Chapter 3

3-1. **(a)** SQRT returns the square root of a number or result of a calculation.

(b) AVERAGE returns the arithmetic mean of a series of numbers.

(c) PI returns the value of pi accurate to 15 digits

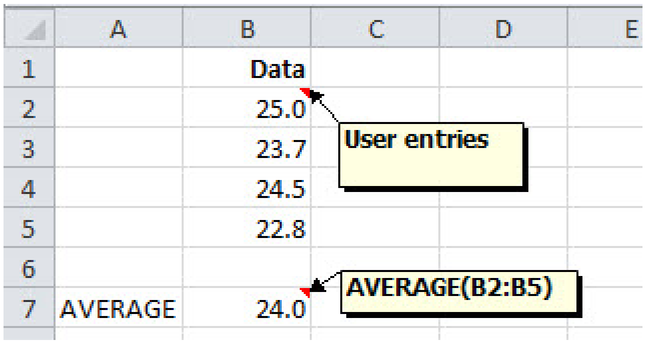
(d) FACT returns the factorial of a number, equal to 1 × 2 × 3 × … × number.

(e) EXP returns e raised to the value of a given number.

(f) LOG returns the logarithm of a number to a base specified by the user.

3-2. Count(value 1, value2,…) returns the number of cells that contain numbers and numbers within the list of arguments. As it appears in Figure 3-10, the COUNT function should return a value of 8 for the number of data values in each column of the spreadsheet.

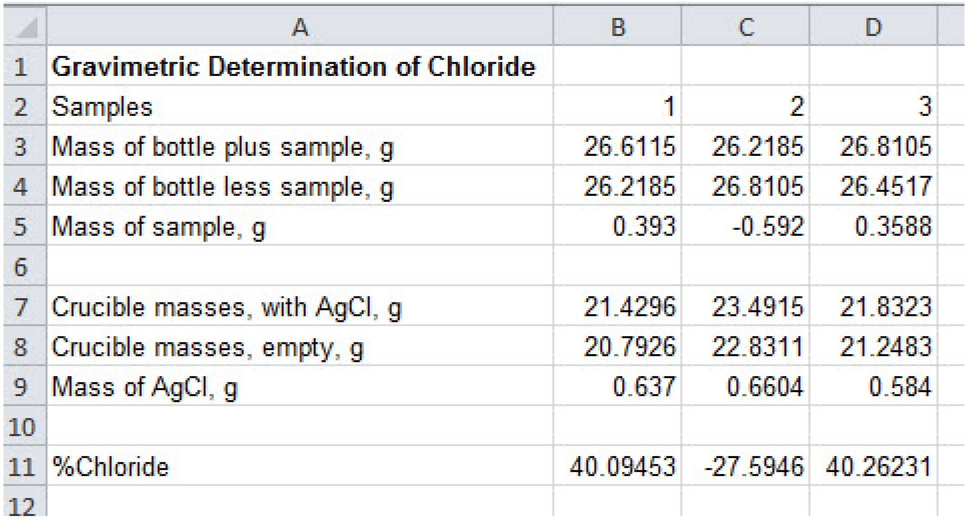
3-3. One method is to add comments for the appropriate cells. The comment group is found under the Review tab. An example for finding the mean (average) of four numbers is shown below.



	A	B	C	D	E
1		Data			
2		25.0			
3		23.7			
4		24.5			
5		22.8			
6					
7	AVERAGE	24.0			

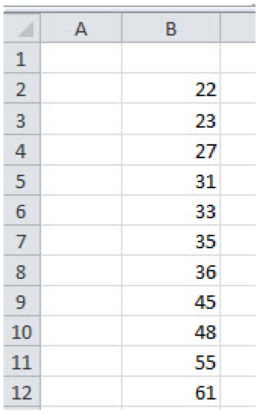
Another method is to add a text box to the worksheet by clicking on Text Box in the Insert tab. An arrow could be added pointing to the appropriate cell by clicking on Shapes in the Illustrations group under the Insert tab.

3-4. Replacing these values gives the worksheet below. Obviously, Column C has a nonsensical result with the replacement.



	A	B	C	D
1	**Gravimetric Determination of Chloride**			
2	Samples	1	2	3
3	Mass of bottle plus sample, g	26.6115	26.2185	26.8105
4	Mass of bottle less sample, g	26.2185	26.8105	26.4517
5	Mass of sample, g	0.393	-0.592	0.3588
6				
7	Crucible masses, with AgCl, g	21.4296	23.4915	21.8323
8	Crucible masses, empty, g	20.7926	22.8311	21.2483
9	Mass of AgCl, g	0.637	0.6604	0.584
10				
11	%Chloride	40.09453	-27.5946	40.26231
12				

3-5. The result is:



	A	B
1		
2		22
3		23
4		27
5		31
6		33
7		35
8		36
9		45
10		48
11		55
12		61

3-6. The answer is contained in the problem.

Chapter 4

4-1. **(a)** The *millimole* is an amount of a chemical species, such as an atom, an ion, a molecule or an electron. There are

$$6.02\times10^{23}\,\frac{\text{particles}}{\text{mole}} \quad\times\quad 10^{-3}\,\frac{\text{mole}}{\text{millimole}} \quad=\quad 6.02\times10^{20}\,\frac{\text{particles}}{\text{millimole}}$$

(b) The molar mass is the mass in grams of one mole of a chemical species.

(c) The *millimolar mass* is the mass in grams of one millimole of a chemical species.

(d) Parts per million, c_{ppm}, is a term expressing the concentration of dilute solutions.

Thus,

$$c_{\text{ppm}} = \frac{\text{mass of solute}}{\text{mass of solution}} \quad\times\quad 10^{6}\,\text{ppm}$$

The units of mass in the numerator and the denominator must be the same.

4-2. The molar species concentration is number of moles of that species contained in one liter of solution. The molar analytical concentration is the total number of moles of a solute in 1 liter of the solution, regardless of the solute's chemical state.

4-3. The liter: $1\text{ L} = \dfrac{1000\text{ mL}}{1\text{ L}} \times \dfrac{1\text{ cm}^3}{1\text{ mL}} \times \left(\dfrac{1\text{ m}}{100\text{ cm}}\right)^3 = 10^{-3}\text{m}^3$

Molar concentration: $1\text{ M} = \dfrac{1\text{ mol}}{1\text{ L}} \times \dfrac{1\text{ L}}{10^{-3}\text{m}^3} = \dfrac{1\text{ mol}}{10^{-3}\text{m}^3}$

4-4. **(a)** $3.2\times10^{8}\text{Hz} \times \dfrac{1\text{ MHz}}{10^{6}\text{Hz}} = 320\text{ MHz}$

(b) $4.56\times10^{-7}\text{g} \times \dfrac{10^{9}\text{ng}}{1\text{ g}} = 456\text{ ng}$

(c) $8.43\times10^{7}\,\mu\text{mol} \times \dfrac{1\text{ mol}}{10^{6}\ \mu\text{mol}} = 84.3\text{ mol}$

(d) $6.5\times10^{10}\text{s} \times \dfrac{1\text{ Gs}}{10^{9}\text{s}} = 65\text{ Gs}$

(e) $8.96\times10^{6}\text{nm} \times \dfrac{1\text{ mm}}{10^{6}\text{nm}} = 8.96\text{ mm}$

(f) $48{,}000\text{ g} \times \dfrac{1\text{ kg}}{1000\text{ g}} = 48\text{ kg}$

4-5. For oxygen, for example 15.999 u/atom = 15.999 g/6.022 ×10^{23} atoms = 15.999 g/mol.

So 1 u = 1 g/mol.

Thus, 1g = 1mol u.

4-6. From Pb. 4-5, 1 g = 1 mol u = 6.022 × 10^{23} u

1 u = 1/12 mass of ^{12}C atom

So 1 kg = 1000 g = 1000× Avogadro's number of u =

1000 × Avogadro's number × 1/12 mass of ^{12}C atom =

1000/12 × Avogadro's number × mass of ^{12}C atom

4-7. $$2.92\text{ g Na}_3\text{PO}_4\times\frac{1\text{ mol Na}_3\text{PO}_4}{163.94\text{ g}}\times\frac{3\text{ mol Na}^+}{1\text{ mol Na}_3\text{PO}_4}\times\frac{6.022\times10^{23}\ \text{Na}^+}{1\text{ mol Na}^+}=3.22\ \times\ 10^{22}\ \text{Na}^+$$

4-8. $$3.41\text{ mol K}_2\text{HPO}_4\times\frac{2\text{ mol K}^+}{1\text{ mol K}_2\text{HPO}_4}\times\frac{6.022\times10^{23}\ \text{K}^+}{1\text{ mol K}^+}=4.11\times10^{24}\ \text{K}^+$$

4-9. **(a)** $8.75\text{ g B}_2\text{O}_3 \times \dfrac{2\text{ mol B}}{1\text{ mol B}_2\text{O}_3} \times \dfrac{1\text{ mol B}_2\text{O}_3}{69.62\text{ g B}_2\text{O}_3} = 0.251\text{ mol B}$

(b) $$167.2\text{ mg Na}_2\text{B}_4\text{O}_7\bullet10\text{H}_2\text{O}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{7\text{ mol O}}{1\text{ mol Na}_2\text{B}_4\text{O}_7\bullet10\text{H}_2\text{O}}$$
$$\times\frac{1\text{ mol Na}_2\text{B}_4\text{O}_7\bullet10\text{H}_2\text{O}}{381.37\text{ g}}=3.07\ \times\ 10^{-3}\text{mol O} = 3.07\text{ mmol}$$

(c) $$4.96\text{ g Mn}_3\text{O}_4\times\frac{1\text{ mol Mn}_3\text{O}_4}{228.81\text{ g Mn}_3\text{O}_4}\times\frac{3\text{ mol Mn}}{1\text{ mol Mn}_3\text{O}_4}=6.50\times10^{-2}\text{ mol Mn}$$

(d) $$333\text{ mg CaC}_2\text{O}_4\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{\text{mol CaC}_2\text{O}_4}{128.10\text{ g CaC}_2\text{O}_4}\times\frac{2\text{ mol C}}{1\text{ mol CaC}_2\text{O}_4}=5.20\times10^{-3}\text{ mol C}$$
$$=5.20\text{ mmol}$$

4-10. **(a)** $$850\text{ mg P}_2\text{O}_5\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol P}_2\text{O}_5}{141.94\text{ g P}_2\text{O}_5}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{2\text{ mol P}}{1\text{ mol P}_2\text{O}_5}$$
$$=11.98\text{ mmol P}$$

(b) $$40.0\text{ g CO}_2\times\frac{1\text{ mol CO}_2}{44.01\text{ g CO}_2}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{1\text{ mol C}}{1\text{ mol CO}_2}=909\text{ mmol C}$$

(c) $$12.92\text{ g NaHCO}_3\times\frac{1\text{ mol NaHCO}_3}{84.01\text{ g NaHCO}_3}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{3\text{ mol O}}{1\text{ mol NaHCO}_3}=461.4\text{ mmol O}$$

(d) $$57\text{ mg MgNH}_4\text{PO}_4\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol MgNH}_4\text{PO}_4}{137.32\text{ g MgNH}_4\text{PO}_4}\times\frac{1000\text{ mmol}}{1\text{ mol}}$$
$$\times\frac{1\text{ mol Mg}}{1\text{ mol MgNH}_4\text{PO}_4}=0.42\text{ mmol Mg}$$

4-11. **(a)** $$\frac{0.0555\text{ mol KMnO}_4}{\text{L}}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times2.00\text{ L}=111\text{ mmol KMnO}_4$$

(b) $$\frac{3.25\times10^{-3}\text{ M KSCN}}{\text{L}}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{\text{L}}{1000\text{ mL}}\times750\text{ mL}$$
$$=2.44\text{ mmol KSCN}$$

(c) $$\frac{3.33\text{ mg CuSO}_4}{1\text{ L}}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol CuSO}_4}{159.61\text{ g CuSO}_4}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times3.50\text{ L}$$
$$=7.30\times10^{-2}\text{ mmol CuSO}_4$$

(d) $$\frac{0.414\text{ mol KCl}}{1\text{ L}}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{1\text{ L}}{1000\text{ mL}}\times250\text{ mL}=103.5\text{ mmol KCl}$$

4-12. **(a)** $$\frac{0.320\text{ mol HClO}_4}{1\text{ L}}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 226\text{ mL}$$
$$= 72.3\text{ mmol HClO}_4$$

(b) $$\frac{8.05\times10^{-3}\text{mol K}_2\text{CrO}_4}{1\text{ L}}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times 25.0\text{ L}$$
$$= 201\text{ mmol K}_2\text{CrO}_4$$

(c) $$\frac{6.75\text{ mg AgNO}_3}{1\text{ L}}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol AgNO}_3}{169.87\text{ g AgNO}_3}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times 6.00\text{ L}$$
$$= 0.238\text{ mmol AgNO}_3$$

(d) $$\frac{0.0200\text{ mol KOH}}{1\text{ L}}\times\frac{1000\text{ mmol}}{1\text{ mol}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 537\text{ mL}$$
$$= 10.7\text{ mmol KOH}$$

4-13. **(a)** $$0.367\text{ mol HNO}_3\times\frac{63.01\text{ g HNO}_3}{1\text{ mol HNO}_3}\times\frac{1000\text{ mg}}{1\text{ g}} = 2.31\times10^4\text{mg HNO}_3$$

(b) $$245\text{ mmol MgO}\times\frac{1\text{ mol}}{1000\text{ mmol}}\times\frac{40.30\text{ g MgO}}{1\text{ mol MgO}}\times\frac{1000\text{ mg}}{1\text{ g}} = 9.87\times10^3\text{mg MgO}$$

(c) $$12.5\text{ mol NH}_4\text{NO}_3\times\frac{80.04\text{ g NH}_4\text{NO}_3}{1\text{ mol NH}_4\text{NO}_3}\times\frac{1000\text{ mg}}{1\text{ g}} = 1.00\times10^6\text{mg NH}_4\text{NO}_3$$

(d) $$4.95\text{ mol (NH}_4)_2\text{Ce(NO}_3)_6\times\frac{548.23\text{ g (NH}_4)_2\text{Ce(NO}_3)_6}{1\text{ mol (NH}_4)_2\text{Ce(NO}_3)_6}\times\frac{1000\text{ mg}}{1\text{ g}}$$
$$= 2.71\times10^6\text{mg (NH}_4)_2\text{Ce(NO}_3)_6$$

4-14. **(a)** $$3.20\text{ mol KBr}\times\frac{119.0\text{ g KBr}}{1\text{ mol KBr}} = 381\text{ g KBr}$$

(b) $$18.9\text{ mmol PbO}\times\frac{1\text{ mol}}{1000\text{ mmol}}\times\frac{223.20\text{ g PbO}}{1\text{ mol PbO}} = 4.22\text{ g PbO}$$

(c) $6.02\text{ mol MgSO}_4 \times \dfrac{120.37\text{ g MgSO}_4}{1\text{ mol MgSO}_4} = 725\text{ g MgSO}_4$

(d) $10.9\text{ mmol Fe(NH}_4)_2(\text{SO}_4)_2{\bullet}6\text{H}_2\text{O} \times \dfrac{1\text{ mol}}{1000\text{ mmol}} \times \dfrac{392.23\text{ g Fe(NH}_4)_2(\text{SO}_4)_2{\bullet}6\text{H}_2\text{O}}{1\text{ mol Fe(NH}_4)_2(\text{SO}_4)_2{\bullet}6\text{H}_2\text{O}}$

$= 4.28\text{ g Fe(NH}_4)_2(\text{SO}_4)_2{\bullet}6\text{H}_2\text{O}$

4-15. **(a)** $\dfrac{0.350\text{ mol sucrose}}{1\text{ L}} \times \dfrac{1\text{ L}}{1000\text{ mL}} \times \dfrac{342\text{ g sucrose}}{1\text{ mol sucrose}} \times \dfrac{1000\text{ mg}}{1\text{ g}}$

$\times\ 16.0\text{ mL} = 1.92{\times}10^3\text{ mg sucrose}$

(b) $\dfrac{3.76{\times}10^{-3}\text{ mol H}_2\text{O}_2}{1\text{ L}} \times \dfrac{34.02\text{ g H}_2\text{O}_2}{1\text{ mol H}_2\text{O}_2} \times \dfrac{1000\text{ mg}}{1\text{ g}}$

$\times\ 1.92\text{ L} = 246\text{ mg H}_2\text{O}_2$

(c) $\dfrac{2.96\text{ mg Pb(NO}_3)_2}{1\text{ L}} \times \dfrac{1\text{ L}}{1000\text{ mL}} \times 356\text{ mL}$

$= 1.05\text{ mg Pb(NO}_3)_2$

(d) $\dfrac{0.0819\text{ mol KNO}_3}{1\text{ L}} \times \dfrac{101.10\text{ g KNO}_3}{1\text{ mol}} \times \dfrac{1000\text{ mg}}{1\text{ g}} \times \dfrac{1\text{ L}}{1000\text{ mL}}$

$\times\ 5.75\text{ mL} = 47.6\text{ mg KNO}_3$

4-16. **(a)** $\dfrac{0.264\text{ mol H}_2\text{O}_2}{1\text{ L}} \times \dfrac{1\text{ L}}{1000\text{ mL}} \times \dfrac{34.02\text{ g H}_2\text{O}_2}{1\text{ mol H}_2\text{O}_2} \times 250\text{ mL}$

$= 2.25\text{ g H}_2\text{O}_2$

(b) $$\frac{5.75\times10^{-4}\text{mol benzoic acid}}{1\text{ L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times\frac{122\text{ g benzoic acid}}{1\text{ mol benzoic acid}}$$

$$\times\ 37.0\text{ mL} = 2.60\times10^{-3}\text{g benzoic acid}$$

(c) $$\frac{31.7\text{ mg SnCl}_2}{1\text{ L}}\times\frac{1\text{ g}}{1000\text{ mg}}\times4.50\text{ L} = 0.143\text{ g SnCl}_2$$

(d) $$\frac{0.0225\text{ mol KBrO}_3}{1\text{ L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times\frac{167\text{ g KBrO}_3}{1\text{ mol KBrO}_3}\times11.7\text{ mL}$$

$$= 4.40\times10^{-2}\text{g KBrO}_3$$

4-17. **(a)** $\text{pNa} = -\log(0.0635 + 0.0403) = -\log(0.1038) = 0.9838$

$\text{pCl} = -\log(0.0635) = 1.197$

$\text{pOH} = -\log(0.0403) = 1.395$

(b) $\text{pBa} = -\log(4.65\times10^{-3}) = 2.333$

$\text{pMn} = -\log(2.54) = -0.405$

$\text{pCl} = -\log(2\times4.65\times10^{-3} + 2\times2.54) = -\log(5.089) = -0.707$

(c)

$\text{pH} = -\log(0.400) = 0.398$

$\text{pCl} = -\log(0.400 + 2\times0.100) = -\log(0.600) = 0.222$

$\text{pZn} = -\log(0.100) = 1.00$

(d)

$\text{pCu} = -\log(5.78\times10^{-2}) = 1.238$

$\text{pZn} = -\log(0.204) = 0.690$

$\text{pNO}_3 = -\log(2\times0.0578 + 2\times0.204) = -\log(0.5236) = 0.281$

(e)

$$\text{pK} = -\log(4\times1.62\times10^{-7}\ +\ 5.12\times10^{-7}) = -\log(1.16\times10^{-6}) = \ 5.936$$

$$\text{pOH} = -\log(5.12\times10^{-7}) = 6.291$$

$$\text{pFe(CN)}_6 = -\log(1.62\times10^{-7}) = 6.790$$

(f)

$$\text{pH} = -\log(4.75\times10^{-4}) = 3.32$$

$$\text{pBa} = -\log(2.35\times10^{-4}) = 3.63$$

$$\text{pClO}_4 = -\log(2\times2.35\times10^{-4} + 4.75\times10^{-4}) = -\log(9.45\times10^{-4}) = 3.02$$

4-18. **(a)** pH = 4.31, $\log[H_3O^+] = -4.31$, $[H_3O^+] = 4.9 \times 10^{-5}$ M

as in part (a)

(b) $[H_3O^+] = 3.3 \times 10^{-5}$ M

(c) $[H_3O^+] = 0.26$ M

(d) $[H_3O^+] = 1.3 \times 10^{-14}$ M

(e) $[H_3O^+] = 2.4 \times 10^{-8}$ M

(f) $[H_3O^+] = 4.8 \times 10^{-6}$ M

(g) $[H_3O^+] = 5.8$ M

(h) $[H_3O^+] = 2.6$ M

4-19. **(a)** pNa = pBr = −log(0.0300) = 1.523

(b) pBa = −log(0.0200) = 1.699; pBr = −log(2 × 0.0200) = 1.398

(c) pBa = $-\log(5.5 \times 10^{-3})$ = 2.26; pOH = $-\log(2 \times 5.5 \times 10^{-3})$ = 1.96

(d) pH = −log(0.020) = 1.70: pNa = −log(0.010) = 2.00

$\text{pCl} = -\log(0.020 + 0.010) = -\log(0.030) = 1.52$

(e) $\text{pCa} = -\log(8.7 \times 10^{-3}) = 2.06$; $\text{pBa} = -\log(6.6 \times 10^{-3}) = 2.18$

$\text{pCl} = -\log(2 \times 8.7 \times 10^{-3} + 2 \times 6.6 \times 10^{-3}) = -\log(0.0306) = 1.51$

(f) $\text{pZn} = -\log(2.8 \times 10^{-8}) = 7.55$; $\text{pCd} = -\log(6.6 \times 10^{-7}) = 6.18$

$\text{pNO}_3 = -\log(2.8 \times 10^{-8} + 2 \times 6.6 \times 10^{-7}) = 5.87$

4-20. **(a)** $\text{pH} = 1.020$**;** $\log[\text{H}_3\text{O}^+] = -1.020$; $[\text{H}_3\text{O}^+] = 0.0955$ M

(b) $\text{pOH} = 0.0025$; $\log[\text{OH}^-] = -0.0025$; $[\text{OH}^-] = 0.99$ M

(c) $\text{pBr} = 7.77$; $[\text{Br}^-] = 1.70 \times 10^{-8}$ M

(d) $\text{pCa} = -0.221$; $[\text{Ca}^{2+}] = 1.66$ M

(e) $\text{pLi} = 12.35$; $[\text{Li}^+] = 4.5 \times 10^{-13}$ M

(f) $\text{pNO}_3 = 0.034$; $[\text{NO}_3^-] = 0.92$ M

(g) $\text{pMn} = 0.135$; $[\text{Mn}^{2+}] = 0.733$ M

(h) $\text{pCl} = 9.67$; $[\text{Cl}^-] = 2.14 \times 10^{-10}$ M

4-21. **(a)** $$1.08\times10^{3}\,\text{ppm Na}^+ \times \frac{1}{10^6\,\text{ppm}} \times \frac{1.02\text{ g}}{1\text{ mL}} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1\text{ mol Na}^+}{22.99\text{ g}} = 4.79\times10^{-2}\,\text{M Na}^+$$

$$270\text{ ppm SO}_4^{2-} \times \frac{1}{10^6\,\text{ppm}} \times \frac{1.02\text{ g}}{1\text{ mL}} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1\text{ mol SO}_4^{3-}}{96.06\text{ g}} = 2.87\times10^{-3}\,\text{M SO}_4^{2-}$$

(b) $\text{pNa} = -\log(4.79\times10^{-2}) = 1.320$

$\text{pSO}_4 = -\log(2.87\times10^{-3}) = 2.542$

4-22. **(a)** 300 nmol/L = 300×10^{-9} mol/L or 300 nM in plasma

2.2 mmol/L = 2.2×10^{-3} mol/L or 2.2 mM in whole blood

(b) pHb in plasma = $-\log(300 \times 10^{-9}) = 6.52$

pHb in blood = $-\log(2.2 \times 10^{-3}) = 2.66$

4-23. (a)

$$\frac{5.76\text{ g KCl•MgCl}_2\text{•6H}_2\text{O}}{2.00\text{ L}}\times\frac{1\text{ mol KCl•MgCl}_2\text{•6H}_2\text{O}}{277.85\text{ g}}=1.04\times10^{-2}\text{M KCl•MgCl}_2\text{•6H}_2\text{O}$$

(b) There is 1 mole of Mg^{2+} per mole of KCl•$MgCl_2$, so the molar concentration of Mg^{2+}

is the same as the molar concentration of KCl•$MgCl_2$ or 1.04×10^{-2}M

(c) $1.04\times10^{-2}\text{M KCl•MgCl}_2\text{•6H}_2\text{O}\times\dfrac{3\text{ mol Cl}^-}{1\text{ mol KCl•MgCl}_2\text{•6H}_2\text{O}}=3.12\times10^{-2}\text{M Cl}^-$

(d) $\dfrac{5.76\text{ g KCl•MgCl}_2\text{•6H}_2\text{O}}{2.00\text{ L}}\times\dfrac{1\text{ L}}{1000\text{ mL}}\times100\%=0.288\%\text{ (w/v)}$

(e) $\dfrac{3.12\times10^{-2}\text{ mol Cl}^-}{1\text{ L}}\times\dfrac{1\text{ L}}{1000\text{ mL}}\times\dfrac{1000\text{ mmol}}{1\text{ mol}}\times25\text{ mL} = 7.8\times10^{-1}\text{mmol Cl}^-$

(f) $1.04\times10^{-2}\text{M KCl•MgCl}_2\text{•6H}_2\text{O}\times\dfrac{1\text{ mol K}^+}{1\text{ mol KCl•MgCl}_2\text{•6H}_2\text{O}}\times\dfrac{39.10\text{ g K}^+}{1\text{ mol K}^+}\times\dfrac{1000\text{ mg}}{1\text{ g}}$

