{\text{b}} = 10V_{\text{e}}/11$.

For anilinium ion, $\text{p}K_{\text{a}} = 4.601$. For the titration of 100 mL of 0.100 M anilinium ion with 0.100 M OH^- , the reaction is



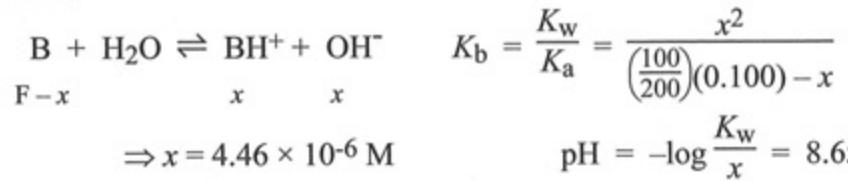
$$\frac{x^2}{0.100 - x} = K_{\text{a}} = 10^{-4.60} \Rightarrow x = 1.57 \times 10^{-3} \Rightarrow \text{pH} = 2.80$$

$V_{\text{e}}/11 = 9.09 \text{ mL}$: $\text{pH} = \text{p}K_{\text{a}} - 1 = 3.60$

$V_{\text{e}}/2 = 50.0 \text{ mL}$: $\text{pH} = \text{p}K_{\text{a}} = 4.60$

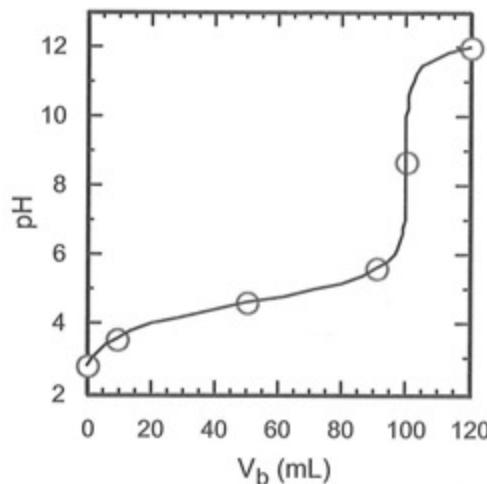
$10V_{\text{e}}/11 = 90.91 \text{ mL}$: $\text{pH} = \text{p}K_{\text{a}} + 1 = 5.60$

$V_{\text{e}} = 100.0 \text{ mL}$: BH^+ has been converted to B.

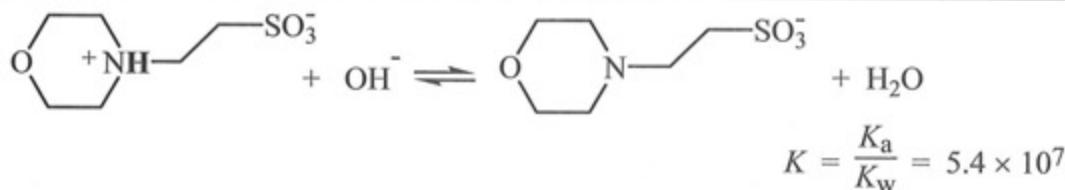
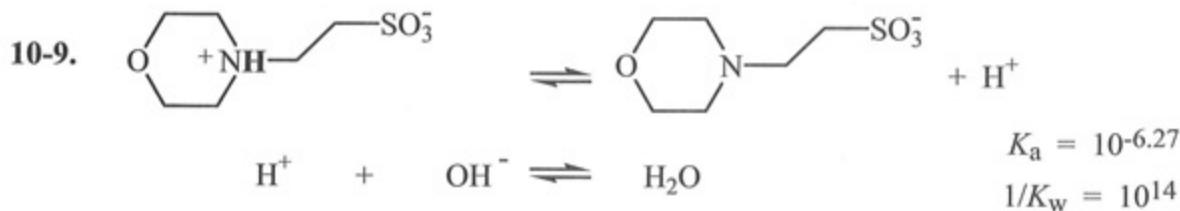
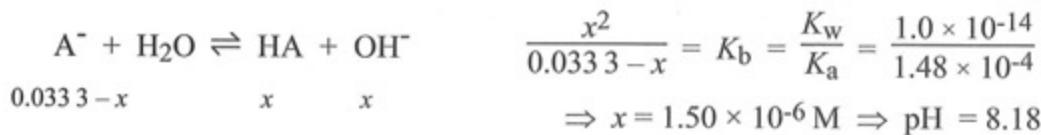


$1.2V_{\text{e}} = 120.0 \text{ mL}$: There are 20.0 mL of excess NaOH.

$$[\text{OH}^-] = \left(\frac{20}{220}\right)(0.100) = 9.09 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.96$$



- 10-8. The titration reaction is $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$. A volume of V mL of HA will require $2V$ mL of KOH to reach the equivalence point, because $[\text{HA}] = 0.100 \text{ M}$ and $[\text{KOH}] = 0.0500 \text{ M}$. The formal concentration of A^- at the equivalence point will be $\left(\frac{V}{V+2V}\right)(0.100) = 0.0333 \text{ M}$. The pH is found by writing



Initial mmol:	5.857	x	—
Final mmol:	$5.857 - x$	—	x

$$\text{pH} = 9.24 = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 9.39 + \log \frac{x}{5.857 - x} \Rightarrow x = 2.428 \text{ mmol}$$

$$[\text{OH}^-] = \frac{2.428 \text{ mmol}}{22.63 \text{ mL}} = 0.107 \text{ M}$$

10-11.	$(\text{CH}_3)_3\text{NH}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{N} + \text{H}_2\text{O}$	
Initial mmol:	1.00	0.40
Final mmol:	0.60	—

First, find the ionic strength:

$$[(\text{CH}_3)_3\text{NH}^+] = 0.60 \text{ mmol}/14.0 \text{ mL} = 0.04286 \text{ M}$$

$$[\text{Br}^-] = 1.00 \text{ mmol}/14.0 \text{ mL} = 0.07143 \text{ M}$$

$$[\text{Na}^+] = 0.40 \text{ mmol}/14.0 \text{ mL} = 0.02857 \text{ M}$$

$$\mu = \frac{1}{2} \sum c_i z_i^2 = 0.071 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{B}] \gamma_{\text{B}}}{[\text{BH}^+] \gamma_{\text{BH}^+}}$$

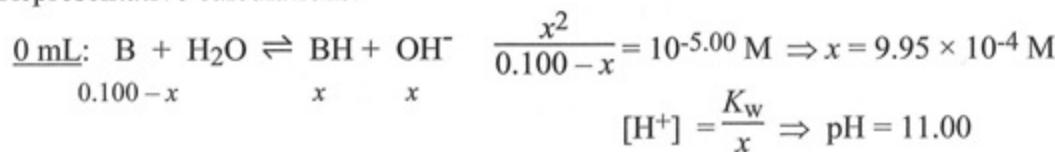
$$\text{pH} = 9.799 + \log \frac{(0.0286)(1.00)}{(0.0429)(0.80)} = 9.72$$

In the previous calculation, we used the size of $(\text{CH}_3)_3\text{NH}^+$ (400 pm) and the activity coefficient interpolated from Table 7-1.

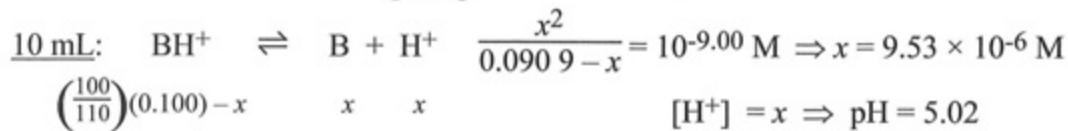
- 10-12. The sketch should look like Figure 10-9. Before base is added, the pH is determined by the base hydrolysis reaction of B with H_2O . Between the initial point and the equivalence point, each mole of H^+ converts an equivalent quantity of B into BH^+ . The resulting buffer containing B and BH^+ determines the pH. At the equivalence point, all B has been converted to BH^+ . The pH is controlled by the acid dissociation reaction of BH^+ . After the equivalence point, excess H^+ is being added to the solution. To a good approximation, the pH is determined just by the concentration of excess H^+ .
- 10-13. At the equivalence point, the weak base, B, is converted completely to the conjugate acid, BH^+ , which is necessarily acidic.

10-14.	V_a	0	1	5	9	9.9	10	10.1	12
	pH	11.00	9.95	9.00	8.05	7.00	5.02	3.04	1.75

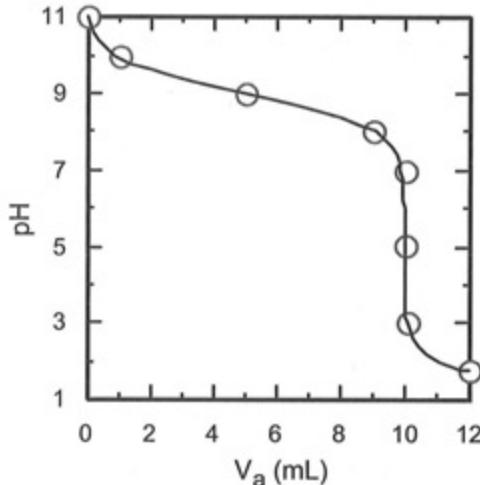
Representative calculations:



$$\underline{1 \text{ mL}}: \text{pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 9.00 + \log \frac{9}{1} = 9.95$$

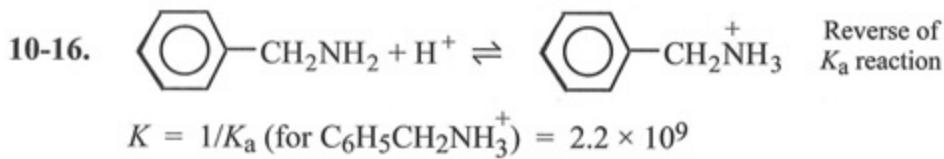


$$\underline{10.1 \text{ mL}}: [\text{H}^+] = \left(\frac{0.1}{110.1} \right) (1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.04$$

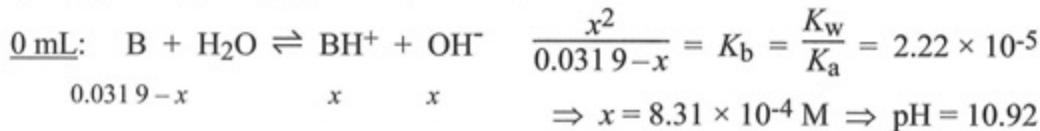


- 10-15. The maximum buffer capacity is reached when

$$V = \frac{1}{2}V_e, \text{ at which time } \frac{[\text{B}]}{[\text{BH}^+]} = 1 \text{ and pH} = \text{p}K_a \text{ (for BH⁺)}.$$



- 10-17. Titration reaction: $\text{B} + \text{H}^+ \rightarrow \text{BH}^+$. To find the equivalence point, we write $(50.0)(0.0319) = (V_e)(0.0500) \Rightarrow V_e = 31.9 \text{ mL}$.



12.0 mL:	B	+	H ⁺	→	BH ⁺
Initial:	31.9	12.0	—		
Final:	19.9	—	12.0		

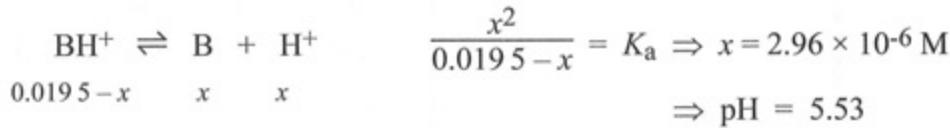
$$\text{pH} = \text{p}K_a + \log \frac{[\text{B}]}{[\text{BH}^+]} = 9.35 + \log \frac{19.9}{12.0} = 9.57$$

$$\underline{1/2V_e}: \text{pH} = \text{p}K_a = 9.35$$

$$\underline{30 \text{ mL}}: \text{pH} = \text{p}K_a + \log \frac{1.9}{30.0} = 8.15$$

V_e : B has been converted to BH^+ at a concentration of $\left(\frac{50.0}{81.9}\right)(0.0319)$

$$= 0.0195 \text{ M}$$



$$\underline{35.0 \text{ mL}}: [\text{H}^+] = \left(\frac{3.1}{85.0}\right)(0.0500) = 1.82 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.74$$

10-18. Titration reaction: $\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$

At the equivalence point, moles of CN^- = moles of H^+

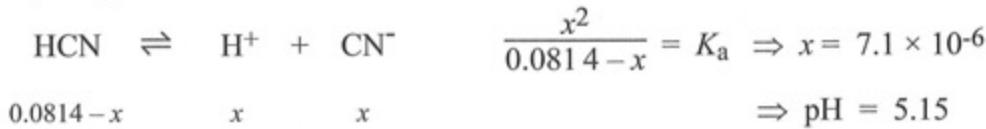
$$(0.100 \text{ M})(50.00 \text{ mL}) = (0.438 \text{ M})(V_e) \Rightarrow V_e = 11.42 \text{ mL}$$

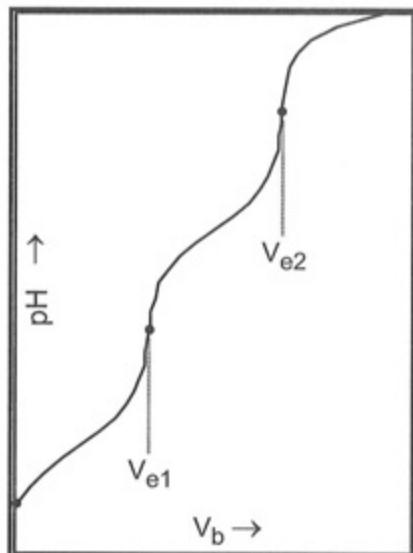
(a)	CN^-	+	H^+	\rightarrow	HCN
Initial:	11.42		4.20		—
Final:	7.22		—		4.20
$\text{pH} = \text{p}K_a + \log \frac{7.22}{4.20} = 9.45$					

(b) 11.82 mL is 0.40 mL past the equivalence point.

$$[\text{H}^+] = \left(\frac{0.40}{61.82}\right)(0.438 \text{ M}) = 2.83 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.55$$

(c) At the equivalence point, we have made HCN at a formal concentration of $\left(\frac{50.00}{61.42}\right)(0.100) = 0.0814 \text{ M}$.

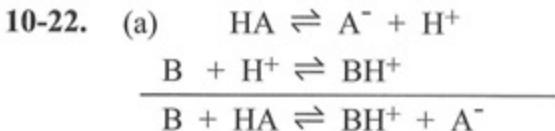


10-19.

The pH of the initial solution before base is added is determined by the first acid dissociation reaction of H₂A. As base is added, it converts H₂A into an equivalent amount of HA⁻. The buffer consisting of H₂A and HA⁻ governs the pH. At the first equivalence point, we have a solution of "pure" HA⁻, the intermediate form of a diprotic acid. The pH is determined by the competitive acid and base reactions of HA⁻. Between the two equivalence points there is a mixture of HA⁻ and A²⁻, which is another buffer. At the second equivalence point, we have converted all HA⁻ into A²⁻, whose base hydrolysis reaction determines the pH. After the second equivalence point, the excess OH⁻ added from the buret is mainly responsible for determining the pH, with negligible contribution from A²⁻.

10-20. The protein has an average charge of 0 at the isoelectric point. Since the isoionic point occurs at a lower pH, the average charge of the protein must be positive at the isoionic point.

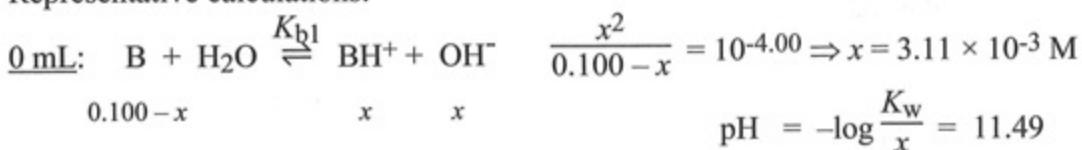
10-21. The equivalence point could be attained by mixing pure HA plus NaCl. Neglecting effects of ionic strength, the pH is equivalent to that of a solution of pure HA. This is the isoionic pH.



(b) In the upper curve, $\frac{3}{2}V_e$ is halfway between the first and second equivalence points. The pH is simply pK₂, since there is a 1:1 mixture of HA⁻ and A²⁻. In the lower curve, pK₂ (= pK_{BH⁺}) occurs when there is a 1:1 mixture of B and BH⁺. To achieve this condition, all of B is first transformed into BH⁺ by reaction with HA until V_e is reached. Then, at $2V_e$ one more equivalent of B has been added, giving a 1:1 mole ratio B:BH⁺, so pH = pK_{BH⁺}.

10-23.	V_a	0	1	5	9	10	11	15	19	20	22
	pH	11.49	10.95	10.00	9.05	8.00	6.95	6.00	5.05	3.54	1.79

Representative calculations:



$$\text{1 mL: pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 10.00 + \log \frac{9}{1} = 10.95$$

$$\text{10 mL: Predominant form is BH}^+ \text{ with formal concentration } \frac{100}{110}(0.100) = 0.0909 \text{ M}$$

$$[\text{H}^+] \approx \sqrt{\frac{10^{-6.00} 10^{-10.00} (0.0909) + 10^{-6.00} 10^{-14.00}}{10^{-6.00} + 0.0909}}$$

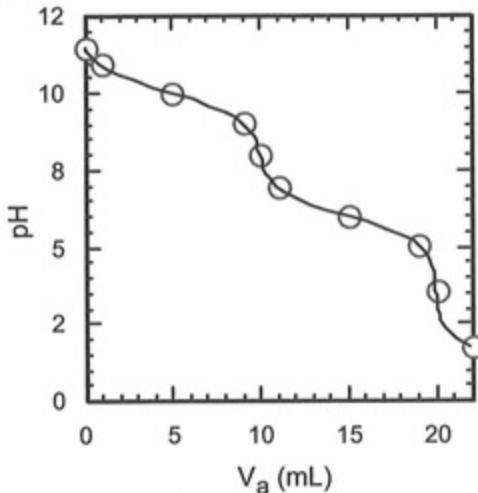
$$= 1.00 \times 10^{-8} \Rightarrow \text{pH} = 8.00$$

$$\text{11 mL: pH} = \text{p}K_{\text{BH}_2^{2+}} + \log \frac{[\text{BH}_2^{2+}]}{[\text{BH}_2^{2+}]} = 6.00 + \log \frac{9}{1} = 6.95$$

$$\text{20 mL: } \text{BH}_2^{2+} \rightleftharpoons \text{BH}^+ + \text{H}^+ \quad \frac{x^2}{0.0833-x} = 10^{-6.00} \Rightarrow x = 2.88 \times 10^{-4}$$

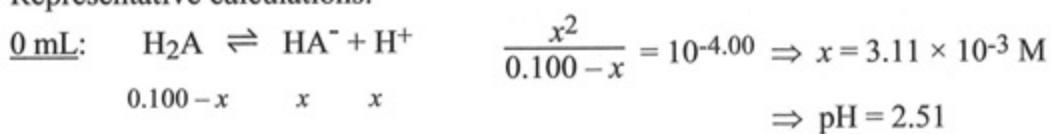
$$\frac{100}{120}(0.100) - x \qquad x \qquad x \qquad \Rightarrow \text{pH} = 3.54$$

$$\text{22 mL: } [\text{H}^+] = \left(\frac{2}{122}\right)(1.00) = 1.64 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 1.79$$



10-24.	V_b	0	1	5	9	10	11	15	19	20	22
	pH	2.51	3.05	4.00	4.95	6.00	7.05	8.00	8.95	10.46	12.21

Representative calculations:



$$\underline{1 \text{ mL}}: \quad \text{pH} = \text{p}K_1 + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]} = 4.00 + \log \frac{1}{9} = 3.05$$

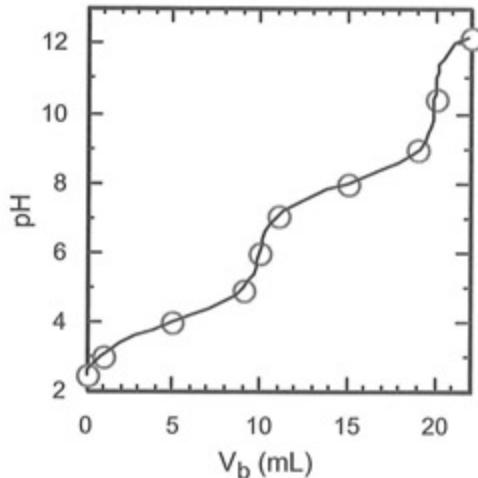
$$\underline{10 \text{ mL}}: \quad \text{Predominant form is HA}^- \text{ with formal concentration } \left(\frac{100}{110}\right)(0.100) \\ = 0.0909 \text{ M.}$$

$$[\text{H}^+] \approx \sqrt{\frac{10^{-4.00} 10^{-8.00} (0.0909) + 10^{-4.00} 10^{-14.00}}{10^{-4.00} + 0.0909}} \\ = 9.99 \times 10^{-7} \Rightarrow \text{pH} = 6.00$$

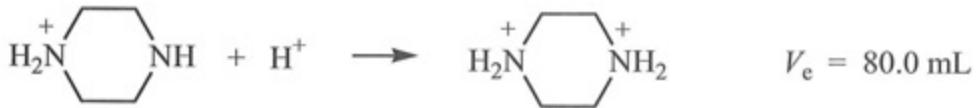
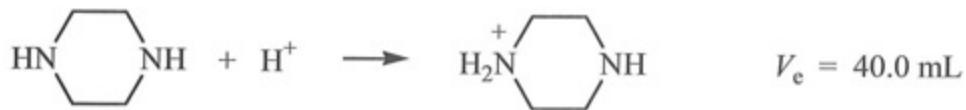
$$\underline{11 \text{ mL}}: \quad \text{pH} = \text{p}K_2 + \log \frac{[\text{A}^{2-}]}{[\text{HA}^-]} = 8.00 + \log \frac{1}{9} = 7.05$$

$$\underline{20 \text{ mL}}: \quad \text{A}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HA}^- + \text{OH}^- \quad \frac{x^2}{0.0833 - x} = \frac{K_w}{K_2} \Rightarrow x = 2.88 \times 10^{-4} \text{ M} \\ \text{pH} = -\log \frac{K_w}{x} = 10.46$$

$$\underline{22 \text{ mL}}: \quad [\text{OH}^-] = \left(\frac{2}{122}\right)(1.00) = 1.64 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 12.21$$



10-25. Titration reactions:



$$\underline{0 \text{ mL}}: \quad \text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \quad \frac{x^2}{0.100 - x} = K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{1.86 \times 10^{-10}} \\ \Rightarrow x = 2.29 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.36$$

$$\underline{10.0 \text{ mL}}: \text{pH} = \text{p}K_2 + \log \frac{[\text{B}]}{[\text{BH}^+]} = 9.731 + \log \frac{3}{1} = 10.21$$

$$\underline{20.0 \text{ mL}}: \text{pH} = \text{p}K_2 = 9.73$$

$$\underline{30.0 \text{ mL}}: \text{pH} = \text{p}K_2 + \log \frac{1}{3} = 9.25$$

40.0 mL: B has been converted to BH⁺ at a formal concentration of

$$F = \left(\frac{40.0}{80.0} \right) (0.100) = 0.0500 \text{ M}$$

$$[\text{H}^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

$$= \sqrt{\frac{(4.65 \times 10^{-6})(1.86 \times 10^{-10})(0.0500) + (4.65 \times 10^{-6})(1.0 \times 10^{-14})}{4.65 \times 10^{-6} + 0.0500}}$$

$$\Rightarrow \text{pH} = 7.53$$

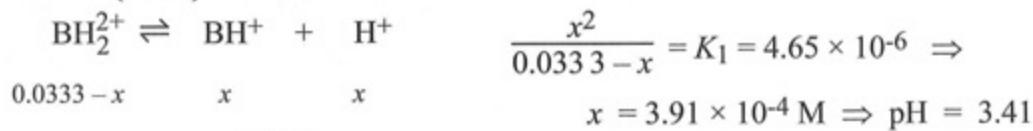
$$\underline{50.0 \text{ mL}}: \text{pH} = \text{p}K_1 + \log \frac{[\text{BH}^+]}{[\text{BH}_2^{2+}]} = 5.333 + \log \frac{3}{1} = 5.81$$

$$\underline{60.0 \text{ mL}}: \text{pH} = \text{p}K_1 = 5.33$$

$$\underline{70.0 \text{ mL}}: \text{pH} = \text{p}K_1 + \log \frac{1}{3} = 4.86$$

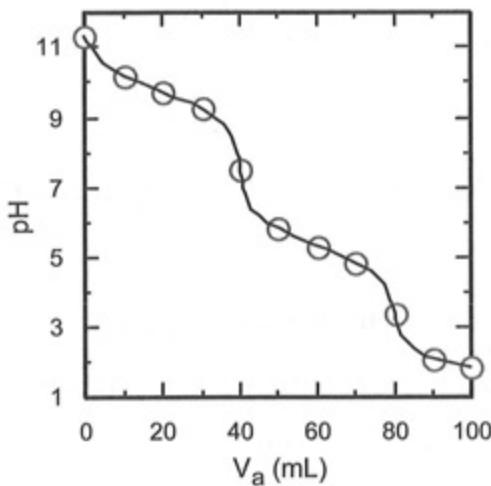
80.0 mL: B has been converted to BH₂²⁺ at a formal concentration of

$$\left(\frac{40.0}{120.0} \right) (0.100) = 0.0333 \text{ M}$$

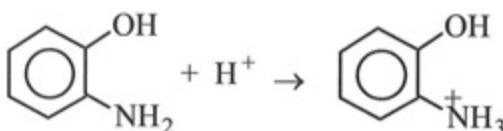


$$\underline{90.0 \text{ mL}}: [\text{H}^+] = \left(\frac{10.0}{130.0} \right) (0.100) \Rightarrow \text{pH} = 2.11$$

$$\underline{100.0 \text{ mL}}: [\text{H}^+] = \left(\frac{20.0}{140.0} \right) (0.100) \Rightarrow \text{pH} = 1.85$$



10-26.



Initial mmol:	0.500	0.164	—
Final mmol:	0.336	—	0.164

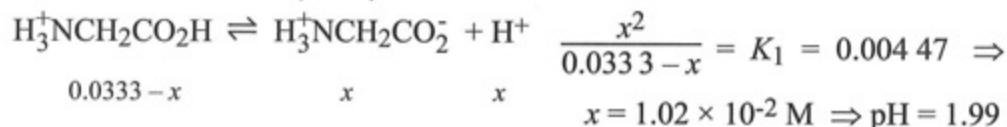
$$\text{pH} = \text{p}K_1 + \log \frac{[\text{B}]}{[\text{BH}^+]} = 4.70 + \log \frac{0.336}{0.164} = 5.01$$

10-27. (a) Titration reactions:



At the second equivalence point, the formal concentration of

$$\text{H}_3^+\text{NCH}_2\text{CO}_2\text{H} \text{ is } \left(\frac{50.0}{150.0}\right)(0.100) = 0.0333 \text{ M}$$

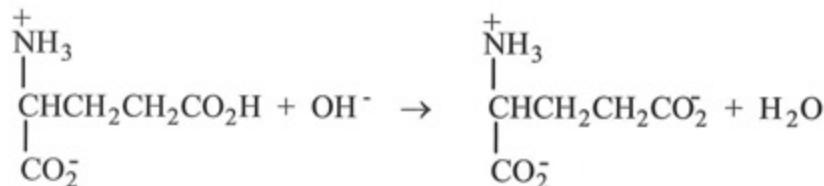
(b) At $V_a = 90.0 \text{ mL}$, the approximation gives $\text{pH} = \text{p}K_1 + \log \frac{[\text{HG}]}{[\text{H}_2\text{G}^+]} = 2.35 +$ $\log \frac{1}{4} = 1.75$, which is lower than the correct value at 100.0 mL . The pH

calculated with the equation in Table 10-5 is 2.16, which is higher than the equivalence point pH of 1.99.

At $V_a = 101.0 \text{ mL}$, the approximation gives $[\text{H}^+] = \left(\frac{1.0}{151.0}\right)(0.100) = 6.62$ $\times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.18$, which is higher than the correct value at 100.0 mL .

The pH calculated with the equation in Table 10-5 is 1.98, which is lower than the equivalence point pH of 1.99.

10-28. (a)

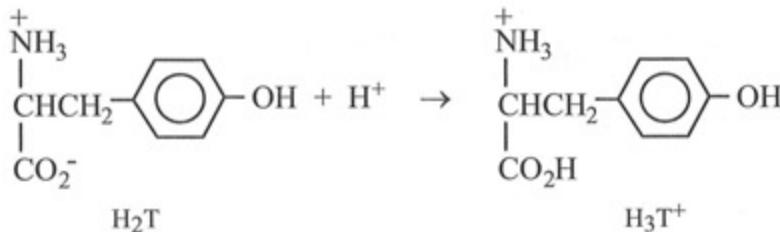
(b) $V \text{ mL}$ of glutamic acid will require $\frac{0.100}{0.025} V = 4.00 V \text{ mL}$ of RbOH to reach

the equivalence point. The formal concentration of product will be

$$\left(\frac{V}{V+4.00V}\right)(0.100) = 0.0200 \text{ M.}$$

$$\begin{aligned} [\text{H}^+] &= \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}} \\ &= \sqrt{\frac{(5.0 \times 10^{-5})(1.1 \times 10^{-10})(0.0200) + (5.0 \times 10^{-5})(1.0 \times 10^{-14})}{(5.0 \times 10^{-5}) + 0.0200}} \\ &= 7.42 \times 10^{-8} \text{ M} \Rightarrow \text{pH} = 7.13 \end{aligned}$$

10-29.



One volume of tyrosine (0.0100 M) requires 2.5 volumes of HClO_4 (0.00400 M), so the formal concentration of tyrosine at the equivalence point is $(\frac{1}{1+2.5})(0.0100 \text{ M}) = 0.00286 \text{ M}$. The pH is calculated from the acid dissociation of H_3T^+ .

$$\begin{array}{ccc} \text{H}_3\text{T}^+ & \rightleftharpoons & \text{H}_2\text{T} + \text{H}^+ \\ 0.00286-x & & x & x \\ & & & \frac{x^2}{0.00286-x} = K_1 = 3.9 \times 10^{-3} \Rightarrow \\ & & & x = 0.00192 \text{ M} \Rightarrow \text{pH} = 2.72 \end{array}$$

10-30. (a) $\text{C}^{2-} + \text{H}^+ \rightarrow \text{HC}^-$. $V_e = 20.0 \text{ mL}$. At the equivalence point, the formal concentration of HC^- is $(\frac{40.0}{60.0})(0.0300) = 0.0200 \text{ M}$.