$=\dfrac{407\text{ mg}}{1\text{ L}} = 407\text{ ppm K}^+$

(g) pMg = $-\log(1.04 \times 10^{-2}) = 1.983$

(h) pCl = $-\log(3.12 \times 10^{-2}) = 1.506$

4-24. **(a)**

$$\frac{1210\text{ mg K}_3\text{Fe(CN)}_6}{775\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}}\times\frac{1\text{ g}}{1000\text{ mg}}=\frac{1210\text{ g K}_3\text{Fe(CN)}_6}{775\text{ L}}$$

$$\frac{1210\text{ g K}_3\text{Fe(CN)}_6}{775\text{ L}}\times\frac{\text{mol K}_3\text{Fe(CN)}_6}{329.2\text{ g}}=4.74\times10^{-3}\text{M K}_3\text{Fe(CN)}_6$$

(b) $4.74\times10^{-3}\text{M K}_3\text{Fe(CN)}_6\times\frac{3\text{ mol K}^+}{\text{mol K}_3\text{Fe(CN)}_6}=1.42\times10^{-2}\text{ M K}^+$

(c) $4.74\times10^{-3}\text{M K}_3\text{Fe(CN)}_6\times\frac{\text{mol Fe(CN)}_6^{\ 3-}}{\text{mol K}_3\text{Fe(CN)}_6}=4.74\times10^{-3}\text{M Fe(CN)}_6^{\ 3-}$

(d) $\frac{1210\text{mgK}_3\text{Fe(CN)}_6}{775\text{mL}}\times\frac{\text{g}}{1000\text{mg}}\times100\% = 0.156\%\text{ (w/v)}$

(e) $\frac{1.42\times10^{-2}\text{mol K}^+}{\text{L}}\times\frac{\text{L}}{1000\text{ mL}}\times\frac{1000\text{ mmolK}^+}{\text{mol K}^+}\times50\text{ mL} = 7.1\times10^{-1}\text{mmol K}^+$

(f)

$$\frac{4.74\times10^{-3}\text{mol K}_3\text{Fe(CN)}_6}{\text{L}}\times\frac{\text{mol Fe(CN)}_6^{\ 3-}}{\text{mol K}_3\text{Fe(CN)}_6}\times\frac{211.95\text{ g Fe(CN)}_6^{\ 3-}}{\text{mol Fe(CN)}_6^{\ 3-}}$$

$$\times\frac{1000\text{ mg}}{\text{g}}=\frac{1005\text{ mg}}{\text{L}}\text{Fe(CN)}_6^{\ 3-}=1005\text{ ppm Fe(CN)}_6^{\ 3-}$$

(g) pK = $-\log(1.42\times10^{-2}) = 1.848$

(h) pFe(CH)$_6$ = $-\log(4.74\times10^{-3}) = 2.324$

4-25. **(a)**

$$6.42\%\text{ Fe(NO}_3)_3=\frac{6.42\text{ g Fe(NO}_3)_3}{100\text{ g solution}}\times\frac{1.059\text{ g}}{\text{mL}}\times\frac{1000\text{ mL}}{1\text{ L}}\times\frac{1\text{ mol Fe(NO}_3)_3}{241.86\text{ g}}$$

$$=\ 2.81\times10^{-1}\text{ M Fe(NO}_3)_3 = 0.281\text{ M}$$

(b)

$$2.81\times10^{-1}\text{M Fe(NO}_3)_3=\frac{2.81\times10^{-1}\text{mol Fe(NO}_3)_3}{\text{L}}\times\frac{3\text{ mol NO}_3^{\ -}}{1\text{ mol Fe(NO}_3)_3}=8.43\times10^{-1}\text{M NO}_3^{\ -}$$

(c) $\frac{2.81\times10^{-1}\text{mol Fe(NO}_3)_3}{\text{L}}\times\frac{241.86\text{ g Fe(NO}_3)_3}{1\text{ mol}}\times\ 1\text{ L}=6.80\times10^{1}\text{g Fe(NO}_3)_3 = 68.0\text{ g}$

4-26. **(a)** $12.5\%\ \text{NiCl}_2 = \frac{12.5\ \text{g NiCl}_2}{100\ \text{g solution}} \times \frac{1.149\ \text{g}}{1\ \text{mL}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{1\ \text{mol NiCl}_2}{129.61\ \text{g}} = 1.11\ \text{M NiCl}_2$

(b) $1.11\ \text{M NiCl}_2 = \frac{1.11\ \text{mol NiCl}_2}{\text{L}} \times \frac{2\ \text{mol Cl}^-}{1\ \text{mol NiCl}_2} = 2.22\ \text{M Cl}^-$

(c) $\frac{1.11\ \text{mol NiCl}_2}{\text{L}} \times \frac{129.61\ \text{g NiCl}_2}{\text{mol}} \times 1\ \text{L} = 1.44\times10^2\ \text{g NiCl}_2$

4-27. **(a)** $\frac{4.75\ \text{g C}_2\text{H}_5\text{OH}}{100\ \text{mL soln}} \times 500\ \text{mL soln} = 2.38\times10^1\ \text{g C}_2\text{H}_5\text{OH}$

Weigh 23.8 g ethanol and add enough water to give a final volume of 500 mL

$4.75\%\ (\text{w/w})\ \text{C}_2\text{H}_5\text{OH} = \frac{4.75\ \text{g C}_2\text{H}_5\text{OH}}{100\ \text{g soln}} \times 500\ \text{g soln} = 2.38\times10^1\ \text{g C}_2\text{H}_5\text{OH}$

(b) $500\ \text{g soln} = 23.8\ \text{g C}_2\text{H}_5\text{OH} + x\ \text{g water}$

$x\ \text{g water} = 500\ \text{g soln} - 23.8\ \text{g C}_2\text{H}_5\text{OH} = 476.2\ \text{g water}$

Mix 23.8 g ethanol with 476.2 g water

(c) $4.75\%\ (\text{v/v})\ \text{C}_2\text{H}_5\text{OH} = \frac{4.75\ \text{mL C}_2\text{H}_5\text{OH}}{100\ \text{mL soln}}$

$\frac{4.75\ \text{mL C}_2\text{H}_5\text{OH}}{100\ \text{mL soln}} \times 500\ \text{mL soln} = 2.38\times10^1\ \text{mL C}_2\text{H}_5\text{OH}$

Dilute 23.8 mL ethanol with enough water to give a final volume of 500 mL.

4-28. **(a)** $\frac{21.0\ \text{g C}_3\text{H}_8\text{O}_3}{100\ \text{mL soln}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times 2.50\ \text{L soln} = 5.25\times10^2\ \text{g C}_3\text{H}_8\text{O}_3$

Weigh 525 g glycerol and add enough water to give a final volume of 2.50 L.

$21.0\%\ (\text{w/w})\ \text{C}_3\text{H}_8\text{O}_3 = \frac{21.0\ \text{g C}_3\text{H}_8\text{O}_3}{100\ \text{g soln}} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times 2.50\ \text{kg soln} = 5.25\times10^2\ \text{g C}_3\text{H}_8\text{O}_3$

(b) $2.50\ \text{kg soln} = 0.525\ \text{kg C}_3\text{H}_8\text{O}_3 + x\ \text{kg water}$

$x\ \text{kg water} = 2.50\ \text{kg soln} - 0.525\ \text{kg C}_3\text{H}_8\text{O}_3 = 1.98\ \text{kg water}$

Mix 525 g glycerol with 1.98 kg water.

(c)

$$21.0\%\ (\text{v/v})\ \text{C}_3\text{H}_8\text{O}_3 = \frac{21.0\ \text{mL C}_3\text{H}_8\text{O}_3}{100\ \text{mL soln}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times 2.50\ \text{L soln} = 5.25\times10^{2}\ \text{mL C}_3\text{H}_8\text{O}_3$$

Dilute 525 mL glycerol with enough water to give a final volume of 2.50 L.

4-29.

$$\frac{6.00\ \text{mol H}_3\text{PO}_4}{\text{L}} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times 750\ \text{mL} = 4.50\ \text{mol H}_3\text{PO}_4$$

$$\frac{86\ \text{g H}_3\text{PO}_4}{100\ \text{g reagent}} \times \frac{1.71\ \text{g reagent}}{\text{g water}} \times \frac{\text{g water}}{\text{mL}} \times \frac{1000\ \text{mL}}{\text{L}} \times \frac{\text{mol H}_3\text{PO}_4}{98.0\ \text{g}}$$

$$= \frac{1.50\times10^{1}\text{mol H}_3\text{PO}_4}{\text{L}}$$

$$\text{volume 86\% (w/w) H}_3\text{PO}_4\text{ required} = 4.50\ \text{mol H}_3\text{PO}_4 \times \frac{\text{L}}{1.50\times10^{1}\text{mol H}_3\text{PO}_4} = 3.00\times10^{-1}\text{L}$$

4-30.

$$\frac{3.00\ \text{mol HNO}_3}{\text{L}} \times \frac{\text{L}}{1000\ \text{mL}} \times 900\ \text{mL} = 2.70\ \text{mol HNO}_3$$

$$\frac{70.5\ \text{g HNO}_3}{100\ \text{g reagent}} \times \frac{1.42\ \text{g reagent}}{\text{g water}} \times \frac{1\ \text{g water}}{1\ \text{mL}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{\text{mol HNO}_3}{63.0\ \text{g}}$$

$$= \frac{1.59\times10^{1}\text{mol HNO}_3}{\text{L}}$$

$$\text{volume 70.5\% HNO}_3\text{ required} = 2.70\ \text{mol HNO}_3 \times \frac{\text{L}}{1.59\times10^{1}\text{mol HNO}_3} = 1.70\times10^{-1}\text{L}$$

Dilute 170 mL of the concentrated reagent to 900 mL with water.

4-31. **(a)**

$$0.0750\ \text{M AgNO}_3 = \frac{0.0750\ \text{mol AgNO}_3}{\text{L}}$$

$$= \frac{0.0750\ \text{mol AgNO}_3}{\text{L}} \times \frac{169.87\ \text{g AgNO}_3}{1\ \text{mol}} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times 500\ \text{mL}$$

$$= 6.37\ \text{g AgNO}_3$$

Dissolve 6.37 g AgNO_3 in enough water to give a final volume of 500 mL.

(b)

$$\frac{0.285\text{ mol HCl}}{\text{L}}\times 1\text{ L} = 0.285\text{ mol HCl}$$

$$0.285\text{ mol HCl}\times\frac{1\text{ L}}{6.00\text{ mol HCl}} = 4.75\times10^{-2}\text{ L HCl}$$

Take 47.5 mL of the 6.00 M HCl and dilute to 1.00 L with water.

(c)

$$\frac{0.0810\text{ mol K}^{+}}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 400\text{ mL} = 3.24\times10^{-2}\text{ mol K}^{+}$$

$$3.24\times10^{-2}\text{ mol K}^{+}\times\frac{1\text{ mol K}_4\text{Fe(CN)}_6}{4\text{ mol K}^{+}}\times\frac{368.43\text{ g K}_4\text{Fe(CN)}_6}{\text{mol}} = 2.98\text{ g K}_4\text{Fe(CN)}_6$$

Dissolve 2.98 g $K_4Fe(CN)_6$ in enough water to give a final volume of 400 mL.

(d)

$$\frac{3.00\text{ g BaCl}_2}{100\text{ mL soln}}\times 600\text{ mL} = 1.8\times10^{1}\text{g BaCl}_2$$

$$1.8\times10^{1}\text{g BaCl}_2\times\frac{1\text{ mol BaCl}_2}{208.23\text{ g}}\times\frac{\text{L}}{0.400\text{ mol BaCl}_2} = 2.16\times10^{-1}\text{ L}$$

Take 216 mL of the 0.400 M $BaCl_2$ solution and dilute to 600 mL with water

(e)

$$\frac{0.120\text{ mol HClO}_4}{\text{L}}\times 2.00\text{ L} = 0.240\text{ mol HClO}_4$$

$$\frac{71\text{ g HClO}_4}{100\text{ g reagent}}\times\frac{1.67\text{ g reagent}}{1\text{ g water}}\times\frac{1\text{ g water}}{1\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}}\times\frac{\text{mol HClO}_4}{100.46\text{ g}}$$

$$=\frac{1.18\times10^{1}\text{mol HClO}_4}{\text{L}}$$

volume 71% (w/w) $HClO_4$ required $= 0.240\text{ mol HClO}_4\times\frac{\text{L}}{1.18\times10^{1}\text{mol HClO}_4} = 2.03\times10^{-2}\text{ L}$

Take 20.3 mL of the concentrated reagent and dilute to 2.00 L with water.

(f)

$$60\text{ ppm Na}^+ = \frac{60\text{ mg Na}^+}{\text{L soln}}$$

$$\frac{60\text{ mg Na}^+}{\text{L soln}}\times 9.00\text{ L} = 5.4\times10^2\text{mg Na}^+$$

$$5.4\times10^2\text{ mg Na}^+\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol Na}^+}{22.99\text{ g}} = 2.35\times10^{-2}\text{mol Na}^+$$

$$2.35\times10^{-2}\text{mol Na}^+ \times \frac{1\text{ mol Na}_2\text{SO}_4}{2\text{ mol Na}^+} \times \frac{142.04\text{ g Na}_2\text{SO}_4}{1\text{ mol}} = 1.7\text{ g Na}_2\text{SO}_4$$

Dissolve 1.7 g Na_2SO_4 in enough water to give a final volume of 9.00 L.

4-32. **(a)** $$\frac{0.0500\text{ mol KMnO}_4}{\text{L}} \times 5.00\text{ L} \times \frac{158.03\text{ g KMnO}_4}{1\text{ mol}} = 3.95\times10^1\text{g KMnO}_4$$

Dissolve 39.5 g $KMnO_4$ in enough water to give a final volume of 5.00 L.

(b)

$$\frac{0.250\text{ mol HClO}_4}{\text{L}} \times 4.00\text{ L} = 1.00\text{ mol HClO}_4$$

$$1.00\text{ mol HClO}_4\times \frac{1\text{ L}}{8.00\text{ mol reagent}} = 1.25\times10^{-1}\text{L reagent}$$

Take 125 mL of the 8.00 M reagent and dilute a final of volume of 4.00 L with water.

(c)

$$\frac{0.0250\text{ mol I}^-}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 400\text{ mL} = 1.00\times10^{-2}\text{mol I}^-$$

$$1.00\times10^{-2}\text{mol I}^- \times \frac{1\text{ mol MgI}_2}{2\text{ mol I}^-} \times \frac{278.11\text{ g MgI}_2}{1\text{ mol}} = 1.39\text{ g MgI}_2$$

Dissolve 1.39 g MgI_2 in enough water to give a final volume of 400 mL

(d)

$$1.00\%\text{ (w/v) CuSO}_4 = \frac{1.00\text{ g CuSO}_4}{100\text{ mL soln}}$$

$$\frac{1.00\text{ g CuSO}_4}{100\text{ mL soln}}\times 200\text{ mL} = 2.00\text{ g CuSO}_4$$

$$2.00\text{ g CuSO}_4 \times \frac{1\text{ mol CuSO}_4}{159.60\text{ g}} \times \frac{\text{L}}{0.365\text{ mol CuSO}_4} = 3.43\times10^{-2}\text{ L}$$

Take 34.3 mL of the 0.365 M $CuSO_4$ and dilute to a final volume of 200 mL with water

(e)

$$\frac{0.215\text{ mol NaOH}}{\text{L}}\times 1.50\text{ L} = 0.322\text{ mol NaOH}$$

$$50\%\text{ (w/w) NaOH}=\frac{50\text{ g NaOH}}{100\text{ g reagent}}$$

$$\frac{50\text{ g NaOH}}{100\text{ g reagent}}\times\frac{1.525\text{ g reagent}}{1\text{ g water}}\times\frac{1\text{ g water}}{1\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}}\times\frac{\text{mol NaOH}}{40.00\text{ g}}$$

$$=\frac{1.9\times 10^{1}\text{mol NaOH}}{\text{L}}$$

$$\text{volume 50\% (w/w) NaOH required} = 0.322\text{ mol NaOH}\times\frac{\text{L}}{1.9\times 10^{1}\text{mol NaOH}} = 1.7\times 10^{-2}\text{ L}$$

Take 17 mL of the concentrated reagent and dilute to a final volume of 1.50 L

with water

(f)

$$12.0\text{ ppm K}^{+} = \frac{12\text{ mg K}^{+}}{\text{L soln}}$$

$$\frac{12\text{ mg K}^{+}}{\text{L soln}}\times 1.50\text{ L} = 1.8\times 10^{1}\text{ mg K}^{+}$$

$$1.8\times 10^{1}\text{ mg K}^{+}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol K}^{+}}{39.10\text{ g}} = 4.60\times 10^{-4}\text{ mol K}^{+}$$

$$4.60\times 10^{-4}\text{ mol K}^{+}\times\frac{1\text{ mol K}_4\text{Fe(CN)}_6}{4\text{ mol K}^{+}}\times\frac{368.35\text{ g K}_4\text{Fe(CN)}_6}{1\text{ mol}} = 4.24\times 10^{-2}\text{ g K}_4\text{Fe(CN)}_6$$

Dissolve 42.4 mg $K_4Fe(CN)_6$ in enough water to give a final volume of 1.50 L.

4-33.

$$\frac{0.250\text{ mol La}^{3+}}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 50.0\text{ mL} = 1.25\times 10^{-2}\text{mol La}^{3+}$$

$$0.302\text{ M IO}_3^{-} = \frac{0.302\text{ mol IO}_3^{-}}{1\text{ L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 75.0\text{ mL} = 2.27\times 10^{-2}\text{ mol IO}_3^{-}$$

Because each mole of $La(IO_3)_3$ requires three moles IO_3^-, IO_3^- is the limiting reagent.

Thus,

$$2.27\times10^{-2}\,\text{mol IO}_3^- \times\frac{1\text{ mol La(IO}_3)_3}{3\text{ mol IO}_3^-}\times\frac{663.6\text{ g La(IO}_3)_3}{1\text{ mol}} = 5.01\text{ g La(IO}_3)_3\text{formed}$$

4-34

$$\frac{0.125\text{ mol Pb}^{2+}}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 200\text{ mL} = 2.50\times10^{-2}\,\text{mol Pb}^{2+}$$

$$\frac{0.175\text{ mol Cl}^-}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 400\text{ mL} = 7.00\times10^{-2}\text{ mol Cl}^-$$

Because each mole of $PbCl_2$ requires two moles Cl^-, Pb^{2+} is the limiting reagent. Thus,

$$2.50\times10^{-2}\text{ mol Pb}^{2+}\times\frac{1\text{ mol PbCl}_2}{1\text{ mol Pb}^{2+}}\times\frac{278.10\text{ g PbCl}_2}{1\text{ mol}} = 6.95\text{ g PbCl}_2\text{formed}$$

4-35. A balanced chemical equation can be written as:

$$\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2\,(g)$$

(a)

$$0.2220\text{ g Na}_2\text{CO}_3\times\frac{1\text{ mol Na}_2\text{CO}_3}{105.99\text{ g}} = 2.094\times10^{-3}\text{mol Na}_2\text{CO}_3$$

$$\frac{0.0731\text{ mol HCl}}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 100.0\text{ mL} = 7.31\times10^{-3}\text{ mol HCl}$$

Because one mole of CO_2 is evolved for every mole Na_2CO_3 reacted, Na_2CO_3 is the limiting reagent. Thus

$$2.094\times10^{-3}\text{ mol Na}_2\text{CO}_3\times\frac{1\text{ mol CO}_2}{1\text{ mol Na}_2\text{CO}_3}\times\frac{44.00\text{ g CO}_2}{1\text{ mol}} = 9.214\times10^{-2}\text{ g CO}_2\text{ evolved}$$

(b)

$$\text{amnt HCl left} = 7.31\times10^{-3}\,\text{mol} - (2\times2.094\times10^{-3}\,\text{mol}) = 3.12\times10^{-3}\,\text{mol}$$

$$\frac{3.12\times10^{-3}\text{ mol HCl}}{100.0\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}} = 3.12\times10^{-2}\text{ M HCl}$$

4-36. A balanced chemical equation can be written as

$$\text{Na}_3\text{PO}_4 + 3\text{HgNO}_3 \rightarrow 3\text{NaNO}_3 + \text{Hg}_3\text{PO}_4$$

(a)

$$\frac{0.3757\text{ mol Na}_3\text{PO}_4}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 25.0\text{ mL} = 9.39\times10^{-3}\text{ mol Na}_2\text{PO}_4$$

$$\frac{0.5151\text{ mol HgNO}_3}{\text{L}}\times\frac{1\text{ L}}{1000\text{ mL}}\times 100.0\text{ mL} = 5.151\times10^{-2}\text{ mol HgNO}_3$$

The limiting reagent is Na_2PO_4. Thus,

$$9.39\times10^{-3}\text{ mol Na}_2\text{PO}_4\times\frac{1\text{ mol Hg}_3\text{PO}_4}{1\text{ mol Na}_3\text{PO}_4}\times\frac{696.74\text{ g Hg}_3\text{PO}_4}{\text{mol}} = 6.54\text{ g Hg}_3\text{PO}_4\text{ formed}$$

(b)

$$\text{mol HgNO}_3\text{ unreacted} = 5.151\times10^{-2}\text{ mol} - (3\times9.39\times10^{-3}\,\text{mol}) = 2.33\times10^{-2}\,\text{mol}$$

$$\frac{2.33\times10^{-2}\,\text{mol HgNO}_3}{125.0\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}} = 1.87\times10^{-1}\,\text{M HgNO}_3$$

4-37 A balanced chemical equation can be written as:

$$\text{Na}_2\text{SO}_3 + 2\text{HClO}_4 \rightarrow 2\text{NaClO}_4 + \text{H}_2\text{O} + \text{SO}_2(g)$$

(a)

$$0.3132\text{ M Na}_2\text{SO}_3 = \frac{0.3132\text{ mol Na}_2\text{SO}_3}{\text{L}}\times\frac{\text{L}}{1000\text{ mL}}\times 75\text{ mL} = 2.3\times10^{-2}\text{mol Na}_2\text{SO}_3$$

$$0.4025\text{ M HClO}_4 = \frac{0.4025\text{ mol HClO}_4}{\text{L}}\times\frac{\text{L}}{1000\text{ mL}}\times 150.0\text{ mL} = 6.038\times10^{-2}\text{mol HClO}_4$$

Because one mole SO_2 is evolved per mole Na_2SO_3, Na_2SO_3 is the limiting reagent.

Thus,

$$2.3\times10^{-2}\text{mol Na}_2\text{SO}_3\times\frac{\text{mol SO}_2}{\text{mol Na}_2\text{SO}_3}\times\frac{64.06\text{ g SO}_2}{\text{mol}} = 1.5\text{ g SO}_2\text{ evolved}$$

(b)

$$\text{mol HClO}_4\text{ unreacted} = (6.038\times10^{-2}\text{mol} - (2\times2.3\times10^{-2}) = 1.4\times10^{-2}\text{ mol}$$

$$\frac{1.4\times10^{-2}\text{mol HClO}_4}{225\text{ mL}}\times\frac{1000\text{ mL}}{\text{L}} = 6.4\times10^{-2}\text{ M HClO}_4 = 0.064\text{ M}$$

4-38. A balanced chemical equation can be written as:

$$\text{MgCl}_2 + \text{Na}_3\text{PO}_4 + \text{NH}_4^+ \rightarrow \text{MgNH}_4\text{PO}_4(\text{s}) + 3\text{Na}^+ + 2\text{Cl}^-$$

$$\frac{1.000\text{ g MgCl}_2}{100\text{ mL}}\times200.0\text{ mL}\times\frac{1\text{ mol MgCl}_2}{95.21\text{ g}}$$
$$= 2.101\times10^{-2}\text{ mol MgCl}_2$$

$$\frac{0.1753\text{ mol Na}_2\text{PO}_4}{\text{L}}\times\frac{\text{L}}{1000\text{ mL}}\times40.0\text{ mL} = 7.01\times10^{-3}\text{ mol Na}_2\text{PO}_4$$ Na_2PO_4 is the

limiting reagent. Thus,

$$\text{amnt MgCl}_2\text{ unreacted} = (2.101\times10^{-2} - 7.01\times10^{-3}) = 1.40\times10^{-2}\text{ mol}$$

$$\frac{1.40\times10^{-2}\text{mol MgCl}_2}{240.0\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}} = 5.83\times10^{-2}\text{ M MgCl}_2$$

4-39. A balanced chemical equation can be written as:

$AgNO_3 + KI \rightarrow AgI(s) + KNO_3$

$$24.31\text{ ppt KI}\times\frac{1}{10^3\text{ppt}}\times\frac{1\text{ g}}{1\text{ mL}}\times200.0\text{ mL}\times\frac{1\text{ mol KI}}{166.0\text{ g}} = 2.93\times10^{-2}\text{ mol KI}$$

$$2.93\times10^{-2}\text{ mol KI}\times\frac{1\text{ mol AgNO}_3}{1\text{ mol KI}}\times\frac{1\text{ L}}{0.0100\text{ mol AgNO}_3} = 2.93\text{ L AgNO}_3$$

2.93 L of 0.0100 M $AgNO_3$ would be required to precipitate I^- as AgI.

4-40. A balanced chemical equation can be written as

$$3Ba(NO_3)_2 + Al_2(SO_4)_3 \rightarrow 3BaSO_4 + 2Al^{+3} + 6NO_3^-$$

(a)

$$480.4 \text{ ppm } Ba(NO_3)_2 \times \frac{1}{10^6 \text{ppm}} \times \frac{1 \text{ g}}{1 \text{ mL}} \times 750.0 \text{ mL} \times \frac{\text{mol } Ba(NO_3)_2}{261.34 \text{ g}}$$

$$= 1.38 \times 10^{-3} \text{ mol } Ba(NO_3)_2$$

$$\frac{0.03090 \text{ mol } Al_2(SO_4)_3}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 200.0 \text{ mL}$$

$$= 6.18 \times 10^{-3} \text{ mol } Al_2(SO_4)_3$$

$Ba(NO_3)_2$ is the limiting reagent. Thus,

$$1.38 \times 10^{-3} \text{mol } Ba(NO_3)_2 \times \frac{3 \text{ mol } BaSO_4}{3 \text{ mol } Ba(NO_3)_2} \times \frac{233.39 \text{ g } BaSO_4}{1 \text{ mol}} = 3.22 \times 10^{-1} \text{ g } BaSO_4 \text{ formed}$$

(b) Since 3 moles of $Ba(NO_3)_2$ react with 1 mole of $Al_2(SO_4)_3$,

$$\text{amnt } Al_2(SO_4)_3 \text{ unreacted} = (6.18 \times 10^{-3} \text{ mol } - (1/3 \times 1.38 \times 10^{-3} \text{mol}) = 5.72 \times 10^{-3} \text{ mol}$$

$$\frac{5.72 \times 10^{-3} \text{mol } Al_2(SO_4)_3}{950.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 6.02 \times 10^{-3} \text{ M } Al_2(SO_4)_3$$

Chapter 5

5-1. **(a)** Random error causes data to be scattered more or less symmetrically around a mean value while systematic error causes the mean of a data set to differ from the accepted value.