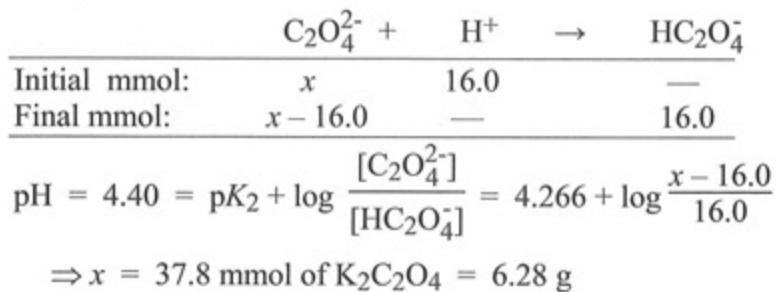
$$\begin{aligned} [\text{H}^+] &= \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}} \\ &= \sqrt{\frac{(4.4 \times 10^{-9})(1.82 \times 10^{-11})(0.0200) + (4.4 \times 10^{-9})(1.0 \times 10^{-14})}{(4.4 \times 10^{-9}) + 0.0200}} \\ &= 2.86 \times 10^{-10} \text{ M} \Rightarrow \text{pH} = 9.54 \end{aligned}$$

$$\begin{array}{ccc} \text{(b)} \quad \text{H}_3\text{C}^+ & \rightleftharpoons & \text{H}_2\text{C} + \text{H}^+ \\ 0.0500-x & & x & x \\ & & & \frac{x^2}{0.0500-x} = K_1 = 0.02 \\ & & & \Rightarrow x = 0.023 \text{ M} \Rightarrow \text{pH} = 1.64 \end{array}$$

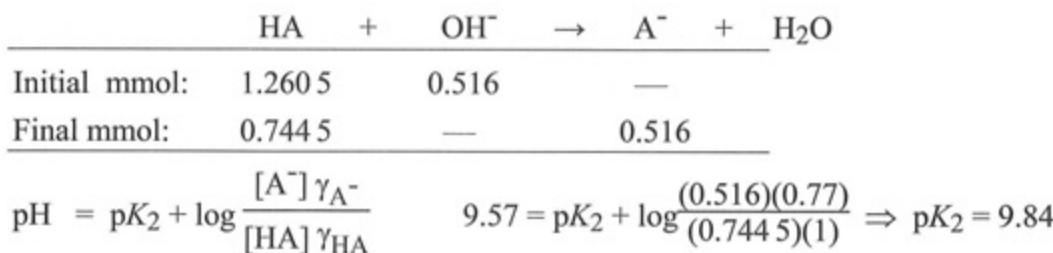
$$\text{pH} = \text{p}K_3 + \log \frac{[\text{C}^{2-}]}{[\text{HC}^-]}$$

$$1.64 = 10.74 + \log \frac{[\text{C}^{2-}]}{[\text{HC}^-]} \Rightarrow \frac{[\text{C}^{2-}]}{[\text{HC}^-]} = 7.9 \times 10^{-10}$$

- 10-31.** The two values of pK_a for oxalic acid are 1.250 and 4.266. At a pH of 4.40, the $C_2O_4^{2-}$ has not yet been half-neutralized.



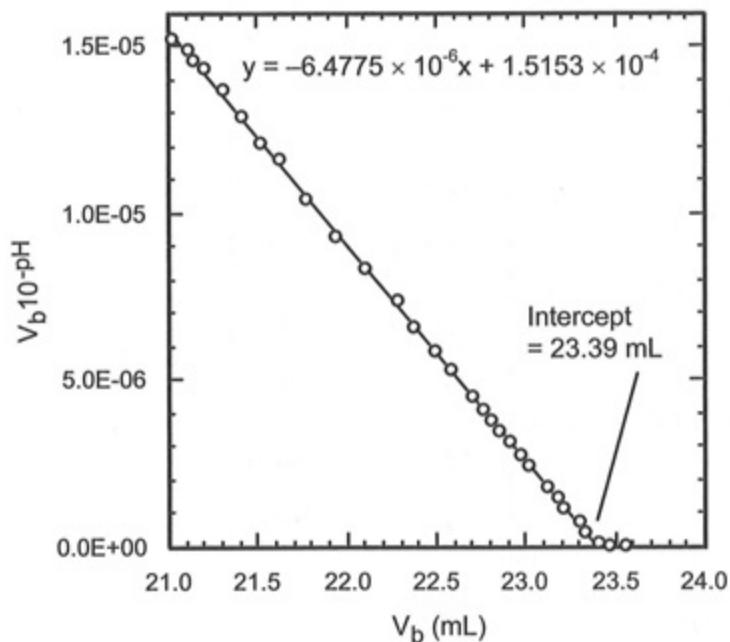
- 10-32.** Neutral alanine is designated HA.



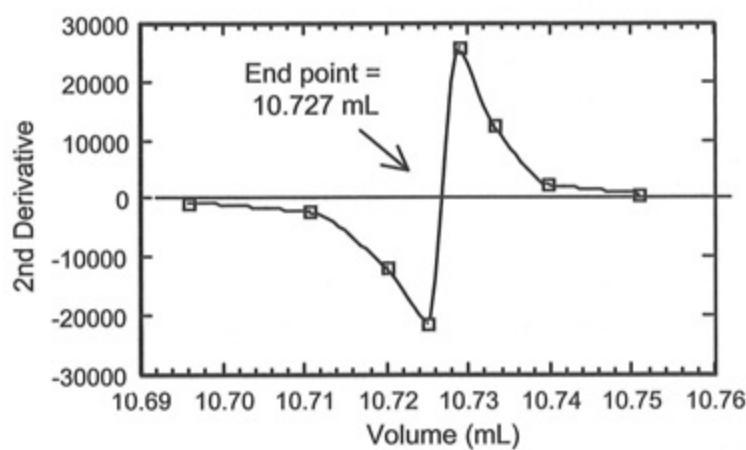
- 10-33.** A Gran plot allows us to find the equivalence point by extrapolating from points measured prior to the equivalence point.

- 10-34.** It is evident from the following table of data that the end point is near 23.4 mL, where the derivative $d\text{pH}/dV_b$ is greatest. A graph of $V_b 10^{-\text{pH}}$ versus V_b follows. The points from 21.01 to 23.30 mL were fit by the method of least squares to give the equation shown in the graph. The intercept is found by setting $y = 0$ in the equation, giving $x = V_e = 23.39 \text{ mL}$.

V_b (mL)	$V_b 10^{-\text{pH}}$	V_b (mL)	$V_b 10^{-\text{pH}}$	V_b (mL)	$V_b 10^{-\text{pH}}$
21.01	15.22×10^{-6}	22.10	8.40×10^{-6}	22.97	2.76×10^{-6}
21.10	14.94	22.27	7.37	23.01	2.41
21.13	14.62	22.37	6.60	23.11	1.79
21.20	14.33	22.48	5.91	23.17	1.46
21.30	13.75	22.57	5.29	23.21	1.16
21.41	12.90	22.70	4.53	23.30	0.75
21.51	12.10	22.76	4.14	23.32	0.42
21.61	11.61	22.80	3.78	23.40	0.12
21.77	10.42	22.85	3.46	23.46	0.01
21.93	9.35	22.91	3.16	23.55	0.003



10-35.



Calculations are shown in the spreadsheet:

	A	B	C	D	E	F
1	Derivatives in a titration curve					
2	Data		1st derivative		2nd derivative	
3	mL NaOH	pH	mL	$\Delta \text{pH}/\Delta \text{mL}$	mL	$\Delta(\Delta \text{pH}/\Delta \text{mL})$
4	10.679	7.643				ΔmL
5			10.6875	-11.5		
6	10.696	7.447	10.7045	-20.9	10.6960	-553.6
7			10.7108	-48.9		
8	10.713	7.091	10.7200	-11770.8		
9			10.7250	-21375.0		
10	10.721	6.700	10.7230	-119.5		
11			10.7270	-205.0		
12	10.725	6.222	10.7310	-102.2	10.7290	25687.5
13			10.7355	-46.4	10.7333	12411.1
14	10.729	5.402	10.7440	-26.4	10.7398	2351.0
15			10.7508	885.2		
16	10.733	4.993	10.7575	-14.5		
17						
18	10.738	4.761				
19						
20	10.750	4.444				
21						
22	10.765	4.227				
23	Representative formulas:					
24	$C_5 = (A_6+A_4)/2$		$E_6 = (C_7+C_5)/2$			
25	$D_5 = (B_6-B_4)/(A_6-A_4)$		$F_6 = (D_7-D_5)/(C_7-C_5)$			

- 10-36.** The quotient $[\text{HIn}]/[\text{In}^-]$ changes from 10:1 when $\text{pH} = \text{p}K_{\text{HIn}} - 1$ to 1:10 when $\text{pH} = \text{p}K_{\text{HIn}} + 1$. This change is generally sufficient to cause a complete color change.
- 10-37.** The indicator has its acidic color when $\text{pH} = \text{p}K_{\text{HIn}} - 1$ because HIn is the dominant species. The indicator has its basic color when $\text{pH} = \text{p}K_{\text{HIn}} + 1$ because In^- is the dominant species. The color changes from the acidic color to the intermediate color to the basic color as the pH rises through the range $\text{p}K_{\text{HIn}} - 1$ to $\text{p}K_{\text{HIn}} + 1$. If the indicator is chosen correctly for the titration, this indicator pH transition range coincides with the steep part of the titration curve. The color change occurs near the equivalence point, which is the center of the steep portion of the titration curve.
- 10-38.** The Henderson-Hasselbalch equation for the indicator, HIn, is $\text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$. If we know $\text{p}K_{\text{HIn}}$ and we measure $\frac{[\text{In}^-]}{[\text{HIn}]}$ spectroscopically, then we can calculate the pH.

10-39. Strong acids, such as H₂SO₄, HCl, HNO₃, and HClO₄ have pK_a < 0.

10-40. yellow, green, blue

10-41. (a) red (b) orange (c) yellow

10-42. (a) red (b) orange (c) yellow (d) red

10-43. No. When a weak acid is titrated with a strong base, the solution contains A⁻ at the equivalence point. A solution of A⁻ must have a pH above 7.

10-44. (a) The titration reaction is F⁻ + H⁺ → HF.

If V mL of NaF are used, $V_e = \frac{1}{2}V$, since the concentration of HClO₄ is twice as great as the concentration of NaF. The formal concentration of HF at the equivalence point is $\left(\frac{V}{V + \frac{1}{2}V}\right)(0.030\ 0) = 0.020\ 0\text{ M}$.

The pH is determined by the acid dissociation of HF.



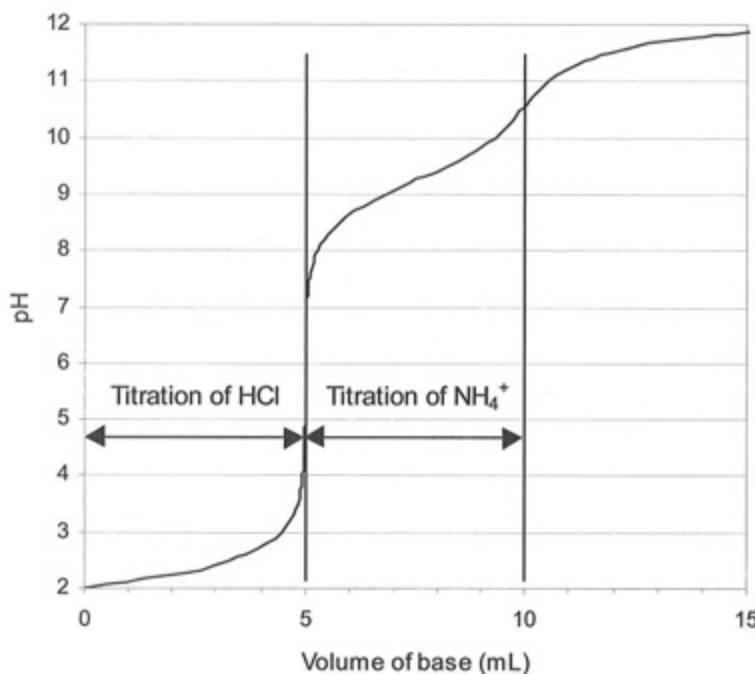
(b) The pH is so low that there would not be much (if any) break (inflection) in the titration curve at the equivalence point. A sharp change in indicator color will not be seen.

10-45. (a) violet (red + blue) (b) blue (c) yellow



(b) One possible indicator is methyl red, using the yellow end point.

For a more complete analysis of this problem, we could compute the titration curve for a mixture of HCl and NH₄⁺. For simplicity, we consider the mixture to be a “diprotic” acid with $K_1 = 100$ (i.e., a “strong” acid) and $K_2 = 5.7 \times 10^{-10}$ for the ammonium ion. We use the spreadsheet equation in Table 10-5 for titrating H₂A with strong base, taking $C_a = 0.01\text{ M}$ and $C_b = 0.1\text{ M}$. An indicator with a color change in the range ~4.5–7.0 would find the HCl end point without titrating a significant amount of NH₄⁺.



- 10-47. Grams of cleaner titrated = $\left(\frac{4.373}{10.231 + 39.466}\right)(10.231 \text{ g}) = 0.9003 \text{ g}$
 mol HCl used = mol NH₃ present = $(0.01422 \text{ L})(0.1063 \text{ M}) = 1.512 \text{ mmol}$
 1.512 mmol NH₃ = 25.74 mg NH₃
 wt% NH₃ = $\frac{2.574 \times 10^{-2} \text{ g}}{0.9003 \text{ g}} \times 100 = 2.859\%$
- 10-48. Alkalinity is the capacity of natural water to react with H⁺ to reach pH 4.5, which is the second equivalence point in the titration of carbonate (CO₃²⁻) with H⁺. Alkalinity measures [OH⁻] + [CO₃²⁻] + [HCO₃⁻] plus any other bases that are present. Bromocresol green is blue above pH 5.4 and yellow below pH 3.8. It will be at its green end-point color between these two pH values, which approximates pH 4.5.
- 10-49. Tris(hydroxymethyl) aminomethane (H₂NC(CH₂OH)₃), mercuric oxide (HgO), sodium carbonate (Na₂CO₃), and borax (NaB₄O₇ · 10H₂O) can be used to standardize HCl. Potassium acid phthalate (HO₂C-C₆H₄-CO₂K⁺), HCl azeotrope, potassium hydrogen iodate (KH(IO₃)₂), sulfosalicylic acid double salt (C₇H₅SO₆K·C₇H₄SO₆K₂), and sulfamic acid (H₃NSO₃⁻) can be used to standardize NaOH.

- 10-50.** The greater the equivalent mass, the more primary standard is required. There is less relative error in weighing a large mass of reagent than a small mass.
- 10-51.** Potassium acid phthalate is dried at 105° and weighed accurately into a flask. It is titrated with NaOH, using a pH electrode or phenolphthalein to observe the end point.
- 10-52.** Grams of tris titrated = $\frac{4.963}{(1.023 + 99.367)} (1.023) = 0.050\ 57 = 0.417\ 5 \text{ mmol}$
 Concentration of HNO₃ = $\frac{0.417\ 5 \text{ mmol}}{5.262 \text{ g solution}} = 0.079\ 34 \text{ mol/kg solution}$
- 10-53.** True mass = $m = \frac{(1.023) \left(1 - \frac{0.001\ 2}{8.0}\right)}{\left(1 - \frac{0.001\ 2}{1.33}\right)} = 1.023\ 8 \text{ g}$
- Failure to account for buoyancy introduces a systematic error of $100 \times (1.023\ 8 - 1.023) / 1.023 = 0.08\%$ in the calculated molarity of HCl.
 The true mass is higher than the measured mass of Tris, so the calculated HCl molarity is too low.
- 10-54.** The mmoles of HgO in 0.194 7 g = 0.898 9, which will make 1.798 mmol of OH⁻ by reaction with Br⁻ plus H₂O. HCl molarity = 1.798 mmol/17.98 mL = 0.100 0 M.
- 10-55.** 30 mL of 0.05 M OH⁻ = 1.5 mmol = 0.31 g of potassium acid phthalate.
- 10-56.** (a) From a graph of weight percent vs pressure,
 HCl = 20.254% when $P = 746 \text{ Torr}$.
- (b) We need 0.100 00 mole of HCl = 3.646 1 g
 $\frac{3.646\ 1 \text{ g HCl}}{0.202\ 54 \text{ g HCl/g solution}} = 18.0019 \text{ g of solution.}$
- The mass required (weighed in air) is given by Equation 2-1.
- $$m' = \frac{(18.0019) \left(1 - \frac{0.001\ 2}{1.096}\right)}{\left(1 - \frac{0.001\ 2}{8.0}\right)} = 17.985 \text{ g}$$
- 10-57.** (a) For a rectangular distribution of uncertainty in atomic mass, divide the uncertainty listed in the periodic table by $\sqrt{3}$ to find the standard uncertainty:

$$C: 12.010\ 7 \pm 0.000\ 8/\sqrt{3} = 12.010\ 7 \pm 0.000\ 4_6$$

$$H: 1.007\ 94 \pm 0.000\ 07/\sqrt{3} = 1.007\ 94 \pm 0.000\ 04_0$$

$$O: 15.999\ 4 \pm 0.000\ 3/\sqrt{3} = 15.999\ 4 \pm 0.000\ 1_7$$

$$K: 39.098\ 3 \pm 0.000\ 1/\sqrt{3} = 39.098\ 3 \pm 0.000\ 0_{58}$$

$$8C: 8(12.010\ 7 \pm 0.000\ 4_6) = 96.085\ 6 \pm 0.003\ 7$$

$$5H: 5(1.007\ 94 \pm 0.000\ 04_0) = 5.039\ 7 \pm 0.000\ 20$$

$$4O: 4(15.999\ 4 \pm 0.000\ 1_7) = 63.997\ 6 \pm 0.000\ 69$$

$$1K: 1(39.098\ 3 \pm 0.000\ 0_{58}) = 39.098\ 3 \pm 0.000\ 0_{58}$$

$$\text{C}_8\text{H}_5\text{O}_4\text{K}: \quad 204.221\ 2 \pm ?$$

$$\text{Uncertainty} = \sqrt{0.003\ 7^2 + 0.000\ 20^2 + 0.000\ 69^2 + 0.000\ 058^2} = 0.003\ 8$$

$$\text{Answer: } 204.221 \pm 0.004 \text{ g/mol}$$

- (b) For a rectangular distribution, divide the stated uncertainty by $\sqrt{3}$ to find the standard uncertainty. Purity = $1.000\ 00 \pm 0.000\ 05/\sqrt{3} = 1.000\ 00 \pm 0.000\ 03$

10-58. $5.00 \text{ mL of } 0.033\ 6 \text{ M HCl} = 0.168\ 0 \text{ mmol}$. $6.34 \text{ mL of } 0.010\ 0 \text{ M NaOH} = 0.063\ 4 \text{ mmol}$. HCl consumed by NH₃ = $0.168\ 0 - 0.063\ 4 = 0.104\ 6 \text{ mmol} = 1.465 \text{ mg of nitrogen}$. $256 \mu\text{L of protein solution contains } 9.702 \text{ mg protein}$. $1.465 \text{ mg of N}/9.702 \text{ mg protein} = 15.1 \text{ wt\%}$.

10-59. When an acid that is stronger than H₃O⁺ is added to H₂O, it reacts to give H₃O⁺ and is “leveled” to the strength of H₃O⁺. Similarly, bases stronger than OH⁻ are leveled to the strength of OH⁻.

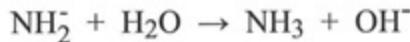
10-60. Methanol and ethanol have nearly the same acidity as water. Both of the following equilibria are driven to the right because of the high concentration of H₂O:

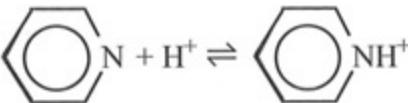


- 10-61.** (a) In acetic acid, strong acids are not leveled to the strength of CH₃CO₂H₂⁺. Therefore, very weak bases can be titrated in acetic acid.
 (b) If tetrabutylammonium hydroxide were added to an acetic acid solution, most of the hydroxide would react with acetic acid instead of analyte. However, OH⁻ will not react with pyridine, so this solvent would be suitable.

- 10-62.** Sodium amide and phenyl lithium are stronger bases than OH⁻. Each reacts with

H_2O to give OH^- :



- 10-63. The reaction of pyridine with acid is 

Methanol is less polar than water. If methanol is added to the aqueous solution, the neutral pyridine molecule will tend to be favored over the protonated pyridinium cation. It will take a higher concentration of acid (a lower pH) to protonate pyridine in the mixed solvent. pK_a for pyridinium ion is lowered when methanol is added to the solution.

- 10-64. Titration reaction: $\text{K}^+\text{HP}^- + \text{Na}^+\text{OH}^- \rightarrow \text{K}^+\text{Na}^+\text{P}^{2-} + \text{H}_2\text{O}$

Begin with $C_a V_a$ moles of K^+HP^- and add $C_b V_b$ moles of NaOH

$$\text{Fraction of titration} = \phi = \frac{C_b V_b}{C_a V_a}$$

Charge balance: $[\text{H}^+] + [\text{Na}^+] + [\text{K}^+] = [\text{HP}^-] + 2[\text{P}^{2-}] + [\text{OH}^-]$

$$\text{Substitutions: } [\text{K}^+] = \frac{C_a V_a}{V_a + V_b} \quad [\text{Na}^+] = \frac{C_b V_b}{V_a + V_b}$$

$$[\text{HP}^-] = \alpha_{\text{HP}^-} \frac{C_a V_a}{V_a + V_b} \quad [\text{P}^{2-}] = \alpha_{\text{P}^{2-}} \frac{C_a V_a}{V_a + V_b}$$

Putting these expressions into the charge balance gives

$$[\text{H}^+] + \frac{C_b V_b}{V_a + V_b} + \frac{C_a V_a}{V_a + V_b} = \alpha_{\text{HP}^-} \frac{C_a V_a}{V_a + V_b} + 2\alpha_{\text{P}^{2-}} \frac{C_a V_a}{V_a + V_b} + [\text{OH}^-]$$

Multiply by $V_a + V_b$ and collect terms:

$$[\text{H}^+]V_a + [\text{H}^+]V_b + C_b V_b + C_a V_a = \alpha_{\text{HP}^-}C_a V_a + 2\alpha_{\text{P}^{2-}}C_a V_a + [\text{OH}^-]V_a + [\text{OH}^-]V_b$$

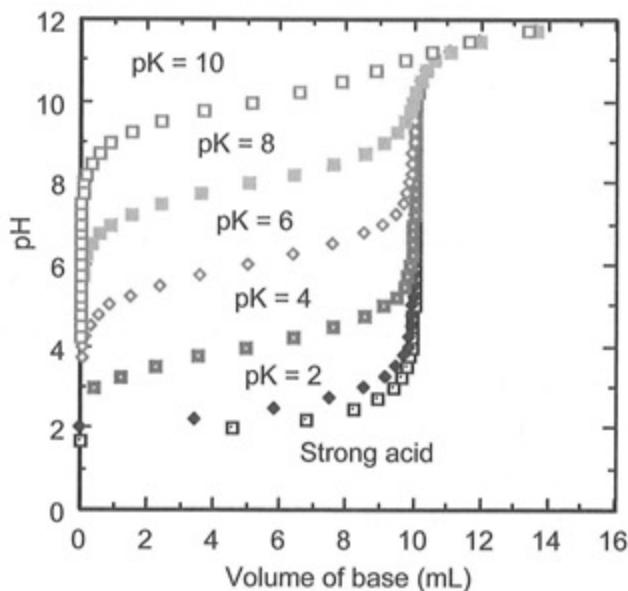
$$V_a ([\text{H}^+] + C_a - \alpha_{\text{HP}^-}C_a - 2\alpha_{\text{P}^{2-}}C_a - [\text{OH}^-]) = V_b([\text{OH}^-] - [\text{H}^+] - C_b)$$

$$\frac{V_b}{V_a} = \frac{\alpha_{\text{HP}^-}C_a + 2\alpha_{\text{P}^{2-}}C_a - C_a - [\text{H}^+] + [\text{OH}^-]}{C_b + [\text{H}^+] - [\text{OH}^-]}$$

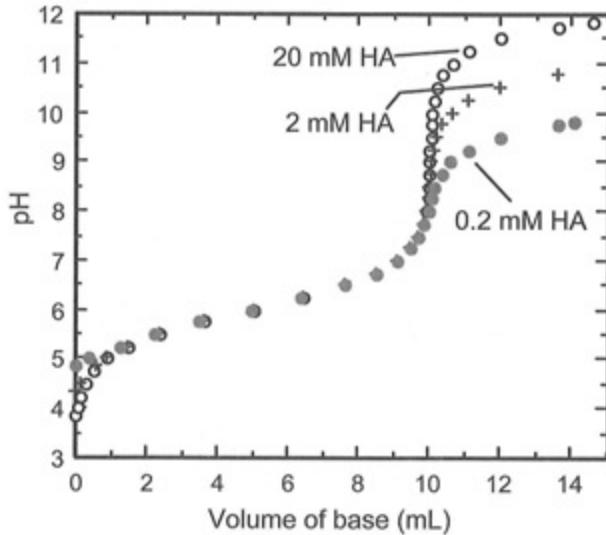
Multiply both sides by $\frac{1/C_a}{1/C_b}$:

$$\phi = \frac{C_b V_b}{C_a V_a} = \frac{\alpha_{\text{HP}^-} + 2\alpha_{\text{P}^{2-}} - 1 - \frac{[\text{H}^+] - [\text{OH}^-]}{C_a}}{1 + \frac{[\text{H}^+] - [\text{OH}^-]}{C_b}}$$

10-65.

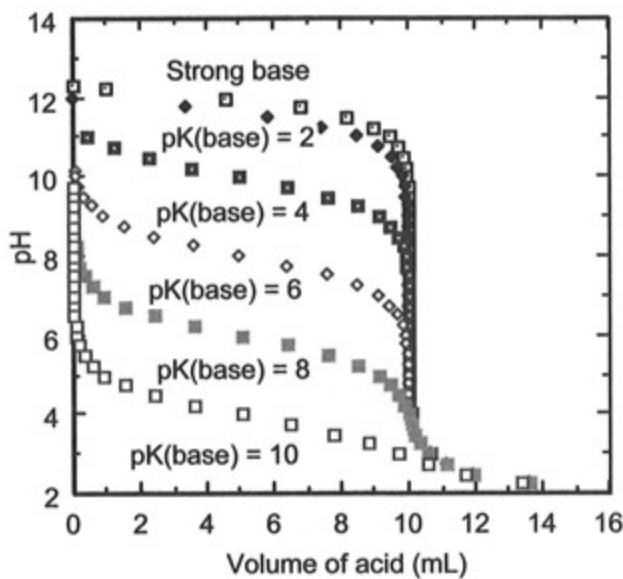


10-66.



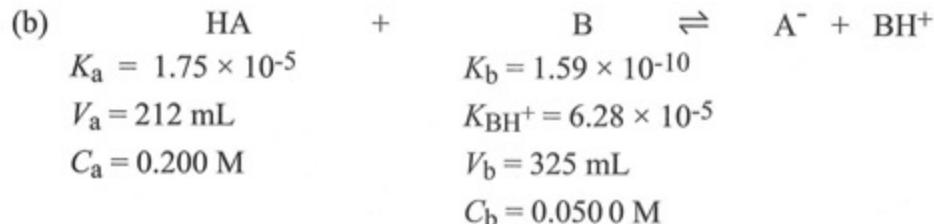
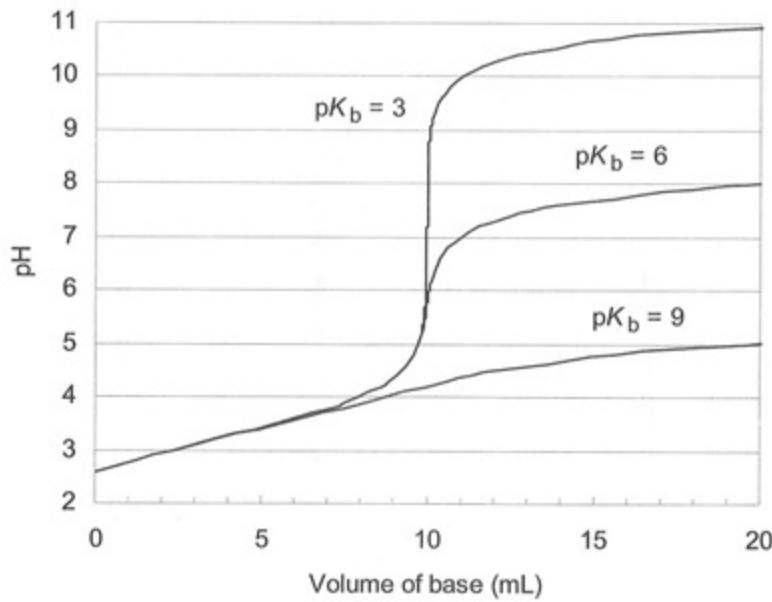
10-67.

	A	B	C	D	E	F	G
1	Effect of pK_b in the titration of weak base with strong acid						
2							
3	Ca =	pH	[H ⁺]	[OH ⁻]	Alpha(BH ⁺)	Phi	V _a (mL)
4	0.1	2.00	1.00E-02	1.00E-12	9.90E-01	1.66E+00	16.557
5	C _b =	2.90	1.26E-03	7.94E-12	9.26E-01	1.00E+00	10.020
6	0.02	3.50	3.16E-04	3.16E-11	7.60E-01	7.78E-01	7.780
7	V _b =	4.00	1.00E-04	1.00E-10	5.00E-01	5.06E-01	5.055
8	50	4.50	3.16E-05	3.16E-10	2.40E-01	2.42E-01	2.419
9	K(BH ⁺) =	6.00	1.00E-06	1.00E-08	9.90E-03	9.95E-03	0.100
10	1E-04	8.15	7.08E-09	1.41E-06	7.08E-05	5.17E-07	0.000
11	K _w =						
12	1E-14			E4 = C4/(C4+\$A\$10)			
13		C4 = 10 ^{-B4}		F4 = (E4+(C4-D4)/\$A\$6)/(1-(C4-D4)/\$A\$4)			
14		D4 = \$A\$12/C4		G4 = F4*\$A\$6*\$A\$8/\$A\$4			



10-68. (a)

	A	B	C	D	E	F	G	H
1	Titrating weak acid with weak base							
2								
3	$C_b =$	pH	$[H^+]$	$[OH^-]$	$\text{Alpha}(A^-)$	$\text{Alpha}(BH^+)$	Φ	$V_b \text{ (mL)}$
4	0.1	2.86	1.4E-03	7.2E-12	6.76E-02	1.00E+00	-1.4E-03	-0.01
5	$C_a =$	3.00	1.0E-03	1.0E-11	9.09E-02	1.00E+00	4.1E-02	0.41
6	0.02	4.00	1.0E-04	1.0E-10	5.00E-01	1.00E+00	4.9E-01	4.95
7	$V_a =$	5.00	1.0E-05	1.0E-09	9.09E-01	9.99E-01	9.1E-01	9.09
8	50	6.00	1.0E-06	1.0E-08	9.90E-01	9.90E-01	1.0E+00	10.00
9	$K_a =$	7.00	1.0E-07	1.0E-07	9.99E-01	9.09E-01	1.1E+00	10.99
10	1E-04	8.00	1.0E-08	1.0E-06	1.00E+00	5.00E-01	2.0E+00	20.00
11	$K_w =$							
12	1E-14		$A16 = \$A\$12/\$A\14		$D4 = \$A\$12/C4$			
13	$K_b =$		$C4 = 10^{-B4}$		$E4 = \$A\$10/(C4+\$A\$10)$			
14	1E-06			$F4 = C4/(C4+\$A\$16)$				
15	$K(BH^+) =$			$G4 = (E4-(C4-D4)/\$A\$6)/(F4+(C4-D4)/\$A\$4)$				
16	1E-08			$H4 = G4 * \$A\$6 * \$A\$8 / \$A\4				



To find the equilibrium constant we write

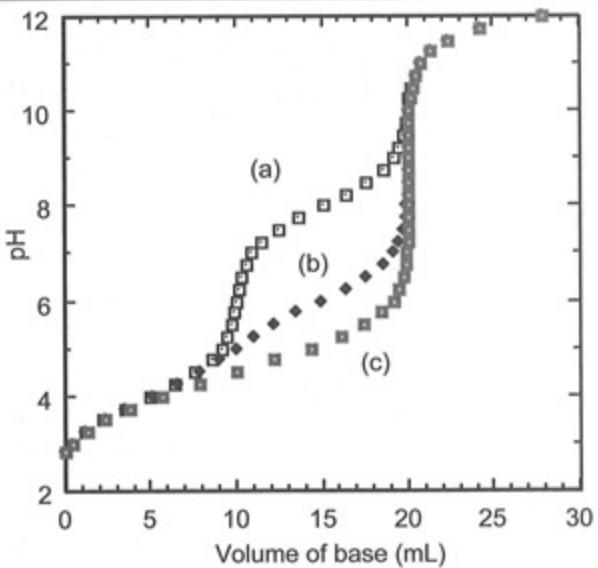
$$\begin{array}{c} \text{HA} \rightleftharpoons \text{A}^- + \text{H}^+ \\ \text{H}^+ + \text{B} \rightleftharpoons \text{BH}^+ \\ \hline \text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{BH}^+ \end{array} \quad \begin{array}{l} K_a \\ 1/K_{\text{BH}^+} \\ \hline K = K_a/K_{\text{BH}^+} = 0.279 \end{array}$$

A pH of 4.16 gives $V_b = 325.0 \text{ mL}$ in the following spreadsheet:

	A	B	C	D	E	F	G	H
1	Mixing acetic acid and sodium benzoate							
2								
3	$C_b =$	pH	$[\text{H}^+]$	$[\text{OH}^-]$	$\text{Alpha}(\text{A}^-)$	$\text{Alpha}(\text{BH}^+)$	Phi	$V_b (\text{mL})$
4	0.05	4.00	1.0E-04	1.0E-10	1.49E-01	6.14E-01	2.4E-01	204.28
5	$C_a =$	4.2	6.3E-05	1.6E-10	2.17E-01	5.01E-01	4.3E-01	365.98
6	0.2	4.1	7.9E-05	1.3E-10	1.81E-01	5.58E-01	3.2E-01	272.78
7	$V_a =$	4.15	7.1E-05	1.4E-10	1.98E-01	5.30E-01	3.7E-01	315.79
8	212	4.1598	6.9E-05	1.4E-10	2.02E-01	5.24E-01	3.8E-01	325.03
9	$K_a =$							
10	1.750E-05		A16 = \$A\$12/\$A\$14					
11	$K_w =$		C4 = 10^-B4					
12	1.E-14		D4 = \$A\$12/C4					
13	$K_b =$		E4 = \$A\$10/(C4+\$A\$10)					
14	1.592E-10		F4 = C4/(C4+\$A\$16)					
15	$K(\text{BH}^+) =$		G4 = (E4-(C4-D4)/\$A\$6)/(F4+(C4-D4)/\$A\$4)					
16	6.281E-05		H4 = G4*\$A\$6*\$A\$8/\$A\$4					

10-69.

	A	B	C	D	E	F	G	H
1	Titrating diprotic acid with strong base							
2								
3	Cb =	pH	[H+]	[OH-]	Alpha(HA-)	Alpha(A2-)	Phi	Vb (mL)
4	0.1	2.865	1.4E-03	7.3E-12	6.83E-02	5.00E-07	5.0E-05	0.000
5	Ca =	4.00	1.0E-04	1.0E-10	5.00E-01	5.00E-05	4.9E-01	4.946
6	0.02	6.00	1.0E-06	1.0E-08	9.80E-01	9.80E-03	1.0E+00	9.999
7	Va =	8.00	1.0E-08	1.0E-06	5.00E-01	5.00E-01	1.5E+00	15.000
8	50	10.0	1.0E-10	1.0E-04	9.90E-03	9.90E-01	2.0E+00	19.971
9	Kw =	12.0	1.0E-12	1.0E-02	1.00E-04	1.00E+00	2.8E+00	27.777
10	1E-14							
10	K1 =		C4 = 10^-B4			D4 = \$A\$12/C4		
12	1E-4		E4 = C4*\$A\$12/(C4^2+C4*\$A\$12+\$A\$12*\$A\$14)					
13	K2 =		F4 = \$A\$12*\$A\$14/(C4^2+C4*\$A\$12+\$A\$12*\$A\$14)					
14	1.E-08		G4 = (E4+2*F4-(C4-D4)/\$A\$6)/(1+(C4-D4)/\$A\$4)					
15			H4 = G4*\$A\$6*\$A\$8/\$A\$4					

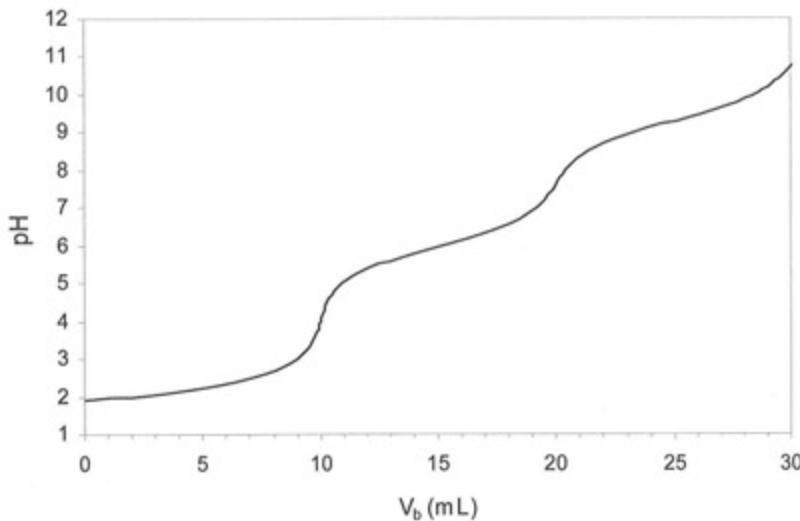


10-70.

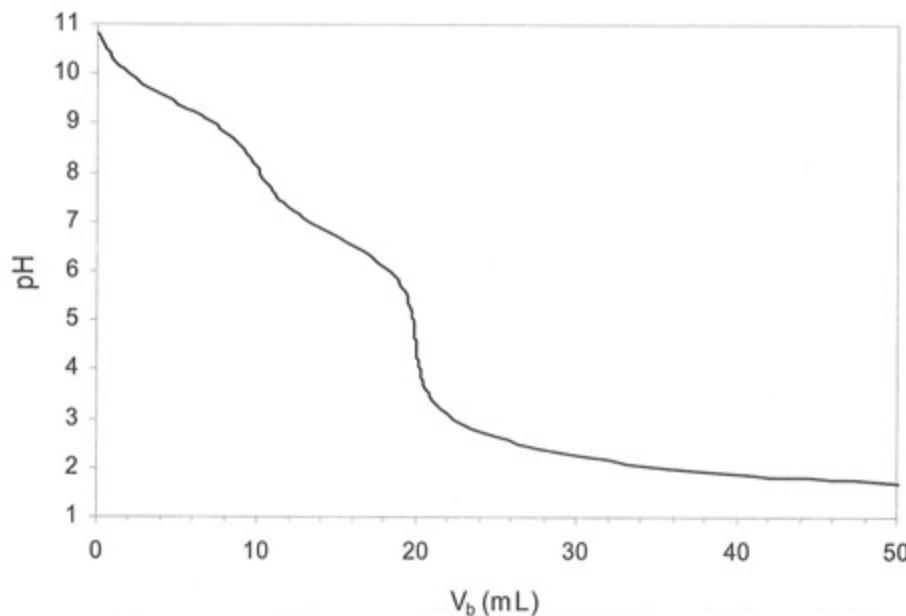
	A	B	C	D	E	F	G	H
1	Titrating nicotine with strong acid							
2								
3	$C_b =$	pH	$[H^+]$	$[OH^-]$	$\text{Alpha}(BH_2)$	$\text{Alpha}(BH)$	Phi	$V_a \text{ (mL)}$
4	0.1	1.75	1.8E-02	5.6E-13	9.62E-01	3.83E-02	2.6E+00	26.023
5	$C_a =$	2.00	1.0E-02	1.0E-12	9.34E-01	6.61E-02	2.3E+00	22.599
6	0.1	3.00	1.0E-03	1.0E-11	5.86E-01	4.14E-01	1.6E+00	16.117
7	$V_b =$	4.00	1.0E-04	1.0E-10	1.24E-01	8.76E-01	1.1E+00	11.258
8	10	5.00	1.0E-05	1.0E-09	1.39E-02	9.85E-01	1.0E+00	10.127
9	$K_w =$	6.00	1.0E-06	1.0E-08	1.39E-03	9.85E-01	9.9E-01	9.875
10	1.E-14	7.00	1.0E-07	1.0E-07	1.24E-04	8.76E-01	8.8E-01	8.764
11	$K_{B1} =$	8.00	1.0E-08	1.0E-06	5.86E-06	4.14E-01	4.1E-01	4.145
12	7.079E-7	9.00	1.0E-09	1.0E-05	9.34E-08	6.61E-02	6.6E-02	0.660
13	$K_{B2} =$	10.00	1.0E-10	1.0E-04	9.93E-10	7.03E-03	6.0E-03	0.060
14	1.41E-11	10.42	3.8E-11	2.6E-04	1.44E-10	2.68E-03	5.4E-05	0.001
15	$K_{A1} =$							
16	7.077E-4		$C_4 = 10^{-B4}$			$D4 = \$A\$12/C4$		
17	$K_{A2} =$				$E4 = C4 * C4 / (C4^2 + C4 * \$A\$16 + \$A\$16 * \$A\$18)$			
18	1.413E-8				$F4 = C4 * \$A\$16 / (C4^2 + C4 * \$A\$16 + \$A\$16 * \$A\$18)$			
19					$G4 = (F4 + 2 * E4 + (C4 - D4) / \$A\$4) / (1 - (C4 - D4) / \$A\$6)$			
20					$H4 = G4 * \$A\$4 * \$A\$8 / \$A\6			

10-71.

	A	B	C	D	E	F	G	H	I
1	Titrating H_3A with NaOH								
2									
3	$C_b =$	pH	$[H^+]$	$[OH^-]$	$\text{Alpha}(H_2A')$	$\text{Alpha}(HA^{2-})$	$\text{Alpha}(A^{3-})$	Phi	$V_b \text{ (mL)}$
4	0.1	1.89	1.29E-02	7.76E-13	6.61E-01	5.50E-05	2.24E-12	1.50E-02	0.150
5	$C_a =$	2.00	1.00E-02	1.00E-12	7.15E-01	7.66E-05	4.02E-12	1.96E-01	1.958
6	0.02	3.00	1.00E-03	1.00E-11	9.61E-01	1.03E-03	5.40E-10	9.04E-01	9.037
7	$V_a =$	4.00	1.00E-04	1.00E-10	9.86E-01	1.06E-02	5.54E-08	1.00E+00	10.006
8	50	5.00	1.00E-05	1.00E-09	9.03E-01	9.67E-02	5.08E-06	1.10E+00	10.958
9	$K_w =$	6.00	1.00E-06	1.00E-08	4.83E-01	5.17E-01	2.71E-04	1.52E+00	15.176
10	1E-14	7.00	1.00E-07	1.00E-07	8.50E-02	9.10E-01	4.78E-03	1.92E+00	19.198
11	$K_1 =$	8.00	1.00E-08	1.00E-06	8.79E-03	9.42E-01	4.94E-02	2.04E+00	20.407
12	2.51E-02	9.00	1.00E-09	1.00E-05	6.12E-04	6.55E-01	3.44E-01	2.34E+00	23.441
13	$K_2 =$	10.00	1.00E-10	1.00E-04	1.49E-05	1.60E-01	8.40E-01	2.85E+00	28.478
14	1.07E-06	11.00	1.00E-11	1.00E-03	1.75E-07	1.87E-02	9.81E-01	3.06E+00	30.619
15	$K_3 =$	12.00	1.00E-12	1.00E-02	1.77E-09	1.90E-03	9.98E-01	3.89E+00	38.868
16	5.25E-10		$C_4 = 10^{-B4}$						
17	$pK_1 =$			$D4 = \$A\$10/C4$					
18	1.60				$E4 = \$C4^2 * \$A\$12 / (\$C4^3 + \$C4^2 * \$A\$12 + \$C4 * \$A\$12 * \$A\$14 + \$A\$12 * \$A\$14 * \$A\$16)$				
19	$pK_2 =$				$F4 = \$C4 * \$A\$12 * \$A\$14 / (\$C4^3 + \$C4^2 * \$A\$12 + \$C4 * \$A\$12 * \$A\$14 + \$A\$12 * \$A\$14 * \$A\$16)$				
20	5.97				$G4 = \$A\$12 * \$A\$14 * \$A\$16 / (\$C4^3 + \$C4^2 * \$A\$12 + \$C4 * \$A\$12 * \$A\$14 + \$A\$12 * \$A\$14 * \$A\$16)$				
21	$pK_3 =$				$H4 = (E4 + 2 * F4 + 3 * G4 - (C4 - D4) / \$A\$4) / (1 + (C4 - D4) / \$A\$4)$				
22	9.28			$I4 = H4 * \$A\$6 * \$A\$8 / \$A\4					



$$10-72. \quad \phi = \frac{C_a V_a}{C_b V_b} = \frac{\alpha_{\text{BH}^+} + 2\alpha_{\text{BH}_2^{2+}} + 3\alpha_{\text{BH}_3^{3+}} + 4\alpha_{\text{BH}_4^{4+}} + \frac{[\text{H}^+] - [\text{OH}^-]}{C_b}}{1 - \frac{[\text{H}^+] - [\text{OH}^-]}{C_a}}$$



$$10-73. \quad A_{604} = \epsilon_{In^-} [In^-] (1.00) \Rightarrow [In^-] = \frac{0.118}{4.97 \times 10^4} = 2.37 \times 10^{-6} \text{ M}$$

Since the indicator was diluted with KOH solution, the formal concentration of indicator is $0.700 \times 10^{-5} \text{ M}$.

$$[\text{HIn}] = 7.00 \times 10^{-6} - 2.37 \times 10^{-6} = 4.63 \times 10^{-6} \text{ M}$$

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} = 7.95 + \log \frac{2.37}{4.63} = 7.66$$

Call benzene-1,2,3-tricarboxylic acid H₃A, with pK₁ = 2.88, pK₂ = 4.75, and pK₃ = 7.13. Since the pH is 7.66, the main species is A³⁻ and the second main species is HA²⁻. Enough KOH to react with H₃A and H₂A⁻ must have been added, and there is enough KOH to react with part of the HA²⁻.

	HA ²⁻	+	OH ⁻	→	A ³⁻	+	H ₂ O
Initial mmol:	1.00		x		—		
Final mmol:	1.00 - x		—		x		

$$\text{pH} = \text{p}K_3 + \log \frac{[\text{A}^{3-}]}{[\text{HA}^{2-}]}$$

$$7.66 = 7.13 + \log \frac{x}{1.00 - x} \Rightarrow x = 0.772 \text{ mmol of OH}^-$$

The total KOH added is 0.772 mmol. The molarity is $\frac{0.772 \text{ mmol}}{20.0 \text{ mL}} = 0.0386 \text{ M}$.

- 10-74. The pH of the solution is 7.50, and the total concentration of indicator is 5.00×10^{-5} M. At pH 7.50, there is a negligible amount of H_2In , since $\text{p}K_1 = 1.00$. We can write

$$[\text{HIn}^-] + [\text{In}^{2-}] = 5.0 \times 10^{-5}$$

$$\text{pH} = \text{p}K_2 + \log \frac{[\text{In}^{2-}]}{[\text{HIn}^-]}$$

$$7.50 = 7.95 + \log \frac{[\text{In}^{2-}]}{5.00 \times 10^{-5} - [\text{In}^{2-}]} \Rightarrow [\text{In}^{2-}] = 1.31 \times 10^{-5} \text{ M}$$

$$[\text{HIn}] = 3.69 \times 10^{-5} \text{ M}$$

$$A_{435} = \epsilon_{435}[\text{HIn}^-] + \epsilon_{435}[\text{In}^{2-}]$$

$$= (1.80 \times 10^4)(3.69 \times 10^{-5}) + (1.15 \times 10^4)(1.31 \times 10^{-5}) = 0.815$$

CHAPTER 11

EDTA TITRATIONS

11-1. The chelate effect is the observation that multidentate ligands form more stable metal complexes than do similar, monodentate ligands.

11-2. $\alpha_{Y^{4-}}$ gives the fraction of all free EDTA in the form Y^{4-} .

(a) At pH 3.50:

$$\alpha_{Y^{4-}} = \frac{10^{-0.0} 10^{-1.5} 10^{-2.0} 10^{-2.69} 10^{-6.13} 10^{-10.37}}{(10^{-3.50})^6 + (10^{-3.50})^5 10^{-0.0} + \dots + 10^{-0.0} 10^{-1.5} \dots 10^{-10.37}} = 2.7 \times 10^{-10}$$

(b) At pH 10.50:

$$\alpha_{Y^{4-}} = \frac{10^{-0.0} 10^{-1.5} 10^{-2.0} 10^{-2.69} 10^{-6.13} 10^{-10.37}}{(10^{-10.50})^6 + (10^{-10.50})^5 10^{-0.0} + \dots + 10^{-0.0} 10^{-1.5} \dots 10^{-10.37}} = 0.57$$

11-3. (a) $K_f' = \alpha_{Y^{4-}} K_f = 0.041 \times 10^{8.79} = 2.5 \times 10^7$



$$\begin{array}{ccc} x & x & 0.050 - x \\ \frac{0.050 - x}{x^2} = 2.5 \times 10^7 \Rightarrow [\text{Mg}^{2+}] = 4.5 \times 10^{-5} \text{ M} \end{array}$$

11-4. $[\text{Ca}^{2+}] = 10^{-9.00} \text{ M}$, so essentially all calcium in solution is CaY^{2-} .

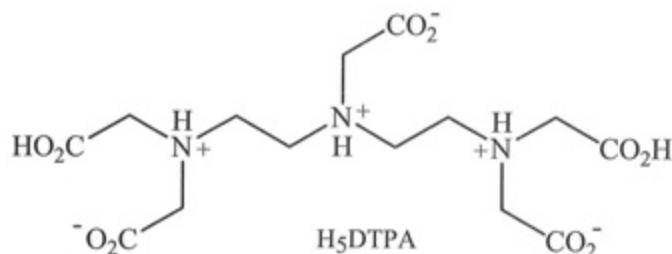
$$[\text{CaY}^{2-}] = \frac{1.95 \text{ g}}{(200.12 \text{ g/mol})(0.500 \text{ L})} = 0.01949 \text{ M}$$

$$K_f' = (0.041)(10^{10.65}) = \frac{[\text{CaY}^{2-}]}{[\text{EDTA}] [\text{Ca}^{2+}]} = \frac{(1.949 \times 10^{-2})}{[\text{EDTA}] (10^{-9.00})}$$

$$\Rightarrow [\text{EDTA}] = 0.0106 \text{ M}$$

$$\begin{aligned} \text{Total EDTA needed} &= \text{mol CaY}^{2-} + \text{mol free EDTA} \\ &= (0.01949 \text{ M})(0.500 \text{ L}) + (0.0106 \text{ M})(0.500 \text{ L}) = 0.01504 \text{ mol} \\ &= 5.60 \text{ g Na}_2\text{EDTA} \cdot 2 \text{ H}_2\text{O} \end{aligned}$$

11-5.



Neutral H_5DTPA 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 ~ 3 and ammonium pK_a values to be above ~ 6 . At pH 14, we expect all acidic protons of DTPA to be dissociated, so the predominant

species will be DTPA⁵⁻. At pH 3-4, nitrogen should be protonated, but carboxyl groups should be deprotonated. The predominant species is probably H₃DTPA²⁻.

For HSO₄⁻, pK_a = 2.0. At pH 14 and at pH 3, sulfate is in the form SO₄²⁻.

At pH 14, DTPA⁵⁻ is apparently a strong enough ligand to chelate Ba²⁺ and dissolve BaSO₄(s). At pH 3-4, H₃DTPA²⁻ is not a strong enough ligand to dissolve BaSO₄(s). An equivalent statement is that H⁺ at a concentration of 10⁻³-10⁻⁴ M competes with Ba²⁺ for binding sites on DTPA, but H⁺ at a concentration of 10⁻¹⁴ M does not compete with Ba²⁺ for binding sites on DTPA.

Now that you have seen my reasoning, I'll provide some more information. The pK_a values for DTPA, beginning with the fully protonated H₈DTPA³⁺, are

H ₈ DTPA ³⁺	pK ₁ = -0.1	CO ₂ H	H ₄ DTPA ⁻	pK ₅ = 2.7	CO ₂ H
H ₇ DTPA ²⁺	pK ₂ = 0.7	CO ₂ H	H ₃ DTPA ²⁻	pK ₆ = 4.3	NH ⁺
H ₆ DTPA ⁺	pK ₃ = 1.6	CO ₂ H	H ₂ DTPA ³⁻	pK ₇ = 8.6	NH ⁺
H ₅ DTPA	pK ₄ = 2.0	CO ₂ H	HDTPA ⁴⁻	pK ₈ = 10.5	NH ⁺

As pH is lowered from 14, the three nitrogen atoms are 50% protonated at pH 10.5, 8.6, and 4.3. The third nitrogen atom is not quite fully protonated at pH 3-4. The predominant species is H₃DTPA²⁻, as I guessed correctly. The species H₄DTPA⁻ and H₂DTPA³⁻ are also present to some extent in the pH range 3-4.

- 11-6. (a) mmol EDTA = mmol Mⁿ⁺

$$(V_e)(0.0500 \text{ M}) = (100.0 \text{ mL})(0.0500 \text{ M}) \Rightarrow V_e = 100.0 \text{ mL}$$

$$\text{(b)} \quad [\text{M}^{n+}] = \frac{\left(\frac{1}{2}\right)}{\text{fraction remaining}} \cdot (0.0500 \text{ M}) \cdot \frac{\left(\frac{100}{150}\right)}{\text{original concentration}} = 0.0167 \text{ M}$$

dilution factor

- (c) 0.041 (Table 11-1)

$$\text{(d)} \quad K_f' = (0.041)(10^{12.00}) = 4.1 \times 10^{10}$$

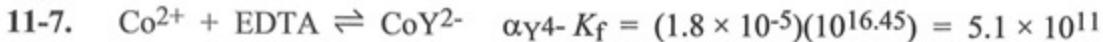
$$\text{(e)} \quad [\text{MY}^{n-4}] = (0.0500 \text{ M}) \left(\frac{100}{200}\right) = 0.0250 \text{ M}$$

$$\frac{[\text{MY}^{n-4}]}{[\text{M}^{n+}][\text{EDTA}]} = \frac{0.0250 - x}{x^2} = 4.1 \times 10^{10} \Rightarrow x = [\text{M}^{n+}] = 7.8 \times 10^{-7} \text{ M}$$

$$\text{(f)} \quad [\text{EDTA}] = (0.0500 \text{ M}) \left(\frac{10.0}{210.0}\right) = 2.38 \times 10^{-3} \text{ M}$$

$$[\text{MY}^{n-4}] = (0.0500 \text{ M}) \left(\frac{100.0}{210.0}\right) = 2.38 \times 10^{-2} \text{ M}$$

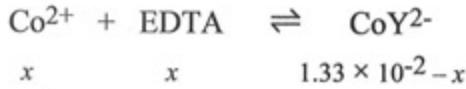
$$\frac{[\text{MY}^{n-4}]}{[\text{M}^{n+}][\text{EDTA}]} = \frac{(2.38 \times 10^{-2})}{(7.8 \times 10^{-7})(2.38 \times 10^{-3})} = 4.1 \times 10^{10} \Rightarrow [\text{M}^{n+}] = 2.4 \times 10^{-10} \text{ M}$$



$$V_e = (25.00) \left(\frac{0.02026 \text{ M}}{0.03855 \text{ M}} \right) = 13.14 \text{ mL}$$

$$\begin{aligned} \text{(a)} \quad \underline{12.00 \text{ mL}}: [\text{Co}^{2+}] &= \left(\frac{13.14 - 12.00}{13.14} \right) (0.02026 \text{ M}) \left(\frac{25.00}{37.00} \right) \\ &= 1.19 \times 10^{-3} \text{ M} \Rightarrow p\text{Co}^{2+} = 2.93 \end{aligned}$$

$$\text{(b)} \quad \underline{V_e}: \text{Formal concentration of CoY}^{2-} \text{ is } \left(\frac{25.00}{38.14} \right) (0.02026 \text{ M}) = 1.33 \times 10^{-2} \text{ M}$$



$$\frac{1.33 \times 10^{-2} - x}{x^2} = \alpha_{\text{Y}4^-} K_f \Rightarrow x = 1.6 \times 10^{-7} \text{ M} \Rightarrow p\text{Co}^{2+} = 6.79$$

$$\begin{aligned} \text{(c)} \quad \underline{14.00 \text{ mL}}: \text{Formal concentration of CoY}^{2-} &\text{ is } \left(\frac{25.00}{39.00} \right) (0.02026 \text{ M}) \\ &= 1.30 \times 10^{-2} \text{ M} \end{aligned}$$

$$\text{Formal concentration of EDTA is } \left(\frac{14.0 - 13.14}{39.00} \right) (0.03855 \text{ M}) = 8.50 \times 10^{-4} \text{ M}$$

$$\begin{aligned} [\text{Co}^{2+}] &= \frac{[\text{CoY}^{2-}]}{[\text{EDTA}] K_f'} = \frac{1.30 \times 10^{-2}}{8.50 \times 10^{-4} (5.1 \times 10^{11})} = 3.0 \times 10^{-11} \text{ M} \\ &\Rightarrow p\text{Co}^{2+} = 10.52 \end{aligned}$$



$$K_f' = \alpha_{\text{Y}4^-} K_f = (4.2 \times 10^{-3})(10^{13.89}) = 3.3 \times 10^{11}$$

The equivalence point is 50.0 mL. Sample calculations:

20.0 mL: The fraction of Mn^{2+} that has reacted is $2/5$ and the fraction remaining is $3/5$.

$$[\text{Mn}^{2+}] = \left(\frac{30.0}{50.0} \right) (0.0200 \text{ M}) \left(\frac{25.0}{45.0} \right) = 6.67 \times 10^{-3} \text{ M} \Rightarrow p\text{Mn}^{2+} = 2.18$$

50.0 mL: The formal concentration of MnY^{2-} is

$$[\text{MnY}^{2-}] = \left(\frac{25.0}{75.0} \right) (0.0200 \text{ M}) = 0.00667 \text{ M}$$



$$\frac{0.00667 - x}{x^2} = \alpha_{\text{Y}4^-} K_f \Rightarrow x = 1.4 \times 10^{-7} \Rightarrow p\text{Mn}^{2+} = 6.85$$

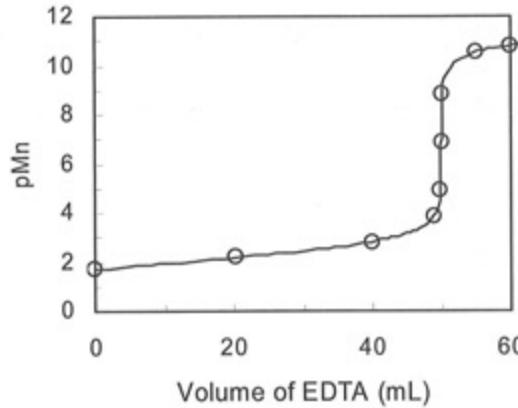
60.0 mL: There are 10.0 mL of excess EDTA.

$$[\text{EDTA}] = \left(\frac{10.0}{85.0}\right)(0.0100 \text{ M}) = 1.176 \times 10^{-3} \text{ M}$$

$$[\text{MnY}^{2-}] = \left(\frac{25.0}{85.0}\right)(0.0200 \text{ M}) = 5.88 \times 10^{-3} \text{ M}$$

$$[\text{Mn}^{2+}] = \frac{[\text{MnY}^{2-}]}{[\text{EDTA}]K_f'} = 1.5 \times 10^{-11} \Rightarrow \text{pMn}^{2+} = 10.82$$

Volume (mL)	pMn ²⁺	Volume	pMn ²⁺	Volume	pMn ²⁺
0	1.70	49.0	3.87	50.1	8.82
20.0	2.18	49.9	4.87	55.0	10.51
40.0	2.81	50.0	6.85	60.0	10.82



11-9. Titration reaction: $\text{Ca}^{2+} + \text{EDTA} \rightleftharpoons \text{CaY}^{2-}$

$$K_f' = \alpha_{\text{Y}^{4-}} K_f = (0.30)(10^{10.65}) = 1.34 \times 10^{10}$$

The equivalence point is 50.0 mL. Sample calculations:

20.0 mL: The fraction of EDTA consumed is 2/5.

$$[\text{EDTA}] = \left(\frac{30.0}{50.0}\right)(0.0200 \text{ M}) \left(\frac{25.0}{45.0}\right) = 0.00667 \text{ M}$$

$$[\text{CaY}^{2-}] = \left(\frac{20.0}{50.0}\right)(0.0200 \text{ M}) \left(\frac{25.0}{45.0}\right) = 0.00444 \text{ M}$$

$$[\text{Ca}^{2+}] = \frac{[\text{CaY}^{2-}]}{[\text{EDTA}]K_f'} = 4.97 \times 10^{-11} \Rightarrow \text{pCa}^{2+} = 10.30$$

50.0 mL: The formal concentration of CaY^{2-} is

$$[\text{CaY}^{2-}] = \left(\frac{25.0}{75.0} \right) (0.0200 \text{ M}) = 0.00667 \text{ M}$$

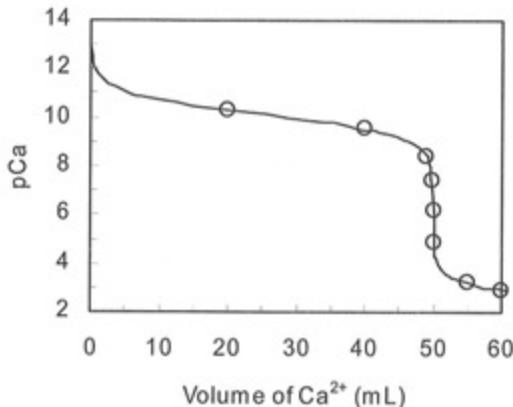


$$\frac{0.00667 - x}{x^2} = \alpha_{\text{Y}} K_f \Rightarrow x = 7.05 \times 10^{-7} \text{ M} \Rightarrow \text{pCa}^{2+} = 6.15$$

50.1 mL: There is an excess of 0.1 mL of Ca^{2+} .

$$[\text{Ca}^{2+}] = \left(\frac{0.1}{75.1} \right) (0.0100 \text{ M}) = 1.33 \times 10^{-5} \text{ M} \Rightarrow \text{pCa}^{2+} = 4.88$$

Volume (mL)	pCa ²⁺	Volume	pCa ²⁺	Volume	pCa ²⁺
0	(∞)	49.0	8.44	50.1	4.88
20.0	10.30	49.9	7.43	55.0	3.20
40.0	9.52	50.0	6.15	60.0	2.93



- 11-10.** There is more VO^{2+} than EDTA in this solution.

$$[\text{VO}^{2+}] = \left(\frac{0.10}{29.9} \right) (0.0100 \text{ M}) = 3.34 \times 10^{-5} \text{ M}$$

$$[\text{VOY}^{2-}] = \left(\frac{9.90}{29.90} \right) (0.0100 \text{ M}) = 3.31 \times 10^{-3} \text{ M}$$

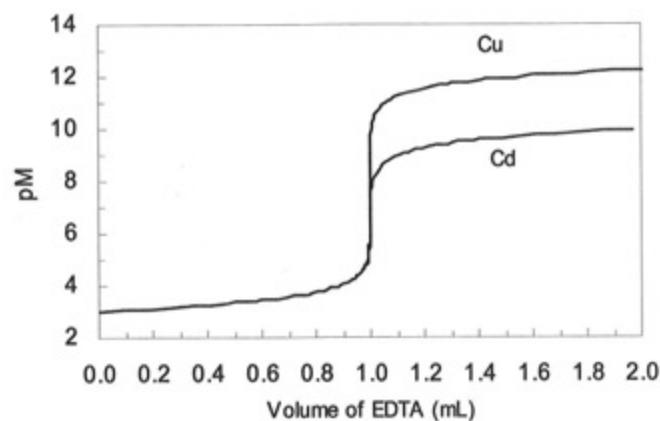
K_f for VOY^{2-} = $10^{18.7}$; $\text{p}K_6$ for H_6Y^{2+} = 10.37; pH = 4.00

$$[\text{Y}^{4-}] = \frac{[\text{VOY}^{2-}]}{[\text{VO}^{2+}] K_f} = 1.98 \times 10^{-17} \text{ M}$$

$$[\text{HY}^{3-}] = \frac{[\text{H}^+] [\text{Y}^{4-}]}{K_6} = 4.6 \times 10^{-11} \text{ M}$$

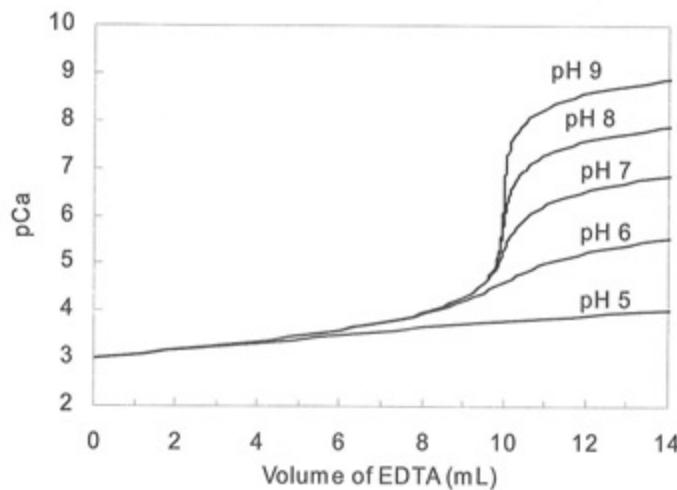
11-11.