(b) The magnitude of a constant error stays essentially the same as the size of the quantity measured is varied while proportional errors increase or decrease according to the size of the sample taken for analysis.

(c) The absolute error of a measurement is the difference between the measured value and the true value while the relative error is the absolute error divided by the true value.

(d) The mean of a data set is obtained by dividing the sum of replicate measurements by the number of measurements in the set while the median is the middle result when replicate data are arranged according to increasing or decreasing value.

5-2. (1) Meter stick slightly longer or shorter than 1.0 m – systematic error.

(2) Markings on the meter stick always read from a given angle – systematic error.

(3) Variability in the sequential movement of the 1-m metal rule to measure the full 3-m table width – random error.

(4) Variability in interpolation of the finest division of the meter stick – random error.

5-3. (1) Instrumental errors

(2) Method errors

(3) Personal errors

5-4. (1) The analytical balance is miscalibrated.

(2) After weighing an empty vial, fingerprints are placed on the vial while adding sample to the vial.

(3) A hygroscopic sample absorbs water from the atmosphere while placing it in a weighing vial.

5-5. (1) The pipet is miscalibrated and holds a slightly different volume of liquid than the indicated volume.

(2) The user repetitively reads the volume marking on the pipet from an angle rather than at eye level.

(3) The inner surfaces of the pipet are contaminated.

5-6. Systematic method errors are detected by application of the method to the analysis of a standard reference material having one or more analytes at known concentration levels.

5-7. Both constant and proportional systematic errors can be detected by varying the sample size. Constant errors do not change with the sample size while proportional errors increase or decrease with increases or decreases in the samples size.

5-8. **(a)** (– 0.4 mg/500 mg) × 100% = – 0.08%

As in part (a)

(b) – 0.16%

(c) – 0.27%

(d) – 0.57%

5-9. **(a)** First determine how much gold is needed to achieve the desired relative error.

(– 0.4 mg/– 0.1%) × 100% = 400 mg gold

Then determine how much ore is needed to yield the required amount of gold.

(400 mg/1.2%) × 100% = 33,000 mg ore **or** 33 g ore

(b) 8.3 g ore

(c) 4.2 g ore

(d) 3.0 g ore

5-10 **(a**) (0.03/50.00) × 100% = 0.060%

As in part (a)

(b) 0.30%

(c) 0.12%

(d) 0.10%

5-11. **(a)** (– 0.4/30) × 100% = – 1.3%

As in part (a)

(b) – 0.27%

(c) – 0.13%

(d) – 0.08%

5-12. mean = $\left(\dfrac{0.0110 + 0.0104 + 0.0105}{3}\right) = 0.01063 \approx 0.0106$

Arranging the numbers in increasing value the median is:

0.0104

0.0105 ← median

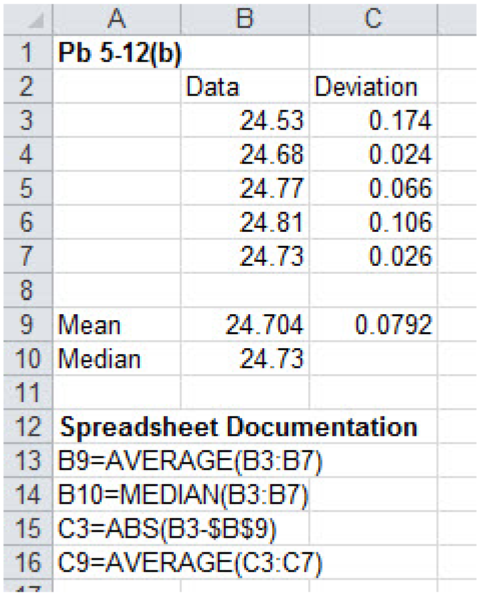
0.0110

The deviations from the mean are:

$$\begin{aligned}|0.0104 - 0.01063| &= 0.00023\\ |0.0105 - 0.01063| &= 0.00013\\ |0.0110 - 0.01063| &= 0.00037\end{aligned}$$

$$\text{mean deviation} = \left(\frac{0.00023+0.00013+0.00037}{3}\right) = 0.00024 \approx 0.0002$$

(b) Using a spreadsheet



	A	B	C
1	**Pb 5-12(b)**		
2		Data	Deviation
3		24.53	0.174
4		24.68	0.024
5		24.77	0.066
6		24.81	0.106
7		24.73	0.026
8			
9	Mean	24.704	0.0792
10	Median	24.73	
11			
12	**Spreadsheet Documentation**		
13	B9=AVERAGE(B3:B7)		
14	B10=MEDIAN(B3:B7)		
15	C3=ABS(B3-\$B\$9)		
16	C9=AVERAGE(C3:C7)		

(c) mean = 190 median = 189 mean deviation = 2

deviations 1.75, 0.25, 4.25, 2.75. rounded to 2, 0, 4, 3

(d) mean = 4.54×10^{-3} median = 4.53×10^{-3} mean deviation = 4.7×10^{-5}

deviations, 1.5×10^{-5}, 6.5×10^{-5}, 9.5×10^{-5}, 5.5×10^{-5}, 5.0×10^{-6}, 4.5×10^{-5}

(e) mean = 39.59 median = 39.65 mean deviation = 0.17

rounded deviations 0.24, 0.02, 0.34, 0.09

(f) mean = 859 median = 862 mean deviation = 7.6

deviations 9, 3, 10, 10, 6

Chapter 6

6-1. **(a)** The *standard error of the mean* is the standard deviation of the mean and is given by the standard deviation of the data set divided by the square root of the number of measurements.

(b) The *coefficient of variation* is the percent relative standard deviation or ($s/\bar{x}$) × 100%.

(c) The *variance* is the square of the standard deviation.

(d) *Significant figures* are all the digits in a number that are known with certainty plus the first uncertain digit.

6-2. **(a)** The term *parameter* refers to quantities such as the mean and standard deviation of a population or distribution of data. The term *statistic* refers to an estimate of a parameter that is made from a sample of data.

(b) The population mean is the true mean for the population of data. The sample mean is the arithmetic average of a limited sample drawn from the population.

(c) *Random errors* result from uncontrolled variables in an experiment while *systematic errors* are those that can be ascribed to a particular cause and can usually be determined.

(d) *Accuracy* represents the agreement between an experimentally measured value and the true or accepted value. *Precision* describes the agreement among measurements that have been performed in exactly the same way.

6-3. **(a)** The *sample standard deviation s* is the standard deviation of a sample drawn from the population. It is given by $s = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \bar{x}\right)^2}{N-1}}$, where $\bar{x}$ is the sample mean.

The *population standard deviation* σ is the standard deviation of an entire population

given by $\sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \mu)^2}{N}}$, where μ is the population mean.

(b) In statistics, a sample is a small set of replicate measurements. In chemistry, a sample is a portion of a material that is taken for analysis.

6-4. The standard error of a mean, $s_{m,}$ is the standard deviation of the set of data, *s*, divided by the square root of the number of data in the set, i.e. $s_m = s/\sqrt{N}$. The standard error of the mean s_m is lower than the standard deviation of the data points in a set *s* because a set of data made up of means will have less spread than a set of data made up of data points. In the equations for s_m, the denominator ($\sqrt{N}$) always has a value greater than 1 so that s_m will always be less than *s*.

6-5. Since the probability that a result lies between -1σ and +1σ is 0.683, the probability that a result will lie between 0 and +1σ will be half this value or 0.342. The probability that a result will lie between +1σ and +2σ will be half the difference between the probability of the result being between -2σ and +2σ, and -1σ and +1σ, or ½ (0.954-0.683) = 0.136.

6-6. Since the probability that a result lies between -2σ and +2σ is 0.954, the probability that a result will lie outside this range is (1 – 0.954) = 0.046. The probability that a result will be more negative than -2σ will be half this value, or 0.023.

6-7. Listing the data from Set A in order of increasing value:

x_i`	x_i^2
9.5	90.25
8.5	72.25
9.1	82.81
9.3	86.49
9.1	82.81
$\Sigma x_i = 45.5$	$\Sigma x_i^2 = 414.61$

(a) mean: $\bar{x} = 45.5/5 = 9.1$

(b) median = 9.1

(c) spread: $w = 9.5 - 8.5 = 1.0$

(d) standard deviation: $s = \sqrt{\dfrac{414.61 - (45.5)^2/5}{5-1}} = 0.37$

(e) coefficient of variation: CV = (0.37/9.1) × 100% = 4.1%

Results for Sets A through F, obtained in a similar way, are given in the following table.

	A	B	C	D	E	F
$\bar{x}$	9.1	55.29	0.650	5.1	20.61	0.958
median	9.1	55.32	0.653	5.0	20.64	0.954
w	1.0	0.15	0.108	1.5	0.14	0.049
s	0.37	0.08	0.056	0.6	0.07	0.02
CV, %	4.1	0.14	8.5	12.2	0.32	2.1

6-8. For Set A, $E = 9.1 - 9.0 = 0.1$

$E_r = (0.1/9.0) \times 1000$ ppt $= 11.1$ ppt

Set B, $E = -0.040$ $E_r = -0.7$ ppt

Set C $E = 0.0195$ $E_r = 31$ ppt

Set D $E = -0.34$ $E_r = -63$ ppt

Set E $E = 0.03$ $E_r = 1.3$ ppt

Set F $E = -0.007$ $E_r = -6.8$ ppt

6-9. **(a)** $s_y = \sqrt{(0.03)^2 + (0.001)^2 + (0.001)^2} = 0.030$

CV = (0.03/–2.082) × 100% = –1.4%

y = –2.08(±0.03)

(b) $s_y = \sqrt{(0.04)^2 + (0.0001)^2 + (0.08)^2} = 0.089$

CV = (0.089/19.1637) × 100% = 0.46%

y = 19.16(±0.09)

(c) $$\frac{s_y}{y} = \sqrt{\left(\frac{0.3}{29.2}\right)^2 + \left(\frac{0.02\times10^{-17}}{2.034\times10^{-17}}\right)^2} = 0.01422$$

CV = (0.0142) × 100% = 1.42%

$s_y = (0.0142) \times (5.93928 \times 10^{-16}) = 0.08446 \times 10^{-16}$

$y = 5.94(\pm0.08) \times 10^{-16}$

(d) $$\frac{s_y}{y} = \sqrt{\left(\frac{1}{326}\right)^2 + \left(\frac{2}{740}\right)^2 + \left(\frac{0.006}{1.964}\right)^2} = 0.00510$$

CV = (0.00510) × 100% = 0.510%

s_y = (0.00510) × (122830.9572) = 626

$y = 1.228(\pm0.006) \times 10^5$

(e) $s_{num} = \sqrt{(6)^2 + (3)^2} = 6.71$ $y_{num} = 187 - 89 = 98$

$s_{den} = \sqrt{(1)^2 + (8)^2} = 8.06$ $y_{den} = 1240 + 57 = 1297$

$$\frac{s_y}{y} = \sqrt{\left(\frac{6.71}{98}\right)^2 + \left(\frac{8.06}{1297}\right)^2} = 0.0688$$

CV = (0.0688) × 100% =6.88%

s_y = (0.0688) × (0.075559) = 0.00520

$y = 7.6(\pm 0.5) \times 10^{-2}$

(f) $$\frac{s_y}{y} = \sqrt{\left(\frac{0.01}{3.56}\right)^2 + \left(\frac{3}{522}\right)^2} = 0.006397$$

CV = (0.006397) × 100% = 0.6397%

$s_y = (0.006397) \times (6.81992 \times 10^{-3}) = 4.36 \times 10^{-5}$

$y = 6.82(\pm 0.04) \times 10^{-3}$

6-10. **(a)** $$s_y = \sqrt{\left(0.02\times10^{-8}\right)^2 + \left(0.2\times10^{-9}\right)^2} = 2.83\times10^{-10}$$

$y = 1.02\times10^{-8} - 3.54\times10^{-9} = 6.66\times10^{-9}$

$$\text{CV} = \frac{2.83\times10^{-10}}{6.66\times10^{-9}}\times100\% = 4.25\%$$

$y = 6.7 \pm 0.3 \times 10^{-9}$

(b) $$s_y = \sqrt{(0.08)^2 + (0.06)^2 + (0.004)^2} = 0.10$$

$y = 90.31 - 89.32 + 0.200 = 1.190$

$$\text{CV} = \frac{0.10}{1.190}\times100\% = 8.41\%$$

$y = 1.2(\pm 0.1)$

(c) $$\frac{s_y}{y} = \sqrt{\left(\frac{0.0005}{0.0040}\right)^2 + \left(\frac{0.02}{10.28}\right)^2 + \left(\frac{1}{347}\right)} = 0.1250$$

CV = (0.1250) × 100% = 12.5%

$y = 0.0040 \times 10.28 \times 347 = 14.27$

s_y = (0.125) × (14.27) = 1.78

y = 14(±2)

(d) $$\frac{s_y}{y}=\sqrt{\left(\frac{0.03\times10^{-14}}{223\times10^{-14}}\right)^2+\left(\frac{0.04\times10^{-16}}{1.47\times10^{-16}}\right)^2}=0.0272$$

CV = (0.027) × 100% = 2.7%

$y = 1.63\times10^{-14} / 1.03\times10^{-16} = 1.517 \times 10^4$

$s_\mathrm{y} = (0.0272) \times (1.517 \times 10^4) = 0.0413 \times 10^4$

$y = 1.52(\pm0.04) \times 10^4$

(e) $$\frac{s_y}{y}=\sqrt{\left(\frac{1}{100}\right)^2+\left(\frac{1}{2}\right)^2}=0.500$$

CV = (0.500) × 100% = 50.0%

y = 100 / 2 = 50.0

s_y = (0.500) × (50.0) = 25

y = 50(±25)

(f) $$s_\mathrm{num}=\sqrt{\left(0.02\ \times\ 10^{-2}\right)^2+\left(0.06\ \times\ 10^{-3}\right)^2}=2.09\ \times\ 10^{-4}$$

num = 0.0149 – 0.00497 = 0.00993

$$s_\mathrm{den}=\sqrt{\left(0.7\right)^2+\left(0.08\right)^2}=0.704$$

den = 27.1 + 8.99 = 36.09

$$\frac{s_y}{y} = \sqrt{\left(\frac{0.000209}{0.00993}\right)^2 + \left(\frac{0.704}{36.09}\right)^2} = 0.0287$$

CV = (0.0287) × 100% = 2.87%

$y = 0.00993/36.09 = 2.751 \times 10^{-4}$

$s_y = (0.0287) \times (2.751 \times 10^{-4}) = 7.899 \times 10^{-6}$

$y = 2.75(\pm 0.08) \times 10^{-4}$

6-11. **(a)** $y = \log(2.00 \times 10^{-4}) = -3.6989$ $\quad s_y = \frac{(0.434)(0.03\times10^{-4})}{(2.00\times10^{-4})} = 6.51\times10^{-3}$

$y = -3.699 \pm 0.0065$

CV = (0.0065/3.699) × 100% = 0.18%

(b) As in part (a): $y = 37.645 \pm 0.001$

CV = 0.003%

(c) $y = \text{antilog}(1.200) = 15.849$ $\quad \frac{s_y}{y} = (2.303)(0.003) = 0.0069$

$s_y = (0.0069)(15.849) = 0.11$ $\quad y = 15.8 \pm 0.1$

CV = (0.11/15.8) × 100% = 0.69%

(d) As in part (c): $y = 3.5(\pm 0.3) \times 10^{49}$

CV = 9.2%

6-12. **(a)** $y = (4.17 \times 10^{-4})^3 = 7.251 \times 10^{-11}$ $\quad \dfrac{s_y}{y} = 3\left(\dfrac{0.03\times10^{-4}}{4.17\times10^{-4}}\right) = 0.0216$

$s_y = (0.0216)(7.251 \times 10^{-11}) = 1.565 \times 10^{-12}$ $\quad y = 7.3(\pm0.2) \times 10^{-11}$

$\text{CV} = (1.565 \times 10^{-12}/7.251 \times 10^{-11}) \times 100\% = 2.2\%$

(b) As in part (a): $y = 1.3090(\pm0.0002)$

CV = 0.02%

6-13. From the equation for the volume of a sphere, we have

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi\left(\frac{2.15}{2}\right)^3 = 5.20\ \text{cm}^3$$

Hence, we may write

$$\frac{s_V}{V} = 3\times\frac{s_d}{d} = 3\times\frac{0.02}{2.15} = 0.0279$$

$s_V = 5.20 \times 0.0279 = 0.145$

$V = 5.2(\pm0.1)\ \text{cm}^3$

6-14. The mean diameter of the tank is $\bar{d} = \dfrac{5.2+5.7+5.3+5.5}{4} = 5.425\ \text{m}$ The standard deviation of the diameter is $s_d = \sqrt{\dfrac{\sum_{i=1}^{N}(x_i-\bar{x})^2}{N-1}} = 0.222$. The standard deviation of the mean diameter is $s_d/\sqrt{4} = 0.111$.

The mean height of the tank is $\bar{h} = \dfrac{7.9+7.8+7.6}{3} = 7.767\ \text{m}$ and $s_h = 0.153$. The standard deviation of the mean height is $s_h/\sqrt{3} = 0.0883$

The volume of the tank is given by

$$V = h \times \pi\left(\frac{d}{2}\right)^2 = 7.767(\pm0.0883) \times \pi \times \left(\frac{5.425(\pm0.111)}{2}\right)^2$$

The error in the 3rd term is given by

$\frac{s_y}{y} = \sqrt{\left(\frac{0.111}{5.425}\right)^2} = 0.02046$ y = ½ (5.425) = 2.7125 $s_y = 0.02046 \times 2.7125 = 0.0555$

$V = 7.767(\pm0.0883) \times (3.14159) \times (2.7125(\pm0.0555))^2$

$\frac{s_y}{y} = 2\left(\frac{0.0555}{2.7125}\right) = 0.0409$ $y = (2.7125)^2 = 7.358$ $s_y = (0.0409)(7.358) = 0.301$

$V = 7.767(\pm0.0883) \times (3.14159) \times 7.358(\pm0.301)$

Next, we propagate the error in volume by assuming the error in pi is negligible.

$\frac{s_y}{y} = \sqrt{\left(\frac{0.0883}{7.767}\right)^2 + \left(\frac{0.301}{7.358}\right)^2} = 0.04246$ $y = 7.767 \times 3.14159 \times 7.358 = 179.5$

$s_y = (0.04246)(179.5) = 7.62$

$y = 180(\pm8)\ \text{m}^3$

Converting to liters, we have

$V = 180(\pm8)\ \text{m}^3 \times \frac{1000L}{m^3} = 1.8(\pm0.08) \times 10^5\ L$

6-15. Since the titrant volume equals the final buret reading minus the initial buret reading, we can introduce the values given into the equation for %A.

%A = [9.26(±0.03) – 0.19(±0.02)] × equivalent mass × 100/[45.0(±0.2)]

Obtaining the value of the first term and the error in the first term

$s_y = \sqrt{(0.03)^2 + (0.02)^2} = 0.0361$ $y = 9.26 - 0.19 = 9.07$

We can now obtain the relative error of the calculation

$$\frac{s_{\%A}}{\%A} = \sqrt{\left(\frac{0.036}{9.07}\right)^2 + \left(\frac{0.2}{45.0}\right)^2} = 0.00596$$

The coefficient of variation is then

CV = (0.00596) × 100% = 0.596% or 0.6%

6-16. To obtain a CV in S of 1% or less,

$$\frac{s_S}{S} \le 0.01 = \sqrt{\left(\frac{s_{k'}}{k'}\right)^2 + \left(\frac{s_{e^{-E/kT}}}{e^{-E/kT}}\right)^2}$$

Since k' is a constant, the first term is zero resulting in:

$$0.01 = \frac{s_{e^{-E/kT}}}{e^{-E/kT}} \qquad \text{From Table 6-4} \qquad \frac{s_{e^{-E/kT}}}{e^{-E/kT}} = s_{-E/kT}$$

$s_{-E/kT}$ can be determined by evaluation of the errors in each of the numbers.

$$\frac{s_{-E/kT}}{-E/kT} = \sqrt{\left(\frac{s_E}{E}\right)^2 + \left(\frac{s_k}{k}\right)^2 + \left(\frac{s_T}{T}\right)^2}$$

Since both E and k have no uncertainty, this equation reduces to:

$$s_{-E/kT} = \left(\frac{s_T}{T}\right) \times \frac{-E}{kT} = \left(\frac{s_T}{6500}\right)\left(\frac{-6.12\times10^{-19}}{\left(1.3807\times10^{-23}\right)\left(6500\right)}\right) = 0.01$$

Solving for s_T gives:

$s_T \le 9.5$ K

6-17. We first calculate the mean transmittance and the standard deviation of the mean.

$$\text{mean T} = \left(\frac{0.213+0.216+0.208+0.214}{4}\right) = 0.2128$$

$s_T = 0.0034$

(a) $$c_X = \left(\frac{-\log T}{\varepsilon b}\right) = \frac{-\log(0.2128)}{3312} = 2.029\times10^{-4}\text{ M}$$

(b) For –log$T$, $s_y = (0.434)s_T/T = 0.434 \times (0.0034/0.2128) = 0.00693$

–log(0.2128) = 0.672

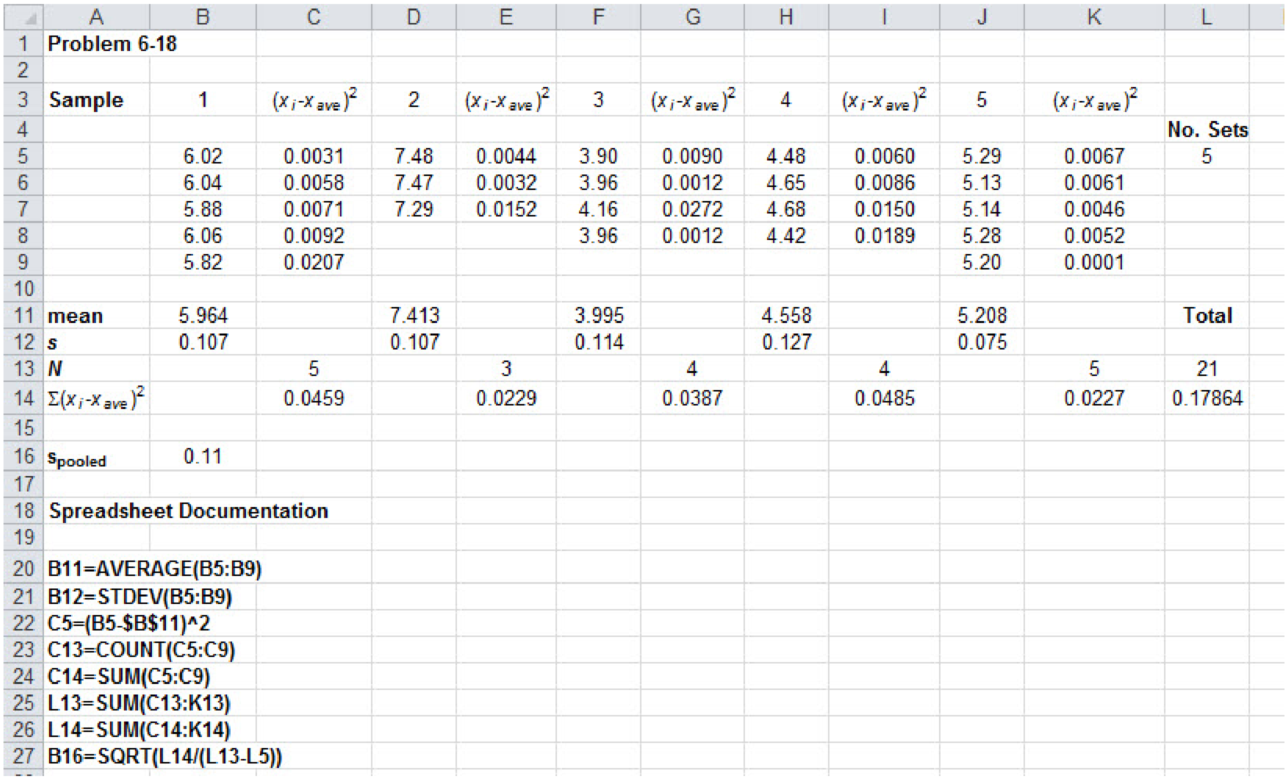
$$c_X = \frac{-\log T}{\varepsilon b} = \frac{0.672 \pm 0.00693}{3312 \pm 12}$$

$$\frac{s_{c_X}}{c_X} = \sqrt{\left(\frac{0.00693}{0.672}\right)^2 + \left(\frac{12}{3312}\right)^2} = 0.0109$$