	A	B	C	D	E	F	G
1	Titration of V_M mL of C_M M Cu^{2+} with $C(\text{ligand})$ M EDTA						
2							
3	$C_M =$	pM	M	Phi	V(EDTA)		
4	0.001	3.0	1.00E-03	0.000	0.000		
5	$V_M =$	4.0	1.00E-04	0.891	0.891		
6	10	5.0	1.00E-05	0.989	0.989		
7	$C(\text{ligand}) =$	6.0	1.00E-06	0.999	0.999		
8	0.01	7.0	1.00E-07	1.000	1.000		
9	$K_f =$	8.0	1.00E-08	1.000	1.000		
10	1.75E+12	9.0	1.00E-09	1.001	1.001		
11	$\alpha(Y^4) =$	10.0	1.00E-10	1.006	1.006		
12	2.90E-07	11.0	1.00E-11	1.057	1.057		
13	$K_f =$	12.0	1.00E-12	1.572	1.572		
14	6.0256E+18	12.3	5.01E-13	2.142	2.142		
15							
16	$A_{10} = A_{12} * A_{14}$						
17	$C_4 = 10^{-B_4}$						
18	$D_4 = (1 + \$A\$10 * C_4 - (C_4 + C_4 * C_4 * \$A\$10) / \$A\$4) / (C_4 * \$A\$10 + (C_4 + C_4 * C_4 * \$A\$10) / \$A\$8)$						
19	$E_4 = D_4 * \$A\$4 * \$A\$6 / \$A\8						



11-12. The spreadsheet below gives representative calculations for the pH 7.

	A	B	C	D	E	F
1	Titration of 10 mL of 1 mM Ca^{2+} with 1 mM EDTA vs pH					
2	pH 7					
3	$C_M =$	pM	M	Phi	V(ligand)	
4	0.001		3.000	1.00E-03	0.000	0.000
5	$V_M =$		3.250	5.62E-04	0.280	2.801
6	10		3.500	3.16E-04	0.520	5.196
7	$C(\text{ligand}) =$		3.750	1.78E-04	0.698	6.982
8	0.001		4.000	1.00E-04	0.819	8.186
9	$K_f' =$		4.500	3.16E-05	0.940	9.404
10	1.70E+07		5.000	1.00E-05	0.986	9.859
11	$\alpha(Y^{4-}) =$		5.500	3.16E-06	1.012	10.121
12	3.80E-04		6.000	1.00E-06	1.057	10.567
13	$K_f =$		6.500	3.16E-07	1.185	11.855
14	4.4668E+10		7.000	1.00E-07	1.589	15.887
15	$A_{10} = A_{12} \cdot A_{14}$					
16	$C_4 = 10^{-B_4}$					
17	$D_4 = (1 + A_{10} \cdot C_4 - (C_4 + C_4 \cdot C_4 \cdot A_{10}) / A_{14}) / (C_4 \cdot A_{10} + (C_4 + C_4 \cdot C_4 \cdot A_{10}) / A_{12})$					
18	$E_4 = D_4 \cdot A_{12} \cdot A_{14} / A_{10}$					



11-13.

	A	B	C	D	E	F	G
1	Titration of EDTA with metal						
2							
3	$C_M =$	pM	M	Phi	V_M		
4	0.08	14.640	2.29E-15	0.004	0.100		
5	$V(\text{ligand}) =$	12.844	1.43E-13	0.200	5.004		
6	50	12.418	3.82E-13	0.400	10.007		
7	$C(\text{ligand}) =$	12.066	8.59E-13	0.600	15.004		
8	0.04	11.640	2.29E-12	0.800	20.003		
9	$K_f' =$	10.860	1.38E-11	0.960	24.005		
10	1.75E+12	6.910	1.23E-07	1.000	25.000		
11	$\alpha(Y^{4-})$	2.978	1.05E-03	1.040	25.999		
12	2.90E-07	2.301	5.00E-03	1.200	30.000		
13	$K_f =$						
14	6.0256E+18						
15							
16	$A_{10} = A_{12} \cdot A_{14}$						
17	$C_4 = 10^{\wedge} B_4$						
18	$D_4 = (C_4 \cdot A_{10} + (C_4 + C_4 \cdot C_4 \cdot A_{10}) / A_{12}) / (1 + A_{10} \cdot C_4 - (C_4 + C_4 \cdot C_4 \cdot A_{10}) / A_{12})$						
19	$E_4 = D_4 \cdot A_{12} \cdot A_{14} / A_{10}$						

11-14. An auxiliary complexing agent forms a weak complex with analyte ion, thereby keeping it in solution without interfering with the EDTA titration. For example, NH_3 keeps Zn^{2+} in solution at high pH, but is easily displaced by EDTA.

11-15. (a) $\beta_2 = K_1 K_2 = \beta_1 K_2 \Rightarrow K_2 = \beta_2 / \beta_1 = 10^{3.63} / 10^{2.23} = 10^{1.40} = 25$

$$(b) \alpha_{\text{Cu}^{2+}} = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2} = \frac{1}{1 + 10^{2.23}(0.100) + 10^{3.63}(0.100)^2} = 0.017$$

11-16. $\text{Cu}^{2+} + Y^{4-} \rightleftharpoons \text{CuY}^{2-} \quad K_f = 10^{18.78} = 6.0_3 \times 10^{18}$

$\alpha_{Y^{4-}} = 0.81$ at pH 11.00 (Table 11-1)

For Cu^{2+} and NH_3 , Appendix I gives $\log \beta_1 = 3.99$, $\log \beta_2 = 7.33$, $\log \beta_3 = 10.06$, and $\log \beta_4 = 12.03$. Therefore, $\beta_1 = 9.8 \times 10^3$, $\beta_2 = 2.1 \times 10^7$, $\beta_3 = 1.15 \times 10^{10}$, and $\beta_4 = 1.07 \times 10^{12}$.

$$\alpha_{\text{Cu}^{2+}} = \frac{1}{1 + \beta_1(1.00) + \beta_2(1.00)^2 + \beta_3(1.00)^3 + \beta_4(1.00)^4} = 9.2_3 \times 10^{-13}$$

$$K_f' = \alpha_{Y^{4-}} K_f = 4.8_8 \times 10^{18}$$

$$K_f'' = \alpha_{Y^{4-}} \alpha_{\text{Cu}^{2+}} K_f = 4.5_1 \times 10^6$$

Equivalence point = 50.00 mL

(a) At 0 mL, the total concentration of copper is $C_{\text{Cu}^{2+}} = 0.00100 \text{ M}$ and

$$[\text{Cu}^{2+}] = \alpha_{\text{Cu}^{2+}} C_{\text{Cu}^{2+}} = 9.2_3 \times 10^{-16} \text{ M} \Rightarrow p\text{Cu}^{2+} = 15.03$$

(b) At 1.00 mL, $C_{\text{Cu}^{2+}} = \left(\frac{49.00}{50.00}\right) (0.00100 \text{ M}) \left(\frac{50.00}{51.00}\right) = 9.61 \times 10^{-4} \text{ M}$

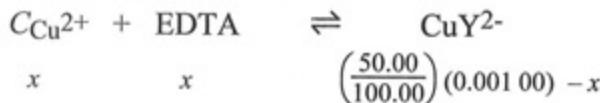
fraction remaining	original concentration	dilution factor
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$$[\text{Cu}^{2+}] = \alpha_{\text{Cu}^{2+}} C_{\text{Cu}^{2+}} = 8.87 \times 10^{-16} \text{ M} \Rightarrow \text{pCu}^{2+} = 15.05$$

(c) At 45.00 mL, $C_{\text{Cu}^{2+}} = \left(\frac{5.00}{50.00}\right) (0.00100) \left(\frac{50.00}{95.00}\right) = 5.26 \times 10^{-5} \text{ M}$

$$[\text{Cu}^{2+}] = \alpha_{\text{Cu}^{2+}} C_{\text{Cu}^{2+}} = 5.04 \times 10^{-17} \text{ M} \Rightarrow \text{pCu}^{2+} = 16.30$$

(d) At the equivalence point, we can write



$$\frac{0.000500 - x}{x^2} = K_f'' = 4.51 \times 10^6 \Rightarrow x = C_{\text{Cu}^{2+}} = 1.04 \times 10^{-5} \text{ M}$$

$$[\text{Cu}^{2+}] = \alpha_{\text{Cu}^{2+}} C_{\text{Cu}^{2+}} = 9.62 \times 10^{-18} \text{ M} \Rightarrow \text{pCu}^{2+} = 17.02$$

(e) Past the equivalence point at 55.00 mL, we can say

$$[\text{EDTA}] = \left(\frac{5.00}{105.00}\right) (0.00100 \text{ M}) = 4.76 \times 10^{-5} \text{ M}$$

$$[\text{CuY}^{2-}] = \left(\frac{50.00}{105.00}\right) (0.00100 \text{ M}) = 4.76 \times 10^{-4} \text{ M}$$

$$K_f' = \frac{[\text{CuY}^{2-}]}{[\text{Cu}^{2+}][\text{EDTA}]} = \frac{(4.76 \times 10^{-4})}{[\text{Cu}^{2+}] (4.76 \times 10^{-5})}$$

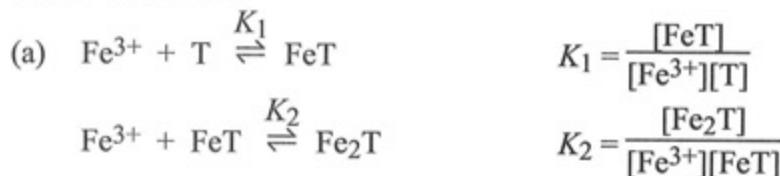
$$\Rightarrow [\text{Cu}^{2+}] = 2.05 \times 10^{-18} \text{ M} \Rightarrow \text{pCu}^{2+} = 17.69$$

11-17. (a) $\alpha_{\text{ML}} = \frac{[\text{ML}]}{C_{\text{M}}} = \frac{\beta_1[\text{M}][\text{L}]}{[\text{M}]\{1+\beta_1[\text{L}] + \beta_2[\text{L}]^2\}} = \frac{\beta_1[\text{L}]}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2}$

$$\alpha_{\text{ML}_2} = \frac{[\text{ML}_2]}{C_{\text{M}}} = \frac{\beta_2[\text{M}][\text{L}]^2}{[\text{M}]\{1+\beta_1[\text{L}] + \beta_2[\text{L}]^2\}} = \frac{\beta_2[\text{L}]^2}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2}$$

(b) For $[\text{L}] = 0.100 \text{ M}$, $\beta_1 = 1.7 \times 10^2$, and $\beta_2 = 4.3 \times 10^3$, we get $\alpha_{\text{ML}} = 0.28$ and $\alpha_{\text{ML}_2} = 0.70$.

11-18. Let T = transferrin



(b) $K_1 = \frac{[\text{Fe}_a\text{T}] + [\text{Fe}_b\text{T}]}{[\text{Fe}^{3+}][\text{T}]} = \frac{[\text{Fe}_a\text{T}]}{[\text{Fe}^{3+}][\text{T}]} + \frac{[\text{Fe}_b\text{T}]}{[\text{Fe}^{3+}][\text{T}]} = k_{1a} + k_{1b}$

$$\frac{1}{K_2} = \frac{[\text{Fe}^{3+}]([\text{Fe}_a\text{T}] + [\text{Fe}_b\text{T}])}{[\text{Fe}_2\text{T}]} = \frac{[\text{Fe}^{3+}][\text{Fe}_a\text{T}]}{[\text{Fe}_2\text{T}]} + \frac{[\text{Fe}^{3+}][\text{Fe}_b\text{T}]}{[\text{Fe}_2\text{T}]} = \frac{1}{k_{2b}} + \frac{1}{k_{2a}}$$

$$(c) \quad k_{1a} k_{2b} = \frac{[\text{Fe}_a\text{T}]}{[\text{Fe}^{3+}][\text{T}]} \frac{[\text{Fe}_2\text{T}]}{[\text{Fe}^{3+}][\text{Fe}_a\text{T}]} = \frac{[\text{Fe}_b\text{T}]}{[\text{Fe}^{3+}][\text{T}]} \frac{[\text{Fe}_2\text{T}]}{[\text{Fe}^{3+}][\text{Fe}_b\text{T}]} = k_{1b} k_{2a}$$

(d) Substituting from Eq. (A) into Eq. (C) gives

$$19.44 = \frac{[\text{FeT}]^2}{(1 - [\text{FeT}] - [\text{Fe}_2\text{T}]) [\text{Fe}_2\text{T}]} \quad (D)$$

Substituting from Eq. (B) into Eq. (D) gives

$$19.44 = \frac{(0.8 - 2[\text{Fe}_2\text{T}])^2}{\{1 - (0.8 - 2[\text{Fe}_2\text{T}]) - [\text{Fe}_2\text{T}]\} [\text{Fe}_2\text{T}]} \xrightarrow{\substack{\text{solve} \\ \text{quadratic} \\ \text{equation}}} [\text{Fe}_2\text{T}] = 0.0773$$

Using this value for $[\text{Fe}_2\text{T}]$ in Eqns. (A) and (B) gives $[\text{FeT}] = 0.645$ and

$[\text{T}] = 0.2773$. Now we also know that $\frac{k_{1a}}{k_{1b}} = \frac{[\text{Fe}_a\text{T}]}{[\text{Fe}_b\text{T}]} = 6.0$, which tells us that $[\text{Fe}_a\text{T}] = \left(\frac{6.0}{7.0}\right)[\text{FeT}] = 0.5532$ and $[\text{Fe}_b\text{T}] = \left(\frac{1.0}{7.0}\right)[\text{FeT}] = 0.0922$.

Final result: $[\text{T}] = 0.277$, $[\text{Fe}_a\text{T}] = 0.553$, $[\text{Fe}_b\text{T}] = 0.092$, $[\text{Fe}_2\text{T}] = 0.077$.

11-19. In place of Equation 11-8, we write



where $[\text{M}]_{\text{free}}$ is the concentration of all metal not bound to EDTA. $[\text{EDTA}]$ is the concentration of all EDTA not bound to metal. The mass balances are

$$\text{Metal:} \quad [\text{M}]_{\text{free}} + [\text{M(EDTA)}] = \frac{C_M V_M}{V_M + V_{\text{EDTA}}}$$

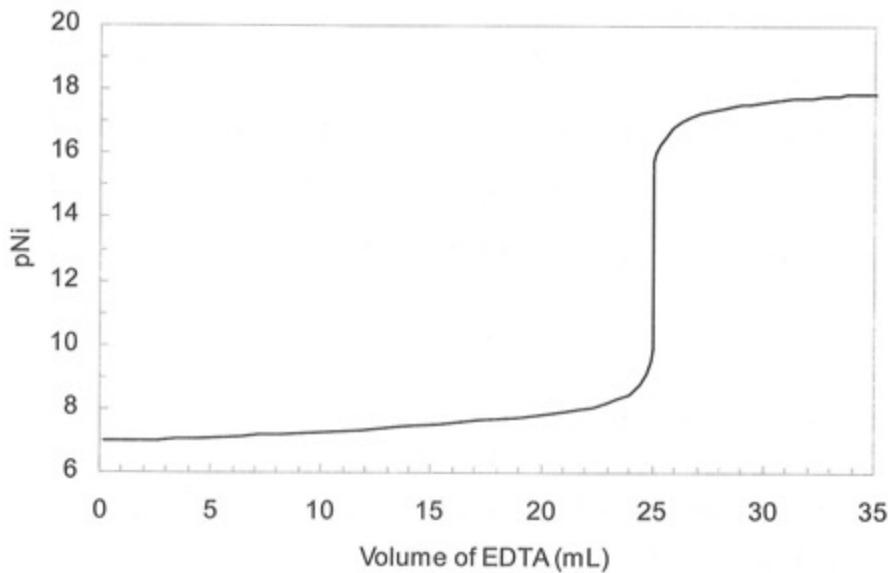
$$\text{EDTA:} \quad [\text{EDTA}] + [\text{M(EDTA)}] = \frac{C_{\text{EDTA}} V_{\text{EDTA}}}{V_M + V_{\text{EDTA}}}$$

These equations have the same form as the first three equations in Section 11-4, with K_f replaced by K_f'' , $[\text{M}]$ replaced by $[\text{M}]_{\text{free}}$, and $[\text{L}]$ replaced by $[\text{EDTA}]$. The derivation therefore leads to Equation 11-11, with K_f replaced by K_f'' , $[\text{M}]$ replaced by $[\text{M}]_{\text{free}}$, and C_L replaced by C_{EDTA} .

11-20. (a)

	A	B	C	D	E	F
1	Titration of 50 mL of 0.001 M Zn^{2+} with 0.001 M EDTA/pH 10 with NH_3					
2						
3	$C_M =$	pM	M	$[M]_{tot}$	ϕ	V_{EDTA}
4	0.001	8.115	7.67E-09	4.29E-04	0.400	19.9814
5	$V_M =$	12.014	9.68E-13	5.41E-08	1.000	50.0000
6	50	15.278	5.27E-16	2.95E-11	1.200	59.9965
7	$C_{EDTA} =$					
8	0.001					
9	$K_f'' =$	$A10 = A12^*A16^*10^A14$				
10	1.70E+11	$A12 = 1/(1+A20^*A18+B20^*A18^2+C20^*A18^3+D20^*A18^4)$				
11	$\alpha(Zn^{2+}) =$					
12	1.79E-05	$C4 = 10^B4$				
13	$\log K_f =$	$D4 = C4/\$A\12				
14	16.5	$E4 = (1+\$A\$10^*D4-(D4+D4^2*\$A\$10)/\$A\$4)/$				
15	$\alpha(Y^{4-}) =$	$(D4*\$A\$10+(D4+D4^2*\$A\$10)/\$A\$8)$				
16	0.30	$F4 = E4*\$A\$4*\$A\$6/\$A\8				
17	$[NH_3] =$					
18	0.1					
19	$\beta_1 =$	$\beta_2 =$	$\beta_3 =$	$\beta_4 =$		
20	1.51E+02	2.69E+04	5.50E+06	5.01E+08		

(b)



	A	B	C	D	E	F
1	Titration of 50 mL of 0.05 M Ni^{2+} with 0.1 M EDTA/ pH 11/ 0.1 M Oxalate					
2						
3	$C_M =$	pM	M	$[M]_{\text{tot}}$	ϕ	V_{EDTA}
4	0.005	6.97	1.07E-07	4.94E-03	0.008	0.210
5	$V_M =$	7.00	1.00E-07	4.61E-03	0.054	1.342
6	50	7.20	6.31E-08	2.91E-03	0.324	8.106
7	$C_{\text{EDTA}} =$	7.50	3.16E-08	1.46E-03	0.618	15.461
8	0.01	8.00	1.00E-08	4.61E-04	0.868	21.696
9	$K_f'' =$	8.40	3.98E-09	1.83E-04	0.946	23.649
10	4.42E+13	8.80	1.58E-09	7.30E-05	0.978	24.456
11	$\alpha(\text{Ni}^{2+}) =$	9.50	3.16E-10	1.46E-05	0.996	24.891
12	2.17E-05	10.50	3.16E-11	1.46E-06	1.000	24.989
13	$\log K_f =$	12.80	1.58E-13	7.30E-09	1.000	25.000
14	18.4	14.00	1.00E-14	4.61E-10	1.000	25.001
15	$\alpha(Y^{4-}) =$	15.00	1.00E-15	4.61E-11	1.000	25.012
16	0.81	16.00	1.00E-16	4.61E-12	1.005	25.123
17	$[\text{Oxalate}^{2-}] =$	17.00	1.00E-17	4.61E-13	1.049	26.229
18	0.1	17.40	3.98E-18	1.83E-13	1.123	28.086
19	$\beta_1 =$	17.60	2.51E-18	1.16E-13	1.196	29.892
20	1.45E+05	17.80	1.58E-18	7.30E-14	1.310	32.753
21	$\beta_2 =$	17.90	1.26E-18	5.80E-14	1.390	34.760
22	3.16E+06	18.00	1.00E-18	4.61E-14	1.491	37.287
23						
24	$A10 = A16 * A12 * 10^A14$					
25	$A12 = 1 / (1 + A20 * A18 + A22 * A18^2)$					
26	$C4 = 10^{-B4}$					
27	$D4 = C4 / \$A\12					
28	$E4 = (1 + \$A\$10 * D4 - (D4 + D4 * D4 * \$A\$10) / \$A\$4) /$					
29	$(D4 * \$A\$10 + (D4 + D4 * D4 * \$A\$10) / \$A\$8)$					
30	$F4 = E4 * \$A\$4 * \$A\$6 / \$A\8					

$$11-21. \quad [L] + [ML] + 2[ML_2] = \frac{C_L V_L}{V_M + V_L}$$

$$[L] + \alpha_{ML} \frac{C_M V_M}{V_M + V_L} + 2\alpha_{ML_2} \frac{C_M V_M}{V_M + V_L} = \frac{C_L V_L}{V_M + V_L}$$

Multiply both sides by $V_M + V_L$:

$$[L]V_M + [L]V_L + \alpha_{ML}C_M V_M + 2\alpha_{ML_2}C_M V_M = C_L V_L$$

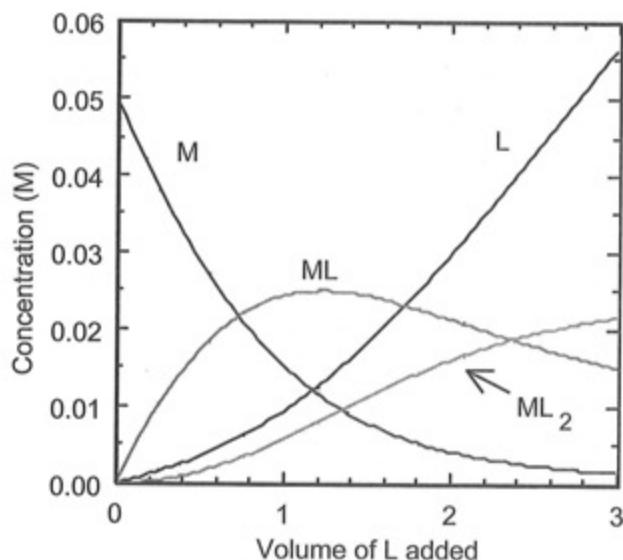
$$\text{Collect terms } V_L ([L] - C_L) = V_M (-[L] - \alpha_{ML}C_M - 2\alpha_{ML_2}C_M)$$

$$\frac{V_L}{V_M} = \frac{[L] + \alpha_{ML}C_M + 2\alpha_{ML_2}C_M}{C_L - [L]}$$

Divide the denominator by C_L and divide the numerator by C_M to obtain ϕ , the fraction of the way to the equivalence point:

$$\phi = \frac{C_L V_L}{C_M V_M} = \frac{\frac{[L]}{C_M} + \alpha_{ML} + 2\alpha_{ML_2}}{1 - \frac{[L]}{C_L}}$$

11-22.



	A	B	C	D	E	F	G	H	I	J	K
1	Copper-acetate complexes ML and ML_2										
2											
3	$C_M =$	pL	[L]	α_M	α_{ML}	α_{ML_2}	ϕ	V(ligand)	[M]	[ML]	[ML ₂]
4	0.05	4.0	0.0001	0.983	0.017	0.000	0.019	0.019	0.0491	0.0008	0.0000
5	$V_M =$	3.0	0.0010	0.852	0.145	0.004	0.172	0.172	0.0419	0.0071	0.0002
6	10	2.8	0.0016	0.781	0.210	0.008	0.260	0.260	0.0381	0.0103	0.0004
7	C(ligand)	2.6	0.0025	0.688	0.294	0.019	0.383	0.383	0.0331	0.0141	0.0009
8	0.5	2.4	0.0040	0.573	0.388	0.039	0.550	0.550	0.0272	0.0184	0.0019
9	$\beta_1 =$	2.2	0.0063	0.446	0.478	0.076	0.766	0.766	0.0207	0.0222	0.0035
10	170	2.0	0.0100	0.319	0.543	0.137	1.039	1.039	0.0145	0.0246	0.0062
11	$\beta_2 =$	1.9	0.0126	0.262	0.560	0.178	1.199	1.199	0.0117	0.0250	0.0080
12	4300	1.8	0.0158	0.209	0.564	0.226	1.377	1.377	0.0092	0.0248	0.0099
13		1.7	0.0200	0.164	0.556	0.280	1.579	1.579	0.0071	0.0240	0.0121
14		1.6	0.0251	0.125	0.535	0.340	1.808	1.808	0.0053	0.0226	0.0144
15		1.5	0.0316	0.094	0.504	0.403	2.073	2.073	0.0039	0.0209	0.0167
16		1.4	0.0398	0.069	0.464	0.467	2.385	2.385	0.0028	0.0187	0.0189
17		1.3	0.0501	0.049	0.419	0.532	2.761	2.761	0.0019	0.0164	0.0208
18		1.3	0.0562	0.041	0.396	0.563	2.981	2.981	0.0016	0.0152	0.0217
19											
20	$C4 = 10^{-B4}$						$H4 = G4 * A4 * A6 / A8$				
21	$D4 = 1 / (1 + A10 * C4 + A12 * C4 * C4)$						$I4 = D4 * A4 * A6 / (A6 + H4)$				
22	$E4 = A10 * C4 / (1 + A10 * C4 + A12 * C4 * C4)$						$J4 = E4 * A4 * A6 / (A6 + H4)$				
23	$F4 = A12 * C4 * C4 / (1 + A10 * C4 + A12 * C4 * C4)$						$K4 = F4 * A4 * A6 / (A6 + H4)$				
24	$G4 = (C4 / A4 + E4 + 2 * F4) / (1 - C4 / A8)$										

- 11-23. Only a small amount of indicator is employed. Most of the Mg^{2+} is not bound to the indicator. Free Mg^{2+} reacts with EDTA before $MgIn$ reacts. Therefore, the concentration of $MgIn$ is constant until all of Mg^{2+} has been consumed. Only when $MgIn$ begins to react does the color change.
- 11-24. 1. With metal ion indicators
2. With a mercury electrode
3. With an ion-selective electrode
4. With a glass electrode
- 11-25. HIn^{2-} , wine red, blue
- 11-26. Buffer (a) (pH 6-7) will give a yellow → blue color change that will be easier to observe than the violet → blue change expected with the other buffers.
- 11-27. A back titration is necessary if the analyte precipitates in the absence of EDTA, if it reacts too slowly with EDTA, or if it blocks the indicator.
- 11-28. In a displacement titration, analyte displaces a metal ion from a complex. The displaced metal ion is then titrated. An example is the liberation of Ni^{2+} from $Ni(CN)_4^{2-}$ by the analyte Ag^+ . The liberated Ni^{2+} is then titrated by EDTA to find out how much Ag^+ was present.
- 11-29. The Mg^{2+} in a solution of Mg^{2+} and Fe^{3+} can be titrated by EDTA if the Fe^{3+} is masked with CN^- to form $Fe(CN)_6^{3-}$, which does not react with EDTA.
- 11-30. Hardness refers to the total concentration of alkaline earth cations in water, which normally means $[Ca^{2+}] + [Mg^{2+}]$. Hardness gets its name from the reaction of these cations with soap to form insoluble curds. Temporary hardness, due to $Ca(HCO_3)_2$, is lost by precipitation of $CaCO_3(s)$ upon heating. Permanent hardness derived from other salts, such as $CaSO_4$, is not affected by heat.
- 11-31. $(50.0 \text{ mL})(0.0100 \text{ mmol/mL}) = 0.500 \text{ mmol } Ca^{2+}$, which requires 0.500 mmol EDTA = 10.0 mL EDTA.
0.500 mmol Al^{3+} requires the same amount of EDTA, 10.0 mL.
- 11-32. mmol EDTA = mmol Ni^{2+} + mmol Zn^{2+}
 $1.250 = x + 0.250 \Rightarrow 1.000 \text{ mmol } Ni^{2+} \text{ in } 50.0 \text{ mL} = 0.0200 \text{ M}$

- 11-33.** The formula mass of MgSO₄ is 120.37. The 50.0 mL aliquot contains

$$\left(\frac{50.0 \text{ mL}}{500 \text{ mL}}\right) \left(\frac{0.450 \text{ g}}{120.37 \text{ g/mol}}\right) = 0.3738 \text{ mmol of Mg}^{2+}$$

37.6 mL of EDTA reacts with this much Mg²⁺, so the EDTA solution contains 0.3738 mmol / 37.6 mL = 9.943 × 10⁻³ mmol/mL. The formula mass of CaCO₃ is 100.09. 1.00 mL of EDTA will react with 9.943 × 10⁻³ mmol of CaCO₃ = 0.995 mg.