$$s_{c_X} = (0.0109)\left(2.029\times10^{-4}\right) = 2.22\times10^{-6}$$

(c) CV = $(2.22 \times 10^{-6}/2.029 \times 10^{-4}) \times 100\% = 1.1\%$

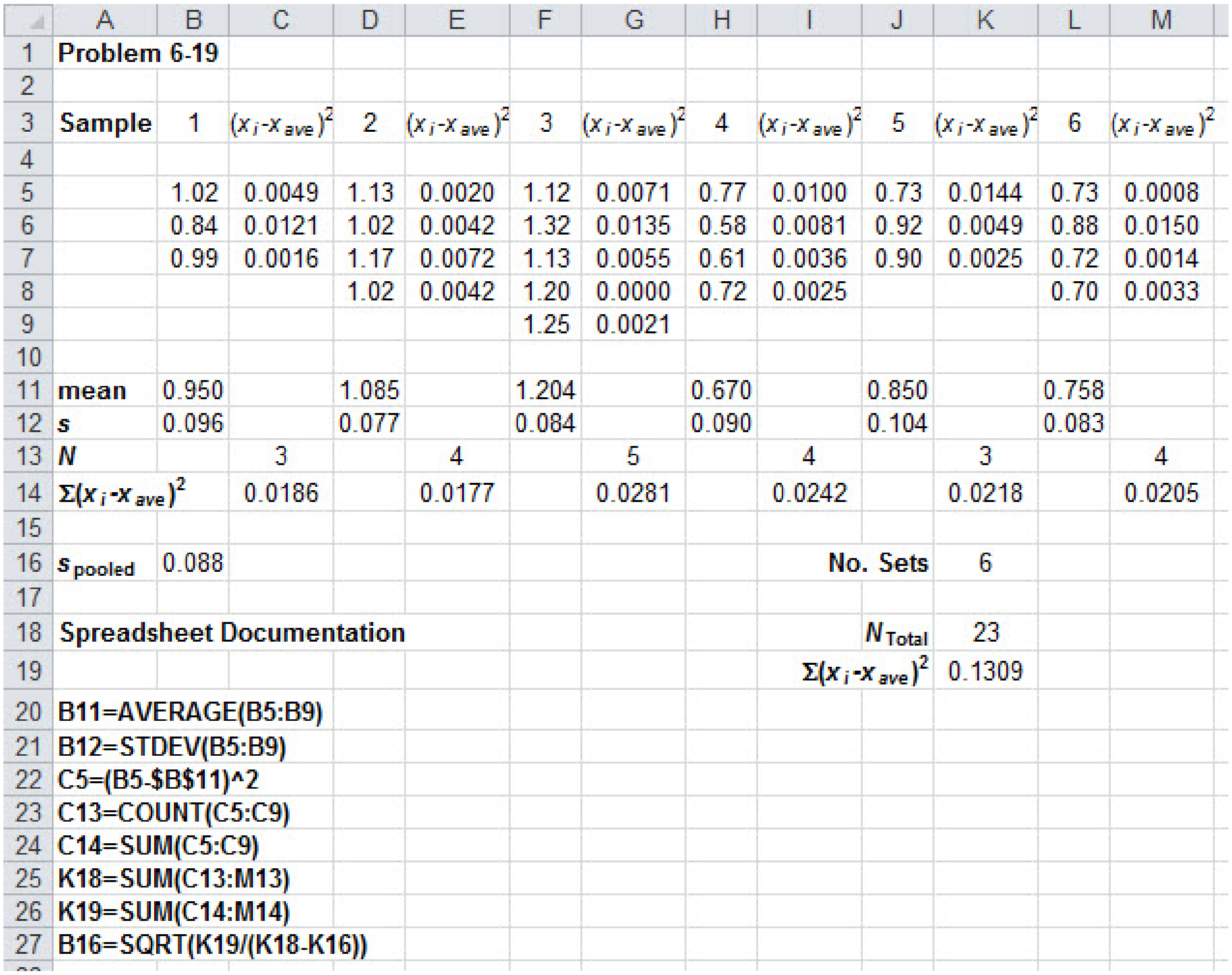
6-18. **(a)** and **(b)**



	A	B	C	D	E	F	G	H	I	J	K	L
1	**Problem 6-18**											
2												
3	**Sample**	1	$(x_i\text{-}x_{ave})^2$	2	$(x_i\text{-}x_{ave})^2$	3	$(x_i\text{-}x_{ave})^2$	4	$(x_i\text{-}x_{ave})^2$	5	$(x_i\text{-}x_{ave})^2$	
4												**No. Sets**
5		6.02	0.0031	7.48	0.0044	3.90	0.0090	4.48	0.0060	5.29	0.0067	5
6		6.04	0.0058	7.47	0.0032	3.96	0.0012	4.65	0.0086	5.13	0.0061	
7		5.88	0.0071	7.29	0.0152	4.16	0.0272	4.68	0.0150	5.14	0.0046	
8		6.06	0.0092			3.96	0.0012	4.42	0.0189	5.28	0.0052	
9		5.82	0.0207							5.20	0.0001	
10												
11	**mean**	5.964		7.413		3.995		4.558		5.208		**Total**
12	***s***	0.107		0.107		0.114		0.127		0.075		
13	***N***		5		3		4		4		5	21
14	$\Sigma(x_i\text{-}x_{ave})^2$		0.0459		0.0229		0.0387		0.0485		0.0227	0.17864
15												
16	**s_{pooled}**	0.11										
17												
18	**Spreadsheet Documentation**											
19												
20	**B11=AVERAGE(B5:B9)**											
21	**B12=STDEV(B5:B9)**											
22	**C5=(B5-$B$11)^2**											
23	**C13=COUNT(C5:C9)**											
24	**C14=SUM(C5:C9)**											
25	**L13=SUM(C13:K13)**											
26	**L14=SUM(C14:K14)**											
27	**B16=SQRT(L14/(L13-L5))**											

(c) Pooling the variations in %K from the five samples gives a better estimate of σ because several data sets are used. Thus the pooled standard deviation uses a larger number of data points and can reflect variations that arise because of sample selection and sample preparation.

6-19.

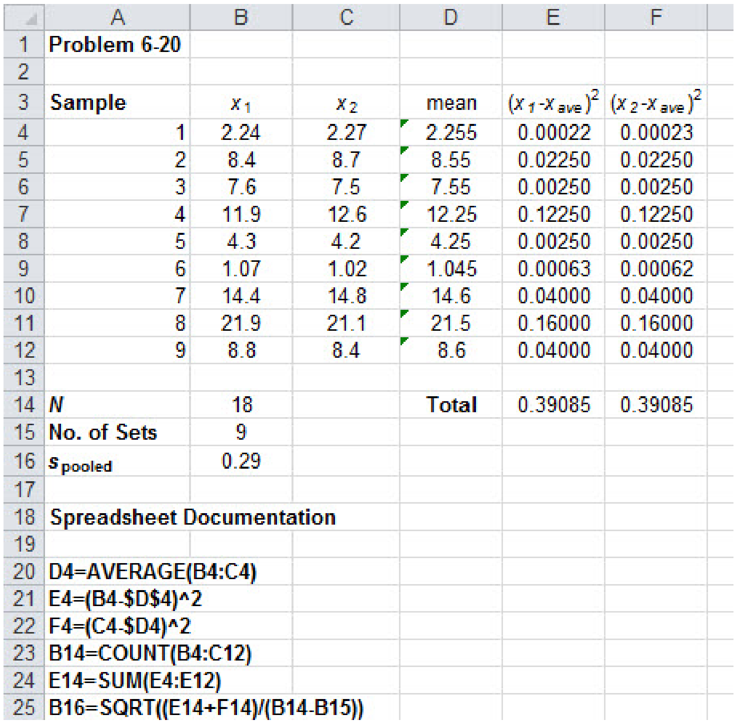


	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Problem 6-19**												
2													
3	**Sample**	1	$(x_i\text{-}x_{ave})^2$	2	$(x_i\text{-}x_{ave})^2$	3	$(x_i\text{-}x_{ave})^2$	4	$(x_i\text{-}x_{ave})^2$	5	$(x_i\text{-}x_{ave})^2$	6	$(x_i\text{-}x_{ave})^2$
4													
5		1.02	0.0049	1.13	0.0020	1.12	0.0071	0.77	0.0100	0.73	0.0144	0.73	0.0008
6		0.84	0.0121	1.02	0.0042	1.32	0.0135	0.58	0.0081	0.92	0.0049	0.88	0.0150
7		0.99	0.0016	1.17	0.0072	1.13	0.0055	0.61	0.0036	0.90	0.0025	0.72	0.0014
8				1.02	0.0042	1.20	0.0000	0.72	0.0025			0.70	0.0033
9						1.25	0.0021						
10													
11	**mean**	0.950		1.085		1.204		0.670		0.850		0.758	
12	***s***	0.096		0.077		0.084		0.090		0.104		0.083	
13	***N***		3		4		5		4		3		4
14	$\Sigma(x_i\text{-}x_{ave})^2$		0.0186		0.0177		0.0281		0.0242		0.0218		0.0205
15													
16	s_{pooled}	0.088								**No. Sets**	6		
17													
18	**Spreadsheet Documentation**									N_{Total}	23		
19										$\Sigma(x_i\text{-}x_{ave})^2$	0.1309		
20	**B11=AVERAGE(B5:B9)**												
21	**B12=STDEV(B5:B9)**												
22	**C5=(B5-$B$11)^2**												
23	**C13=COUNT(C5:C9)**												
24	**C14=SUM(C5:C9)**												
25	**K18=SUM(C13:M13)**												
26	**K19=SUM(C14:M14)**												
27	**B16=SQRT(K19/(K18-K16))**												

(a) The standard deviations are $s_1 = 0.096$, $s_2 = 0.077$, $s_3 = 0.084$, $s_4 = 0.090$, $s_5 = 0.104$, $s_6 = 0.083$

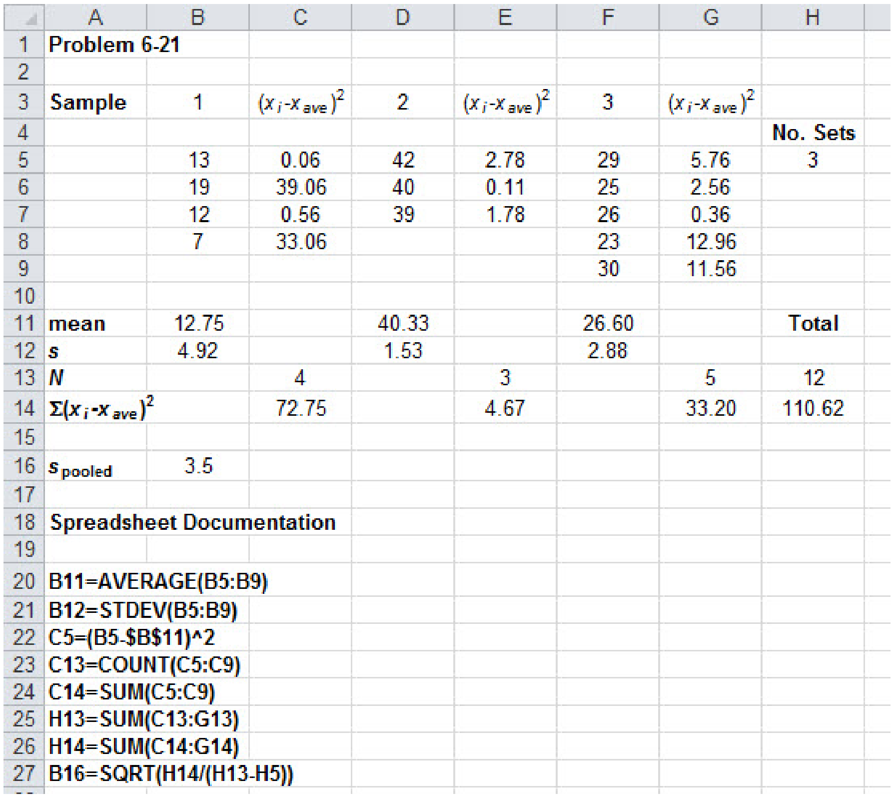
(b) $s_{\text{pooled}} = 0.088$ or 0.09

6-20.



	A	B	C	D	E	F
1	Problem 6-20					
2						
3	Sample	x_1	x_2	mean	$(x_1\text{-}x_{ave})^2$	$(x_2\text{-}x_{ave})^2$
4	1	2.24	2.27	2.255	0.00022	0.00023
5	2	8.4	8.7	8.55	0.02250	0.02250
6	3	7.6	7.5	7.55	0.00250	0.00250
7	4	11.9	12.6	12.25	0.12250	0.12250
8	5	4.3	4.2	4.25	0.00250	0.00250
9	6	1.07	1.02	1.045	0.00063	0.00062
10	7	14.4	14.8	14.6	0.04000	0.04000
11	8	21.9	21.1	21.5	0.16000	0.16000
12	9	8.8	8.4	8.6	0.04000	0.04000
13						
14	*N*	18		Total	0.39085	0.39085
15	No. of Sets	9				
16	s_{pooled}	0.29				
17						
18	Spreadsheet Documentation					
19						
20	D4=AVERAGE(B4:C4)					
21	E4=(B4-$D$4)^2					
22	F4=(C4-$D4)^2					
23	B14=COUNT(B4:C12)					
24	E14=SUM(E4:E12)					
25	B16=SQRT((E14+F14)/(B14-B15))					

6-21.



	A	B	C	D	E	F	G	H
1	Problem 6-21							
2								
3	Sample	1	$(x_i\text{-}x_{ave})^2$	2	$(x_i\text{-}x_{ave})^2$	3	$(x_i\text{-}x_{ave})^2$	
4								No. Sets
5		13	0.06	42	2.78	29	5.76	3
6		19	39.06	40	0.11	25	2.56	
7		12	0.56	39	1.78	26	0.36	
8		7	33.06			23	12.96	
9						30	11.56	
10								
11	mean	12.75		40.33		26.60		Total
12	*s*	4.92		1.53		2.88		
13	*N*		4		3		5	12
14	$\Sigma(x_i\text{-}x_{ave})^2$		72.75		4.67		33.20	110.62
15								
16	s_{pooled}	3.5						
17								
18	Spreadsheet Documentation							
19								
20	B11=AVERAGE(B5:B9)							
21	B12=STDEV(B5:B9)							
22	C5=(B5-$B$11)^2							
23	C13=COUNT(C5:C9)							
24	C14=SUM(C5:C9)							
25	H13=SUM(C13:G13)							
26	H14=SUM(C14:G14)							
27	B16=SQRT(H14/(H13-H5))							

6-22.

	Excel value	**NIST value**
Mean	2.001856000000000	2.001856000000000
SD	0.000429123454003085	0.000429123454003053

The means are the same in both cases. There is some difference, however, in the standard deviations in the last two digits. The differences could arise because of the different algorithms used to calculate the SD and to roundoff errors in the calculations. The first 16 digits are identical.

Chapter 7

7-1. The distribution of means is narrower than the distribution of single results. Hence, the standard error of the mean of 5 measurements is smaller than the standard deviation of a single result. The mean is thus known with more confidence than is a single result

7-2 **(a)** Looking at Table 7-1, we find that for $z = 2.58$, CL = 99%

(b) CL = 95%

(c) CL = 99.9%

(d) CL = 68%

7-3. **(a)** Since CI = $\bar{x} \pm \frac{z\sigma}{\sqrt{N}}$, as the standard deviation, σ, increases the confidence interval increases.

(b) As the desired confidence level increases, z inceases and thus the confidence interval increases.

(c). as the sample size, N, increases the confidence interval decreases.

7-4. For Set A

x_i	x_i^2
2.7	7.29
3.0	9.00
2.6	6.76
2.8	7.84
3.2	10.24
$\Sigma x_i = 14.3$	$\Sigma x_i^2 = 41.13$

mean: $\bar{x} = 14.3/5 = 2.86$

standard deviation: $s = \sqrt{\dfrac{41.13 - (14.3)^2/5}{5-1}} = 0.24$

Since, for a small set of measurements we cannot be certain *s* is a good approximation of σ, we should use the *t* statistic for confidence intervals. From Table 7-3, at 95% confidence *t* for 4 degrees of freedom is 2.78, therefore for set A,

$$\text{CI for } \mu = 2.86 \pm \frac{(2.78)(0.24)}{\sqrt{5}} = 2.86 \pm 0.30$$

Similarly, for the other data sets, we obtain the results shown in the following table:

	A	**B**	**C**	**D**	**E**	**F**
$\bar{x}$	2.86	0.494	70.19	3.1	0.824	70.53
s	0.24	0.016	0.08	0.37	0.051	0.22
CI	2.86 ±0.30	0.494 ±0.020	70.19 ±0.20	3.1 ±0.46	0.824 ±0.081	70.53± 0.34

The 95% confidence interval is the range within which the population mean is expected to lie with a 95% probability.

7-5. If *s* is a good estimate of σ then we can use $z = 1.96$ for the 95% confidence level. For set A, at the 95% confidence,

CI for $\mu = 2.86 \pm \dfrac{(1.96)(0.30)}{\sqrt{5}}$ = 2.86 ±0.26. Similarly for sets B-F, the limits are:

	A	**B**	**C**	**D**	**E**	**F**
CI	2.86±0.26	0.494±0.013	70.19±0.079	3.1±0.18	0.824±0.009	70.53 ±0.015

7-6. For set A: $Q = \dfrac{|3.2 - 3.0|}{3.2 - 2.6} = 0.33$ and $Q_{\text{crit}} = 0.710$ for 5 observations at the 95% confidence level.

Since $Q < Q_{\text{crit}}$ the outlier value 2.5 cannot be rejected with 95% confidence.

	A	B	C	D	E	F
Q	0.33	0.33	0.86	0.60	0.81	0.95
Q_{crit}	0.710	0.710	0.970	0.710	0.829	0.829
Decision	Keep	Keep	Keep	Keep	Keep	Reject

7-7. **(a)** 99% CI = 18.5 ± 2.58 × 3.6 = 18.5 ± 9.3 μg Fe/mL

95% CI = 18.5 ± 1.96 × 3.6 = 18.5 ± 7.1 μg Fe/mL

(b) $99\%\ \text{CI} = 18.5 \pm \dfrac{2.58 \times 3.6}{\sqrt{2}} = 18.5 \pm 6.6\ \mu\text{g Fe/mL}$

$95\%\ \text{CI} = 18.5 \pm \dfrac{1.96 \times 3.6}{\sqrt{2}} = 18.5 \pm 5.0\ \mu\text{g Fe/mL}$

(c) $99\%\ \text{CI} = 18.5 \pm \dfrac{2.58 \times 3.6}{\sqrt{4}} = 18.5 \pm 4.6\ \mu\text{g Fe/mL}$

$95\%\ \text{CI} = 18.5 \pm \dfrac{1.96 \times 3.6}{\sqrt{4}} = 18.5 \pm 3.5\ \mu\text{g Fe/mL}$

7-8. **(a)** 95% CI = 7.91 ± 1.96 × 0.27 = 7.91 ± 0.53 μg Cu/mL

99% CI = 7.91 ± 2.58 × 0.27 = 7.91 ± 0.70 μg Cu/mL

(b) $95\%\ \text{CI} = 7.91 \pm \dfrac{1.96 \times 0.27}{\sqrt{4}} = 7.91 \pm 0.26\ \mu\text{g Cu/mL}$

$99\%\ \text{CI} = 7.91 \pm \dfrac{2.58 \times 0.27}{\sqrt{4}} = 7.91 \pm 0.35\ \mu\text{g Cu/mL}$

(c) $95\%\ \text{CI} = 7.91 \pm \dfrac{1.96 \times 0.27}{\sqrt{16}} = 7.91 \pm 0.13\ \mu\text{g Cu/mL}$

$99\%\ \text{CI} = 7.91 \pm \dfrac{2.58 \times 0.32}{\sqrt{16}} = 7.91 \pm 0.17\ \mu\text{g Cu/mL}$

7-9. $2.2 = \dfrac{1.96 \times 3.6}{\sqrt{N}}$ For a 95% CI, $N = 10.3 \cong 11$

$2.2 = \dfrac{2.58 \times 3.6}{\sqrt{N}}$ For a 99% CI, $N = 17.8 \cong 18$

7-10. **(a)** $0.20 = \dfrac{1.96 \times 0.27}{\sqrt{N}}$ For the 95% CI, $N = 7$

(b) $0.20 = \dfrac{2.58 \times 0.27}{\sqrt{N}}$ For a 99% CI, $N = 12.13 \cong 13$

7-11. For the data set, $\bar{x} = 3.22$ and $s = 0.06$

(a) 95% CI = $3.22 \pm \dfrac{4.30 \times 0.06}{\sqrt{3}} = 3.22 \pm 0.15$ meq Ca/L

(b) 95% CI = $3.22 \pm \dfrac{1.96 \times 0.056}{\sqrt{3}} = 3.22 \pm 0.06$ meq Ca/L

7-12. For the data set, $\bar{x} = 7.24$ and $s = 0.29$

(a) 90% CI = $7.24 \pm \dfrac{2.92 \times 0.29}{\sqrt{3}} = 7.24 \pm 0.49$ % lindane

(b) 90% CI = $7.24 \pm \dfrac{1.64 \times 0.28}{\sqrt{3}} = 7.24 \pm 0.27$ % lindane

7-13 **(a)** $0.3 = \dfrac{2.58 \times 0.38}{\sqrt{N}}$ For the 99% CI, $N = 10.7 \cong 11$

(b) $0.3 = \dfrac{1.96 \times 0.38}{\sqrt{N}}$ For the 95% CI, $N = 6.1 \cong 7$

(c) $0.2 = \dfrac{1.64 \times 0.38}{\sqrt{N}}$ For the 90% CI, $N = 9.7 \cong 10$

7-14. This is a two-tailed test and from Table 7-1, $z_{\text{crit}} = 1.96$ for the 95% confidence level.

For carbon,

$$z = \frac{68.5 - 68.8}{0.004 \times 68.8\% / \sqrt{2}} = -1.54 \geq -1.96$$

Systematic error is NOT indicated at 95% confidence level.

For hydrogen, $z = \dfrac{4.882 - 4.953}{0.006 \times 4.953\% / \sqrt{2}} = -3.38 \leq -1.96$

Systematic error IS indicated at 95% confidence level.

7-15. This is a two-tailed test where s $\rightarrow \sigma$ and from Table 7-1, $z_{\text{crit}} = 2.58$ for the 99% confidence level.

For As: $z = \dfrac{129 - 119}{9.5\sqrt{\dfrac{3+3}{3 \times 3}}} = 1.28 \leq 2.58$

No significant difference exists at the 99% confidence level .

Proceeding in a similar fashion for the other elements

Element	*z*	Significant Difference?
As	1.28	No
Co	–3.43	Yes
La	2.45	No
Sb	0.20	No
Th	-3.42	Yes

For two of the elements there is a significant difference, but for three there are not. Thus, the defendant might have grounds for claiming reasonable doubt. It would be prudent, however, to analyze other windows and show that these elements are good diagnostics for the rare window.

7-16. The null hypothesis is that $\mu = 5.0$ ppm dissolved O_2 and the alternative hypothesis is that $\mu < 5.0$ ppm dissolved O_2. This is a one-tailed test and from Table 7-1, $t_{crit} = 1.90$ for the 95% confidence level and 7 degrees of freedom.

For the data set, $\bar{x} = 4.888$ and $s = 0.40$

$t = \dfrac{4.888 - 5.0}{0.40/\sqrt{8}} = -0.79 \geq -1.64$ Thus, we must accept the null hypothesis that the mean dissolved O_2 is 5.0 ppm at the 95% confidence level.

7-17. $Q = \dfrac{|5.6 - 5.1|}{5.6 - 4.3} = 0.385$ and Q_{crit} for 8 observations at 95% confidence = 0.526.

Since $Q < Q_{crit}$ the outlier value 5.6 cannot be rejected at the 95% confidence level.

7-18. H_0: $\mu = 1.0$ ppb for the impurity: H_a: $\mu < 1.0$ ppb for the impurity. This is a one-tailed test. The type I error for this situation would be that we reject the null hypothesis when, in fact, it is true, i.e. we decide the impurity is < 1.0 ppb at some level of confidence when, in fact, it is not < 1.0 ppb. The type II error would be that we accept the null hypothesis when, in fact, it is false, i.e. we decide the impurity is not < 1.0 ppb at some level of confidence when, in fact, it is < 1.0 ppb.

7-19. The null hypothesis is that for the pollutant the current level = the previous level (H_0: $\mu_{current} = \mu_{previous}$). The alternative hypothesis is H_a: $\mu_{current} > \mu_{previous}$ This would be a one-tailed test. The type I error for this situation would be that we reject the null hypothesis when, in fact, it is true, i.e. we decide the level of the pollutant is > the previous level at some level of confidence when, in fact, it is not. The type II error would be that we accept the null hypothesis when, in fact, it is false, i.e. we decide the level of the pollutant = the previous level when, in fact, it is > than the previous level.

7-20. **(a)** H_0: $\mu_{ISE} = \mu_{EDTA}$, H_a: $\mu_{ISE} \neq \mu_{EDTA}$. This would be a two-tailed test. The type I error for this situation would be that we decide the methods agree when they do not. The type II error would be that we decide the methods do not agree when they do.

(b) H_0: $\mu = 7.03$ ppm; H_a: $\mu = < 7.03$ ppm. This is a one-tailed test. The type I error for this situation would be that we reject H_0 decide that a systematic error exists when it does not. The type II error would be that we accept H_0 decide a systematic error does not exist when it does.

(c) H_0:$\sigma^2_X = \sigma^2_Y$; H_a $\sigma^2_X < \sigma^2_Y$. This is a one-tailed test. The type I error would be that we decide that $\sigma^2_X < \sigma^2_Y$ when it is not. The type II error would be that we decide that $\sigma^2_X = \sigma^2_Y$ when actually $\sigma^2_X < \sigma^2_Y$.

(d) H_0: $\sigma^2_{AA} = \sigma^2_{EC}$; H_a: $\sigma^2_{AA} < \sigma^2_{EC}$. This is a one-tailed test. The type I error for this situation would be that we decide AA results are less precise than electrochemistry results, when the precision is the same. The type II error would be that we decide the precision is the same when they electrochemical results are more precise.

7-21. **(a)** For the Top data set, $\bar{x} = 26.338$

For the bottom data set, $\bar{x} = 26.254$

$s_{pooled} = 0.1199$

degrees of freedom = 5 +5 – 2 = 8

For 8 degrees of freedom at 95% confidence t_{crit} = 2.31

$t = \dfrac{26.338 - 26.254}{0.1199\sqrt{\dfrac{5+5}{5\times5}}} = 1.11$ Since $t < t_{crit}$, we conclude that no significant difference exists at 95% confidence level.

(b) From the data, $N = 5$, $\overline{d} = 0.084$ and $s_d = 0.015166$

For 4 degrees of freedom at 95% confidence $t = 2.78$

$$t = \frac{0.084 - 0}{0.015/\sqrt{5}} = 12.52$$

Since 12.52 > 2.78, a significant difference does exist at 95% confidence level.

(c) The large sample to sample variability causes s_{Top} and s_{Bottom} to be large and masks the differences between the samples taken from the top and the bottom.

7-22. **(a)** A paired *t* test should definitely be used in this case due to the large variation in the Cl concentrations resulting from the various contact times and various locations from which the samples were obtained.

(b) H_0: $\mu_d = 0$; H_a: $\mu_A \neq 0$, where μ_d is the mean difference between the methods

From the data $N = 8$, $\overline{d} = -0.414$ and $s_d = 0.32$

For 7 degrees of freedom at 90% confidence level, $t_{\text{crit}} = 1.90$

$$t = \frac{0.414 - 0}{0.32/\sqrt{8}} = 3.65$$

Since $t > t_{\text{crit}}$, a significant difference is indicated at the 90% confidence level

(c) For 7 degrees of freedom at 95% confidence level, $t_{\text{crit}} = 2.36$

Therefore, a significant difference in the 2 methods exists at the 95% confidence level.

For 7 degrees of freedom at the 99% confidence level, $t_{\text{crit}} = 3.50$

Thus, a significant difference is indicated even at the 99% confidence level. The conclusion does not depend on which of the three confidence levels is used.

7-23. For the first data set: $\bar{x} = 2.2978$

For the second data set: $\bar{x} = 2.3106$

$s_{\text{pooled}} = 0.0027$

Degrees of freedom = 4 + 3 – 2 = 5

$$t = \frac{2.2978 - 2.3106}{0.0027\sqrt{\frac{4+3}{4\times 3}}} = -6.207$$

For 5 degrees of freedom at the 99% confidence level, t = 4.03 and at the 99.9% confidence level, t = 6.87. Thus, we can be between 99% and 99.9% confident that the nitrogen prepared in the two ways is different. The Excel TDIST(x,df,tails) function can be used to calculate the probability of getting a t value of –6.207. In this case we find TDIST(6.207,5,2) = 0.0016. Therefore, we can be 99.84% confident that the nitrogen prepared in the two ways is different. There is a 0.16% probability of this conclusion being in error.

7-24. **(a)**

Source	**SS**	**df**	**MS**	**F**
Between soils	0.374 – 0.0972 = 0.2768	3 – 1 = 2	0.2768/2 = 0.1384	0.1384/0.0081 = 17.09
Within soils	12 × 0.0081 = 0.0972	15 – 3 = 12	0.0081	
Total	0.374	15 – 1 = 14		

(b) H_0: $\mu_{\text{samp1}} = \mu_{\text{samp2}} = \mu_{\text{samp3}}$; H_a: at least two of the means differ.

(c) From Table 7-4 the F value for 12 degrees of freedom in the denominator and 2 degrees of freedom in the numerator at the 95% confidence level is 3.89. Since the F value calculated in the table exceeds F critical, we reject H_0 and conclude that the phosphorous contents of the soil samples taken from the 3 locations are different.

7-25 **(a)**

Source	SS	df	MS	F
Between juices	4 × 7.715 = 30.86	5 – 1 = 4	0.913 × 8.45 = 7.715	8.45
Within juices	25 × 0.913 = 22.825	30 – 5 = 25	0.913	
Total	30.86 + 22.82 = 50.68	30 – 1 = 29		

(b) H_0: $\mu_{\text{brand1}} = \mu_{\text{brand2}} = \mu_{\text{brand3}} = \mu_{\text{brand4}} = \mu_{\text{brand5}}$; H_a: at least two of the means differ.

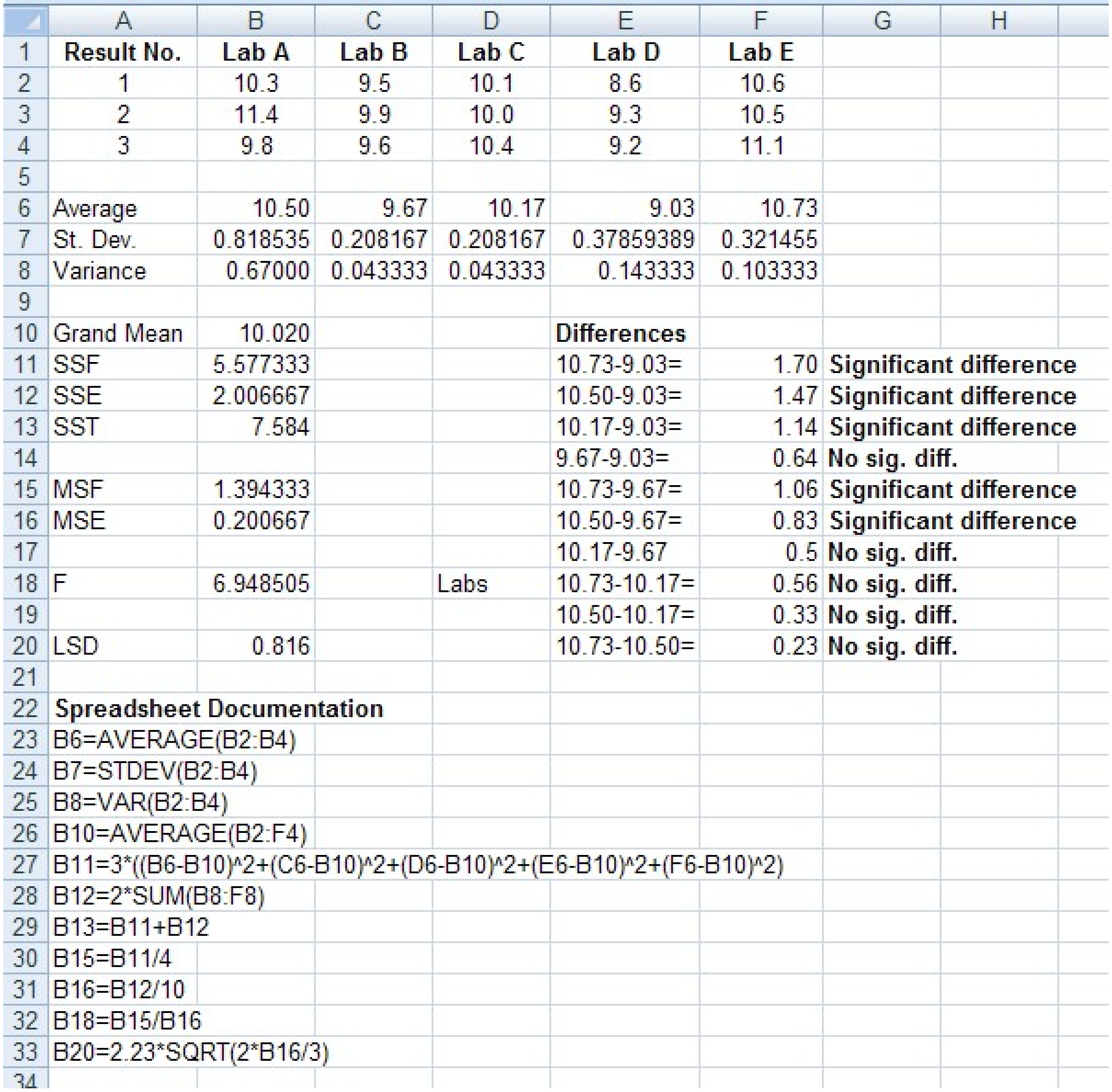
(c) The Excel FINV(prob,df1,df2) function can be used to calculate the *F* value for the above problem. In this case we find FINV(0.05,4,25) = 2.76. Since *F* calculated exceeds *F* critical, we reject the null hypothesis and conclude that the average ascorbic acid contents of the 5 brands of orange juice differ at the 95% confidence level.

7-26. **(a)** H_0: $\mu_{\text{LabA}} = \mu_{\text{LabB}} = \mu_{\text{LabC}} = \mu_{\text{LabD}} = \mu_{\text{LabE}}$; H_a: at least two of the means differ.

(b) See spreadsheet next page. From Table 7-4 the *F* value for 4 degrees of freedom in the numerator and 10 degrees of freedom in the denominator at 95% is 3.48. Since *F* calculated exceeds *F* tabulated we reject H_0 and conclude that the laboratories differ at 95% confidence. We can also be 99% confident that the laboratories differ, but we cannot be 99.9% confident that the laboratories differ.

(c) Based on the calculated LSD value laboratories A, C and E differ from laboratory D, but laboratory B does not. Laboratories E and A differ from laboratory B, but laboratory C does not. No significant difference exists between laboratories E and A.

Spreadsheet for Pb. 7-26.



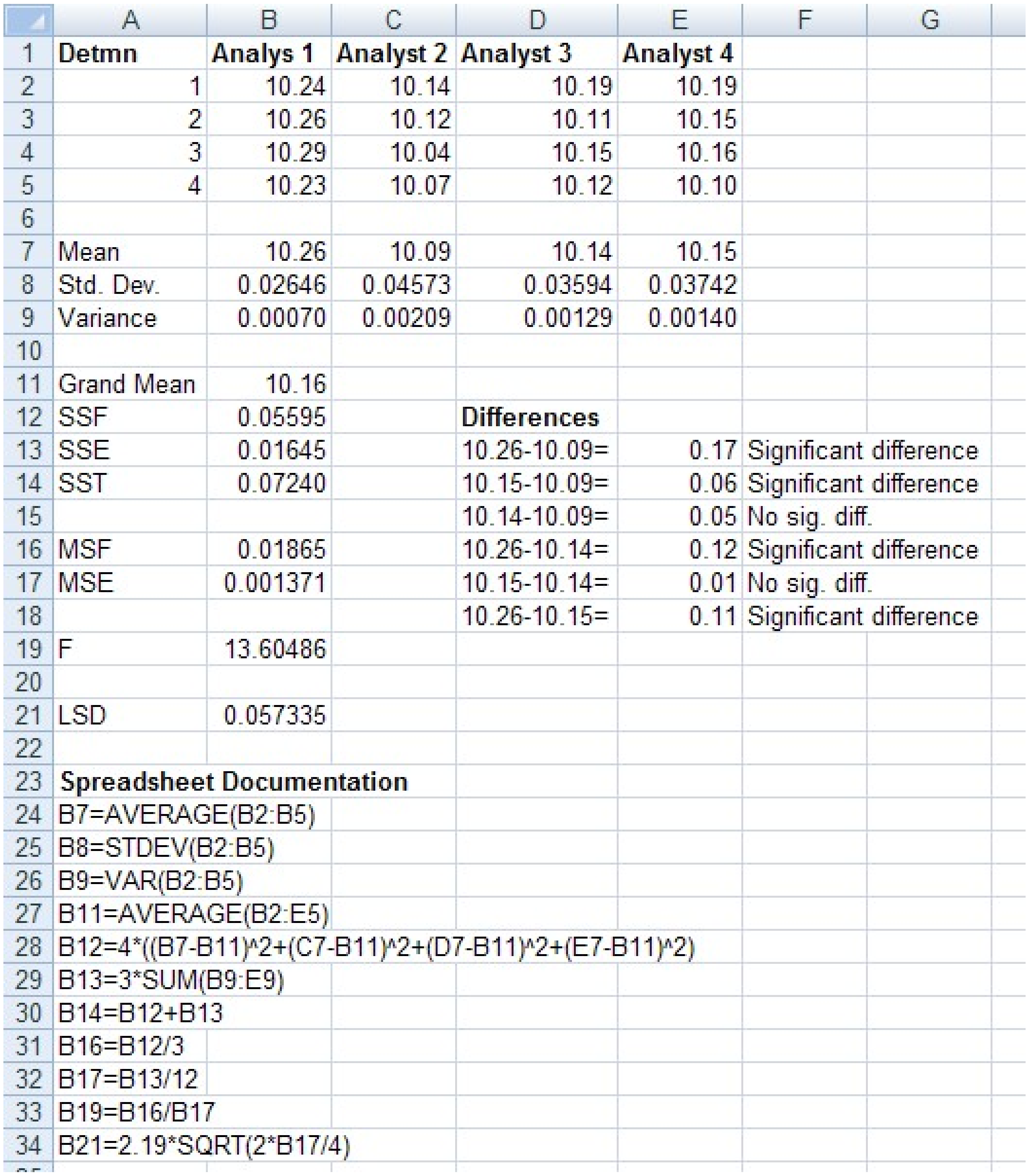
	A	B	C	D	E	F	G	H
1	**Result No.**	**Lab A**	**Lab B**	**Lab C**	**Lab D**	**Lab E**		
2	1	10.3	9.5	10.1	8.6	10.6		
3	2	11.4	9.9	10.0	9.3	10.5		
4	3	9.8	9.6	10.4	9.2	11.1		
5								
6	Average	10.50	9.67	10.17	9.03	10.73		
7	St. Dev.	0.818535	0.208167	0.208167	0.37859389	0.321455		
8	Variance	0.67000	0.043333	0.043333	0.143333	0.103333		
9								
10	Grand Mean	10.020			**Differences**			
11	SSF	5.577333			10.73-9.03=	1.70	**Significant difference**	
12	SSE	2.006667			10.50-9.03=	1.47	**Significant difference**	
13	SST	7.584			10.17-9.03=	1.14	**Significant difference**	
14					9.67-9.03=	0.64	**No sig. diff.**	
15	MSF	1.394333			10.73-9.67=	1.06	**Significant difference**	
16	MSE	0.200667			10.50-9.67=	0.83	**Significant difference**	
17					10.17-9.67	0.5	**No sig. diff.**	
18	F	6.948505		Labs	10.73-10.17=	0.56	**No sig. diff.**	
19					10.50-10.17=	0.33	**No sig. diff.**	
20	LSD	0.816			10.73-10.50=	0.23	**No sig. diff.**	
21								
22	**Spreadsheet Documentation**							
23	B6=AVERAGE(B2:B4)							
24	B7=STDEV(B2:B4)							
25	B8=VAR(B2:B4)							
26	B10=AVERAGE(B2:F4)							
27	B11=3*((B6-B10)^2+(C6-B10)^2+(D6-B10)^2+(E6-B10)^2+(F6-B10)^2)							
28	B12=2*SUM(B8:F8)							
29	B13=B11+B12							
30	B15=B11/4							
31	B16=B12/10							
32	B18=B15/B16							
33	B20=2.23*SQRT(2*B16/3)							
34								

7-27. **(a)** H_0: $\mu_{\text{Analyst1}} = \mu_{\text{Analyst2}} = \mu_{\text{Analyst3}} = \mu_{\text{Analyst4}}$; H_a: at least two of the means differ.

(b) See spreadsheet next page. From Table 7-4 the *F* value for 3 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is 3.49. Since *F* calculated exceeds *F* critical, we reject the null hypothesis and conclude that the analysts differ at 95% confidence. The *F* value calculated of 13.60 also exceeds the critical values at the 99% and 99.9% confidence levels so that we can be certain that the analysts differ at these confidence levels.

(c) Based on the calculated LSD value there is a significant difference between analyst 2 and analysts 1 and 4, but not analyst 3. There is a significant difference between analyst 3 and analyst 1, but not analyst 4. There is a significant difference between analyst 1 and analyst 4.

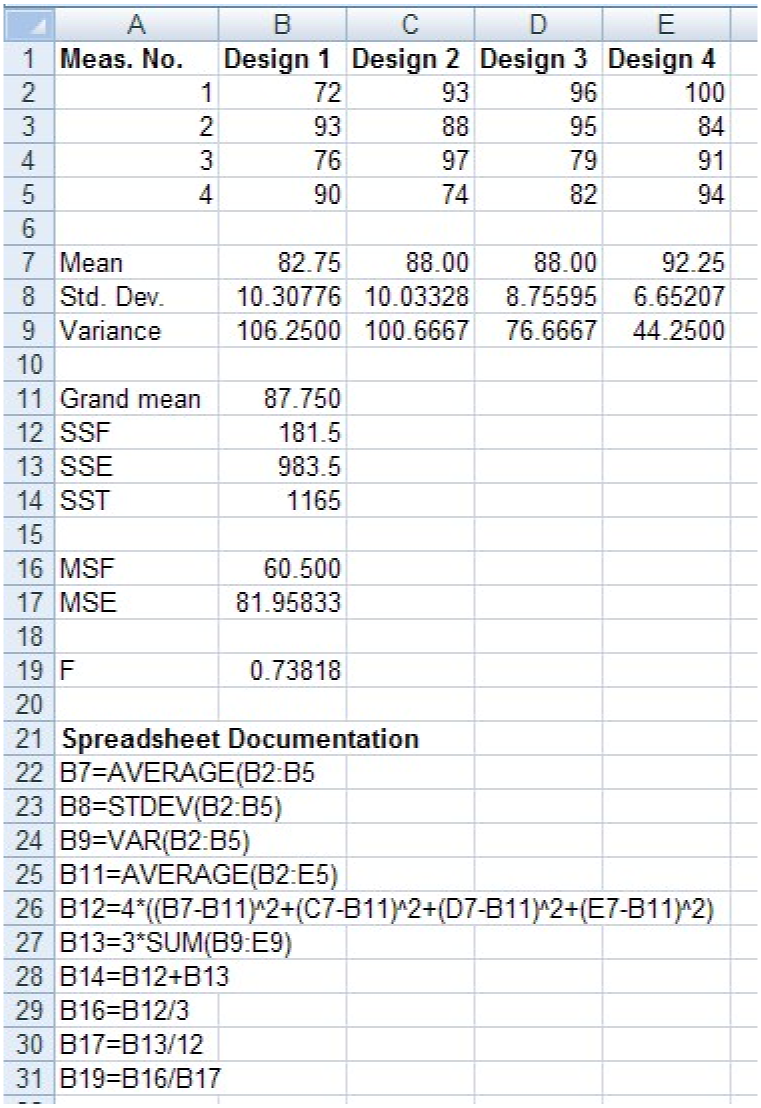
Spreadsheet for Problem 7-27.



	A	B	C	D	E	F	G
1	**Detmn**	**Analys 1**	**Analyst 2**	**Analyst 3**	**Analyst 4**		
2	1	10.24	10.14	10.19	10.19		
3	2	10.26	10.12	10.11	10.15		
4	3	10.29	10.04	10.15	10.16		
5	4	10.23	10.07	10.12	10.10		
6							
7	Mean	10.26	10.09	10.14	10.15		
8	Std. Dev.	0.02646	0.04573	0.03594	0.03742		
9	Variance	0.00070	0.00209	0.00129	0.00140		
10							
11	Grand Mean	10.16					
12	SSF	0.05595		**Differences**			
13	SSE	0.01645		10.26-10.09=	0.17	Significant difference	
14	SST	0.07240		10.15-10.09=	0.06	Significant difference	
15				10.14-10.09=	0.05	No sig. diff.	
16	MSF	0.01865		10.26-10.14=	0.12	Significant difference	
17	MSE	0.001371		10.15-10.14=	0.01	No sig. diff.	
18				10.26-10.15=	0.11	Significant difference	
19	F	13.60486					
20							
21	LSD	0.057335					
22							
23	**Spreadsheet Documentation**						
24	B7=AVERAGE(B2:B5)						
25	B8=STDEV(B2:B5)						
26	B9=VAR(B2:B5)						
27	B11=AVERAGE(B2:E5)						
28	B12=4*((B7-B11)^2+(C7-B11)^2+(D7-B11)^2+(E7-B11)^2)						
29	B13=3*SUM(B9:E9)						
30	B14=B12+B13						
31	B16=B12/3						
32	B17=B13/12						
33	B19=B16/B17						
34	B21=2.19*SQRT(2*B17/4)						

7-28. **(a)** H_0: $\mu_{\mathrm{Des1}} = \mu_{\mathrm{Des2}} = \mu_{\mathrm{Des3}} = \mu_{\mathrm{Des4}}$; H_a: at least two of the means differ.

(b) See Spreadsheet.



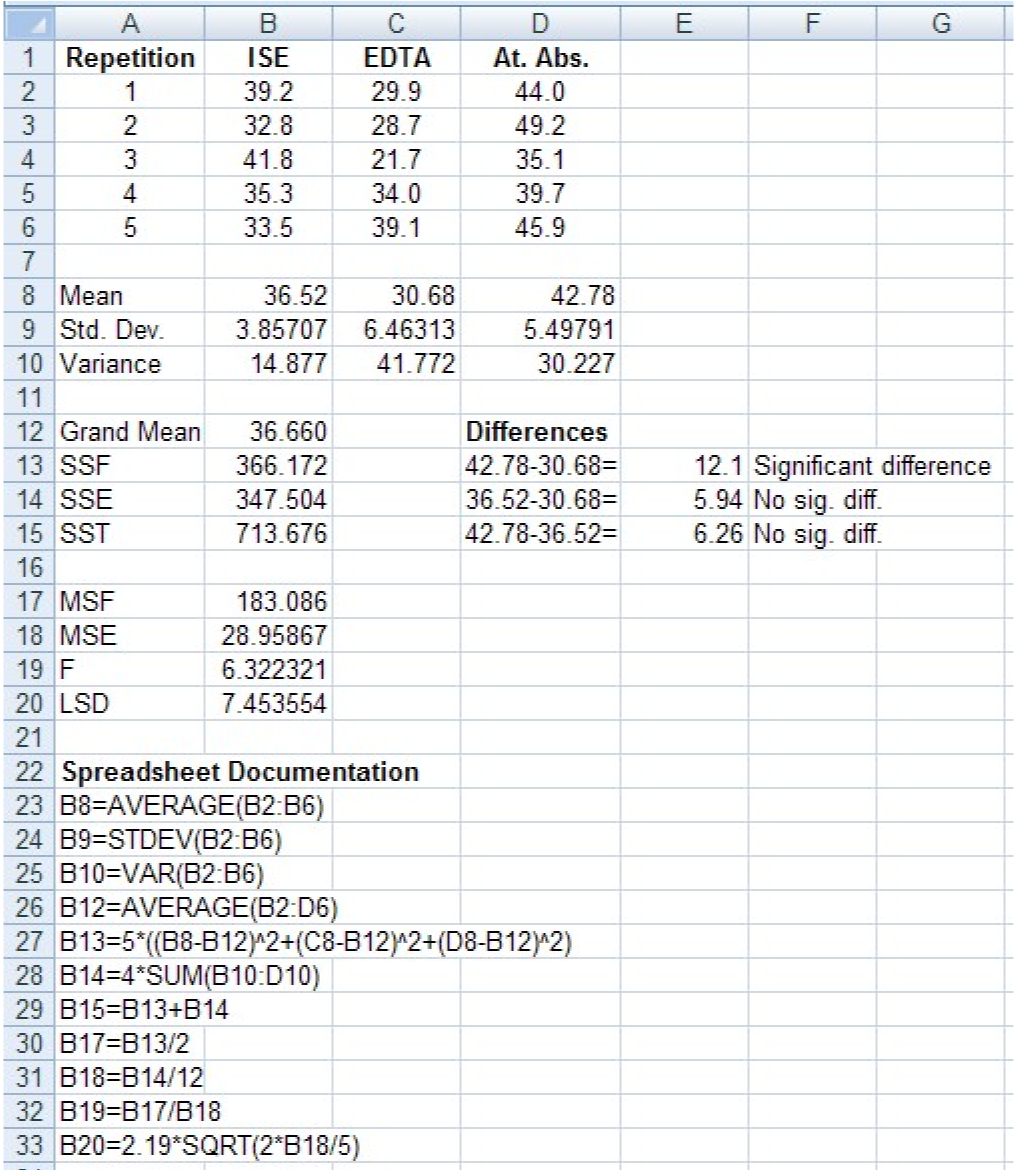
	A	B	C	D	E
1	**Meas. No.**	**Design 1**	**Design 2**	**Design 3**	**Design 4**
2	1	72	93	96	100
3	2	93	88	95	84
4	3	76	97	79	91
5	4	90	74	82	94
6					
7	Mean	82.75	88.00	88.00	92.25
8	Std. Dev.	10.30776	10.03328	8.75595	6.65207
9	Variance	106.2500	100.6667	76.6667	44.2500
10					
11	Grand mean	87.750			
12	SSF	181.5			
13	SSE	983.5			
14	SST	1165			
15					
16	MSF	60.500			
17	MSE	81.95833			
18					
19	F	0.73818			
20					
21	**Spreadsheet Documentation**				
22	B7=AVERAGE(B2:B5				
23	B8=STDEV(B2:B5)				
24	B9=VAR(B2:B5)				
25	B11=AVERAGE(B2:E5)				
26	B12=4*((B7-B11)^2+(C7-B11)^2+(D7-B11)^2+(E7-B11)^2)				
27	B13=3*SUM(B9:E9)				
28	B14=B12+B13				
29	B16=B12/3				
30	B17=B13/12				
31	B19=B16/B17				

From Table 7-4 the *F* value for 3 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is 3.49. Since *F* calculated is less than *F* critical, we accept the null hypothesis and conclude that 4 flow cell designs give the same results at the 95% confidence level.

(c) No differences were detected.

7-29. **(a)** H_0: $\mu_{\text{ISE}} = \mu_{\text{EDTA}} = \mu_{\text{AA}}$; H_a: at least two of the means differ.