- 11-34.** 30.10 mL Ni²⁺ reacted with 39.35 mL 0.01307 M EDTA, so Ni²⁺ molarity is

$$[\text{Ni}^{2+}] = \frac{(39.35 \text{ mL})(0.01307 \text{ mol/L})}{30.10 \text{ mL}} = 0.01709 \text{ M.}$$

25.00 mL Ni²⁺ contains 0.4272 mmol Ni²⁺. 10.15 mL EDTA = 0.1327 mmol EDTA. The Ni²⁺ which must have reacted with CN⁻ was 0.4272 – 0.1327 = 0.2945 mmol. Cyanide reacting with Ni²⁺ must have been (4)(0.2945 mmol) = 1.178 mmol. Original [CN⁻] = 1.178 mmol/12.73 mL = 0.09254 M.

- 11-35.** For 1.00 mL of unknown:

$$\begin{array}{r} 25.00 \text{ mL of EDTA} = 0.9680 \text{ mmol} \\ - 23.54 \text{ mL of Zn}^{2+} = 0.5007 \text{ mmol} \\ \hline \text{Co}^{2+} + \text{Ni}^{2+} = 0.4673 \text{ mmol} \end{array}$$

For 2.000 mL of unknown:

$$\begin{array}{r} 25.00 \text{ mL of EDTA} = 0.9680 \text{ mmol} \\ - 25.63 \text{ mL of Zn}^{2+} = 0.5452 \text{ mmol} \\ \hline \text{Ni}^{2+} \text{ in } 2.000 \text{ mL} = 0.4228 \text{ mmol} \end{array}$$

Co²⁺ in 2.000 mL of unknown = 2(0.4673) – 0.4228 = 0.5118 mmol. The Co²⁺ will react with 0.5118 mmol of EDTA, leaving 0.9680 – 0.5118 = 0.4562 mmol EDTA. mL Zn needed = $\frac{0.4562 \text{ mmol}}{0.02127 \text{ mmol/mL}} = 21.45 \text{ mL}$

- 11-36.** Total EDTA = (25.0 mL)(0.0452 M) = 1.130 mmol

$$\begin{array}{r} - \text{Mg}^{2+} \text{ required} = (12.4 \text{ mL})(0.0123 \text{ M}) = 0.153 \text{ mmol} \\ \hline \text{Ni}^{2+} + \text{Zn}^{2+} = 0.977 \text{ mmol} \end{array}$$

Zn²⁺ = EDTA displaced by 2,3-dimercapto-1-propanol

$$= (29.2 \text{ mL}) (0.0123 \text{ M}) = 0.359 \text{ mmol}$$

$$\Rightarrow \text{Ni}^{2+} = 0.977 - 0.359 = 0.618 \text{ mmol}; [\text{Ni}^{2+}] = \frac{0.618 \text{ mmol}}{50.0 \text{ mL}} = 0.0124 \text{ M}$$

$$[\text{Zn}^{2+}] = \frac{0.359 \text{ mmol}}{50.0 \text{ mL}} = 0.00718 \text{ M}$$

- 11-37.** The precipitation reaction is $\text{Cu}^{2+} + \text{S}^{2-} \rightarrow \text{CuS} (s)$.

$$\text{Total Cu}^{2+} \text{ used} = (25.00 \text{ mL}) (0.04332 \text{ M}) = 1.0830 \text{ mmol}$$

$$\begin{array}{rcl} \text{Excess Cu}^{2+} & = (12.11 \text{ mL}) (0.03927 \text{ M}) & = 0.4756 \text{ mmol} \\ \hline \text{mmol of S}^{2-} & & = 0.6074 \text{ mmol} \end{array}$$

$$[\text{S}^{2-}] = 0.6074 \text{ mmol}/25.00 \text{ mL} = 0.02430 \text{ M}$$

- 11-38.** mmol Bi in reaction = $(25.00 \text{ mL}) (0.08640 \text{ M}) = 2.160 \text{ mmol}$

$$\text{EDTA required} = (14.24 \text{ mL}) (0.0437 \text{ M}) = 0.622 \text{ mmol}$$

$$\text{mmol Bi that reacted with Cs} = 2.160 - 0.622 = 1.538 \text{ mmol}$$

Since 2 mol Bi react with 3 mol Cs to give $\text{Cs}_3\text{Bi}_2\text{I}_9$,

$$\text{mmol Cs}^+ \text{ in unknown} = \frac{3}{2}(1.538) = 2.307 \text{ mmol}$$

$$[\text{Cs}^+] = \frac{2.307 \text{ mmol}}{25.00 \text{ mL}} = 0.09228 \text{ M.}$$

- 11-39.** Total standard $\text{Ba}^{2+} + \text{Zn}^{2+}$ added to the sulfate was $(5.000 \text{ mL})(0.01463 \text{ M BaCl}_2) + (1.000 \text{ mL})(0.01000 \text{ M ZnCl}_2) = 0.08315 \text{ mmol}$. Total EDTA required was $(2.39 \text{ mL})(0.00963 \text{ M}) = 0.02302 \text{ mmol}$. Therefore, the original solid must have contained $0.08315 - 0.02302 = 0.06013 \text{ mmol}$ sulfur (which made 0.06013 mmol sulfate that precipitated 0.06013 mmol Ba^{2+}). The mass of sulfur was $(0.06013 \text{ mmol})(32.066 \text{ mg}/\text{mmol}) = 1.928 \text{ mg}$. $\text{wt\% S} = 100 \times (1.928 \text{ mg S}/5.89 \text{ mg sphalerite}) = 32.7 \text{ wt\%}$. Theoretical wt\% S in pure $\text{ZnS} = 100 \times (32.066 \text{ g S} / 97.46 \text{ g ZnS}) = 32.90 \text{ wt\%}$.

CHAPTER 12

ADVANCED TOPICS IN EQUILIBRIUM

- 12-1.** As pH is lowered, $[H^+]$ increases. H^+ reacts with basic anions to increase the solubility of their salts. Dissolution of minerals such as galena and cerussite increases the concentration of Pb^{2+} in the environment.



- 12-2.** (a) Hydroxybenzene = HA with $pK_{HA} = 9.997$

Mixture contains 0.010 0 mol HA and 0.005 0 mol KOH in 1.00 L.

Chemical reactions:

$$\text{HA} \rightleftharpoons A^- + H^+ \quad K_{HA} = \frac{[H^+][A^-]}{[HA]} = 10^{-9.997}$$

$$\text{H}_2\text{O} \rightleftharpoons H^+ + OH^- \quad K_w = [H^+][OH^-] = 10^{-14.00}$$

Charge balance:

$$[H^+] + [K^+] = [OH^-] + [A^-]$$

Mass balances:

$$[K^+] = 0.005 \text{ M}$$

$$[HA] + [A^-] = 0.010 \text{ M} = F_A$$

We have 5 equations and 5 chemical species.

Fractional composition equations:

$$[HA] = \alpha_{HA} F_A = \frac{[H^+] F_A}{[H^+] + K_{HA}}$$

$$[A^-] = \alpha_{A^-} F_A = \frac{K_{HA} F_A}{[H^+] + K_{HA}}$$

Substitute concentration expressions into the charge balance:

$$[H^+] + [0.005 \text{ M}] = K_w/[H^+] + \alpha_{A^-} F_A \tag{A}$$

We could solve Equation A for $[H^+]$ by using the solution to a quadratic equation. Instead, we will use Solver in the following spreadsheet, with an initial guess of $pH = 10$ in cell H9. Select Solver and choose Options. Set Precision to 1e-16 and click OK. In the Solver window, Set Target Cell E12 Equal To Value of 0 By Changing Cells H9. Click Solve and Solver finds $pH = 9.98$ in cell H9, giving a net charge near 0 in cell E12.

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.010 M HA and 0.005 M NaOH								
2									
3	$F_A =$	0.010		$[K^+] =$	0.005				
4	$pK_{HA} =$	9.997		$pK_w =$	14.000				
5	$K_{HA} =$	1.01E-10		$K_w =$	1.00E-14				
6									
7	Species in charge balance:						Other concentrations:		
8	$[H^+] =$	1.05E-10		$[A^-] =$	4.90E-03	$[HA] =$	5.10E-03		
9	$[K^+] =$	5.00E-03		$[OH^-] =$	9.56E-05	$pH =$	9.980		
10						↑ initial value is a guess			
11									
12	Positive charge minus negative charge	-3.00E-18	= B8+B9-E8-E9						
13	Formulas:								
14	$B5 = 10^{-B4}$			$B8 = 10^{-H9}$					
15	$E5 = 10^{-E4}$			$B9 = E3$					
16	$E8 = B5*B3/(B8+B5)$			$E9 = E5/B8$					
17	$H8 = B8*B3/(B8+B5)$								

(b) In Chapter 8, we would have said that there is enough KOH to neutralize half of the HA. Therefore, $[HA] = [A^-]$.

$pH = pK_a + \log([A^-]/[HA]) = pK_a + \log(1) = pK_a = 10.00$. The systematic treatment of equilibrium in the spreadsheet gave $pH = 9.98$.

(c) If we dilute HA to 0.000 10 M and KOH to 0.000 50 in cells B3 and E3, then Solver finds a pH of 9.45. It makes sense that as the solution becomes more dilute, the pH must move toward 7.

12-3. We use effective equilibrium constants, K' , defined as follows:

$$K_{HA} = \frac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}} \Rightarrow K'_{HA} = \frac{[H^+][A^-]}{[HA]} = K_{HA} \frac{\gamma_{HA}}{\gamma_{H^+}\gamma_{A^-}}$$

$$K_w = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} = 10^{-13.995}$$

$$K'_w = \frac{K_w}{\gamma_{H^+}\gamma_{OH^-}} = [H^+][OH^-] \Rightarrow [OH^-] = K'_w/[H^+]$$

$$pH = -\log([H^+]\gamma_{H^+})$$

The following spreadsheet shows the beginning of the first iteration with an initial ionic strength of 0 in cell C17. Execute Solver to find the pH in cell H13 that produces a net charge of 0 in cell E16. Solver finds $pH = 9.98$ and ionic strength = 0.005 0 in cell C18. Write 0.0050 in cell C17 and execute Solver again to find

pH = 9.95 and ionic strength = 0.0050 in cell C18. Since the ionic strength did not change after the 2nd iteration, we are finished. The pH is 9.95.

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.010 M HA and 0.005 M NaOH with activity coefficients								
2									
3	$\gamma_A =$	0.010		$\gamma_K^+ =$	0.005				
4	$pK_{HA} =$	9.997		$pK_w =$	13.995				
5	$K_{HA}' =$	1.01E-10		$K_w' =$	1.01E-14				
6									
7	Activity coefficients:								
8	$H^+ =$	1.00		$A^- =$	1.00				
9	$OH^- =$	1.00		$HA =$	1.00				
10									
11	Species in charge balance:						Other concentrations:		
12	$[H^+] =$	1.00E-10		$[A^-] =$	5.02E-03	$[HA] =$	4.98E-03		
13	$[K^+] =$	0.005		$[OH^-] =$	1.01E-04	$pH =$	10.000		
14						↑ initial value is a guess			
15									
16	Positive charge minus negative charge =	-1.18E-04	= B12+B13-E12-E13						
17	Ionic strength =	0.0000	← initial value is 0						
18	New ionic strength =	0.0051	← substitute this value into cell C17 for next iteration						
19									
20	Formulas:								
21	$B_5 = (10^{-B4}) * E9 / (B8 * E8)$			$E9 = 1$		$B_{13} = E3$			
22	$E_5 = (10^{-E4}) / (B8 * B9)$								
23	$B_8 = B_9 = E_8 = 10^{(-0.51 * 1^2 * (\text{SQRT}(\$C\$17) / (1 + \text{SQRT}(\$C\$17)) - 0.3 * \$C\$17))}$								
24	$B_{12} = (10^{-H13}) / B_8$								
25	$E_{12} = B_5 * B_3 / (B_{12} + B_5)$			$E_{13} = E_5 / B_{12}$					
26	$C_{18} = 0.5 * (B_{12} + B_{13} + E_{12} + E_{13})$			$H_{12} = B_{12} * B_3 / (B_{12} + B_5)$					

12-4. Abbreviating the protonated form of glycine as H_2G^+ , we write

$$H_2G^+ \rightleftharpoons HG + H^+ \quad K_1 = \frac{[HG]\gamma_{HG}[H^+]\gamma_{H^+}}{[H_2G^+]\gamma_{H_2G^+}} \quad pK_1 = 2.350$$

$$HG \rightleftharpoons G^- + H^+ \quad K_2 = \frac{[G^-]\gamma_G[H^+]\gamma_{H^+}}{[HG]\gamma_{HG}} \quad pK_2 = 9.778$$

At $\mu = 0.1$ M, the activity coefficient of a monovalent ion is 0.78. The activity coefficient of a neutral molecule is 1. Putting these coefficients into the expressions for K_1 and K_2 gives

$$K'_1 = \frac{[HG][H^+]}{[H_2G^+]} \text{ (at } \mu = 0.1 \text{ M)} = K_1 \frac{\gamma_{H_2G^+}}{\gamma_{HG}\gamma_{H^+}} = 10^{-2.350} \frac{0.78}{(1)(0.78)} = 10^{-2.350}$$

$$K'_2 = \frac{[G^-][H^+]}{[HG]} \text{ (at } \mu = 0.1 \text{ M)} = K_2 \frac{\gamma_{HG}}{\gamma_G\gamma_{H^+}} = 10^{-9.778} \frac{1}{(0.78)(0.78)} = 10^{-9.562}$$

The predicted values are $pK'_1 = 2.350$ and $pK'_2 = 9.562$. Values from fitting the data in the spreadsheet are 2.312 and 9.625. The change from pK_1 to pK'_1 is expected to be zero and it is observed to be -0.038 . The change from pK_2 to pK'_2 is expected to be -0.216 and it is observed to be -0.153 .

- 12-5.** Ethylenediamine = B from diprotic H_2B^{2+} $pK_1 = 6.848$ $pK_2 = 9.928$

Mixture contains 0.100 mol B and 0.035 mol HBr in 1.00 L.

Chemical reactions:



Charge balance:

$$[\text{H}^+] + 2[\text{H}_2\text{B}^{2+}] + [\text{HB}^+] = [\text{OH}^-] + [\text{Br}^-]$$

Mass balances:

$$[\text{Br}^-] = 0.035 \text{ M}; \quad [\text{H}_2\text{B}^{2+}] + [\text{HB}^+] + [\text{B}] = 0.100 \text{ M} = F_B$$

We have 6 equations and 6 chemical species, so there is enough information.

Fractional composition equations:

$$[\text{H}_2\text{B}^{2+}] = \alpha_{\text{H}_2\text{B}^{2+}} F_B = \frac{[\text{H}^+]^2 F_B}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2}$$

$$[\text{HB}^+] = \alpha_{\text{HB}^+} F_B = \frac{K_1 [\text{H}^+] F_B}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2}$$

$$[\text{B}] = \alpha_B F_B = \frac{K_1 K_2 F_B}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1 K_2}$$

Substitute into charge balance:

$$[\text{H}^+] + 2\alpha_{\text{H}_2\text{B}^{2+}} F_B + \alpha_{\text{HB}^+} F_B = K_w / [\text{H}^+] + [0.035 \text{ M}] \quad (\text{A})$$

We solve Equation A for $[\text{H}^+]$ by using Solver in the following spreadsheet, with an initial guess of $\text{pH} = 10$ in cell H11. Select Solver and choose Options. Set Precision to 1E-16 and click OK. In the Solver window, Set Target Cell E14 Equal To Value of 0 By Changing Cells H11. Click Solve and Solver finds $\text{pH} = 10.194$ in cell H11, giving a net charge of $\sim 10^{-17}$ in cell E14.

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.100 M B and 0.035 M HBr								
2									
3	$F_B =$	0.100		$[Br] =$	0.035				
4	$pK_1 =$	6.848		$pK_w =$	14.000				
5	$pK_2 =$	9.928		$K_w =$	1.00E-14				
6	$K_1 =$	1.42E-07							
7	$K_2 =$	1.18E-10							
8									
9	Concentrations:								
10	$[H^+] =$	6.39E-11		$[H_2B^{2+}] =$	1.58E-05	$[B] =$	6.49E-02		
11	$[Br] =$	3.50E-02		$[HB^+] =$	3.51E-02	$pH =$	10.194		
12	$[OH^-] =$	1.56E-04					↑ initial value is a guess		
13									
14	Positive charge minus negative charge	-1.70E-17							
15	Formulas:								
16	$B6 = 10^{-B4}$	$B7 = 10^{-B5}$		$E5 = 10^{-E4}$					
17	$B10 = 10^{-H11}$	$B11 = E3$		$B12 = E5/B10$					
18	$E10 = B10^{2*}B$3/(B10^{2*}+B10^{*}B$6+B$6^{*}B$7)$								
19	$E11 = B10^{*}B$6^{*}B$3/(B10^{2*}+B10^{*}B$6+B$6^{*}B$7)$								
20	$H10 = B$6^{*}B$7^{*}B$3/(B10^{2*}+B10^{*}B$6+B$6^{*}B$7)$								

In your earlier life, you would have solved this problem by noting that 0.035 mol HBr converts 0.035 mol B into 0.035 mol HB^+ , leaving $(0.100 - 0.035)$ mol B.

$$pH = pK_2 + \log \frac{[B]}{[HB^+]} = 9.928 + \log \frac{0.065}{0.035} = 10.197 \text{ (close to spreadsheet answer)}$$

- 12-6. Benzene-1,2,3-tricarboxylic acid = H_3A with $pK_1 = 2.86$, $pK_2 = 4.30$, $pK_3 = 6.28$; Imidazole = HB from diprotic H_2B^+ with $pK_1 = 6.993$, $pK_2 = 14.5$

Mixture contains 0.040 mol H_3A , 0.030 mol HB, and 0.035 mol NaOH in 1.00 L.

Charge balance:

$$[H^+] + [H_2B^+] + [Na^+] = [OH^-] + [H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + [B^-]$$

Substitute fractional composition equations into charge balance:

$$[H^+] + \alpha_{H_2B^+} F_B + [0.035]$$

$$= K_w/[H^+] + \alpha_{H_2A^-} F_A + 2\alpha_{H_2A^{2-}} F_A + 3\alpha_{HA^{3-}} F_A + \alpha_{B^-} F_B$$

We solve for $[H^+]$ with the following spreadsheet, with an initial guess of $pH = 7$ in cell H14. Select Solver and choose Options. Set Precision to 1e-16 and click OK. In Solver, Set Target Cell E16 Equal To Value of 0 By Changing Cells H14. Click Solve and Solver finds $pH = 4.52$ in cell H14, giving a net charge of $\sim 10^{-16}$ in cell E16.

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.040 M H_3A , 0.030 M HB , and 0.035 M NaOH								
2									
3	$F_A =$	0.040		$F_B =$	0.030	$[\text{Na}^+] =$	0.035		
4	$pK_1 =$	2.86		$pK_{\text{H}_2\text{B}} =$	6.993	$pK_w =$	14.000		
5	$pK_2 =$	4.30		$pK_{\text{HB}} =$	14.5	$K_w =$	1.00E-14		
6	$pK_3 =$	6.28		$K_{\text{H}_2\text{B}} =$	1.02E-07				
7	$K_1 =$	1.4E-03		$K_{\text{HB}} =$	3.16E-15				
8	$K_2 =$	5.0E-05							
9	$K_3 =$	5.2E-07							
10									
11	Concentrations								
12	$[\text{H}^+] =$	3.05E-05		$[\text{A}^{3-}] =$	4.21E-04	$[\text{OH}^-] =$	3.28E-10		
13	$[\text{H}_3\text{A}] =$	3.27E-04		$[\text{H}_2\text{B}^+] =$	2.99E-02	$[\text{Na}^+] =$	0.035		
14	$[\text{H}_2\text{A}^-] =$	1.48E-02		$[\text{HB}] =$	9.98E-05	$\text{pH} =$	4.516		
15	$[\text{HA}^{2-}] =$	2.44E-02		$[\text{B}^-] =$	1.04E-14	\uparrow initial value is a guess			
16	Positive charge minus negative charge :	-2.42E-17							
17									
18	Formulas:								
19	$B7 = 10^{-B4}$			$B8 = 10^{-B5}$		$B9 = 10^{-B6}$			
20	$E6 = 10^{-E4}$			$E7 = 10^{-E5}$					
21	$B12 = 10^{-H14}$			$H12 = H5/B12$		$H13 = H3$			
22									
23									
24									
25									
26									
27									
28									

12-7. Arginine = HA from H_3A^{2+} with $pK_1 = 1.823$, $pK_2 = 8.991$, $pK_3 = 12.1$; glutamic acid = H_2G from H_3G^+ with $pK_1 = 2.160$, $pK_2 = 4.30$, $pK_3 = 9.96$

Mixture contains 0.020 mol arginine, 0.030 mol glutamic acid, and 0.005 mol KOH in 1.00 L. $F_A = 0.020$ M and $F_G = 0.030$ M.

Charge balance:

$$[\text{H}^+] + 2[\text{H}_3\text{A}^{2+}] + [\text{H}_2\text{A}^+] + [\text{H}_3\text{G}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{HG}^-] + 2[\text{G}^{2-}]$$

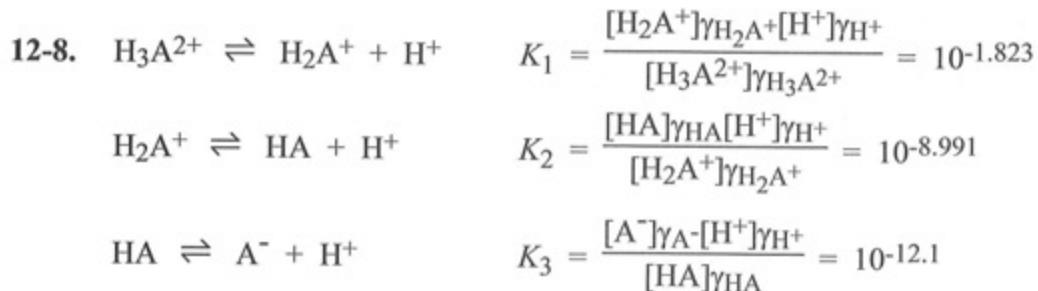
Substitute fractional composition equations into charge balance:

$$[\text{H}^+] + 2\alpha_{\text{H}_3\text{A}^{2+}} F_A + \alpha_{\text{H}_2\text{A}^+} F_A + \alpha_{\text{H}_3\text{G}^+} F_G + [0.005]$$

$$= K_w/[\text{H}^+] + \alpha_{\text{A}^-} F_A + \alpha_{\text{HG}^-} F_G + 2\alpha_{\text{G}^{2-}} F_G$$

	A	B	C	D	E	F	G	H	I	J
1	Mixture of 0.020 M arginine, 0.030 M glutamic acid, and 0.005 M KOH									
2										
3	$F_A =$	0.020	$F_B =$	0.030	$[K^+] =$	0.005				
4	$pK_1 =$	1.823	$pK_{H3G} =$	2.160	$pK_w =$	14.00				
5	$pK_2 =$	8.991	$pK_{H2G} =$	4.30	$K_w =$	1.00E-14				
6	$pK_3 =$	12.1	$pK_{HG} =$	9.96						
7	$K_1 =$	1.5E-02	$K_{H3G} =$	6.9E-03						
8	$K_2 =$	1.0E-09	$K_{H2G} =$	5.0E-05						
9	$K_3 =$	7.9E-13	$K_{HG} =$	1.1E-10						
10										
11	Concentrations									
12	$[H_3A^{2+}] =$	1.32E-05	$[H_3G^+] =$	7.14E-06	$[H^+] =$	9.94E-06				
13	$[H_2A^+] =$	2.00E-02	$[H_2G] =$	4.96E-03	$[OH^-] =$	1.01E-09				
14	$[HA] =$	2.05E-06	$[HG] =$	2.50E-02	$[K^+] =$	0.005				
15	$[A^-] =$	1.64E-13	$[G^{2-}] =$	2.76E-07	$pH =$	5.003				
16										
17	Positive charge minus negative charge			-9.94E-17						
18					= 2*B12+B13+E12+H12+H14-B15-E14-2*E15-H13					
19	Formulas:									
20	$B7 = 10^{-B4}$	$B8 = 10^{-B5}$			$B9 = 10^{-B6}$					
21	$E7 = 10^{-E4}$	$E8 = 10^{-E5}$			$E9 = 10^{-E6}$					
22	$H12 = 10^{-H15}$	$H13 = H5/H12$			$H14 = H3$					
23	$B12 = \$H\$12^3*\$B\$3/(\$H\$12^3+\$H\$12^2*\$B\$7+\$H\$12*\$B\$7*\$B\$8+\$B\$7*\$B\$8*\$B\$9)$									
24	$B13 = \$H\$12^2*\$B\$7*\$B\$3/(\$H\$12^3+\$H\$12^2*\$B\$7+\$H\$12*\$B\$7*\$B\$8+\$B\$7*\$B\$8*\$B\$9)$									
25	$B14 = \$H\$12*\$B\$7*\$B\$8*\$B\$3/(\$H\$12^3+\$H\$12^2*\$B\$7+\$H\$12*\$B\$7*\$B\$8+\$B\$7*\$B\$8*\$B\$9)$									
26	$B15 = \$B\$7*\$B\$8*\$B\$9*\$B\$3/(\$H\$12^3+\$H\$12^2*\$B\$7+\$H\$12*\$B\$7*\$B\$8+\$B\$7*\$B\$8*\$B\$9)$									
27	$E12 = \$H\$12^3*\$E\$3/(\$H\$12^3+\$H\$12^2*\$E\$7+\$H\$12*\$E\$7*\$E\$8+\$E\$7*\$E\$8*\$E\$9)$									
28	$E13 = \$H\$12^2*\$E\$7*\$E\$3/(\$H\$12^3+\$H\$12^2*\$E\$7+\$H\$12*\$E\$7*\$E\$8+\$E\$7*\$E\$8*\$E\$9)$									
29	$E14 = \$H\$12*\$E\$7*\$E\$8*\$E\$3/(\$H\$12^3+\$H\$12^2*\$E\$7+\$H\$12*\$E\$7*\$E\$8+\$E\$7*\$E\$8*\$E\$9)$									
30	$E15 = \$E\$7*\$E\$8*\$E\$9*\$E\$3/(\$H\$12^3+\$H\$12^2*\$E\$7+\$H\$12*\$E\$7*\$E\$8+\$E\$7*\$E\$8*\$E\$9)$									

We solve for $[H^+]$ with the spreadsheet, with an initial guess of pH = 3 in cell H15. Select Solver and choose Options. Set Precision to 1e-16 and click OK. In Solver, Set Target Cell E17 Equal To Value of 0 By Changing Cells H55. Click Solve and Solver finds pH = 5.00 in cell H15, giving a net charge of $\sim 10^{-16}$ in cell E17.



$$K'_1 = K_1 \left(\frac{\gamma_{H_3A^{2+}}}{\gamma_{H_2A^+}\gamma_{H^+}} \right) = \frac{[H_2A^+][H^+]}{[H_3A^{2+}]} \quad K = K_2 \left(\frac{\gamma_{H_2A^+}}{\gamma_{HA}\gamma_{H^+}} \right) = \frac{[HA][H^+]}{[H_2A^+]}$$

$$K'_3 = K_3 \left(\frac{\gamma_{HA}}{\gamma_{A^-}\gamma_{H^+}} \right) = \frac{[A^-][H^+]}{[HA]}$$

$$H_3G^+ \rightleftharpoons H_2G + H^+ \quad K_{H_3G} = \frac{[H_2G]\gamma_{H_2G}[H^+]\gamma_{H^+}}{[H_3G^+]\gamma_{H_3G^+}} = 10^{-2.160}$$

$$H_2G \rightleftharpoons HG^- + H^+ \quad K_{H_2G} = \frac{[HG^-]\gamma_{HG^-}[H^+]\gamma_{H^+}}{[H_2G]\gamma_{H_2G}} = 10^{-4.30}$$

$$HG^- \rightleftharpoons G^{2-} + H^+ \quad K_{HG} = \frac{[G^{2-}]\gamma_{G^{2-}}[H^+]\gamma_{H^+}}{[HG^-]\gamma_{HG^-}} = 10^{-9.96}$$

$$K'_{H_3G} = K_{H_3G} \left(\frac{\gamma_{H_3G^+}}{\gamma_{H_2G}\gamma_{H^+}} \right) = \frac{[H_2G][H^+]}{[H_3G^+]} \quad K'_{H_2G} = K_{H_2G} \left(\frac{\gamma_{H_2G}}{\gamma_{HG^-}\gamma_{H^+}} \right) = \frac{[HG^-][H^+]}{[H_2G]}$$

$$K'_{HG} = K_{HG} \left(\frac{\gamma_{HG^-}}{\gamma_{G^{2-}}\gamma_{H^+}} \right) = \frac{[G^{2-}][H^+]}{[HG^-]}$$

In the next spreadsheet, $[H^+]$ in cell H18 is computed from $(10^{-pH})/\gamma_{H^+}$. Don't forget that activity coefficient! Ionic strength in cell D24 was initially set to 0, and activity coefficients are computed in cells A13:H15. From the activity coefficients, effective equilibrium constants are computed in cells H4:H10. pH = 3 is guessed in cell H21. From pH and the K' values, concentrations are computed in cells A18:H21. Solver is used to vary pH in cell H21 until the net charge in cell H23 is 0. If Solver does not find an answer, try a different initial value for pH or increase Precision in the Options window of Solver. A value of 1e-16 generally works, but for some problems I need larger numbers, such as 1E-10. The ionic strength computed in cell D25 is then entered into cell D24 and Solver is executed again. The process is complete when ionic strength no longer changes. pH computed with activities is 4.95 and $\mu = 0.025$ M. When we found pH without activities in the previous problem, the pH was 5.00.