(b) See Spreadsheet



	A	B	C	D	E	F	G
1	**Repetition**	**ISE**	**EDTA**	**At. Abs.**			
2	1	39.2	29.9	44.0			
3	2	32.8	28.7	49.2			
4	3	41.8	21.7	35.1			
5	4	35.3	34.0	39.7			
6	5	33.5	39.1	45.9			
7							
8	Mean	36.52	30.68	42.78			
9	Std. Dev.	3.85707	6.46313	5.49791			
10	Variance	14.877	41.772	30.227			
11							
12	Grand Mean	36.660		**Differences**			
13	SSF	366.172		42.78-30.68=	12.1	Significant difference	
14	SSE	347.504		36.52-30.68=	5.94	No sig. diff.	
15	SST	713.676		42.78-36.52=	6.26	No sig. diff.	
16							
17	MSF	183.086					
18	MSE	28.95867					
19	F	6.322321					
20	LSD	7.453554					
21							
22	**Spreadsheet Documentation**						
23	B8=AVERAGE(B2:B6)						
24	B9=STDEV(B2:B6)						
25	B10=VAR(B2:B6)						
26	B12=AVERAGE(B2:D6)						
27	B13=5*((B8-B12)^2+(C8-B12)^2+(D8-B12)^2)						
28	B14=4*SUM(B10:D10)						
29	B15=B13+B14						
30	B17=B13/2						
31	B18=B14/12						
32	B19=B17/B18						
33	B20=2.19*SQRT(2*B18/5)						

From Table 7-4 the *F* value for 2 degrees of freedom in the numerator and 12 degrees of freedom in the denominator at 95% is 3.89. Since *F* calculated is greater than *F* critical, we reject the null hypothesis and conclude that the 3 methods give different results at the 95% confidence level.

(c) Based on the calculated LSD value there is a significant difference between the atomic absorption method and the EDTA titration. There is no significant difference between the EDTA titration method and the ion-selective electrode method and there is no significant difference between the atomic absorption method and the ion-selective electrode method.

7-30. **(a)** $Q = \frac{|41.27 - 41.61|}{41.84 - 41.27} = 0.596$ and Q_{crit} for 4 observations at 95% confidence = 0.829.

Since $Q < Q_{\text{crit}}$ the outlier value 41.27 cannot be rejected with 95% confidence.

(b) $Q = \frac{|7.388 - 7.295|}{7.388 - 7.284} = 0.894$ and Q_{crit} for 4 observations at 95% confidence = 0.829.

Since $Q > Q_{\text{crit}}$ the outlier value 7.388 can be rejected with 95% confidence.

7-31. **(a)** $Q = \frac{|85.10 - 84.70|}{85.10 - 84.62} = 0.833$ and Q_{crit} for 3 observations at 95% confidence = 0.970.

Since $Q < Q_{\text{crit}}$ the outlier value 85.10 cannot be rejected with 95% confidence.

(b) $Q = \frac{|85.10 - 84.70|}{85.10 - 84.62} = 0.833$ and Q_{crit} for 4 observations at 95% confidence = 0.829.

Since $Q > Q_{\text{crit}}$ the outlier value 85.10 can be rejected with 95% confidence.

7-32. $Q = \frac{|4.60 - 4.50|}{4.60 - 4.40} = 0.5$ and Q_{crit} for 5 observations at 95% confidence = 0.710.

Since $Q < Q_{\text{crit}}$ the outlier value 4.60 ppm cannot be rejected with 95% confidence.

Chapter 8

8-1. The sample size is in the micro range and the analyte level is in the trace range. Hence, the analysis is a micro analysis of a trace constituent.

8-2. The objective of the sampling step is to produce a homogeneous laboratory sample of a few hundred grams or less having a composition that is identical to the average composition of the bulk of the material being sampled. Statistically, we try to obtain a mean value that is an unbiased estimate of the population mean and a variance that is an unbiased estimate of the population variance.

8-3. Step 1: Identify the population from which the sample is to be drawn.

Step 2: Collect the gross sample.

Step 3: Reduce the gross sample to a laboratory sample, which is a small quantity of homogeneous material

8-4. The gross sample mass is determined by (1) the uncertainty that can be tolerated between the composition of the gross sample and that of the whole, (2) the degree of heterogeneity of the whole, and (3) the level of particle size at which heterogeneity begins.

8-5. $s_o^2 = s_s^2 + s_m^2$

From the NIST sample: $s_m^2 = 0.00947$

From the gross sample: $s_o^2 = 0.15547$

$$s_s = \sqrt{0.15547 - 0.00947} = 0.38$$

The relative standard deviation = $\left(\dfrac{s_s}{\bar{x}}\right)\times 100\% = \left(\dfrac{0.38}{49.92}\right)\times 100\% = 0.76\%$

8-6. **(a)** $\sigma_r = \sqrt{(1-p)/Np}$ (where p = 14/250 = 0.0560)

$$\sigma_r = \sqrt{(1-0.0560)/(250\times 0.0560)} = 0.260 \quad \underline{\underline{\text{or } 26\%}}$$

(b) σ= 14 × 0.26 = 3.6 = $\underline{\underline{\text{4 tablets}}}$

95% CI = $14 \pm z\sigma\sqrt{N} = 14 \pm 1.96 \times 3.6/\sqrt{1} = 14 \pm 7$

(where z = 1.96 was obtained from Table 7-1)

(c) $N = (1 - 0.056)/[(0.05)^2 \times 0.056] = 6743 = 6.743 \times 10^3$

8-7. **(a)** $N = \dfrac{(1-p)}{p\sigma_r^2} = \dfrac{(1-0.02)}{0.02\,(0.20)^2} = \dfrac{49.0}{(0.20)^2} = 1225$

(b) $N = 49.0/(0.12)^2 = 3403$

(c) $N = 49.0/(0.07)^2 = 10000$

(d) $N = 49.0/(0.02)^2 = 122500$

8-8. **(a)** $250 = \dfrac{(1-52/250)}{(52/250)\times\sigma_r^2}$

$\sigma_r = 0.12 = 12\%$

(b) Here, the absolute standard deviation $\sigma$of the estimate is sought.

σ = 750 × 12(52/250)0.12 = 224.6 = 220 broken bottles

(c) 90% CI = 750 × 12 × 52/250 ± $zs/\sqrt{N}$ = $1872 \pm 1.64\times 224.6/\sqrt{1}$

= 1872 ± 368 = 1900 ± 400 broken bottles

(d) $N = \dfrac{(1-0.21)}{0.21(0.05)^2}$ = 1500 bottles

8-9. $N = p(1-p)\left(\dfrac{d_A d_B}{d^2}\right)^2\left(\dfrac{P_A - P_B}{\sigma_r P}\right)^2$

(a) $d = 7.3 \times 0.15 + 2.6 \times 0.85 = 3.3$

$P = 0.15 \times 7.3 \times 0.87 \times 100 / 3.3 = 29\%$

$N = 0.15(1-0.15)\left(\dfrac{7.3\times 2.6}{(3.3)^2}\right)^2\left(\dfrac{87-0}{0.020\times 29}\right)^2$ = 8714 particles

(b) mass = $(4/3)\pi(r)^3 \times d \times N = (4/3)\,\pi\,(0.175\text{ cm})^3 \times 3.3(\text{g/cm}^3) \times 8.714 \times 10^3$

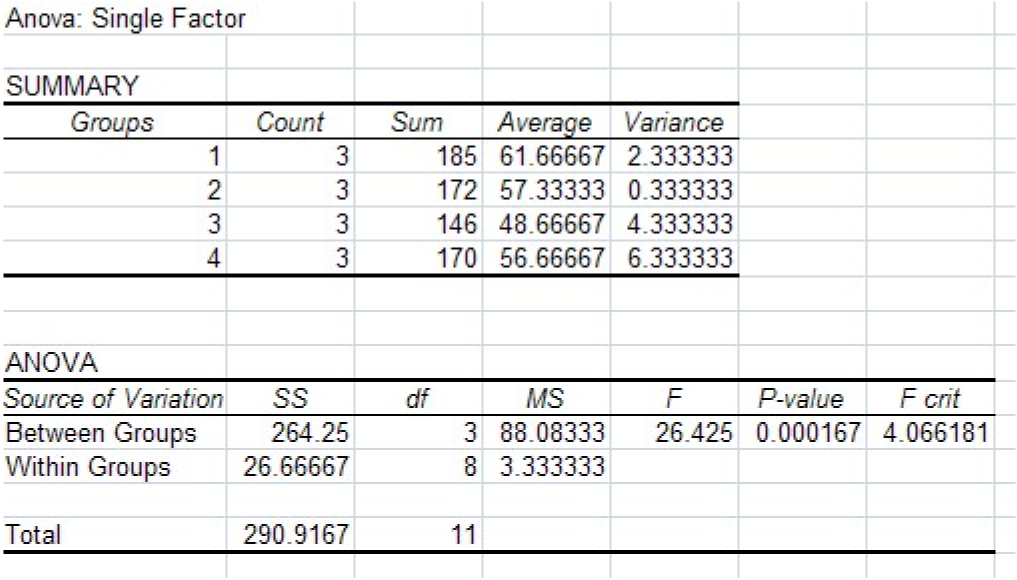
= 650 g

(c) $0.500 = (4/3)\pi(r)^3 \times 3.3(\text{g/cm}^3) \times 8.714 \times 10^3$

$r = 0.016$ cm (diameter = 0.32 mm)

8-10. Recall that $s_o^2 = s_s^2 + s_m^2$. For both Scheme A and Scheme B the contribution of the method variance, s_m^2, will be both small relative to the sampling variance, s_s^2, and essentially the same. The sampling variancewill be lower for Scheme A, however, since 5 samples are blended and then evaluated as opposed to 3 samples that are unblended in Scheme B. Thus, Scheme A will have the lower variance.

8-11. (a) The following single-factor ANOVA table was generated using Excel's Data Analysis Tools:



Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
1	3	185	61.66667	2.333333
2	3	172	57.33333	0.333333
3	3	146	48.66667	4.333333
4	3	170	56.66667	6.333333

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	264.25	3	88.08333	26.425	0.000167	4.066181
Within Groups	26.66667	8	3.333333			
Total	290.9167	11				

The Between Groups *SS* value of 264.25 compared to the Within Groups value of 26.66667 indicates that the mean concentrations vary significantly from day to day.

(b) SST is the total variance and is the sum of the within day variance, SSE, and the day-to-day variance, SSF; SST = SSE + SSF. The within day variance, SSE, reflects the method variance, SSM. The day-to-day variance, SSF, reflects the sum of the method variance, SSM, and the sampling variance, SSS; SSF = SSM + SSS. Thus,

SST = SSM + SSM + SSS and SSS = SST – 2×SSM

SSS = 290.92 – 2×26.67 = 237.58. Dividing 3 degrees of freedom gives a mean square (estimates sampling variance σ_s^2) of 79.19.

(c) The best approach to lowering the overall variance would be to reduce the sampling variance, since this is the major component of the total variance (σ_t^2 = 88.08333).

8-12. See Example 8-1

d = 7.3 × 0.01 + 2.6 × 0.99 = 2.6 g/cm^3

P = 0.01 × 7.3 × 0.87 × 100 / 2.6 = 2.4%

$$N = 0.01(1-0.01)\left(\frac{7.3\times2.6}{2.6\times2.6}\right)^2\left(\frac{87-0}{0.05\times2.4}\right)^2 = 4.1\times10^4 \text{ particles}$$

mass = (4/3)π(0.25)^3× 2.6 × 4.1 × 10^4 / 454 = 15 lb;

Since the seller took only a 5 lb sample and 15 lbs was needed, this is insufficient.

8-13. See Example 8-3

Using t = 1.96 for infinite samples $N = \dfrac{(1.96)^2\times(0.3)^2}{(3.7)^2\times(0.07)^2} = 5.16$

Using t = 2.78 for 5 samples (4 df) $N = \dfrac{(2.78)^2\times(0.3)^2}{(3.7)^2\times(0.07)^2} = 10.36$

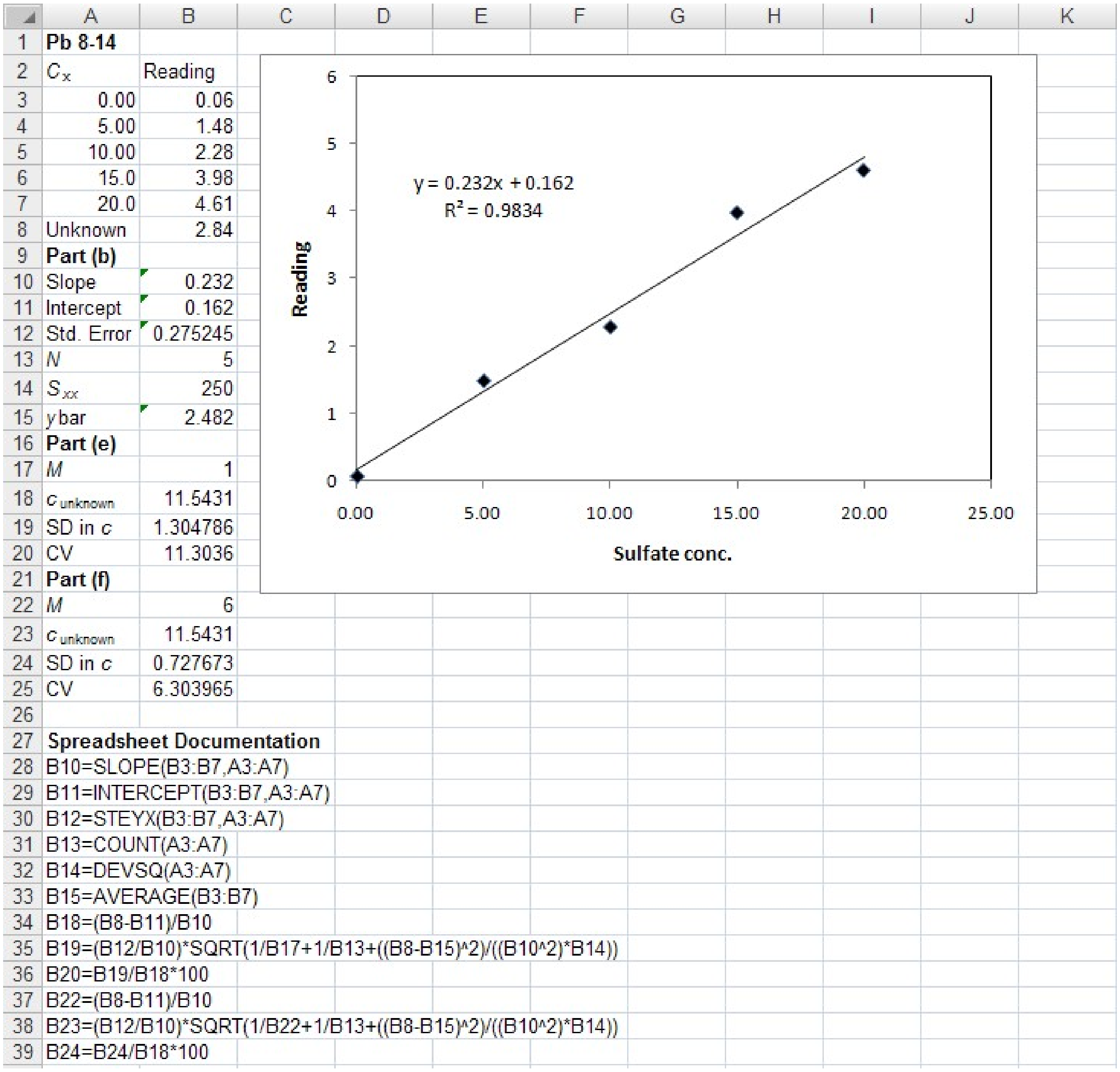
Using t = 2.26 for 10 samples $N = \dfrac{(2.26)^2\times(0.3)^2}{(3.7)^2\times(0.07)^2} = 6.85$

Using t = 2.45 for 7 samples $N = \dfrac{(2.45)^2\times(0.3)^2}{(3.7)^2\times(0.07)^2} = 8.05$

Using t = 2.36 for 8 samples $N = \dfrac{(2.36)^2\times(0.3)^2}{(3.7)^2\times(0.07)^2} = 7.47$

The iterations converge at between 7 and 8 samples, so 8 should be taken for safety.

8-14.



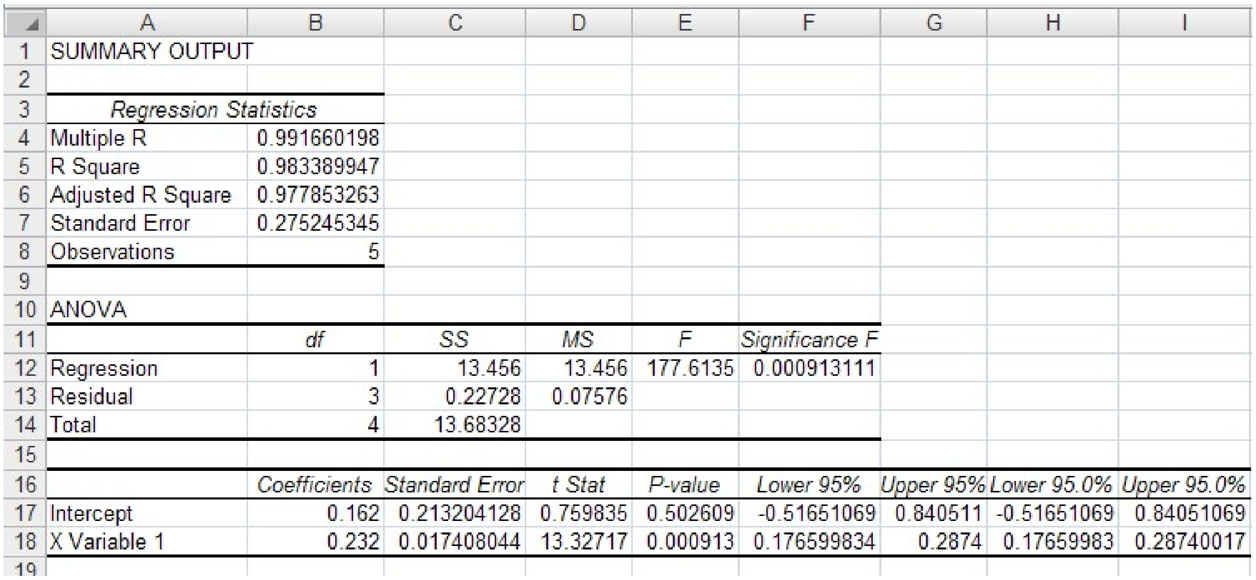
	A	B
1	**Pb 8-14**	
2	C_x	Reading
3	0.00	0.06
4	5.00	1.48
5	10.00	2.28
6	15.0	3.98
7	20.0	4.61
8	Unknown	2.84
9	**Part (b)**	
10	Slope	0.232
11	Intercept	0.162
12	Std. Error	0.275245
13	*N*	5
14	S_{xx}	250
15	ybar	2.482
16	**Part (e)**	
17	*M*	1
18	c_{unknown}	11.5431
19	SD in *c*	1.304786
20	CV	11.3036
21	**Part (f)**	
22	*M*	6
23	c_{unknown}	11.5431
24	SD in *c*	0.727673
25	CV	6.303965
26		
27	**Spreadsheet Documentation**	
28	B10=SLOPE(B3:B7,A3:A7)	
29	B11=INTERCEPT(B3:B7,A3:A7)	
30	B12=STEYX(B3:B7,A3:A7)	
31	B13=COUNT(A3:A7)	
32	B14=DEVSQ(A3:A7)	
33	B15=AVERAGE(B3:B7)	
34	B18=(B8-B11)/B10	
35	B19=(B12/B10)*SQRT(1/B17+1/B13+((B8-B15)^2)/((B10^2)*B14))	
36	B20=B19/B18*100	
37	B22=(B8-B11)/B10	
38	B23=(B12/B10)*SQRT(1/B22+1/B13+((B8-B15)^2)/((B10^2)*B14))	
39	B24=B24/B18*100	

(a) See spreadsheet

(b) m = 0.232 and b = 0.162

(c) See spreadsheet

(d) Regression statistic generated using Excel's Data Analysis Tools



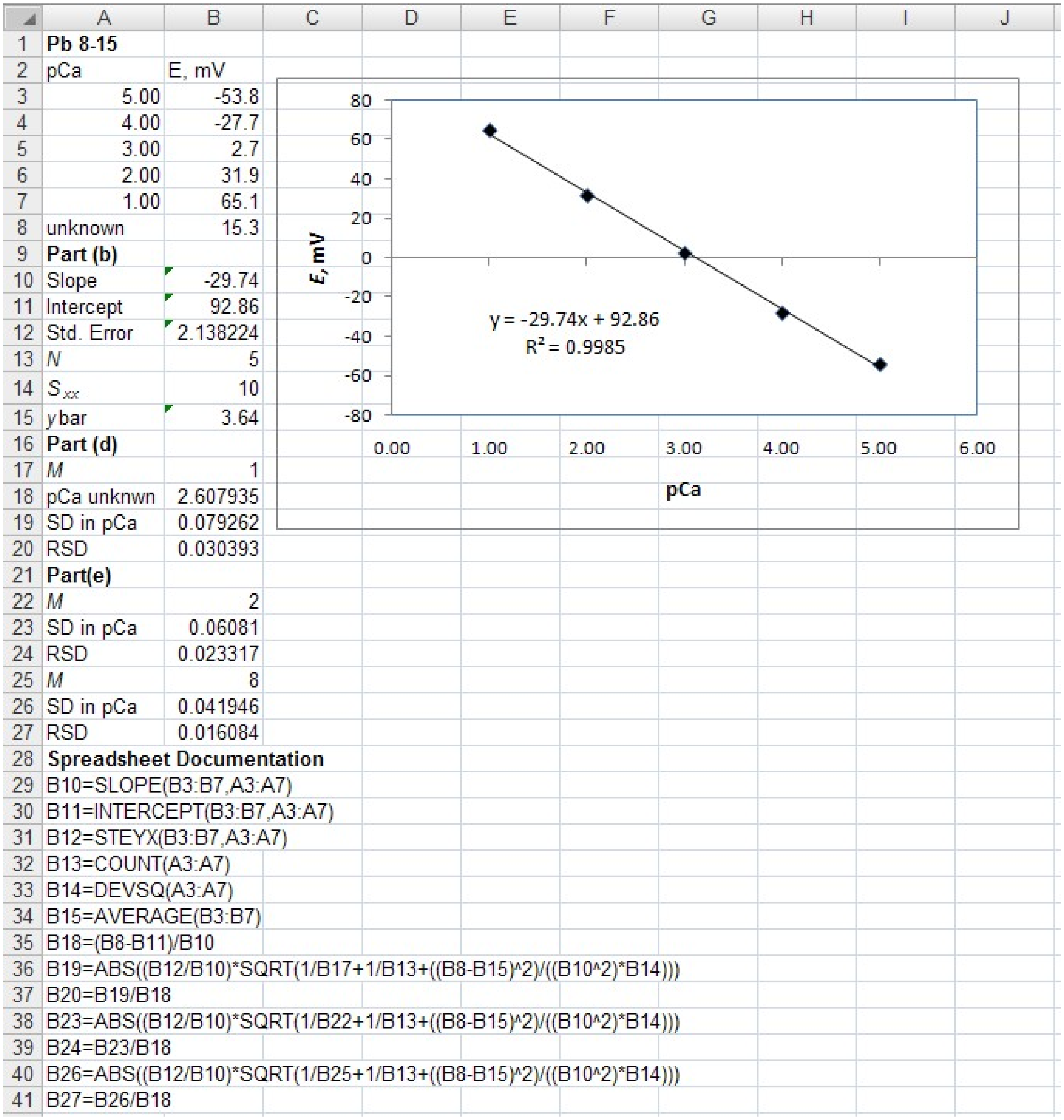
	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.991660198							
5	R Square	0.983389947							
6	Adjusted R Square	0.977853263							
7	Standard Error	0.275245345							
8	Observations	5							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	13.456	13.456	177.6135	0.000913111			
13	Residual	3	0.22728	0.07576					
14	Total	4	13.68328						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	0.162	0.213204128	0.759835	0.502609	-0.51651069	0.840511	-0.51651069	0.84051069
18	X Variable 1	0.232	0.017408044	13.32717	0.000913	0.176599834	0.2874	0.17659983	0.28740017
19									

The large F value of 177.6 indicates that the regression is significant. The R^2 value of 0.9834 measures the fraction of the variation explained by the regression. The adjusted R^2 value of 0.9779 indicates the price to pay for adding an additional parameter.

(e) c_{Unk} = 11.5 mg/mL; s_{Unk} = 1.3 mg/mL; CV = 11.3%

(f) c_{Unk} = 11.5 mg/mL; s_{Unk} = 0.73 mg/mL; CV = 6.3%

8-15.

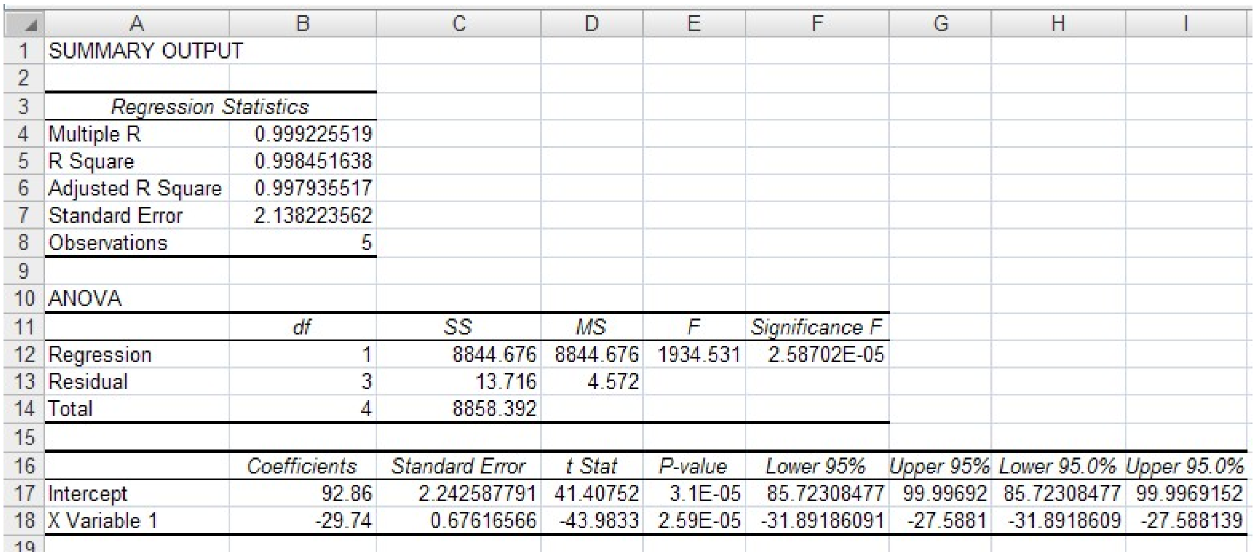


	A	B
1	**Pb 8-15**	
2	pCa	E, mV
3	5.00	-53.8
4	4.00	-27.7
5	3.00	2.7
6	2.00	31.9
7	1.00	65.1
8	unknown	15.3
9	**Part (b)**	
10	Slope	-29.74
11	Intercept	92.86
12	Std. Error	2.138224
13	*N*	5
14	S_{xx}	10
15	*y* bar	3.64
16	**Part (d)**	
17	*M*	1
18	pCa unknwn	2.607935
19	SD in pCa	0.079262
20	RSD	0.030393
21	**Part(e)**	
22	*M*	2
23	SD in pCa	0.06081
24	RSD	0.023317
25	*M*	8
26	SD in pCa	0.041946
27	RSD	0.016084
28	**Spreadsheet Documentation**	
29	B10=SLOPE(B3:B7,A3:A7)	
30	B11=INTERCEPT(B3:B7,A3:A7)	
31	B12=STEYX(B3:B7,A3:A7)	
32	B13=COUNT(A3:A7)	
33	B14=DEVSQ(A3:A7)	
34	B15=AVERAGE(B3:B7)	
35	B18=(B8-B11)/B10	
36	B19=ABS((B12/B10)*SQRT(1/B17+1/B13+((B8-B15)^2)/((B10^2)*B14)))	
37	B20=B19/B18	
38	B23=ABS((B12/B10)*SQRT(1/B22+1/B13+((B8-B15)^2)/((B10^2)*B14)))	
39	B24=B23/B18	
40	B26=ABS((B12/B10)*SQRT(1/B25+1/B13+((B8-B15)^2)/((B10^2)*B14)))	
41	B27=B26/B18	

(a) See spreadsheet

(b) Equation of the line: y = –29.74 x + 92.86

(c) Regression statistics generated with Excel's Data Analysis Tools



	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.999225519							
5	R Square	0.998451638							
6	Adjusted R Square	0.997935517							
7	Standard Error	2.138223562							
8	Observations	5							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	8844.676	8844.676	1934.531	2.58702E-05			
13	Residual	3	13.716	4.572					
14	Total	4	8858.392						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	92.86	2.242587791	41.40752	3.1E-05	85.72308477	99.99692	85.72308477	99.9969152
18	X Variable 1	-29.74	0.67616566	-43.9833	2.59E-05	-31.89186091	-27.5881	-31.8918609	-27.588139

The large *F* value of 1934.5 indicates that the regression is significant. The R^2 value of 0.9985 measures the fraction of the variation explained by the regression. The adjusted R^2 value of 0.9979 indicates the price to pay for adding an additional parameter.

(d) pCa_{Unk} = 2.608; SD in pCa = 0.079; RSD = 0.030 (CV = 3.0%)

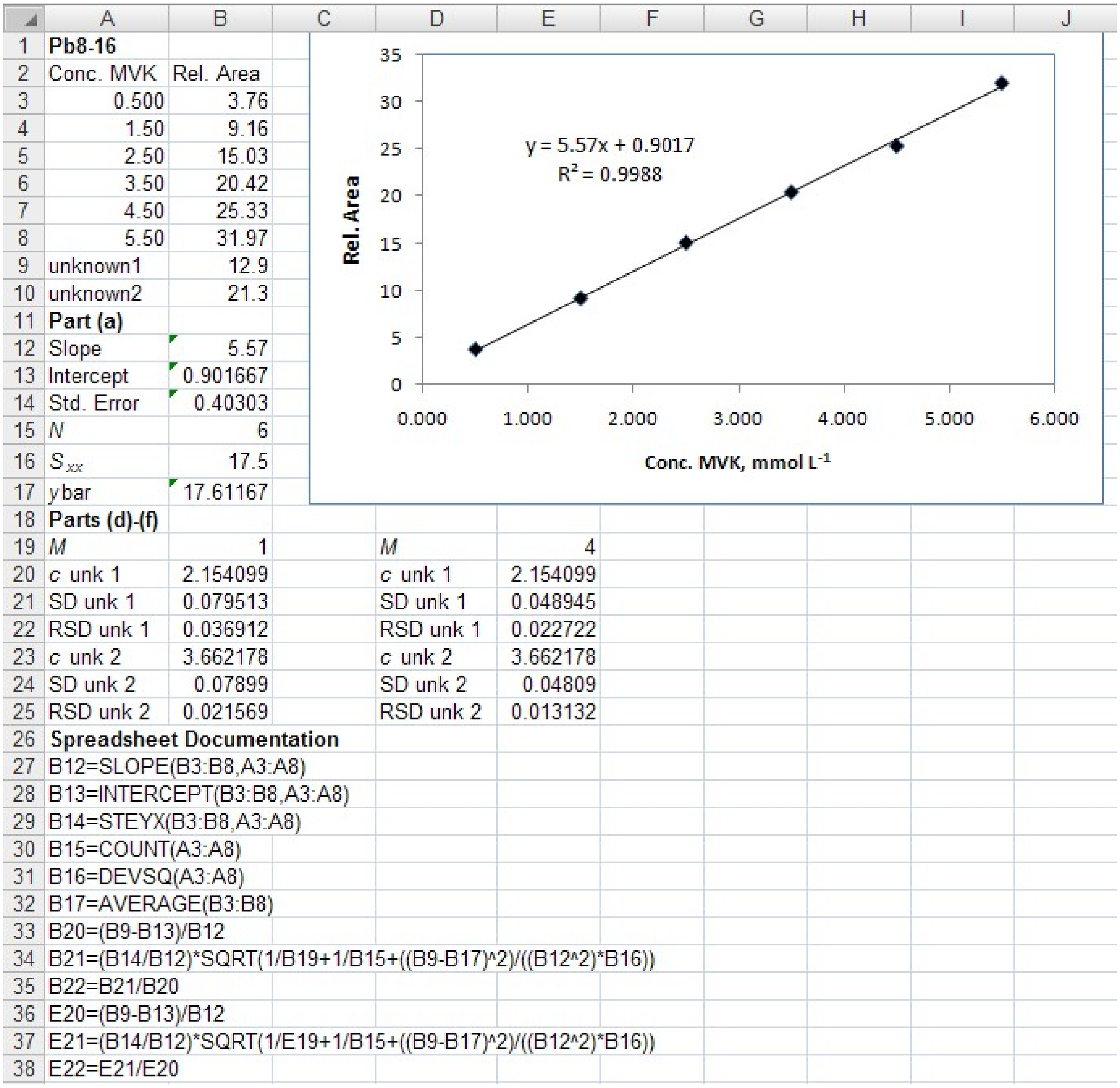
(e) For 2 replicate measurements:

pCa_{Unk} = 2.608; SD in pCa = 0.061; RSD = 0.023 (CV = 2.3%)

For 8 replicate measurements:

pCa_{Unk} = 2.608; SD in pCa = 0.042: RSD = 0.016 (CV = 1.6%)

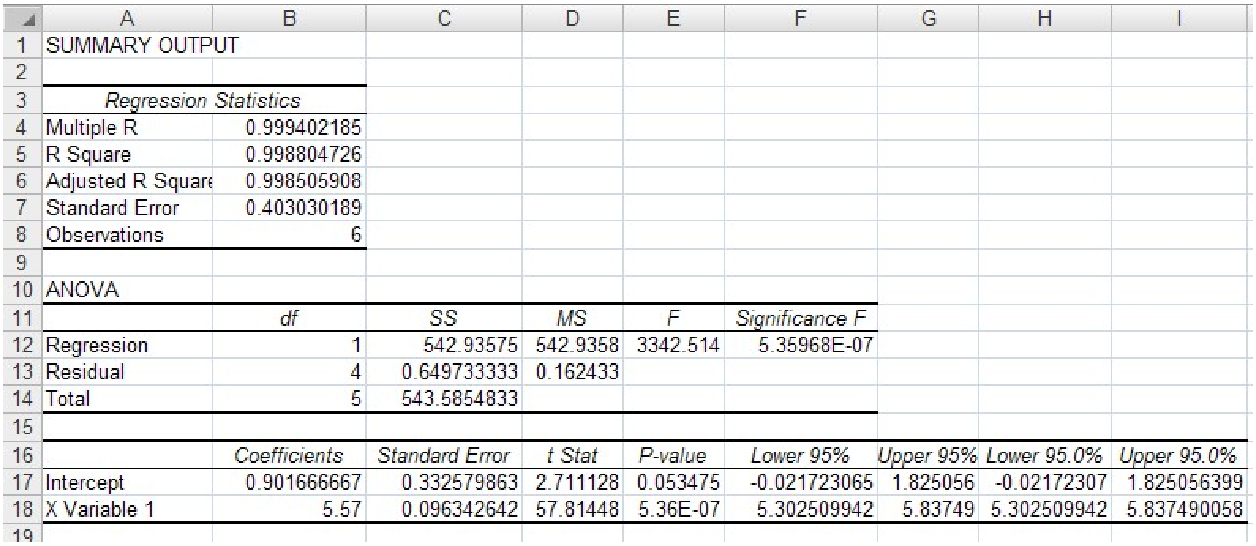
8-16.



	A	B	C	D	E
1	**Pb8-16**				
2	Conc. MVK	Rel. Area			
3	0.500	3.76			
4	1.50	9.16			
5	2.50	15.03			
6	3.50	20.42			
7	4.50	25.33			
8	5.50	31.97			
9	unknown1	12.9			
10	unknown2	21.3			
11	**Part (a)**				
12	Slope	5.57			
13	Intercept	0.901667			
14	Std. Error	0.40303			
15	*N*	6			
16	S_{xx}	17.5			
17	ybar	17.61167			
18	**Parts (d)-(f)**				
19	*M*	1		*M*	4
20	*c* unk 1	2.154099		*c* unk 1	2.154099
21	SD unk 1	0.079513		SD unk 1	0.048945
22	RSD unk 1	0.036912		RSD unk 1	0.022722
23	*c* unk 2	3.662178		*c* unk 2	3.662178
24	SD unk 2	0.07899		SD unk 2	0.04809
25	RSD unk 2	0.021569		RSD unk 2	0.013132
26	**Spreadsheet Documentation**				
27	B12=SLOPE(B3:B8,A3:A8)				
28	B13=INTERCEPT(B3:B8,A3:A8)				
29	B14=STEYX(B3:B8,A3:A8)				
30	B15=COUNT(A3:A8)				
31	B16=DEVSQ(A3:A8)				
32	B17=AVERAGE(B3:B8)				
33	B20=(B9-B13)/B12				
34	B21=(B14/B12)*SQRT(1/B19+1/B15+((B9-B17)^2)/((B12^2)*B16))				
35	B22=B21/B20				
36	E20=(B9-B13)/B12				
37	E21=(B14/B12)*SQRT(1/E19+1/B15+((B9-B17)^2)/((B12^2)*B16))				
38	E22=E21/E20				

(a) m = 5.57 and b = 0.90

(b) Regression statistics



	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.999402185							
5	R Square	0.998804726							
6	Adjusted R Square	0.998505908							
7	Standard Error	0.403030189							
8	Observations	6							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	542.93575	542.9358	3342.514	5.35968E-07			
13	Residual	4	0.649733333	0.162433					
14	Total	5	543.5854833						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	0.901666667	0.332579863	2.711128	0.053475	-0.021723065	1.825056	-0.02172307	1.825056399
18	X Variable 1	5.57	0.096342642	57.81448	5.36E-07	5.302509942	5.83749	5.302509942	5.837490058

(c) See spreadsheet

(d) *c* of MVK in unknown 1 = 2.15 mmol L^{-1}

(e) For 1 measurement, SD = 0.080 mmol L^{-1}; RSD = 0.037

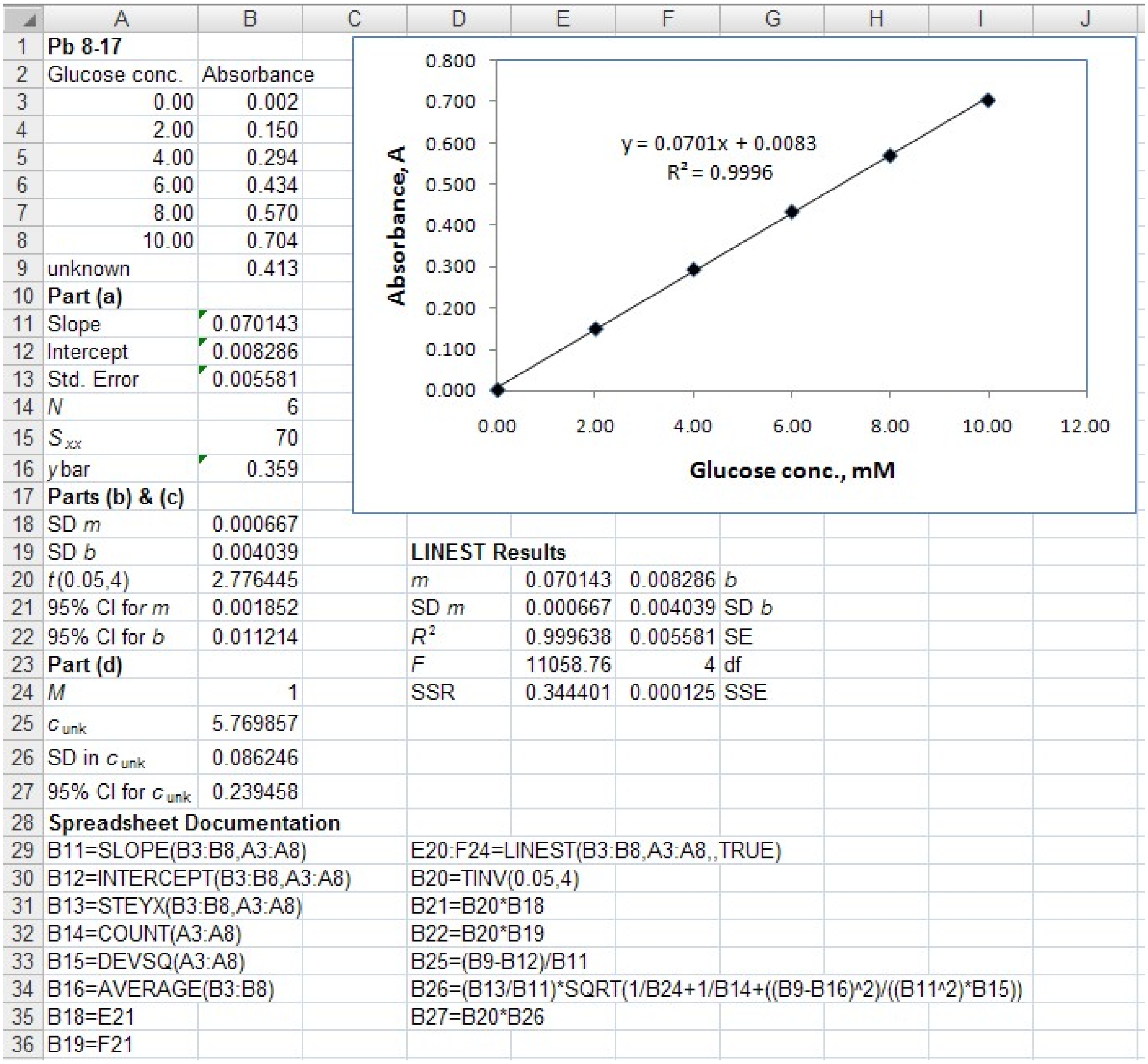
For 4 replicates, SD = 0.049 mmol L^{-1}; RSD = 0.023

(f) *c* of MVK in unknown 2 = 3.66 mmol L^{-1}

SD for 1 measurement = 0.079; RSD = 0.022

SD for 4 replicates = 0.048; RSD = 0.013

8-17.



	A	B	C	D	E	F	G	H	I	J
1	**Pb 8-17**									
2	Glucose conc.	Absorbance								
3	0.00	0.002								
4	2.00	0.150								
5	4.00	0.294								
6	6.00	0.434								
7	8.00	0.570								
8	10.00	0.704								
9	unknown	0.413								
10	**Part (a)**									
11	Slope	0.070143								
12	Intercept	0.008286								
13	Std. Error	0.005581								
14	*N*	6								
15	S_{xx}	70								
16	*y*bar	0.359								
17	**Parts (b) & (c)**									
18	SD *m*	0.000667								
19	SD *b*	0.004039		**LINEST Results**						
20	*t*(0.05,4)	2.776445		*m*	0.070143	0.008286	*b*			
21	95% CI for *m*	0.001852		SD *m*	0.000667	0.004039	SD *b*			
22	95% CI for *b*	0.011214		R^2	0.999638	0.005581	SE			
23	**Part (d)**			*F*	11058.76	4	df			
24	*M*	1		SSR	0.344401	0.000125	SSE			
25	c_{unk}	5.769857								
26	SD in c_{unk}	0.086246								
27	95% CI for c_{unk}	0.239458								
28	**Spreadsheet Documentation**									
29	B11=SLOPE(B3:B8,A3:A8)			E20:F24=LINEST(B3:B8,A3:A8,,TRUE)						
30	B12=INTERCEPT(B3:B8,A3:A8)			B20=TINV(0.05,4)						
31	B13=STEYX(B3:B8,A3:A8)			B21=B20*B18						
32	B14=COUNT(A3:A8)			B22=B20*B19						
33	B15=DEVSQ(A3:A8)			B25=(B9-B12)/B11						
34	B16=AVERAGE(B3:B8)			B26=(B13/B11)*SQRT(1/B24+1/B14+((B9-B16)^2)/((B11^2)*B15))						
35	B18=E21			B27=B20*B26						
36	B19=F21									

(a) $m = 0.07014$ and $b = 0.008286$

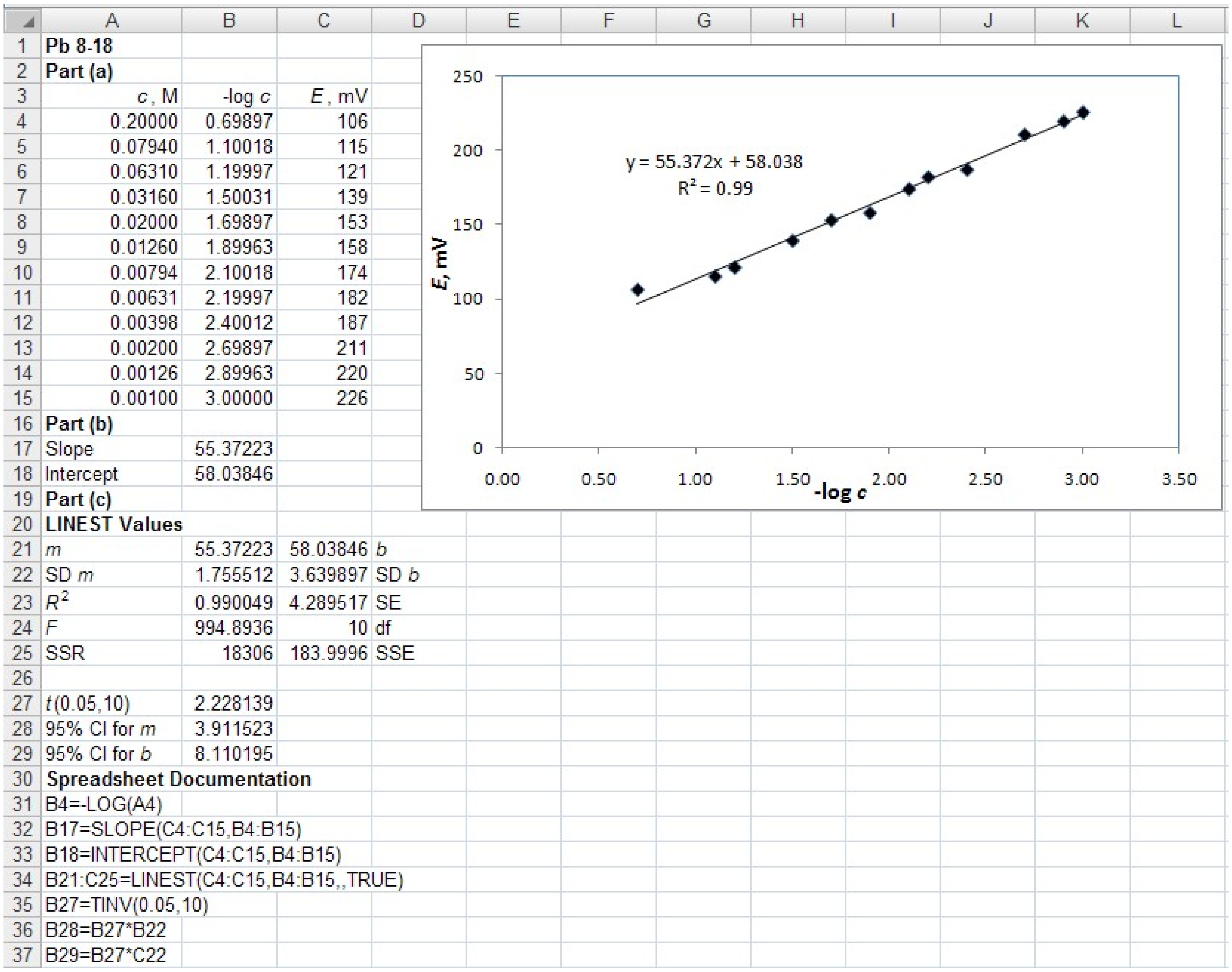
(b) $s_m = 0.00067$; $s_b = 0.004039$; SE = 0.00558

(c) $95\%\ \text{CI}_m = m \pm t \times s_m = 0.07014 \pm 0.0019$

$95\%\ \text{CI}_b = b \pm t \times s_b = 0.0083 \pm 0.0112$

(d) $c_{\text{unk}} = 5.77$ mM; $s_{\text{unk}} = 0.09$; $95\%\ \text{CI}_{\text{unk}} = c_{\text{unk}} \pm t \times s_{\text{Unk}} = 5.77 \pm 0.24$ mM

8-18.



	A	B	C	D
1	**Pb 8-18**			
2	**Part (a)**			
3	*c*, M	-log *c*	*E*, mV	
4	0.20000	0.69897	106	
5	0.07940	1.10018	115	
6	0.06310	1.19997	121	
7	0.03160	1.50031	139	
8	0.02000	1.69897	153	
9	0.01260	1.89963	158	
10	0.00794	2.10018	174	
11	0.00631	2.19997	182	
12	0.00398	2.40012	187	
13	0.00200	2.69897	211	
14	0.00126	2.89963	220	
15	0.00100	3.00000	226	
16	**Part (b)**			
17	Slope	55.37223		
18	Intercept	58.03846		
19	**Part (c)**			
20	**LINEST Values**			
21	*m*	55.37223	58.03846	*b*
22	SD *m*	1.755512	3.639897	SD *b*
23	R^2	0.990049	4.289517	SE
24	*F*	994.8936	10	df
25	SSR	18306	183.9996	SSE
26				
27	*t*(0.05,10)	2.228139		
28	95% CI for *m*	3.911523		
29	95% CI for *b*	8.110195		
30	**Spreadsheet Documentation**			
31	B4=-LOG(A4)			
32	B17=SLOPE(C4:C15,B4:B15)			
33	B18=INTERCEPT(C4:C15,B4:B15)			
34	B21:C25=LINEST(C4:C15,B4:B15,,TRUE)			
35	B27=TINV(0.05,10)			
36	B28=B27*B22			
37	B29=B27*C22			

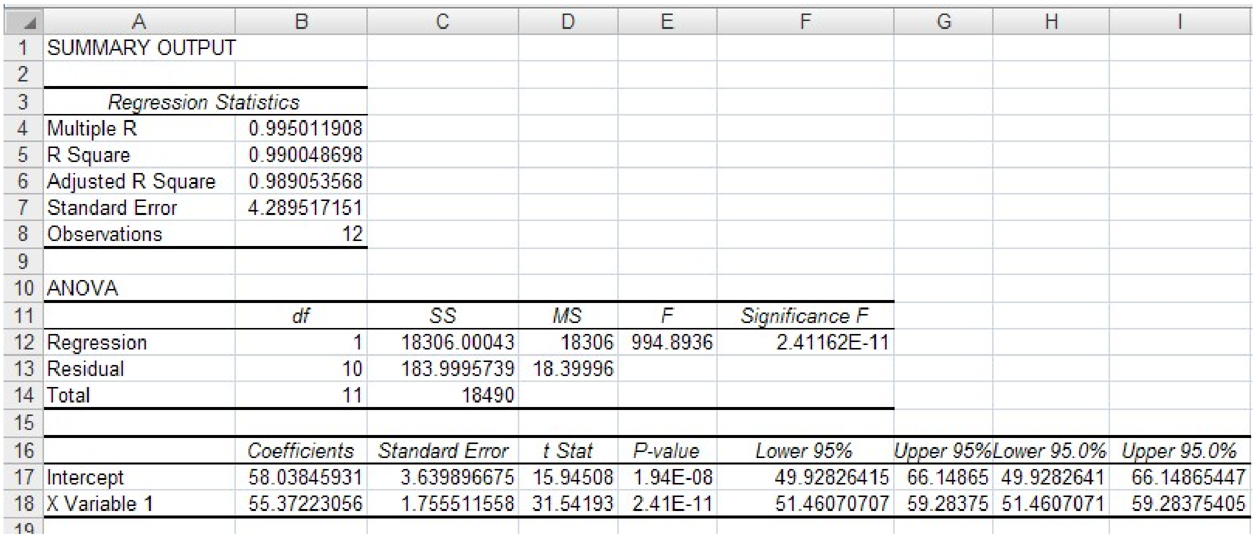
(a). See spreadsheet

(b). *m* **= 55.37;** *b* **= 58.04;** $y = 55.37\,x + 58.04$

(c). 95% CI_m = 55.37 ± 3.91 and 95% CI_b = 58.04 ± 8.11

(d). From the LINEST values, $F = 994.9$. This large value indicates that the regression is significant.