Iteration	ionic strength	pH
1	0	5.003
2	0.025	4.939
3	0.025	4.939

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.020 M arginine, 0.030 M glutamic acid, and 0.005 M KOH								
2	Solved with Davies activity coefficients								
3	$F_A =$	0.020		$F_B =$	0.030		$[K'] =$	0.005	
4	$pK_1 =$	1.823		$pK_{H3G} =$	2.160		$K_1' =$	1.1E-02	
5	$pK_2 =$	8.991		$pK_{H2G} =$	4.30		$K_2' =$	1.0E-09	
6	$pK_3 =$	12.1		$pK_{HG} =$	9.96		$K_3' =$	1.1E-12	
7	$K_1 =$	1.5E-02		$K_{H3G} =$	6.9E-03		$K_{H3G}' =$	6.9E-03	
8	$K_2 =$	1.0E-09		$K_{H2G} =$	5.0E-05		$K_{H2G}' =$	6.8E-05	
9	$K_3 =$	7.9E-13		$K_{HG} =$	1.1E-10		$K_{HG}' =$	2.01E-10	
10	$pK_w =$	13.995		$K_w =$	1.01E-14		$K_w' =$	1.37E-14	
11									
12	Davies activity coefficients								
13	$H_3A^{2+} =$	0.54		$H_3G^+ =$	0.86				
14	$H_2A^+ =$	0.86		$HG^- =$	0.86		$H^+ =$	0.86	
15	$A^- =$	0.86		$G^{2-} =$	0.54		$OH^- =$	0.86	
16									
17	Concentrations								
18	$[H_3A^{2+}] =$	2.41E-05		$[H_3G^+] =$	9.58E-06		$[H^+] =$	1.34E-05	
19	$[H_2A^+] =$	2.00E-02		$[H_2G] =$	4.95E-03		$[OH^-] =$	1.02E-09	
20	$[HA] =$	1.52E-06		$[HG^-] =$	2.50E-02		$[K'] =$	0.005	
21	$[A^-] =$	1.22E-13		$[G^{2-}] =$	3.76E-07		$pH =$	4.939	
22							↑ initial value is a guess		
23	Positive charge minus negative charge =	-8.86E-18							
24	Ionic strength =	0.0251	← initial value is 0						
25	New ionic strength =	0.0251	← substitute this value into cell D24						
26			for next iteration						
27	Formulas								
28	$K_1' = B7*B13/(B14*H14)$			$K_2' = B8*B14/(H14)$			$K_3' = B9/(B15*H14)$		
29	$K_{H3B}' = E7*E13/H14$			$K_{H2B}' = E8/(E14*H14)$			$K_{HB}' = E9*E14/(E15*H14)$		
30	$K_w' = E10/(H14*H15)$			$[H^+] = (10^-H21)/H14$			$[OH^-] = H10/H18$		
31	Activity coefficient = $10^{(-0.51*charge^2*(SQRT(D24)/(1+SQRT(D24))-0.3*D24))}$								
32	Denom1 = $(\$H\$18^3+\$H\$18^2*\$H\$4+\$H\$18*\$H\$4*\$H\$5+\$H\$4*\$H\$5*\$H\$6)$								
33	$[H_3A^{2+}] = \$H\$18^3*B\$3/Denom1$				$[H_2A^+] = \$H\$18^2*\$H\$4*B\$3/Denom1$				
34	$[HA] = \$H\$18*\$H\$4*\$H\$5*B\$3/Denom1$				$[A^-] = \$H\$4*\$H\$5*\$H\$6*B\$3/Denom1$				
35	Denom2 = $(\$H\$18^3+\$H\$18^2*\$H\$7+\$H\$18*\$H\$7*\$H\$8+\$H\$7*\$H\$8*\$H\$9)$								
36	$[H_3G^+] = \$H\$18^3*E\$3/Denom2$				$[H_2G] = \$H\$18^2*\$H\$7*E\$3/Denom2$				
37	$[HG^-] = \$H\$18*\$H\$7*\$H\$8*E\$3/Denom2$				$[G^{2-}] = \$H\$7*\$H\$8*\$H\$9*E\$3/Denom2$				
38	$E23 = 2*B18+B19+E18+H18+H20-B21-E20-2*E21-H19$								
39	$D25 = 0.5*(4*B18+B19+B21+E18+E20+4*E21+H18+H19+H20)$								

- 12-9. (a) This is the same problem that was worked in Section 12-2, but with $[KH_2PO_4] = 0.008\ 695\ m$ and $[Na_2HPO_4] = 0.030\ 43\ m$ in cells B3 and B4 of the spreadsheet in Figure 12-4. Beginning with ionic strength = 0 in cell C19 and pH = 7 in cell H15, we find the value of pH required to make the net charge 0

in cell E18 by using Solver with Precision = 1e-16. The first iteration gives pH = 7.742. The ionic strength in cell C20 after the first (and all subsequent) iterations is 0.100 *m*. Typing this value in cell C19 and performing a second iteration gives pH = 7.420.

- (b) To use the Debye-Hückel equation, we can compute activity coefficients with ion size parameters from Table 7-1 or we can just use activity coefficients from Table 7-1 for $\mu = 0.1 \text{ M}$:

	A	B	C	D	E	F	G	H
8	Activity coefficients from table iin textbook:							
9	$\text{H}^+ =$	0.83	$\text{H}_3\text{P}^- =$		1.00 (fixed at 1)	$\text{HP}^{2-} =$	0.36	
10	$\text{OH}^- =$	0.76	$\text{H}_2\text{P}^{3-} =$		0.78	$\text{P}^{3-} =$	0.10	

These activity coefficients produce a pH of 7.403 after executing Solver to reduce the net charge to 0 in cell E18.

- 12-10.** EDTA = H_4A from hexaproto H₆A²⁺ with $\text{p}K_1 = 0.0$, $\text{p}K_2 = 1.5$, $\text{p}K_3 = 2.00$, $\text{p}K_4 = 2.69$, $\text{p}K_5 = 6.13$, $\text{p}K_6 = 10.37$; Lysine = HL from triprotic H₃L²⁺ with $\text{p}K_1 = 1.77$, $\text{p}K_2 = 9.07$, $\text{p}K_3 = 10.82$

Mixture contains 0.040 mol H₄A, 0.030 mol HL, and 0.050 mol NaOH in 1.00 L.

Charge balance:

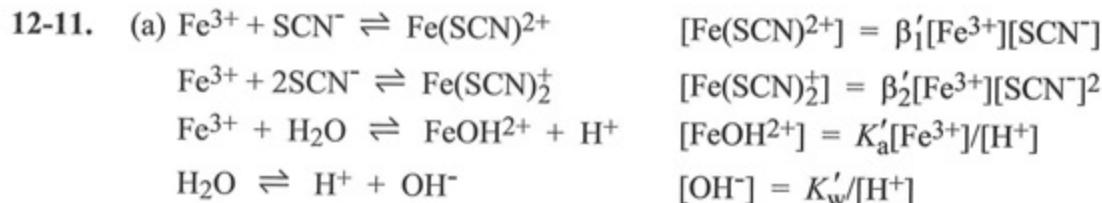
$$\begin{aligned} [\text{H}^+] + 2[\text{H}_6\text{A}^{2+}] + [\text{H}_5\text{A}^+] + 2[\text{H}_3\text{L}^{2+}] + [\text{H}_2\text{L}^+] + [\text{Na}^+] \\ = [\text{OH}^-] + [\text{H}_3\text{A}^-] + 2[\text{H}_2\text{A}^{2-}] + 3[\text{HA}^{3-}] + 4[\text{A}^{4-}] + [\text{L}^-] \end{aligned}$$

Substitute fractional composition equations into charge balance:

$$\begin{aligned} [\text{H}^+] + 2\alpha_{\text{H}_6\text{A}^{2+}} \text{F}_A + \alpha_{\text{H}_5\text{A}^+} \text{F}_A + 2\alpha_{\text{H}_3\text{L}^{2+}} \text{F}_L + \alpha_{\text{H}_2\text{L}^+} \text{F}_L + [0.050] \\ = K_w/[\text{H}^+] + \alpha_{\text{H}_3\text{A}^-} \text{F}_A + 2\alpha_{\text{H}_2\text{A}^{2-}} \text{F}_A + 3\alpha_{\text{HA}^{3-}} \text{F}_A + 4\alpha_{\text{A}^{4-}} \text{F}_A + \alpha_{\text{L}^-} \text{F}_L \end{aligned}$$

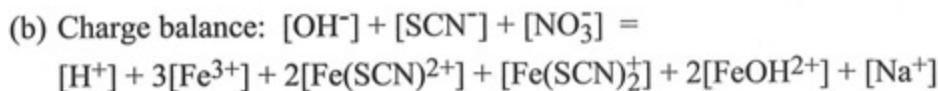
We solve this equation for pH with the following spreadsheet, with an initial guess of pH = 7 in cell H18. In Solver, Set Target Cell E19 Equal To Value of 0 By Changing Cells H18. Click OK and Solver finds pH = 4.44 in cell H18.

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.040 M H ₄ A, 0.030 M HL, and 0.05 M NaOH								
2									
3	F _A =	0.040		F _L =	0.030	[Na ⁺] =	0.050		
4	pK ₁ =	0.0		pK _{L1} =	1.77				
5	pK ₂ =	1.5		pK _{L2} =	9.07				
6	pK ₃ =	2.0		pK _{L3} =	10.82	pK _w =	14.00		
7	pK ₄ =	2.69		K _{L1} =	1.70E-02	K _w =	1.00E-14		
8	pK ₅ =	6.13		K _{L2} =	8.51E-10				
9	pK ₆ =	10.37		K _{L3} =	1.51E-11				
10	K ₁ =	1.00E+00		K ₃ =	1.00E-02	K ₅ =	7.41E-07		
11	K ₂ =	3.16E-02		K ₄ =	2.04E-03	K ₆ =	4.27E-11		
12									
13	Species in charge balance:								
14	[H ⁺] =	3.62E-05		[HA ³⁻] =	7.88E-04	[OH ⁻] =	2.76E-10		
15	[H ₆ A ²⁺] =	1.03E-13		[A ⁴⁻] =	9.28E-10	[Na ⁺] =	0.050		
16	[H ₅ A ⁺] =	2.84E-09		[H ₃ L ²⁺] =	6.39E-05	[H ₄ A] =	2.48E-06		
17	[H ₃ A] =	6.84E-04		[H ₂ L ⁺] =	2.99E-02	[HL] =	7.03E-07		
18	[H ₂ A ²⁻] =	3.85E-02		[L ⁻] =	2.94E-13	pH =	4.441 ← initial value		
19	Positive charge minus negative charge	-9.77E-17							is a guess
20	Formulas:								
21	B10 = 10^-B4 with analogous formulas for K ₂ - K ₆								
22	E7 = 10-E4 with analogous formulas for K _{L2} and K _{L3}								
23	B14 = 10^-H18	H14 = H7/B14		H15 = H3					
24	Denom1 = \$B\$14^6+\$B\$14^5*\$B\$10+\$B\$14^4*\$B\$10*\$B\$11+\$B\$14^3*\$B\$10*\$B\$11*\$E\$10								
25	+\$B\$14^2*\$B\$10*\$B\$11*\$E\$10*\$E\$11+\$B\$14*\$B\$10*\$B\$11*\$E\$10*\$E\$11*\$H\$10								
26	+\$B\$10*\$B\$11*\$E\$10*\$E\$11*\$H\$10*\$H\$11								
27	Denom2 = \$B\$14^3+\$B\$14^2*\$E\$7+\$B\$14*\$E\$7*\$E\$8+\$E\$7*\$E\$8*\$E\$9								
28	B15 = \$B\$14^6*\$B\$3/Denom1								
29	B16 = \$B\$14^5*\$B\$10*\$B\$3/Denom1								
30	B17 = \$B\$14^3*\$B\$10*\$B\$11*\$E\$10*\$B\$3/Denom1								
31	B18 = \$B\$14^2*\$B\$10*\$B\$11*\$E\$10*\$E\$11*\$B\$3/Denom1								
32	E14 = \$B\$14*\$B\$10*\$B\$11*\$E\$10*\$E\$11*\$H\$10*\$B\$3/Denom1								
33	E15 = \$B\$10*\$B\$11*\$E\$10*\$E\$11*\$H\$10*\$H\$11*\$B\$3/Denom1								
34	H16 = \$B\$14^4*\$B\$10*\$B\$11*\$B\$3/Denom1								
35	E16 = \$B\$14^3*\$E\$3/Denom2								
36	E17 = \$B\$14^2*\$E\$7*\$E\$3/Denom2								
37	E18 = \$E\$7*\$E\$8*\$E\$9*\$E\$3/Denom2								
38	H17 = \$B\$14*\$E\$7*\$E\$8*\$E\$3/Denom2								
39	E19 = B14+2*B15+B16+2*E16+E17+H15-B17-2*B18-3*E14-4*E15-E18-H14								



$$\beta'_1 = \beta_1 \frac{\gamma_{\text{Fe}^{3+}} \gamma_{\text{SCN}^-}}{\gamma_{\text{Fe}(\text{SCN})_2^{2+}}} \quad \beta'_2 = \beta_2 \frac{\gamma_{\text{Fe}^{3+}} \gamma_{\text{SCN}^-}^2}{\gamma_{\text{Fe}(\text{SCN})_2^+}} \quad K'_a = K_a \frac{\gamma_{\text{Fe}^{3+}}}{\gamma_{\text{FeOH}^{2+}} \gamma_{\text{H}^+}}$$

$$K'_w = \frac{K_w}{\gamma_{\text{H}^+} \gamma_{\text{OH}^-}} \quad \beta_1 = 10^{3.03} \quad \beta_2 = 10^{4.6} \quad K_a = 10^{-2.195}$$



(c) Mass balances:

$$\text{Total iron} \equiv F_{\text{Fe}} = 5.0 \text{ mM} = [\text{Fe}^{3+}] + [\text{Fe}(\text{SCN})^{2+}] + [\text{Fe}(\text{SCN})_2^+] + [\text{FeOH}^{2+}]$$

$$\text{Total thiocyanate} \equiv F_{\text{SCN}} = 5.0 \mu\text{M} = [\text{Fe}(\text{SCN})^{2+}] + 2[\text{Fe}(\text{SCN})_2^+] + [\text{SCN}^-]$$

$$[\text{Na}^+] = 5.0 \mu\text{M}$$

$$[\text{NO}_3^-] = 3(5.0 \text{ mM}) + 15.0 \text{ mM} = 30.0 \text{ mM}$$

(d) $[\text{Fe}(\text{SCN})^{2+}] + 2[\text{Fe}(\text{SCN})_2^+] + [\text{SCN}^-] = F_{\text{SCN}}$

$$\beta'_1 [\text{Fe}^{3+}] [\text{SCN}^-] + 2\beta'_2 [\text{Fe}^{3+}] [\text{SCN}^-]^2 + [\text{SCN}^-] = F_{\text{SCN}}$$

$$[\text{Fe}^{3+}] (\beta'_1 [\text{SCN}^-] + 2\beta'_2 [\text{SCN}^-]^2) = F_{\text{SCN}} - [\text{SCN}^-]$$

$$[\text{Fe}^{3+}] = \frac{F_{\text{SCN}} - [\text{SCN}^-]}{\beta'_1 [\text{SCN}^-] + 2\beta'_2 [\text{SCN}^-]^2}$$

(e) $[\text{Fe}^{3+}] + [\text{Fe}(\text{SCN})^{2+}] + [\text{Fe}(\text{SCN})_2^+] + [\text{FeOH}^{2+}] = F_{\text{Fe}}$

$$[\text{Fe}^{3+}] + \beta'_1 [\text{Fe}^{3+}] [\text{SCN}^-] + \beta'_2 [\text{Fe}^{3+}] [\text{SCN}^-]^2 + K'_a [\text{Fe}^{3+}] / [\text{H}^+] = F_{\text{Fe}}$$

$$[\text{H}^+] = \frac{K'_a [\text{Fe}^{3+}]}{F_{\text{Fe}} - [\text{Fe}^{3+}] - \beta'_1 [\text{Fe}^{3+}] [\text{SCN}^-] - \beta'_2 [\text{Fe}^{3+}] [\text{SCN}^-]^2}$$

$$\text{or } [\text{H}^+] = \frac{K'_a [\text{Fe}^{3+}]}{F_{\text{Fe}} - [\text{Fe}^{3+}] - [\text{Fe}(\text{SCN})^{2+}] - [\text{Fe}(\text{SCN})_2^+]} \text{ (which is easier to use)}$$

(f), (g), (h), (i) The spreadsheet on the next page shows the following results:

	A	B	C	D	E	F	G	H
13	$[\text{SCN}^-]$	$[\text{Fe}^{3+}]$	$[\text{H}^+]$	$[\text{OH}^-]$	$[\text{Fe}(\text{SCN})^{2+}]$	$[\text{Fe}(\text{SCN})_2^+]$	$[\text{FeOH}^{2+}]$	Net charge
14	2.03E-06	4.20E-03	1.58E-02	9.20E-13	2.97E-06	1.06E-10	8.02E-04	-2.78E-17

$$\text{Ionic strength} = 0.043 \text{ M}$$

$$\text{pH} = 1.88$$

$$\frac{[\text{Fe}(\text{SCN})^{2+}]}{([\text{Fe}^{3+}] + [\text{FeOH}^{2+}]) [\text{SCN}^-]} = 293 \text{ (The graph in the textbook gives 270.)}$$

(j) The next spreadsheet shows the results when the solution also contains 0.20 M KNO_3 :

	A	B	C	D	E	F	G	H
13	[SCN ⁻]	[Fe ³⁺]	[H ⁺]	[OH ⁻]	[FeSCN ²⁺]	[Fe(SCN) ₂ ⁺]	[FeOH ²⁺]	Net charge
14	2.81E-06	4.45E-03	1.55E-02	1.18E-12	2.19E-06	6.82E-11	5.46E-04	0.00E+00

Ionic strength = 0.243 9 M

pH = 1.94

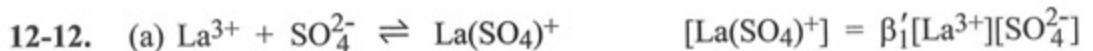
$$\frac{[\text{Fe}(\text{SCN})^{2+}]}{\{[\text{Fe}^{3+}] + [\text{FeOH}^{2+}]\}[\text{SCN}^-]} = 156 \quad (\text{The graph in the textbook gives } 150.)$$

Spreadsheet for 0 M KNO₃:

	A	B	C	D	E	F	G	H
1	Composition of Fe(III)-thiocyanate solution							
2								
3	log β ₁ =	3.03	β ₁ =	1.07E+03	β _{1'} =	1.75E+02	F _{Fe} =	5.0E-03
4	log β ₂ =	4.6	β ₂ =	3.98E+04	β _{2'} =	1.94E+03	F _{SCN} =	5.0E-06
5	log K _a =	-2.195	K _a =	6.38E-03	K _{a'} =	1.90E-03	[Na ⁺] =	5.0E-06
6	log K _w =	-14.00	K _w =	1.00E-14	K _{w'} =	1.83E-14	[NO ₃ ⁻] =	2.3E-01
7							[K ⁺] =	2.0E-01
8	Davies activity coefficients:							
9	Fe ³⁺	0.07	FeOH ²⁺	0.30	OH ⁻			0.74
10	Fe(SCN) ²⁺	0.30	SCN ⁻	0.74	H ⁺			0.74
11	Fe(SCN) ₂ ⁺	0.74						
12								
13	[SCN ⁻]	[Fe ³⁺]	[H ⁺]	[OH ⁻]	[FeSCN ²⁺]	[Fe(SCN) ₂ ⁺]	[FeOH ²⁺]	Net charge
14	2.81E-06	4.45E-03	1.55E-02	1.18E-12	2.19E-06	6.82E-11	5.46E-04	0.00E+00
15								
16	Ionic strength =	0.2439	← Initial value is 0					
17	New ionic strength =	0.2439		[FeSCN ²⁺]/{[Fe ³⁺] + [FeOH ²⁺]})[SCN ⁻] =				
18	pH =	1.94			156			
19	Total Fe =	5.000E-03	= [Fe ³⁺] + [FeSCN ²⁺] + [Fe(SCN) ₂ ⁺] + [FeOH ²⁺]					
20	Total SCN =	5.000E-06	= [SCN ⁻] + [FeSCN ²⁺] + 2[Fe(SCN) ₂ ⁺]					
21								
22	Activity coefficients = 10 ^{-0.51*charge^2*(SQRT(\$C\$16)/(1+SQRT(\$C\$16))-0.3*\$C\$16))}							
23	β _{1'} = D3*B9*E10/B10		K _{a'} = D5*B9/(E9*H10)					
24	β _{2'} = D4*B9*E10^2/B11		K _{w'} = D6/(H9*H10)					
25	[Fe ³⁺] = (H4-A14)/(F3*A14+2*F4*A14^2)							
26	[H ⁺] = F5*B14/(H3-B14-E14-F14)		[OH ⁻] = F6/C14					
27	[FeSCN ²⁺] = F3*B14*A14		[Fe(SCN) ₂ ⁺] = F4*B14*A14^2					
28	[FeOH ²⁺] = F5*B14/C14		pH = -LOG10(C14*H10)					
29	Net charge = 3*B14+C14+2*E14+F14+2*G14+H5-A14-D14-H6+H7							
30	New ionic strength = 0.5*(H5+H6+A14+9*B14+C14+D14+4*E14+F14+4*G14+H7)							

Spreadsheet for 0.20 M KNO₃:

	A	B	C	D	E	F	G	H
1	Composition of Fe(III)-thiocyanate solution							
2								
3	$\log \beta_1 =$	3.03	$\beta_1 =$	1.07E+03	$\beta_1' =$	1.75E+02	$F_{Fe} =$	5.0E-03
4	$\log \beta_2 =$	4.6	$\beta_2 =$	3.98E+04	$\beta_2' =$	1.94E+03	$F_{SCN} =$	5.0E-06
5	$\log K_a =$	-2.195	$K_a =$	6.38E-03	$K_a' =$	1.90E-03	$[Na^+] =$	5.0E-06
6	$\log K_w =$	-14.00	$K_w =$	1.00E-14	$K_w' =$	1.83E-14	$[NO_3^-] =$	2.3E-01
7							$[K^+] =$	2.0E-01
8	Davies activity coefficients:							
9	Fe ³⁺	0.07	FeOH ²⁺	0.30	OH ⁻	0.74		
10	Fe(SCN) ²⁺	0.30	SCN ⁻	0.74	H ⁺	0.74		
11	Fe(SCN) ₂ ⁺	0.74						
12								
13	[SCN ⁻]	[Fe ³⁺]	[H ⁺]	[OH ⁻]	[FeSCN ²⁺]	[Fe(SCN) ₂ ⁺]	[FeOH ²⁺]	Net charge
14	2.81E-06	4.45E-03	1.55E-02	1.18E-12	2.19E-06	6.82E-11	5.46E-04	0.00E+00
15								
16	Ionic strength =	0.2439	← Initial value is 0					
17	New ionic strength =	0.2439		[FeSCN ²⁺]/([Fe ³⁺] + [FeOH ²⁺]) =				
18	pH =	1.94			156			
19	Total Fe =	5.000E-03	= [Fe ³⁺] + [FeSCN ²⁺] + [Fe(SCN) ₂ ⁺] + [FeOH ²⁺]					
20	Total SCN =	5.000E-06	= [SCN ⁻] + [FeSCN ²⁺] + 2[Fe(SCN) ₂ ⁺]					



$$\beta_1' = \beta_1 \frac{\gamma_{La^{3+}} \gamma_{SO_4^{2-}}}{\gamma_{La(SO_4)^+}} \quad \beta_2' = \beta_2 \frac{\gamma_{La^{3+}} \gamma_{SO_4^{2-}}^2}{\gamma_{La(SO_4)_2^-}} \quad K_a' = K_a \frac{\gamma_{La^{3+}}}{\gamma_{LaOH^{2+}} \gamma_{H^+}}$$

$$K_w' = \frac{K_w}{\gamma_{H^+} \gamma_{OH^-}} \quad \beta_1 = 10^{3.64} \quad \beta_2 = 10^{5.3} \quad K_a = 10^{-8.5}$$

Charge balance:

$$[OH^-] + 2[SO_4^{2-}] + [La(SO_4)_2^-] = [H^+] + 3[La^{3+}] + [La(SO_4)^+] + 2[LaOH^{2+}]$$

Mass balances:

$$\text{Lanthanum} \equiv F_{La} = 2.0 \text{ mM} = [La^{3+}] + [La(SO_4)^+] + [La(SO_4)_2^-] + [LaOH^{2+}]$$

$$\text{Sulfate} \equiv F_{SO_4} = 3.0 \text{ mM} = [La(SO_4)^+] + 2[La(SO_4)_2^-] + [SO_4^{2-}]$$

Express [La³⁺] in terms of [SO₄²⁻]:

$$[La(SO_4)^+] + 2[La(SO_4)_2^-] + [SO_4^{2-}] = F_{SO_4}$$

$$\beta_1'[La^{3+}][SO_4^{2-}] + 2\beta_2'[La^{3+}][SO_4^{2-}]^2 + [SO_4^{2-}] = F_{SO_4}$$

$$[\text{La}^{3+}](\beta'_1[\text{SO}_4^{2-}] + 2\beta'_2[\text{SO}_4^{2-}]^2) = F_{\text{SO}_4} - [\text{SO}_4^{2-}]$$

$$[\text{La}^{3+}] = \frac{F_{\text{SO}_4} - [\text{SO}_4^{2-}]}{\beta'_1[\text{SO}_4^{2-}] + 2\beta'_2[\text{SO}_4^{2-}]^2}$$

Express $[\text{H}^+]$ in terms of $[\text{La}^{3+}]$ and $[\text{SO}_4^{2-}]$:

$$[\text{La}^{3+}] + [\text{La}(\text{SO}_4)^+] + [\text{La}(\text{SO}_4)_2^-] + [\text{LaOH}^{2+}] = F_{\text{La}}$$

$$[\text{La}^{3+}] + \beta'_1[\text{La}^{3+}][\text{SO}_4^{2-}] + \beta'_2[\text{La}^{3+}][\text{SO}_4^{2-}]^2 + K_a'[\text{La}^{3+}]/[\text{H}^+] = F_{\text{La}}$$

$$[\text{H}^+] = \frac{K_a'[\text{La}^{3+}]}{F_{\text{La}} - [\text{La}^{3+}] - \beta'_1[\text{La}^{3+}][\text{SO}_4^{2-}] - \beta'_2[\text{La}^{3+}][\text{SO}_4^{2-}]^2}$$

$$\text{or } [\text{H}^+] = \frac{K_a'[\text{La}^{3+}]}{F_{\text{La}} - [\text{La}^{3+}] - [\text{La}(\text{SO}_4)^+] - [\text{La}(\text{SO}_4)_2^-]} \text{ (which is easier to use)}$$

The spreadsheet is shown after (e).

- (b) If $\text{La}_2(\text{SO}_4)_3$ were a strong electrolyte, $\mu = \frac{1}{2} \{ [\text{La}^{3+}] \cdot (+3)^2 + [\text{SO}_4^{2-}] \cdot (-2)^2 \}$
 $= \frac{1}{2} \{ (2.0 \text{ mM} \cdot 9) + (3.0 \text{ mM} \cdot 4) \} = 15.0 \text{ mM}$. The actual ionic strength in cell C17 is 6.3 mM.
- (c) $[\text{La}^{3+}]/F_{\text{La}} = 0.285$
- (d) We expected the solution to have a pH near neutral. pK_a for HSO_4^- is 1.99.

Therefore, we did not expect very much HSO_4^- to be present. With a pH near 6, the fraction on sulfate that is protonated is $\sim 10^{-4}$.

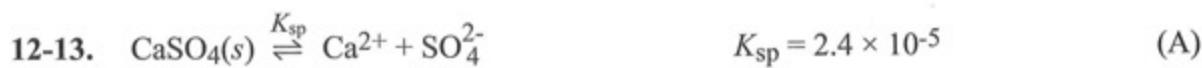
- (e) Evaluate the solubility product expression for $\text{La}(\text{OH})_3$:

$$[\text{La}^{3+}][\text{OH}^-]^3 \gamma_{\text{La}^{3+}} \gamma_{\text{OH}^-}^3 = (5.69 \times 10^{-4})(1.04 \times 10^{-8})^3(0.47)(0.92)^3$$

$$= 2.3 \times 10^{-28} < K_{\text{sp}}$$
 for $\text{La}(\text{OH})_3 = 2 \times 10^{-21}$

$\text{La}(\text{OH})_3(s)$ does not precipitate.

	A	B	C	D	E	F	G	H
1	Composition of La(III)-sulfate solution							
2								
3	$\log \beta_1 =$	3.64	$\beta_1 =$	4.37E+03	$\beta_1' =$	1.59E+03	$F_{La} =$	2.0E-03
4	$\log \beta_2 =$	5.3	$\beta_2 =$	2.00E+05	$\beta_2' =$	5.20E+04	$F_{SO_4} =$	3.0E-03
5	$\log K_a =$	-8.5	$K_a =$	3.16E-09	$K_a' =$	2.26E-09		
6	$\log K_w =$	-14.00	$K_w =$	1.00E-14	$K_w' =$	1.18E-14		
7								
8	Davies activity coefficients:							
9	La ³⁺	0.47	LaOH ²⁺	0.71	OH ⁻			0.92
10	La(SO ₄) ⁺	0.92	SO ₄ ²⁻	0.71	H ⁺			0.92
11	La(SO ₄) ₂ ⁻	0.92						
12								
13	[SO ₄ ²⁻]	[La ³⁺]	[H ⁺]	[OH ⁻]	[La(SO ₄) ⁺]	[La(SO ₄) ₂ ⁻]	[LaOH ²⁺]	Net charge
14	1.50E-03	5.69E-04	1.14E-06	1.04E-08	1.36E-03	6.69E-05	1.13E-06	3.12E-19
15								
16	Ionic strength = 0.00629 ← Initial value is 0							
17	New ionic strength =	0.00629		[La ³⁺]/F _{La} =	0.285		[SO ₄ ²⁻]/F _{SO₄} =	
18	pH =	5.98		[La(SO ₄) ⁺]/F _{La} =	0.681			0.501
19	Total La =	2.000E-03		[La(SO ₄) ₂ ⁻]/F _{La} =	0.033			
20	Total SO ₄ ²⁻ =	3.000E-03		[LaOH ²⁺]/F _{La} =	5.6E-04			
21								
22	Activity coefficients = 10^(-0.51*charge^2*(SQRT(\$C\$16)/(1+SQRT(\$C\$16))-0.3*\$C\$16))							
23	$\beta_1' = D3*B9*E10/B10$		$K_a' = D5*B9/(E9*H10)$					
24	$\beta_2' = D4*B9*E10^2/B11$		$K_w' = D6/(H9*H10)$					
25	[La ³⁺] = (H4-A14)/(F3*A14+2*F4*A14^2)							
26	[H ⁺] = F5*B14/(H3-B14-E14-F14)			[OH ⁻] = F6/C14				
27	[La(SO ₄) ⁺] = F3*B14*A14			[La(SO ₄) ₂ ⁻] = F4*B14*A14^2				
28	[LaOH ²⁺] = F5*B14/C14			pH = -LOG10(C14*H10)				
29	Net charge = 3*B14+C14+ E14+2*G14-2*A14-D14-F14							
30	New ionic strength = 0.5*(4*A14+9*B14+C14+D14+E14+F14+4*G14)							



Charge balance: $2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{OH}^-]$ (F)

Mass balance: [total calcium] = [total sulfate]

$[\text{Ca}^{2+}] + [\text{CaSO}_4(aq)] + [\text{CaOH}^+] = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{CaSO}_4(aq)]$ (G)

Write expressions for effective equilibrium constants K' .

$$K_{\text{sp}} = [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}} \Rightarrow K'_{\text{sp}} = K_{\text{sp}} \frac{1}{\gamma_{\text{Ca}^{2+}} \gamma_{\text{SO}_4^{2-}}} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \quad (\text{H})$$

$$K_{\text{acid}} = \frac{[\text{CaOH}^+] \gamma_{\text{CaOH}^+} [\text{H}^+] \gamma_{\text{H}^+}}{[\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}}} \Rightarrow K'_{\text{acid}} = K_{\text{acid}} \frac{\gamma_{\text{Ca}^{2+}}}{\gamma_{\text{CaOH}^+} \gamma_{\text{H}^+}} = \frac{[\text{CaOH}^+] [\text{H}^+]}{[\text{Ca}^{2+}]} \quad (\text{I})$$

$$K_{\text{base}} = \frac{[\text{HSO}_4^-] \gamma_{\text{HSO}_4^-} [\text{OH}^-] \gamma_{\text{OH}^-}}{[\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}}} \\ \Rightarrow K'_{\text{base}} = K_{\text{base}} \frac{\gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{HSO}_4^-} \gamma_{\text{OH}^-}} = \frac{[\text{HSO}_4^-] [\text{OH}^-]}{[\text{SO}_4^{2-}]} \quad (\text{J})$$

$$K_w = [\text{H}^+] \gamma_{\text{H}^+} [\text{OH}^-] \gamma_{\text{OH}^-} \Rightarrow K'_w = \frac{K_w}{\gamma_{\text{H}^+} \gamma_{\text{OH}^-}} = [\text{H}^+] [\text{OH}^-] \quad (\text{K})$$

Substitute equilibrium expressions into mass balance (G):

$$\begin{aligned} [\text{Ca}^{2+}] + [\text{CaOH}^+] &= [\text{SO}_4^{2-}] + [\text{HSO}_4^-] \\ [\text{Ca}^{2+}] + \frac{K'_{\text{acid}} [\text{Ca}^{2+}]}{[\text{H}^+]} &= [\text{SO}_4^{2-}] + \frac{K'_{\text{base}} [\text{SO}_4^{2-}]}{[\text{OH}^-]} = [\text{SO}_4^{2-}] \left(1 + \frac{K'_{\text{base}}}{[\text{OH}^-]}\right) \end{aligned} \quad (\text{L})$$

Substitute expression for $[\text{SO}_4^{2-}]$ from (H) into right side of (L):

$$[\text{Ca}^{2+}] + \frac{K'_{\text{acid}} [\text{Ca}^{2+}]}{[\text{H}^+]} = \frac{K'_{\text{sp}}}{[\text{Ca}^{2+}]} \left(1 + \frac{K'_{\text{base}}}{[\text{OH}^-]}\right)$$

Express $[\text{OH}^-]$ in terms of $[\text{H}^+]$:

$$[\text{Ca}^{2+}] + \frac{K'_{\text{acid}} [\text{Ca}^{2+}]}{[\text{H}^+]} = \frac{K'_{\text{sp}}}{[\text{Ca}^{2+}]} \left(1 + \frac{K'_{\text{base}} [\text{H}^+]}{K'_w}\right)$$

Multiply both sides by $[\text{Ca}^{2+}]$ and solve for $[\text{Ca}^{2+}]$:

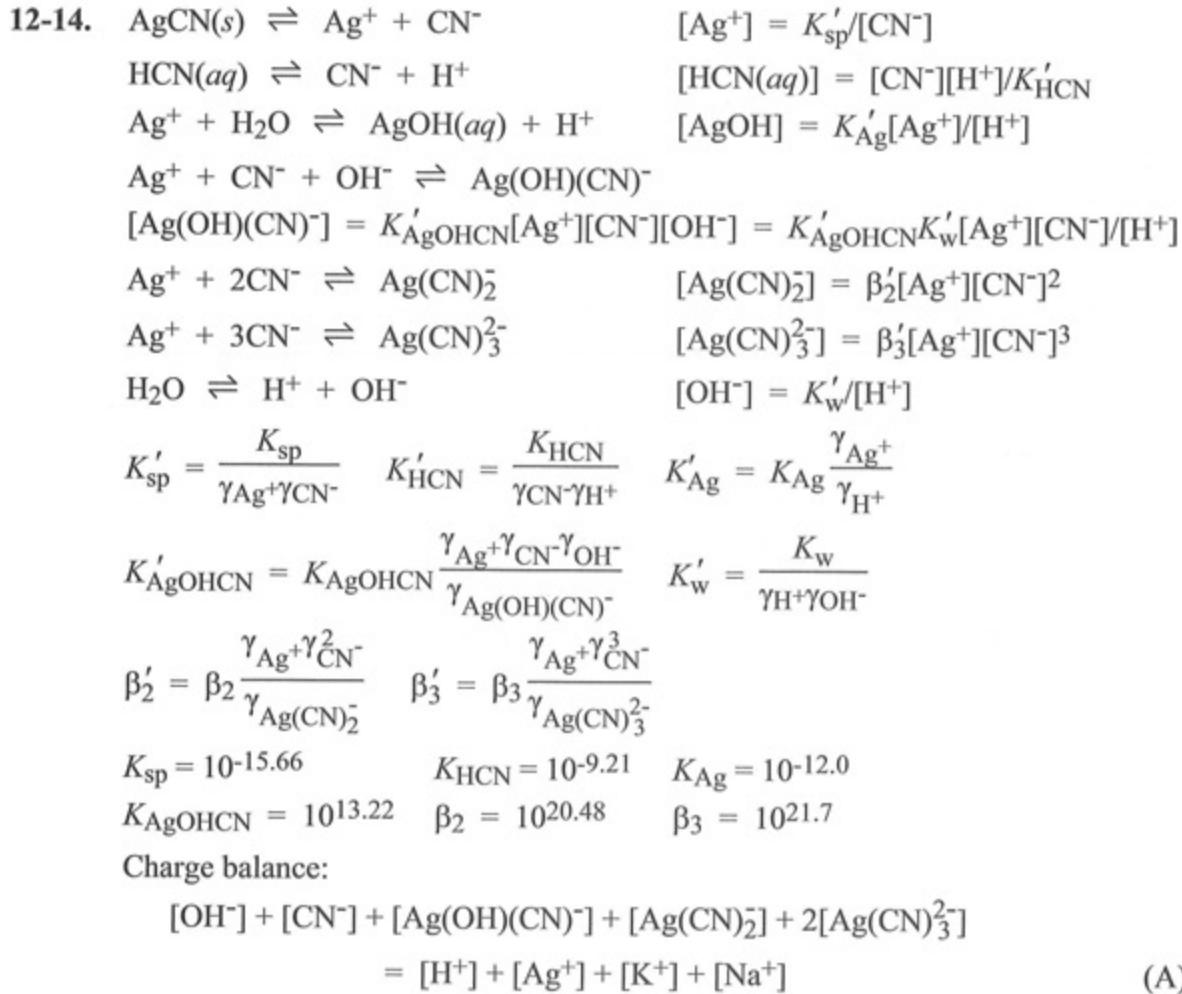
$$\begin{aligned} [\text{Ca}^{2+}]^2 \left(1 + \frac{K'_{\text{acid}}}{[\text{H}^+]}\right) &= K'_{\text{sp}} \left(1 + \frac{K'_{\text{base}} [\text{H}^+]}{K'_w}\right) \\ [\text{Ca}^{2+}]^2 &= K'_{\text{sp}} \left(1 + \frac{K'_{\text{base}} [\text{H}^+]}{K'_w}\right) / \left(1 + \frac{K'_{\text{acid}}}{[\text{H}^+]}\right) \end{aligned} \quad (\text{M})$$

In the following spreadsheet, we begin with a guess of $\text{pH} = 7$ in cell A14 and an ionic strength of 0 in cell C16. The spreadsheet computes the concentrations in row 14 and the sum of charges in cell H14.

	A	B	C	D	E	F	G	H
1	Saturated CaSO ₄							
2								
3	$K_{sp} = 2.4E-05$		$K_{sp} = 2.40E-05$					
4	$K_{ip} = 5.0E-03$		$K_{ip} = 5.00E-03$					
5	$K_{acid} = 2.0E-13$		$K_{acid} = 2.00E-13$					
6	$K_{base} = 9.8E-13$		$K_{base} = 9.80E-13$					
7	$K_w = 1.0E-14$		$K_w = 1.00E-14$					
8								
9	Davies activity coefficients:							
10	Ca ²⁺	1.00	SO ₄ ²⁻	1.00	OH ⁻	1.00		
11	CaOH ⁺	1.00	HSO ₄ ⁻	1.00	H ⁺	1.00		
12								
13	pH	[H ⁺]	[OH ⁻]	[Ca ²⁺]	[CaOH ⁺]	[SO ₄ ²⁻]	[HSO ₄ ⁻]	Net charge
14	7.0000	1.00E-07	1.00E-07	4.90E-03	9.80E-09	4.90E-03	4.80E-08	3.82E-08
15								
16	Ionic strength =	0.000000	← Initial value is 0					
17	New ionic strength =	0.000000						
18								
19	Activity coefficients = $10^{(-0.51 * \text{charge}^2 * (\text{SQRT}(\$C\$16) / (1 + \text{SQRT}(\$C\$16)) - 0.3 * \$C\$16))}$							
20	$K_{sp} = B3 / (B10 * E10)$		$[H^+] = 10^{-A14} / H11$					
21	$K_{ip} = B4$		$[OH^-] = D7 / B14$					
22	$K_{acid} = B5 * B10 / (B11 * H11)$		$[Ca^{2+}] = \text{SQRT}(D3 * (1 + D6 * B14 / D7) / (1 + D5 / B14))$					
23	$K_{base} = B6 * E10 / (E11 * H10)$		$[CaOH^+] = D5 * D14 / B14$					
24	$K_w = B7 / (H11 * H10)$		$[SO_4^{2-}] = D3 / D14$					
25			$[HSO_4^-] = D6 * F14 / C14$					
26	Net charge = $2 * D14 + E14 + B14 - 2 * F14 - G14 - C14$							
27	New ionic strength = $0.5 * (B14 + C14 + 4 * D14 + E14 + 4 * F14 + G14)$							

We then use Solver or Goal Seek to vary pH in cell A14 until the net charge in cell H14 is close to 0. We set a limit of 1E-18 for this calculation. The spreadsheet computes a pH and new set of concentrations and an ionic strength in cell C17. We transcribe the ionic strength from C17 into cell C16 and repeat the cycle several times until ionic strength no longer changes. Final results are displayed in the following spreadsheet. The pH is 7.06 and the ionic strength is 0.041 M.

	A	B	C	D	E	F	G	H
1	Saturated CaSO_4							
2								
3	$K_{sp} = 2.4E-05$		$K_{sp}' = 1.04E-04$					
4	$K_{ip} = 5.0E-03$		$K_{ip}' = 5.00E-03$					
5	$K_{acid} = 2.0E-13$		$K_{acid}' = 1.39E-13$					
6	$K_{base} = 9.8E-13$		$K_{base}' = 6.80E-13$					
7	$K_w = 1.0E-14$		$K_w' = 1.44E-14$					
8								
9	Davies activity coefficients:							
10	Ca^{2+}	0.48	SO_4^{2-}	0.48	OH^-	0.83		
11	CaOH^+	0.83	HSO_4^-	0.83	H^+	0.83		
12								
13	pH	[H^+]	[OH^-]	[Ca^{2+}]	[CaOH^+]	[SO_4^{2-}]	[HSO_4^-]	Net charge
14	7.0648	1.03E-07	1.39E-07	1.02E-02	1.37E-08	1.02E-02	4.96E-08	8.20E-19
15								
16	Ionic strength =	0.04071	← Initial value is 0					
17	New ionic strength =	0.04071						



Mass balances:

$$[K^+] = 0.10 \text{ M} \quad (\text{B})$$

$$\{\text{total silver}\} + [K^+] = \{\text{total cyanide}\}$$

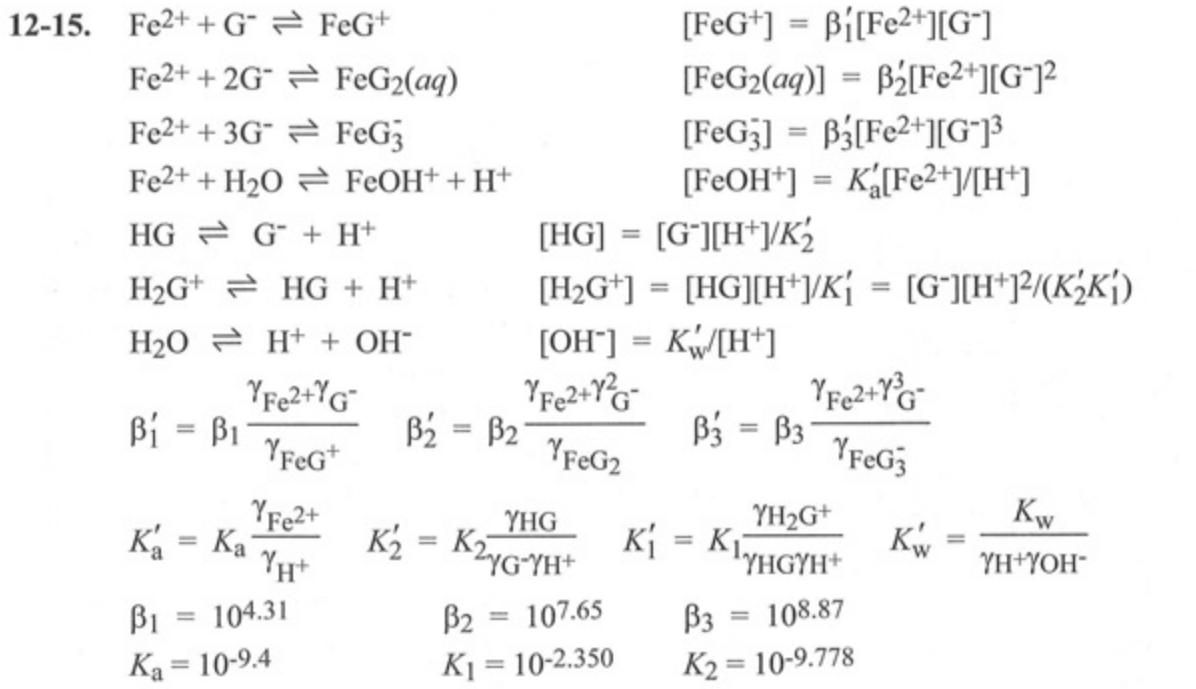
$$\begin{aligned} [\text{Ag}^+] + [\text{AgOH}] + [\text{Ag(OH)(CN)}^-] + [\text{Ag(CN)}_2^-] + [\text{Ag(CN)}_3^{2-}] + [K^+] \\ = [\text{CN}^-] + [\text{HCN}] + [\text{Ag(OH)(CN)}^-] + 2[\text{Ag(CN)}_2^-] + 3[\text{Ag(CN)}_3^{2-}] \end{aligned}$$

which simplifies to

$$[\text{Ag}^+] + [\text{AgOH}] - [\text{Ag(CN)}_2^-] - 2[\text{Ag(CN)}_3^{2-}] + [K^+] - [\text{CN}^-] - [\text{HCN}] = 0 \quad (\text{C})$$

In the following spreadsheet, the initial ionic strength was guessed to be 0.10 M in cell C23. $[\text{CN}^-]$ was then guessed in cell A17. $[\text{H}^+]$ and $[\text{OH}^-]$ in cells B17 and B18 were computed from the known pH. $[\text{Ag}^+]$ in cell D17 was calculated from $[\text{Ag}^+] = K'_{\text{sp}} / [\text{CN}^-]$. $[\text{AgOH}]$, $[\text{Ag(OH)(CN)}^-]$, $[\text{Ag(CN)}_2^-]$, and $[\text{Ag(CN)}_3^{2-}]$ were computed from $[\text{CN}^-]$, $[\text{H}^+]$, $[\text{Ag}^+]$, and $[\text{OH}^-]$ with equilibrium expressions. The mass balance Equation C is evaluated in cell H21. In the key step, the value in cell H21 is set equal to 0 by using Solver to vary $[\text{CN}^-]$ in cell A17. When the mass balance is satisfied, all concentrations must be correct. $[\text{Na}^+]$ is then computed in cell C22 from the charge balance Equation A and the new ionic strength is found in cell C24. The new ionic strength is then entered in cell C23 and the process is repeated until the ionic strength no longer changes. The spreadsheet shows the final concentrations when the mass balance is satisfied.

	A	B	C	D	E	F	G	H
1	Species in silver-cyanide solution							
2								
3	$\log K_{sp} = -15.66$		$K_{sp} = 2.19E-16$		$K_{sp}' = 3.65E-16$	$[K^+] = 0.10$		
4	$\log K_{HCN} = -9.21$		$K_{HCN} = 6.17E-10$		$K_{HCN}' = 1.03E-09$	$pH = 12.00$		
5	$\log K_{Ag} = -12.0$		$K_{Ag} = 1.00E-12$		$K_{Ag}' = 1.00E-12$			
6	$\log K_{AgOH} = 13.22$		$K_{AgOH} = 1.66E+13$		$K_{AgOH}' = 9.95E+12$			
7	$\log \beta_2 = 20.48$		$\beta_2 = 3.02E+20$		$\beta_2' = 1.81E+20$			
8	$\log \beta_3 = 21.7$		$\beta_3 = 5.01E+21$		$\beta_3' = 5.01E+21$			
9	$\log K_w = -14.00$		$K_w = 1.00E-14$		$K_w' = 1.67E-14$			
10								
11	Davies activity coefficients:							
12	Ag^+	0.77	$Ag(OH)(CN)$	0.77	OH^-	0.77		
13	$Ag(CN)_2^-$	0.77	CN^-	0.77	H^+	0.77		
14	$Ag(CN)_3^{2-}$	0.36						
15								
16	$[CN^-]$	$[H^+]$	$[OH^-]$	$[Ag^+]$	$[AgOH]$	$[Ag(OH)(CN)]$		
17	1.513E-06	1.29E-12	1.29E-02	2.410E-10	1.867E-10	4.688E-05		
18				$[Ag(CN)_2^-]$	$[Ag(CN)_3^{2-}]$	$[HCN]$		
19				0.09999	4.187E-06	1.901E-09		
20								
21	Mass balance: $[Ag^+] + [AgOH] - [Ag(CN)_2^-] - 2[Ag(CN)_3^{2-}] + [K^+] - [CN^-] - [HCN] =$							-1.5E-17
22		$[Na^+] = 0.01296$ (from charge balance)						
23	Ionic strength = 0.113	← Initial value is 0.1						
24	New ionic strength = 0.113	← Substitute this value into C23 for next iteration						
25	Total Ag + $K^+ = 0.20004$	check						
26	Total CN = 0.20004	check						
27								
28	Activity coefficients = $10^{(-0.51 * charge^2 * (SQRT(C23)/(1+SQRT(C23))-0.3*C23)))}$							
29	$K_{sp}' = D3/(B12*E13)$	$K_{HCN}' = D4/(E13*H13)$			$K_{Ag}' = D5*B12/H13$			
30	$K_{AgOH} = D6*B12*E13*H12/E12$				$\beta_2' = D7*B12*E13^2/B13$			
31	$K_w' = D9/(H12*H13)$				$\beta_3' = D8*B12*E13^3/B14$			
32	$[H^+] = 10^{-H4/H13}$	$[OH^-] = F9/B17$			$[AgOH] = F5*D17/B17$			
33	$[Ag^+] = F3/A17$							
34	$[Ag(OH)(CN)] = F6*D17*A17*C17$				$[Ag(CN)_2^-] = F7*D17*A17^2$			
35	$[Ag(CN)_3^{2-}] = F8*D17*A17^3$				$[HCN] = A17*B17/F4$			
36	Mass balance = D17+E17-D19-2*E19+H3-A17-F19							
37	$[Na^+] = C17+A17+F17+D19+2*E19-B17-D17-H3$							
38	New ionic strength = 0.5*(A17+B17+C17+D17+F17+D19+4*E19+H3+C22)							



Charge balance:

$$[\text{OH}^-] + [\text{G}^-] + [\text{FeG}_3^-] + [\text{Cl}^-] = [\text{H}^+] + 2[\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{FeG}^+] + [\text{H}_2\text{G}^+] \quad (\text{A})$$

Mass balances:

$$F_{\text{Fe}} = 0.050 \text{ M} = [\text{Fe}^{2+}] + [\text{FeG}^+] + [\text{FeG}_2] + [\text{FeG}_3^-] + [\text{FeOH}^+] \quad (\text{B})$$

$$F_{\text{G}} = 0.100 \text{ M} = [\text{G}^-] + [\text{HG}] + [\text{H}_2\text{G}^+] + [\text{FeG}^+] + 2[\text{FeG}_2] + 3[\text{FeG}_3^-] \quad (\text{C})$$

Substitute equilibrium expressions into the mass balance B to express $[\text{Fe}^{2+}]$ in terms of $[\text{G}^-]$ and $[\text{H}^+]$:

$$\begin{aligned} F_{\text{Fe}} &= [\text{Fe}^{2+}] + \beta'_1 [\text{Fe}^{2+}] [\text{G}^-] + \beta'_2 [\text{Fe}^{2+}] [\text{G}^-]^2 + \beta'_3 [\text{Fe}^{2+}] [\text{G}^-]^3 + K'_a [\text{Fe}^{2+}] / [\text{H}^+] \\ [\text{Fe}^{2+}] &= \frac{F_{\text{Fe}}}{1 + \beta'_1 [\text{G}^-] + \beta'_2 [\text{G}^-]^2 + \beta'_3 [\text{G}^-]^3 + K'_a / [\text{H}^+]} \end{aligned} \quad (\text{D})$$

In the spreadsheet on the next page, we guess a value for $[\text{G}^-]$ in cell A17 and compute $[\text{H}^+] = 10^{-\text{pH}} / \gamma_{\text{H}^+}$ in cell B17. Equation D is used to find $[\text{Fe}^{2+}]$ in cell D17. Other concentrations in rows 17 and 19 are computed from $[\text{G}^-]$, $[\text{H}^+]$, and $[\text{Fe}^{2+}]$. Cell H24 checks that the sum of iron species equals $F_{\text{Fe}} = 0.050 \text{ M}$. By using the mass balance for iron to find Fe^{2+} in cell D17, cell H24 must give F_{Fe} if we have not made a mistake. We use the mass balance for glycine for the first time in cell H25, where we add all the glycine species. Then use Solver to vary $[\text{G}^-]$ in cell A17 to satisfy the mass balance for glycine in cell H25. In Solver, Set Target Cell H25 Equal To Value of 0.1 By Changing Cells A17. $[\text{Cl}^-]$ in cell C20 is then found from the charge balance equation A. The new ionic strength is

Fraction of Fe in each form:

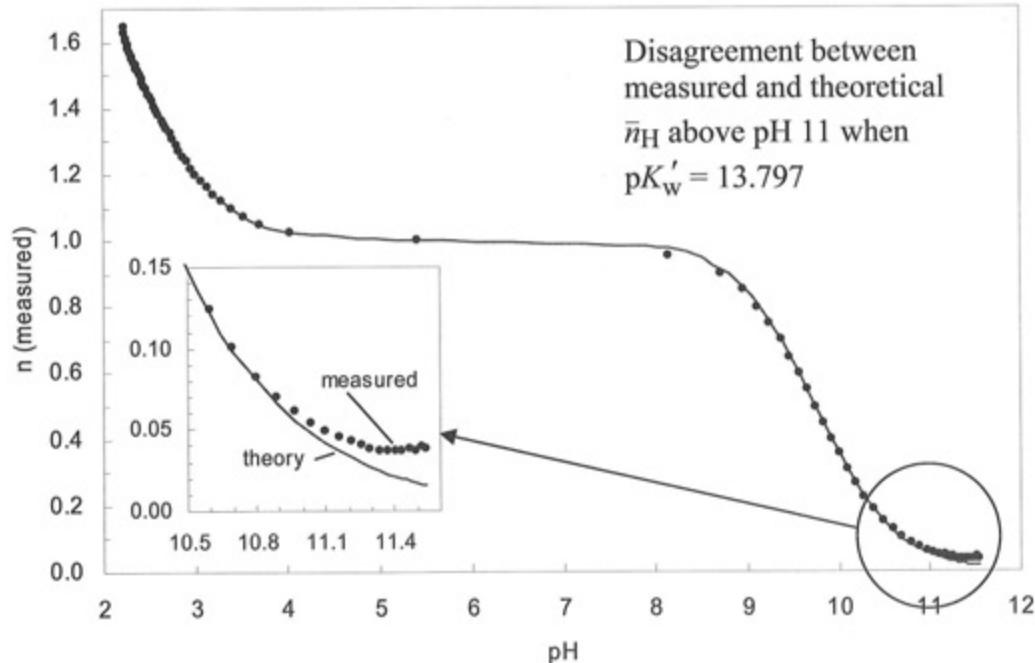
$[Fe^{2+}]$, 2.7%; $[FeG^+]$, 34.0%; $[FeG_2]$, 62.0%; $[FeG_3^-]$, 1.1%; $[FeOH^+]$, 0.2%

Fraction of glycine in each form:

$[G^-]$, 1.1%; $[HG]$, 18.2%; $[H_2G^+]$, 0.000 015%; $[FeG^+]$, 17.0%; $2[FeG_2]$, 62.0%; $3[FeG_3^-]$, 1.7%

The chemistry: We dissolved FeG_2 and found that the principal species are FeG^+ , FeG_2 , and HG . The chemistry that requires HCl to be added to obtain pH 8.5 is $FeG_2 \rightleftharpoons FeG^+ + G^-$ followed by $G^- + H^+ \rightleftharpoons HG$. The base G^- is released when FeG_2 dissolves, so HCl is required to neutralize the base.

- 12-16.** (a) A range of initial values of pK_1 and pK_2 , such as 6 and 6 or 10 and 10, converge to the correct solution. Even choosing a ridiculous value for pK'_w , such as 10, converges to the correct value after executing Solver more than once.
- (b) Fixing pK'_w at 13.797 and using Solver gives the optimized values of pK_1 and $pK_2 = 2.312$ and 9.630 , which are hardly different from the values obtained when pK'_w is allowed to vary. However, inspection of the following curves shows that $\bar{n}_H(\text{measured})$ deviates systematically from $\bar{n}_H(\text{theoretical})$ at the end of the titration when $\bar{n}_H(\text{measured})$ should approach 0.



12-17. (a) $\bar{n}_H = \frac{\text{moles of bound H}^+}{\text{total moles of weak acid}} = \frac{3[H_3A^{3+}] + 2[H_2A^{2+}] + [HA^+]}{[H_3A^{3+}] + [H_2A^{2+}] + [HA^+] + [A]}$

or $\bar{n}_H F_{H_3A} = 3[H_3A^{3+}] + 2[H_2A^{2+}] + [HA^+] \quad (\text{A})$

where $F_{H_3A} = [H_3A^{3+}] + [H_2A^{2+}] + [HA^+] + [A]$

charge balance:

$$[\text{H}^+] + [\text{Na}^+] + 3[\text{H}_3\text{A}^{3+}] + 2[\text{H}_2\text{A}^{2+}] + [\text{HA}^+] = [\text{OH}^-] + [\text{Cl}^-]_{\text{HCl}} + [\text{Cl}^-]_{\text{H}_3\text{A}} \quad (\text{B})$$

$\underbrace{\quad \quad \quad}_{= \bar{n}_H F_{H_3A} \text{ from Eq. (A)}}$ $\underbrace{\quad \quad \quad}_{= 3F_{H_3A}}$

where $[\text{Cl}^-]_{\text{HCl}}$ is from HCl and $[\text{Cl}^-]_{\text{H}_3\text{A}}$ is from H_3A^{3+} .

Each mol of H_3A^{3+} brings 3Cl^- , so $[\text{Cl}^-]_{\text{H}_3\text{A}} = 3F_{H_3A}$

We can rearrange Eq. (B) to solve for \bar{n}_H :

$$[\text{H}^+] + [\text{Na}^+] + \bar{n}_H F_{H_3A} = [\text{OH}^-] + [\text{Cl}^-]_{\text{HCl}} + 3F_{H_3A}$$

$$\bar{n}_H F_{H_3A} = 3F_{H_3A} + [\text{OH}^-] + [\text{Cl}^-]_{\text{HCl}} - [\text{H}^+] - [\text{Na}^+]$$

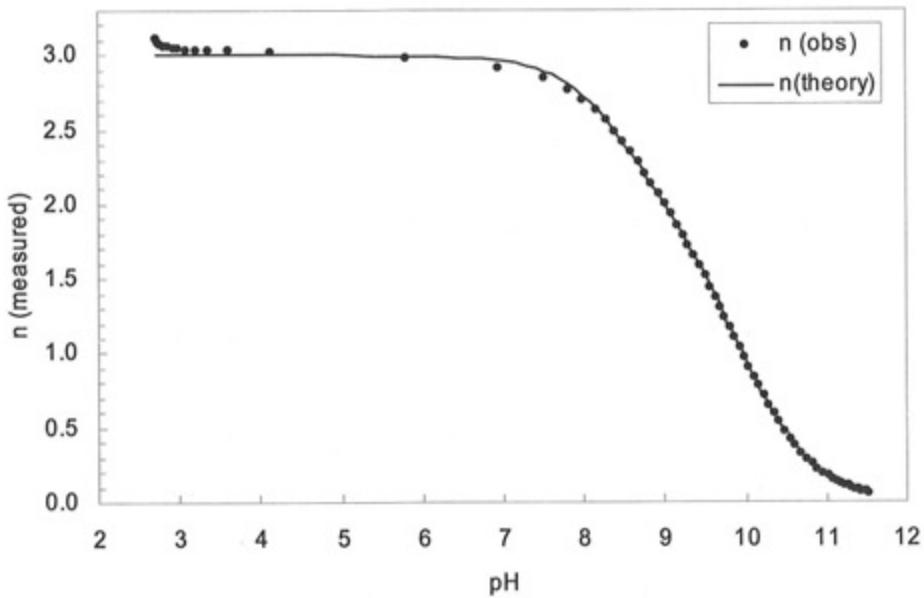
$$\bar{n}_H = 3 + \frac{[\text{OH}^-] + [\text{Cl}^-]_{\text{HCl}} - [\text{H}^+] - [\text{Na}^+]}{F_{H_3A}} \quad (\text{C})$$

Expression (C) is the same equation derived in the text, with $n = 3$.

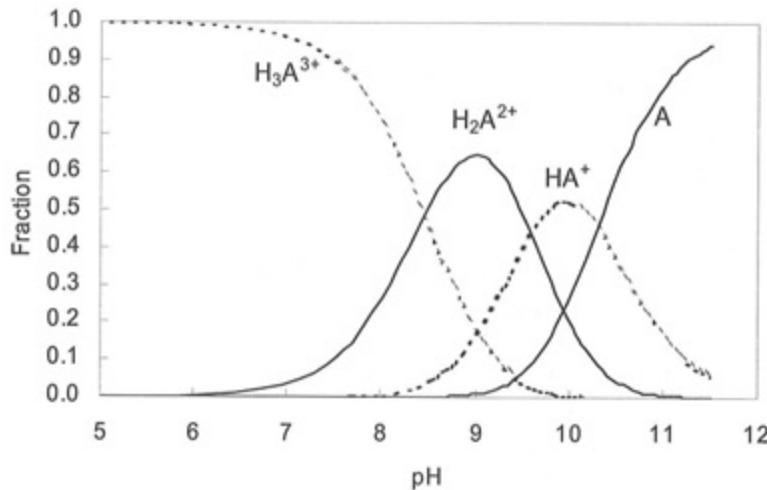
The expression for \bar{n}_H (theoretical) is $\bar{n}_H(\text{theoretical}) = 3\alpha_{H_3A} + 2\alpha_{H_2A} + \alpha_{HA}$.

(b) Optimized values are $pK'_w = 13.819$, $pK_1 = 8.33$, $pK_2 = 9.48$, and $pK_3 = 10.19$ in cells B9:B12 in the following spreadsheet. These were obtained from initial guesses of $pK'_w = 13.797$, $pK_1 = 8$, $pK_2 = 9$, and $pK_3 = 10$, after executing Solver to minimize the sum of squared residuals in column K. The NIST database lists $pK_1 = 7.85$, $pK_2 = 9.13$, and $pK_3 = 10.03$ at $\mu = 0$ and $pK_1 = 8.42$, $pK_2 = 9.43$, and $pK_3 = 10.13$ at $\mu = 0.1$ M. Our observed values at $\mu = 0.1$ M are in reasonable agreement with the NIST values.

	A	B	C	D	E	F	G	H	I	J	K
1	Difference plot for tris(2-aminoethyl)amine										
2				C17 = 10^-B17/\$B\$8		D17 = 10^-\$B\$9/C17					
3	Titrant NaOH =	0.4905	C _b (M)	E17 = \$B\$7+(\$B\$6-\$B\$3*A17-(C17-D17)*(\$B\$4+A17))/\$B\$5							
4	Initial volume =	40	V _o (mL)	denom = \$C17^3+\$C17^2*\$E\$10+\$C17*\$E\$10*\$E\$11+\$E\$10*\$E\$11*\$E\$12							
5	H ₃ A =	0.139	L (mmol)	F17 = \$C17^3/denom							
6	HCl added =	0.115	A (mmol)	G17 = \$C17^2*\$E\$10/denom							
7	Number of H ⁺ =	3	n	H17 = \$C17*\$E\$10*\$E\$11/denom							
8	Activity coeff =	0.78	γ_H	I17 = \$E\$10*\$E\$11*\$E\$12/denom							
9	pK _w ' =	13.819		J17 = 3*F17+2*G17+H17							
10	pK ₁ =	8.334		K ₁ = 4.636E-09 = 10^-B10							
11	pK ₂ =	9.483		K ₂ = 3.289E-10 = 10^-B11							
12	pK ₃ =	10.188		K ₃ = 6.485E-11 = 10^-B12							
13	$\Sigma(\text{resid})^2 =$	0.0510	= sum of column K								
14											
15	v	pH	[H ⁺] = $(10^{-\text{pH}})/\gamma_H$	[OH ⁻] = $(10^{-\text{pKw}})/[\text{H}^+]$	Measured	α_{H3A}	α_{H2A}	α_{HA}	α_A	Theoretical	$(\text{residuals})^2 = (n_{\text{meas}} - n_{\text{theor}})^2$
16	mL NaOH				n _H					n _H	
17	0.00	2.709	2.51E-03	6.06E-12	3.106	1.000	0.000	0.000	0.000	3.000	0.011303
18	0.02	2.743	2.32E-03	6.55E-12	3.090	1.000	0.000	0.000	0.000	3.000	0.008046
19	:										
20	0.34	8.158	8.91E-09	1.70E-06	2.628	0.649	0.338	0.012	0.000	2.637	0.000077
21	0.36	8.283	6.68E-09	2.27E-06	2.558	0.579	0.401	0.020	0.000	2.558	0.000001
22	:										
23	0.54	9.087	1.05E-09	1.45E-05	1.926	0.145	0.641	0.201	0.012	1.919	0.000045
24	0.56	9.158	8.91E-10	1.70E-05	1.856	0.121	0.630	0.232	0.017	1.855	0.000002
25	:										
26	0.78	9.864	1.75E-10	8.66E-05	1.100	0.010	0.277	0.520	0.192	1.106	0.000031
27	0.80	9.926	1.52E-10	9.98E-05	1.034	0.008	0.243	0.525	0.224	1.035	0.000001
28	:										
29	1.00	10.545	3.66E-11	4.15E-04	0.421	0.000	0.039	0.346	0.615	0.424	0.000011
30	1.02	10.615	3.11E-11	4.88E-04	0.372	0.000	0.030	0.314	0.656	0.375	0.000007
31	:										
32	1.38	11.496	4.09E-12	3.71E-03	0.062	0.000	0.001	0.059	0.940	0.061	0.000002
33	1.40	11.521	3.86E-12	3.93E-03	0.057	0.000	0.001	0.056	0.943	0.058	0.000000



- (c) The fractions of each species are computed in columns F, G, H, and I beginning in row 17 in the spreadsheet. Results are shown following graph.



- 12-18.** (a) From the equilibrium expressions, we write

$$[\text{CuSO}_4(aq)] = K'_{\text{ip}} [\text{Cu}^{2+}] [\text{SO}_4^{2-}]$$

$$[\text{HSO}_4^-] = [\text{SO}_4^{2-}] [\text{H}^+] / K'_a$$

$$[\text{CuOH}^+] = \beta'_1 [\text{Cu}^{2+}] [\text{OH}^-]$$

$$[\text{Cu(OH)}_2(aq)] = \beta'_2 [\text{Cu}^{2+}] [\text{OH}^-]^2$$

$$[\text{Cu(OH)}_3^-] = \beta'_3 [\text{Cu}^{2+}] [\text{OH}^-]^3$$

$$[\text{Cu(OH)}_4^{2-}] = \beta'_4 [\text{Cu}^{2+}] [\text{OH}^-]^4$$

$$[\text{Cu}_2(\text{OH})^{3+}] = \beta'_{12} [\text{Cu}^{2+}]^2 [\text{OH}^-]$$

$$[\text{Cu}_2(\text{OH})_2^{2+}] = \beta'_{22} [\text{Cu}^{2+}]^2 [\text{OH}^-]^2$$

$$[\text{Cu}_3(\text{OH})_4^{2+}] = \beta'_{43} [\text{Cu}^{2+}]^3 [\text{OH}^-]^4$$

Mass balances ($F = 0.025 \text{ M}$):

$$\text{Sulfate: } F = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{CuSO}_4(aq)]$$

$$\begin{aligned} \text{Copper: } F &= [\text{Cu}^{2+}] + [\text{CuSO}_4(aq)] + [\text{CuOH}^+] + [\text{Cu(OH)}_2(aq)] + \\ &[\text{Cu(OH)}_3^-] + [\text{Cu(OH)}_4^{2-}] + 2[\text{Cu}_2(\text{OH})^{3+}] + 2[\text{Cu}_2(\text{OH})_2^{2+}] + 3[\text{Cu}_3(\text{OH})_4^{2+}] \end{aligned}$$

Charge balance if the pH is not adjusted:

$$\begin{aligned} [\text{OH}^-] + 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{Cu(OH)}_3^-] + 2[\text{Cu(OH)}_4^{2-}] &= [\text{H}^+] + 2[\text{Cu}^{2+}] \\ + [\text{CuOH}^+] + 3[\text{Cu}_2(\text{OH})^{3+}] + 2[\text{Cu}_2(\text{OH})_2^{2+}] + 2[\text{Cu}_3(\text{OH})_4^{2+}] \end{aligned}$$

Substitute equilibrium expressions into the sulfate mass balance:

$$F = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{CuSO}_4(aq)]$$

$$\begin{aligned}
 &= [\text{SO}_4^{2-}] + [\text{SO}_4^{2-}][\text{H}^+]/K'_a + K'_{\text{ip}}[\text{Cu}^{2+}][\text{SO}_4^{2-}] \\
 \text{or } [\text{SO}_4^{2-}] &= \frac{\text{F}}{1 + [\text{H}^+]/K'_a + K'_{\text{ip}}[\text{Cu}^{2+}]} \tag{A}
 \end{aligned}$$

Therefore, we can find $[\text{SO}_4^{2-}]$ if we know $[\text{Cu}^{2+}]$ and $[\text{H}^+]$. We can also find $[\text{HSO}_4^-]$ from the equilibrium relationship $[\text{HSO}_4^-] = [\text{SO}_4^{2-}][\text{H}^+]/K'_a$. We find the concentrations of copper species from their equilibrium relationships.

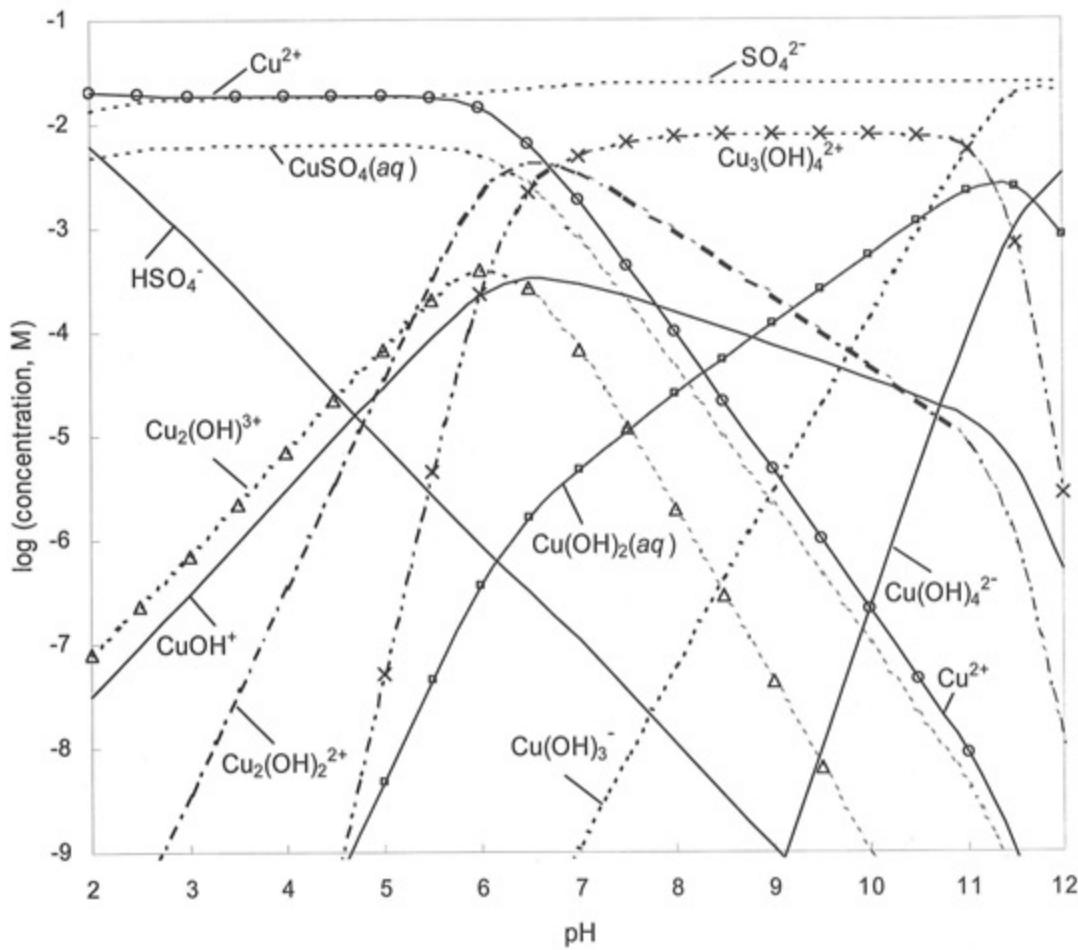
In the spreadsheet on the next page, pH is input in column A beginning at cell A14. $[\text{H}^+]$ and $[\text{OH}^-]$ are computed from pH in columns B and C. The initial value of $[\text{Cu}^{2+}]$ in each row of column D is a *guess*. We use Solver later to find the correct value of $[\text{Cu}^{2+}]$. $[\text{SO}_4^{2-}]$ in column E is computed with Equation A. The remaining concentrations in columns F through N are computed from the equilibrium relationships. The sum of copper species is tallied in column O. The key step is to use Solver to vary $[\text{Cu}^{2+}]$ in column A, so the total copper in column O equals 0.025 M. Solver must be applied separately to each row of the spreadsheet.

- (b) Column P gives the sum of all charges. This sum will be zero at the pH of 0.025 M CuSO_4 , to which no acid or base has been added. Trial-and-error variation of the pH shows that the charge is closest to zero at pH 4.61. Column Q was not necessary for the problem, but it shows that the ionic strength of the solution is near 0.075 M at most pH values, if no solids precipitate.
- (c) To find out if the solubility of any salt has been exceeded, we evaluate the reaction quotient $[\text{Cu}^{2+}][\text{OH}^-]^2$ for $\text{Cu}(\text{OH})_2(s)$ and $\text{CuO}(s)$ and the reaction quotient $[\text{Cu}^{2+}][\text{OH}^-]^{3/2}[\text{SO}_4^{2-}]^{1/4}$ for $\text{Cu}(\text{OH})_{1.5}(\text{SO}_4)_{0.25}(s)$. The solubility of $\text{Cu}(\text{OH})_{1.5}(\text{SO}_4)_{0.25}(s)$ is exceeded above $\text{pH} \approx 4.5$. The solubility of $\text{CuO}(s)$ is exceeded above $\text{pH} \approx 5$. The solubility of $\text{Cu}(\text{OH})_2(s)$ is exceeded above $\text{pH} \approx 5.5$. We predict that 0.025 M CuSO_4 is not a stable solution. At the calculated pH of 4.61, some $\text{Cu}(\text{OH})_{1.5}(\text{SO}_4)_{0.25}(s)$ will precipitate.

	A	B	C	D	E	F	G	H	I
1	Copper-sulfate-hydroxide system								
2	F =	0.025	M						
3	log K _{ip} ' =	1.26	K _{ip} ' =	1.8E+01	log K _{sp} ' (OH-SO ₄) =	-16.68			
4	log K _a ' =	-1.54	K _a ' =	2.9E-02	log K _{sp} ' (OH) =	-18.7			
5	log β ₁ ' =	6.1	β ₁ ' =	1.E+06	log K _{sp} ' (O) =	-19.7			
6	log β ₂ ' =	11.2	β ₂ ' =	2.E+11	K _{sp} ' (OH-SO ₄) =	2.1E-17			
7	log β ₃ ' =	14.5	β ₃ ' =	3.E+14	K _{sp} ' (OH) =	2.E-19			
8	log β ₄ ' =	15.6	β ₄ ' =	4.E+15	K _{sp} ' (O) =	2.E-20			
9	log β ₁₂ ' =	8.2	β ₁₂ ' =	2.E+08	log K _w ' =	-13.79			
10	log β ₂₂ ' =	16.8	β ₂₂ ' =	6.E+16	K _w ' =	1.62E-14			
11	log β ₄₃ ' =	33.5	β ₄₃ ' =	3.E+33	γ _{H+} =	0.78			
12									
13	pH	[H ⁺]	[OH ⁻]	[Cu ²⁺]	[SO ₄ ²⁻]	[HSO ₄ ⁻]	[CuSO ₄]	[CuOH ⁺]	[Cu(OH) ₂]
14	3	1.3E-03	1.3E-11	0.018824	1.8E-02	8.0E-04	6.2E-03	3.0E-07	4.8E-13
15	4	1.3E-04	1.3E-10	0.018665	1.9E-02	8.3E-05	6.3E-03	3.0E-06	4.7E-11
16	4.61	3.1E-05	5.2E-10	0.018602	1.9E-02	2.0E-05	6.3E-03	1.2E-05	7.8E-10
17	5	1.3E-05	1.3E-09	0.018476	1.9E-02	8.3E-06	6.3E-03	2.9E-05	4.7E-09
18	6	1.3E-06	1.3E-08	0.014136	2.0E-02	8.8E-07	5.1E-03	2.3E-04	3.6E-07
19	8	1.3E-08	1.3E-06	9.8E-05	2.5E-02	1.1E-08	4.4E-05	1.6E-04	2.5E-05
20	12	1.3E-12	1.3E-02	3.3E-11	2.5E-02	1.1E-12	1.5E-11	5.2E-07	8.3E-04

	J	K	L	M	N	O	P	Q
12						Total	Charge	Ionic
13	[Cu(OH) ₃ ⁻]	[Cu(OH) ₄ ²⁻]	[Cu ₂ (OH) ³⁺]	[Cu ₂ (OH) ₂ ²⁺]	[Cu ₃ (OH) ₄ ²⁺]	copper	balance	strength
14	1.2E-20	1.9E-30	7.1E-07	3.6E-09	5.4E-16	0.0250000	2.1E-03	0.075
15	1.2E-17	1.9E-26	7.0E-06	3.5E-07	5.3E-12	0.0250000	2.0E-04	0.075
16	8.1E-16	5.2E-24	2.8E-05	5.8E-06	1.4E-09	0.0250000	-1.0E-07	0.075
17	1.2E-14	1.9E-22	6.8E-05	3.4E-05	5.1E-08	0.0250000	-1.5E-04	0.075
18	9.0E-12	1.4E-18	4.0E-04	2.0E-03	2.3E-04	0.0250000	-5.6E-03	0.074
19	6.3E-08	1.0E-12	1.9E-06	9.7E-04	7.6E-03	0.0250000	-3.2E-02	0.067
20	2.1E-02	3.3E-03	2.1E-15	1.1E-08	2.8E-06	0.0250000	-9.0E-02	0.073

	A	B	C	D	E	F	G	H	I
22	[H ⁺]	B14 = 10^-A14/\$G\$11			[OH ⁻]	C14 = \$G\$10/B14			
23	[Cu ²⁺]	Enter guess and find value with SOLVER to make total copper in column 0 = 0.025							
24	[SO ₄ ²⁻]	E14 = \$B\$2/(1+B14/\$D\$4+\$D\$3*D14)			[HSO ₄ ⁻]	F14 = E14*B14/\$D\$4			
25	[CuSO ₄]	G14 = \$D\$3*D14*E14			[CuOH ⁺]	H14 = \$D\$5*D14*C14			
26	[Cu(OH) ₂]	I14 = \$D\$6*D14*C14^2			[Cu(OH) ₃ ⁻]	J14 = \$D\$7*D14*C14^3			
27	[Cu(OH) ₄ ²⁻]	K14 = \$D\$8*D14*C14^4			[Cu ₂ (OH) ³⁺]	L14 = \$D\$9*D14^2*C14			
28	[Cu ₂ (OH) ₂ ²⁺]	M14 = \$D\$10*D14^2*C14^2			[Cu ₃ (OH) ₄ ²⁺]	N14 = \$D\$11*D14^3*C14^4			
29	Total copper	O14 = D14+G14+H14+I14+J14+K14+2*L14+2*M14+3*N14							
30	Charge balance	P14 = B14-C14+2*D14-2*E14-F14+H14-J14-2*K14+3*L14+2*M14+2*N14							
31	Ionic strength	Q14 = 0.5*(B14+C14+4*D14+4*E14+F14+H14+J14+4*K14+9*L14+4*M14+4*N14)							



The following formulas were used when writing this problem to compute equilibrium constants K' for $\mu = 0.1$ M from equilibrium constants K for $\mu = 0$. If K' was reported for another ionic strength, such as 1 M, it was first converted to K for $\mu = 0$ and then converted from K to K' for $\mu = 0.1$ M. Davies activity coefficients were used.

$$K'_{\text{ip}} = K_{\text{ip}} \frac{\gamma_{\text{Cu}^{2+}} \gamma_{\text{SO}_4^{2-}}}{\gamma_{\text{CuSO}_4}} \quad K'_{\text{a}} = K_{\text{a}} \frac{\gamma_{\text{HSO}_4^-}}{\gamma_{\text{SO}_4^{2-}} \gamma_{\text{H}^+}} \quad \beta'_1 = \beta_1 \frac{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}}{\gamma_{\text{CuOH}^+}}$$

$$\beta'_2 = \beta_2 \frac{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}^2}{\gamma_{\text{Cu}(\text{OH})_2}} \quad \beta'_3 = \beta_3 \frac{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}^3}{\gamma_{\text{Cu}(\text{OH})_3^-}} \quad \beta'_4 = \beta_4 \frac{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}^4}{\gamma_{\text{Cu}(\text{OH})_4^{2-}}}$$

$$\beta'_{12} = \beta_{12} \frac{\gamma_{\text{Cu}^{2+}}^2 \gamma_{\text{OH}^-}}{\gamma_{\text{Cu}_2(\text{OH})^{3+}}} \quad \beta'_{22} = \beta_{22} \frac{\gamma_{\text{Cu}^{2+}}^2 \gamma_{\text{OH}^-}^2}{\gamma_{\text{Cu}_2(\text{OH})_2^{2+}}} \quad \beta'_{43} = \beta_{43} \frac{\gamma_{\text{Cu}^{2+}}^3 \gamma_{\text{OH}^-}^4}{\gamma_{\text{Cu}_3(\text{OH})_4^{2+}}}$$

$$K'_{\text{sp}}(\text{OH-SO}_4) = \frac{K_{\text{sp}}(\text{OH-SO}_4)}{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}^{3/2} \gamma_{\text{SO}_4^{2-}}^{1/4}}$$

$$K'_{\text{sp}}(\text{OH}) = \frac{K_{\text{sp}}(\text{OH})}{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}^2} \quad K'_{\text{sp}}(\text{O}) = \frac{K_{\text{sp}}(\text{O})}{\gamma_{\text{Cu}^{2+}} \gamma_{\text{OH}^-}^2}$$

12-19. (a) $[\text{Na}^+] + [\text{NaT}^-] + [\text{NaHT}] = F_{\text{Na}} = F_{\text{H}_2\text{T}}$

Substitute $[\text{NaT}^-] = K_{\text{NaT}}[\text{Na}^+][\text{T}^{2-}]$ and $[\text{NaHT}] = K_{\text{NaHT}}[\text{Na}^+][\text{HT}^-]$:

$$[\text{Na}^+] + K_{\text{NaT}}[\text{Na}^+][\text{T}^{2-}] + K_{\text{NaHT}}[\text{Na}^+][\text{HT}^-] = F_{\text{H}_2\text{T}}$$

$$[\text{Na}^+] \{1 + K_{\text{NaT}}[\text{T}^{2-}] + K_{\text{NaHT}}[\text{HT}^-]\} = F_{\text{H}_2\text{T}}$$

$$[\text{Na}^+] = \frac{F_{\text{H}_2\text{T}}}{1 + K_{\text{NaT}}[\text{T}^{2-}] + K_{\text{NaHT}}[\text{HT}^-]} \quad (\text{A})$$

(b) $[\text{H}_2\text{T}] + [\text{HT}^-] + [\text{T}^{2-}] + [\text{NaT}^-] + [\text{NaHT}] = F_{\text{H}_2\text{T}}$

Make the following substitutions to find expressions in terms of $[\text{T}^{2-}]$, $[\text{Na}^+]$, and $[\text{H}^+]$:

$$[\text{H}_2\text{T}] = \frac{[\text{H}^+]^2}{K_1 K_2} [\text{T}^{2-}]; \quad [\text{HT}^-] = \frac{[\text{H}^+]}{K_2} [\text{T}^{2-}]; \quad [\text{NaT}^-] = K_{\text{NaT}}[\text{Na}^+][\text{T}^{2-}]$$

$$[\text{NaHT}] = K_{\text{NaHT}}[\text{Na}^+][\text{HT}^-] = K_{\text{NaHT}}[\text{Na}^+] \frac{[\text{H}^+]}{K_2} [\text{T}^{2-}]$$

Then put these expressions into the mass balance:

$$\frac{[\text{H}^+]^2}{K_1 K_2} [\text{T}^{2-}] + \frac{[\text{H}^+]}{K_2} [\text{T}^{2-}] + [\text{T}^{2-}] + K_{\text{NaT}}[\text{Na}^+][\text{T}^{2-}] + K_{\text{NaHT}}[\text{Na}^+] \frac{[\text{H}^+]}{K_2} [\text{T}^{2-}] = F_{\text{H}_2\text{T}}$$

and solve for $[\text{T}^{2-}]$:

$$[\text{T}^{2-}] = \frac{F_{\text{H}_2\text{T}}}{\frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1 + K_{\text{NaT}}[\text{Na}^+] + K_{\text{NaHT}}[\text{Na}^+] \frac{[\text{H}^+]}{K_2}} \quad (\text{B})$$

(c) To find $[\text{HT}^-]$, make the following substitutions in the mass balance for H_2T :

$$[\text{H}_2\text{T}] = \frac{[\text{H}^+]}{K_1} [\text{HT}^-]; \quad [\text{T}^{2-}] = \frac{K_2}{[\text{H}^+]} [\text{HT}^-]; \quad [\text{NaHT}] = K_{\text{NaHT}}[\text{Na}^+][\text{HT}^-]$$

$$[\text{NaT}^-] = K_{\text{NaT}}[\text{Na}^+][\text{T}^{2-}] = K_{\text{NaT}}[\text{Na}^+] \frac{K_2}{[\text{H}^+]} [\text{HT}^-]$$

Then put these expressions into the mass balance:

$$\frac{[\text{H}^+]}{K_1} [\text{HT}^-] + [\text{HT}^-] + \frac{K_2}{[\text{H}^+]} [\text{HT}^-] + K_{\text{NaT}}[\text{Na}^+] \frac{K_2}{[\text{H}^+]} [\text{HT}^-] + K_{\text{NaHT}}[\text{Na}^+][\text{HT}^-] = F_{\text{H}_2\text{T}}$$

and solve for $[\text{HT}^-]$:

$$[\text{HT}^-] = \frac{F_{\text{H}_2\text{T}}}{\frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]} + K_{\text{NaT}^-}[\text{Na}^+] \frac{K_2}{[\text{H}^+]} + K_{\text{NaHT}}[\text{Na}^+]} \quad (\text{C})$$

To find $[\text{H}_2\text{T}]$, make the following substitutions in the mass balance for H_2T :

$$[\text{HT}^-] = \frac{K_1}{[\text{H}^+]} [\text{H}_2\text{T}]; \quad [\text{T}^{2-}] = \frac{K_1 K_2}{[\text{H}^+]^2} [\text{H}_2\text{T}]$$

$$[\text{NaT}^-] = K_{\text{NaT}^-}[\text{Na}^+] [\text{T}^{2-}] = K_{\text{NaT}^-}[\text{Na}^+] \frac{K_1 K_2}{[\text{H}^+]^2} [\text{H}_2\text{T}]$$

$$[\text{NaHT}] = K_{\text{NaHT}}[\text{Na}^+] [\text{HT}^-] = K_{\text{NaHT}}[\text{Na}^+] \frac{K_1}{[\text{H}^+]} [\text{H}_2\text{T}]$$

Then put these expressions into the mass balance:

$$[\text{H}_2\text{T}] + \frac{K_1}{[\text{H}^+]} [\text{H}_2\text{T}] + \frac{K_1 K_2}{[\text{H}^+]^2} [\text{H}_2\text{T}] + K_{\text{NaT}^-}[\text{Na}^+] \frac{K_1 K_2}{[\text{H}^+]^2} [\text{H}_2\text{T}] + K_{\text{NaHT}}[\text{Na}^+] \frac{K_1}{[\text{H}^+]} [\text{H}_2\text{T}] \\ = F_{\text{H}_2\text{T}}$$

and solve for $[\text{H}_2\text{T}]$:

$$[\text{H}_2\text{T}] = \frac{F_{\text{H}_2\text{T}}}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} + K_{\text{NaT}^-}[\text{Na}^+] \frac{K_1 K_2}{[\text{H}^+]^2} + K_{\text{NaHT}}[\text{Na}^+] \frac{K_1}{[\text{H}^+]}} \quad (\text{D})$$

- (d) Insert equations A, B, C, and D into the following spreadsheet to compute $[\text{Na}^+]$, $[\text{H}_2\text{T}]$, $[\text{HT}^-]$, and $[\text{T}^{2-}]$ in cells B12, H10, E11, and E12. Excel indicates a circular reference problem with these new formulas. In Excel 2007, click the Microsoft Office button at the upper left of the spreadsheet. Click on Excel Options at the bottom of the window. Select Formulas. In Calculation options, check Enable iterative calculation and set Maximum Change to 1e-16. Click OK. (In earlier versions of Excel, go to the Tools menu and choose Options. Select Calculation and choose Iteration. Set the maximum change to 1e-16 and click OK.) Guess a pH (such as 6) in cell H13. Select Solver and Set Target Cell E15 Equal To Value of 0 By Changing Cells H13. Click Solve and your spreadsheet should find the concentrations in the spreadsheet on the next page.

	A	B	C	D	E	F	G	H	I
1	Mixture of 0.020 M Na^+HT^- , 0.015 M PyH^+Cl^- , and 0.010 M KOH								
2	With some Na^+ ion pairs								
3	$F_{\text{H}_2\text{T}} = 0.020$		$F_{\text{PyH}^+} = 0.015$		$[\text{K}^+] = 0.010$				
4	$pK_1 = 3.036$		$pK_a = 5.20$		$K_w = 1.00\text{E}-14$				
5	$pK_2 = 4.366$		$K_a = 6.31\text{E}-06$		$K_{\text{NaT}^-} = 8$				
6	$K_1 = 9.20\text{E}-04$				$K_{\text{NaHT}} = 1.6$				
7	$K_2 = 4.31\text{E}-05$								
8									
9	Species in charge balance:					Other concentrations:			
10	$[\text{H}^+] = 5.45\text{E}-05$		$[\text{OH}^-] = 1.84\text{E}-10$		$[\text{H}_2\text{T}] = 5.93\text{E}-04$				
11	$[\text{PyH}^+] = 1.34\text{E}-02$		$[\text{HT}^-] = 1.00\text{E}-02$		$[\text{Py}] = 1.56\text{E}-03$				
12	$[\text{Na}^+] = 0.0185$		$[\text{T}^{2-}] = 7.92\text{E}-03$		$[\text{NaHT}] = 2.97\text{E}-04$				
13	$[\text{K}^+] = 0.0100$		$[\text{Cl}^-] = 0.0150$		$\text{pH} = 4.264$	← initial value			
14			$[\text{NaT}^-] = 1.17\text{E}-03$			is a guess			
15	Positive charge minus negative charge =		-3.69E-18						
16				E15 = B10+B11+B12+B13-E10-E11-2*E12-E13-E14					
17	Check: $[\text{PH}^+] + [\text{P}] =$		0.01500						
18	Check: $[\text{H}_2\text{T}] + [\text{HT}^-] + [\text{T}^{2-}] + [\text{NaT}^-] + [\text{NaHT}] =$		0.02000						
19	Check: $[\text{Na}^+] + [\text{NaT}^-] + [\text{NaHT}] =$		0.02000						
20	Formulas:								
21	$B6 = 10^{-B4}$	$B7 = 10^{-B5}$	$E5 = 10^{-E4}$	$E10 = H4/B10$					
22	$B10 = 10^{-H13}$		$B13 = H3$	$E13 = E3$					
23	$E11 = B3/(B10/B6 + 1 + B7/B10 + H5*B12*B7/B10 + H6*B12)$								
24	$E12 = B3/((B10^2(B6*B7))+(B10/B7)+1+H5*B12+H6*B12*B10/B7)$								
25	$H10 = B3/(1 + B6/B10 + B6*B7/B10^2 + H5*B12*B6*B7/B10^2 + H6*B12*B6/B10)$								
26	$B12 = B3/(1 + H5*E12 + H6*E11)$				$B11 = B10*E3/(B10+E5)$				
27	$E14 = H5*B12*E12$				$H11 = E5*E3/(B10+E5)$				
28	$H12 = H6*B12*E11$								
29									
30									
31	Na distribution (%)		H ₂ T distribution (%)						
32	$[\text{Na}^+] = 92.6$		$[\text{H}_2\text{T}] = 3.0$						
33	$[\text{NaT}^-] = 5.9$		$[\text{HT}^-] = 50.1$						
34	$[\text{NaHT}] = 1.5$		$[\text{T}^{2-}] = 39.6$						
35			$[\text{NaT}^-] = 5.9$						
36			$[\text{NaHT}] = 1.5$						