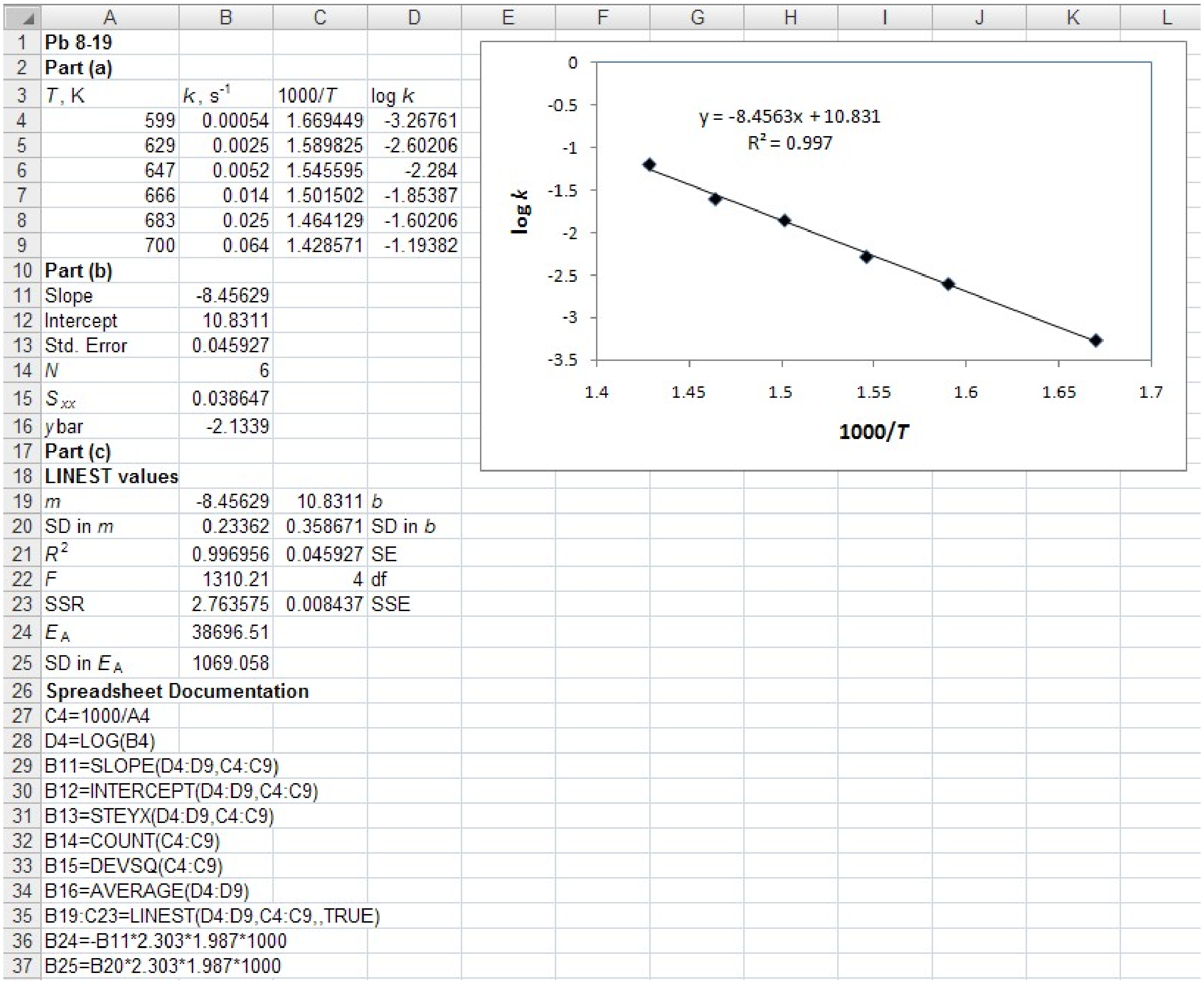
(e). Regression statistics via Excel's Data Analysis Tools:



	A	B	C	D	E	F	G	H	I
1	SUMMARY OUTPUT								
2									
3	*Regression Statistics*								
4	Multiple R	0.995011908							
5	R Square	0.990048698							
6	Adjusted R Square	0.989053568							
7	Standard Error	4.289517151							
8	Observations	12							
9									
10	ANOVA								
11		*df*	*SS*	*MS*	*F*	*Significance F*			
12	Regression	1	18306.00043	18306	994.8936	2.41162E-11			
13	Residual	10	183.9995739	18.39996					
14	Total	11	18490						
15									
16		*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
17	Intercept	58.03845931	3.639896675	15.94508	1.94E-08	49.92826415	66.14865	49.9282641	66.14865447
18	X Variable 1	55.37223056	1.755511558	31.54193	2.41E-11	51.46070707	59.28375	51.4607071	59.28375405

From either LINEST or the regression statistics, the standard error = 4.29. The correlation coefficient $R=\sqrt{R^2}=\sqrt{0.990048698}=0.995$, and the multiple *R* is also 0.995.

8-19.



	A	B	C	D
1	**Pb 8-19**			
2	**Part (a)**			
3	*T*, K	*k*, s^{-1}	1000/*T*	log *k*
4	599	0.00054	1.669449	-3.26761
5	629	0.0025	1.589825	-2.60206
6	647	0.0052	1.545595	-2.284
7	666	0.014	1.501502	-1.85387
8	683	0.025	1.464129	-1.60206
9	700	0.064	1.428571	-1.19382
10	**Part (b)**			
11	Slope	-8.45629		
12	Intercept	10.8311		
13	Std. Error	0.045927		
14	*N*	6		
15	S_{xx}	0.038647		
16	*y*bar	-2.1339		
17	**Part (c)**			
18	**LINEST values**			
19	*m*	-8.45629	10.8311	*b*
20	SD in *m*	0.23362	0.358671	SD in *b*
21	R^2	0.996956	0.045927	SE
22	*F*	1310.21	4	df
23	SSR	2.763575	0.008437	SSE
24	E_A	38696.51		
25	SD in E_A	1069.058		
26	**Spreadsheet Documentation**			
27	C4=1000/A4			
28	D4=LOG(B4)			
29	B11=SLOPE(D4:D9,C4:C9)			
30	B12=INTERCEPT(D4:D9,C4:C9)			
31	B13=STEYX(D4:D9,C4:C9)			
32	B14=COUNT(C4:C9)			
33	B15=DEVSQ(C4:C9)			
34	B16=AVERAGE(D4:D9)			
35	B19:C23=LINEST(D4:D9,C4:C9,,TRUE)			
36	B24=-B11*2.303*1.987*1000			
37	B25=B20*2.303*1.987*1000			

(a) See Spreadsheet

(b) $m = -8.456$; $b = 10.83$ and SE = 0.0459

(c) $E_A = -m \times 2.303 \times R \times 1000$ (Note: m has units of mK) =

$-(-8.456\text{ mK})\times(2.303)\times(1.987\text{ cal mol}^{-1}\text{ K}^{-1})\times(1000\text{ K/mK})$

= 38697 cal/mol

$s_{EA} = s_m \times 2.303 \times R \times 1000$

= 1069 cal/mol

Thus, E_A = 38,697 ± 1069 cal/mol or 38.7 ± 1.1 kcal/mol

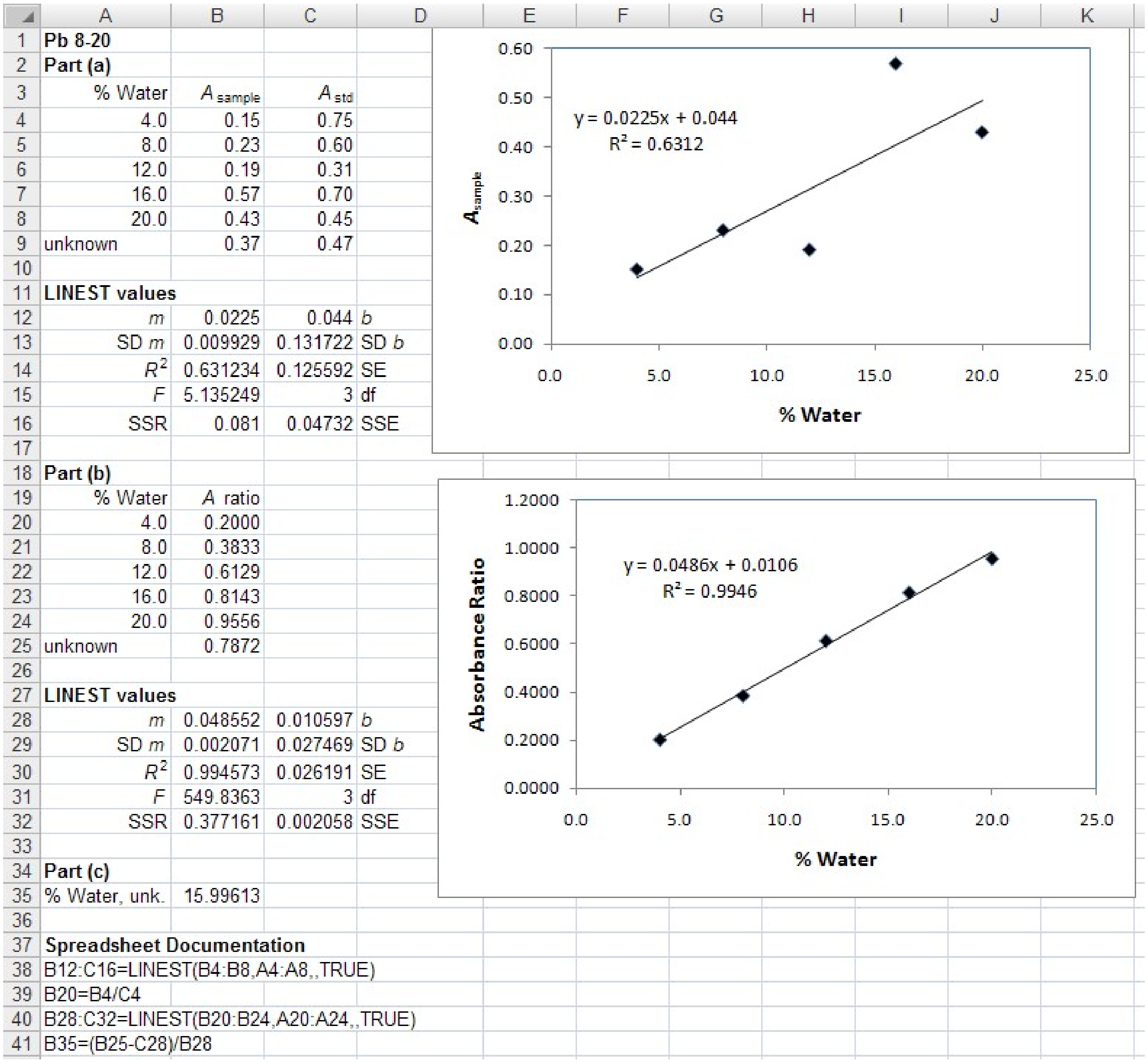
(d) H_0: E_A = 41.00 kcal/mol; H_A: $E_A \neq$ 41.00 kcal/mol.

$t = (38.697 - 41.00)/1.069 = -2.15$

$t(0.025, 4) = 2.776$

Since $t > -t_{crit}$ we retain H_0. There is no reason to doubt that E_A is not 41.00 kcal/mol at the 95% confidence level.

8-20.



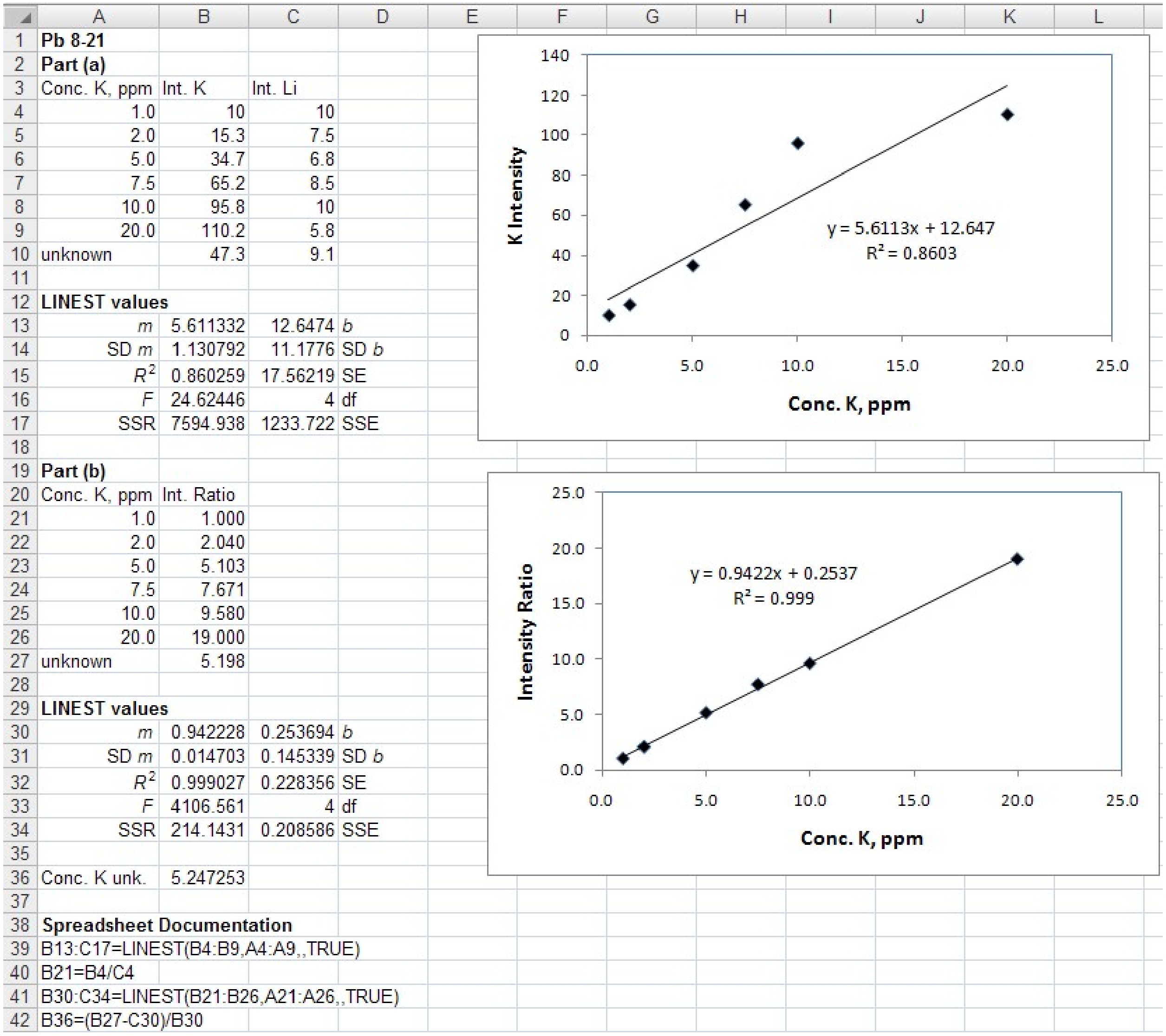
	A	B	C	D
1	**Pb 8-20**			
2	**Part (a)**			
3	% Water	*A* sample	*A* std	
4	4.0	0.15	0.75	
5	8.0	0.23	0.60	
6	12.0	0.19	0.31	
7	16.0	0.57	0.70	
8	20.0	0.43	0.45	
9	unknown	0.37	0.47	
10				
11	**LINEST values**			
12	*m*	0.0225	0.044	*b*
13	SD *m*	0.009929	0.131722	SD *b*
14	R^2	0.631234	0.125592	SE
15	*F*	5.135249	3	df
16	SSR	0.081	0.04732	SSE
17				
18	**Part (b)**			
19	% Water	*A* ratio		
20	4.0	0.2000		
21	8.0	0.3833		
22	12.0	0.6129		
23	16.0	0.8143		
24	20.0	0.9556		
25	unknown	0.7872		
26				
27	**LINEST values**			
28	*m*	0.048552	0.010597	*b*
29	SD *m*	0.002071	0.027469	SD *b*
30	R^2	0.994573	0.026191	SE
31	*F*	549.8363	3	df
32	SSR	0.377161	0.002058	SSE
33				
34	**Part (c)**			
35	% Water, unk.	15.99613		
36				
37	**Spreadsheet Documentation**			
38	B12:C16=LINEST(B4:B8,A4:A8,,TRUE)			
39	B20=B4/C4			
40	B28:C32=LINEST(B20:B24,A20:A24,,TRUE)			
41	B35=(B25-C28)/B28			

(a) See Spreadsheet

(b) The linearity is much better when using internal standards (compare R^2 and *F* values). Taking the ratio compensates for systematic errors that affect both the sample and the internal standard.

(c) 15.996% rounded to 16.0%

8-21.



	A	B	C	D
1	**Pb 8-21**			
2	**Part (a)**			
3	Conc. K, ppm	Int. K	Int. Li	
4	1.0	10	10	
5	2.0	15.3	7.5	
6	5.0	34.7	6.8	
7	7.5	65.2	8.5	
8	10.0	95.8	10	
9	20.0	110.2	5.8	
10	unknown	47.3	9.1	
11				
12	**LINEST values**			
13	*m*	5.611332	12.6474	*b*
14	SD *m*	1.130792	11.1776	SD *b*
15	R^2	0.860259	17.56219	SE
16	*F*	24.62446	4	df
17	SSR	7594.938	1233.722	SSE
18				
19	**Part (b)**			
20	Conc. K, ppm	Int. Ratio		
21	1.0	1.000		
22	2.0	2.040		
23	5.0	5.103		
24	7.5	7.671		
25	10.0	9.580		
26	20.0	19.000		
27	unknown	5.198		
28				
29	**LINEST values**			
30	*m*	0.942228	0.253694	*b*
31	SD *m*	0.014703	0.145339	SD *b*
32	R^2	0.999027	0.228356	SE
33	*F*	4106.561	4	df
34	SSR	214.1431	0.208586	SSE
35				
36	Conc. K unk.	5.247253		
37				
38	**Spreadsheet Documentation**			
39	B13:C17=LINEST(B4:B9,A4:A9,,TRUE)			
40	B21=B4/C4			
41	B30:C34=LINEST(B21:B26,A21:A26,,TRUE)			
42	B36=(B27-C30)/B30			

(a) See Spreadsheet

(b) The linearity is much better when using internal standards (compare R^2 and *F* values). Taking the ratio compensates for systematic errors that affect both the sample and the internal standard.

(c) 5.247 ppm rounded to 5.2 ppm

8-22. **(a)**

$$\frac{c_{\text{Unk}}}{(V_{\text{Std}}c_{\text{Std}} + V_{\text{Unk}}c_{\text{Unk}})/V_{\text{Tot}}} = \frac{A(\text{sample - blank})}{A(\text{sample} + \text{addition - blank})}$$

$$\frac{c_{\text{Unk}}}{\frac{(0.1000\text{ mL} \times 1000\ \mu\text{g/mL} + 100.0\text{ mL} \times c_{\text{Unk}})}{(100.1\text{ mL})}} = \frac{(0.520 - 0.020)}{1.020}$$

$$\frac{c_{\text{Unk}}}{0.99900 + 0.99900c_{\text{Unk}}} = 0.490196$$

c_{Unk} = 0.490196(0.99900 + 0.99900 c_{Unk})

0.510294 c_{Unk} = 0.489706

c_{Unk} = 0.96 μg/mL

(b) $$\frac{c_{\text{Unk}}}{\frac{(0.1000\text{ mL} \times 1000\ \mu\text{g/mL} + 100.0\text{ mL} \times c_{\text{Unk}})}{(100.1\text{ mL})}} = \frac{(0.520 - 0.100)}{(1.020 - 0.080)}$$

Proceeding as in (a) we obtain c_{Unk} = 0.81 μg/mL

%error = (0.96 – 0.81)/0.81 × 100% = 19%

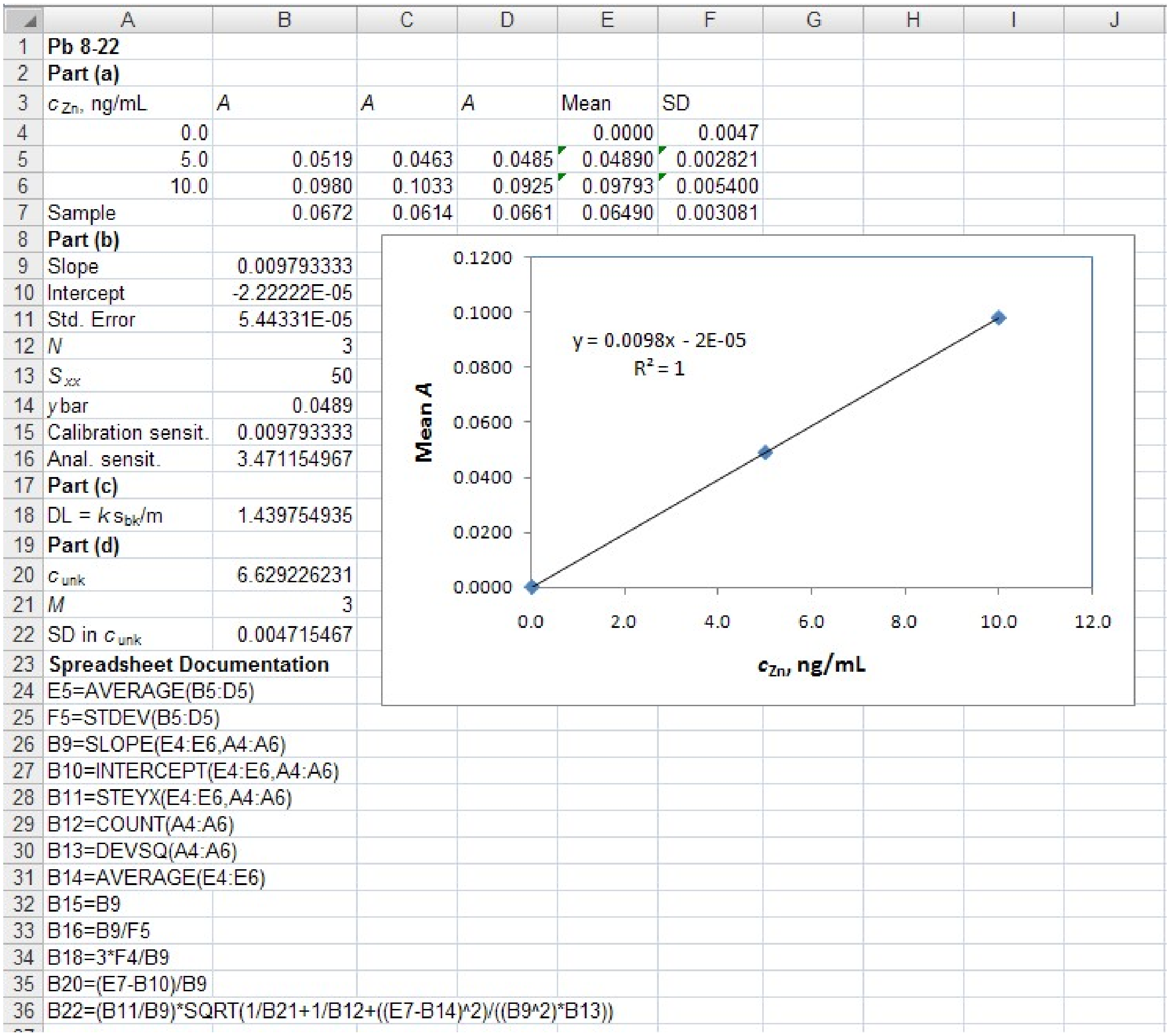
8-23. See Example 8-8

$$c_{\text{u}} = \frac{(0.300)(1.00 \times 10^{-3})(1.00)}{(0.530)(51.00) - (0.300)(50.00)} = 2.4938 \times 10^{-5}\text{ M}$$

To obtain the concentration of the original sample, we need to multiply by 25.00/1.00.

$c_{\text{u}} = (2.4938 \times 10^{-5}\text{ M})(25.00)/(1.00) = 6.23 \times 10^{-4}\text{ M}$

8-24.



	A	B	C	D	E	F	G	H	I	J
1	**Pb 8-22**									
2	**Part (a)**									
3	c_{Zn}, ng/mL	*A*	*A*	*A*	Mean	SD				
4	0.0				0.0000	0.0047				
5	5.0	0.0519	0.0463	0.0485	0.04890	0.002821				
6	10.0	0.0980	0.1033	0.0925	0.09793	0.005400				
7	Sample	0.0672	0.0614	0.0661	0.06490	0.003081				
8	**Part (b)**									
9	Slope	0.009793333								
10	Intercept	-2.22222E-05								
11	Std. Error	5.44331E-05								
12	*N*	3								
13	S_{xx}	50								
14	*y* bar	0.0489								
15	Calibration sensit.	0.009793333								
16	Anal. sensit.	3.471154967								
17	**Part (c)**									
18	DL = $k s_{bk}$/m	1.439754935								
19	**Part (d)**									
20	c_{unk}	6.629226231								
21	*M*	3								
22	SD in c_{unk}	0.004715467								
23	**Spreadsheet Documentation**									
24	E5=AVERAGE(B5:D5)									
25	F5=STDEV(B5:D5)									
26	B9=SLOPE(E4:E6,A4:A6)									
27	B10=INTERCEPT(E4:E6,A4:A6)									
28	B11=STEYX(E4:E6,A4:A6)									
29	B12=COUNT(A4:A6)									
30	B13=DEVSQ(A4:A6)									
31	B14=AVERAGE(E4:E6)									
32	B15=B9									
33	B16=B9/F5									
34	B18=3*F4/B9									
35	B20=(E7-B10)/B9									
36	B22=(B11/B9)*SQRT(1/B21+1/B12+((E7-B14)^2)/((B9^2)*B13))									

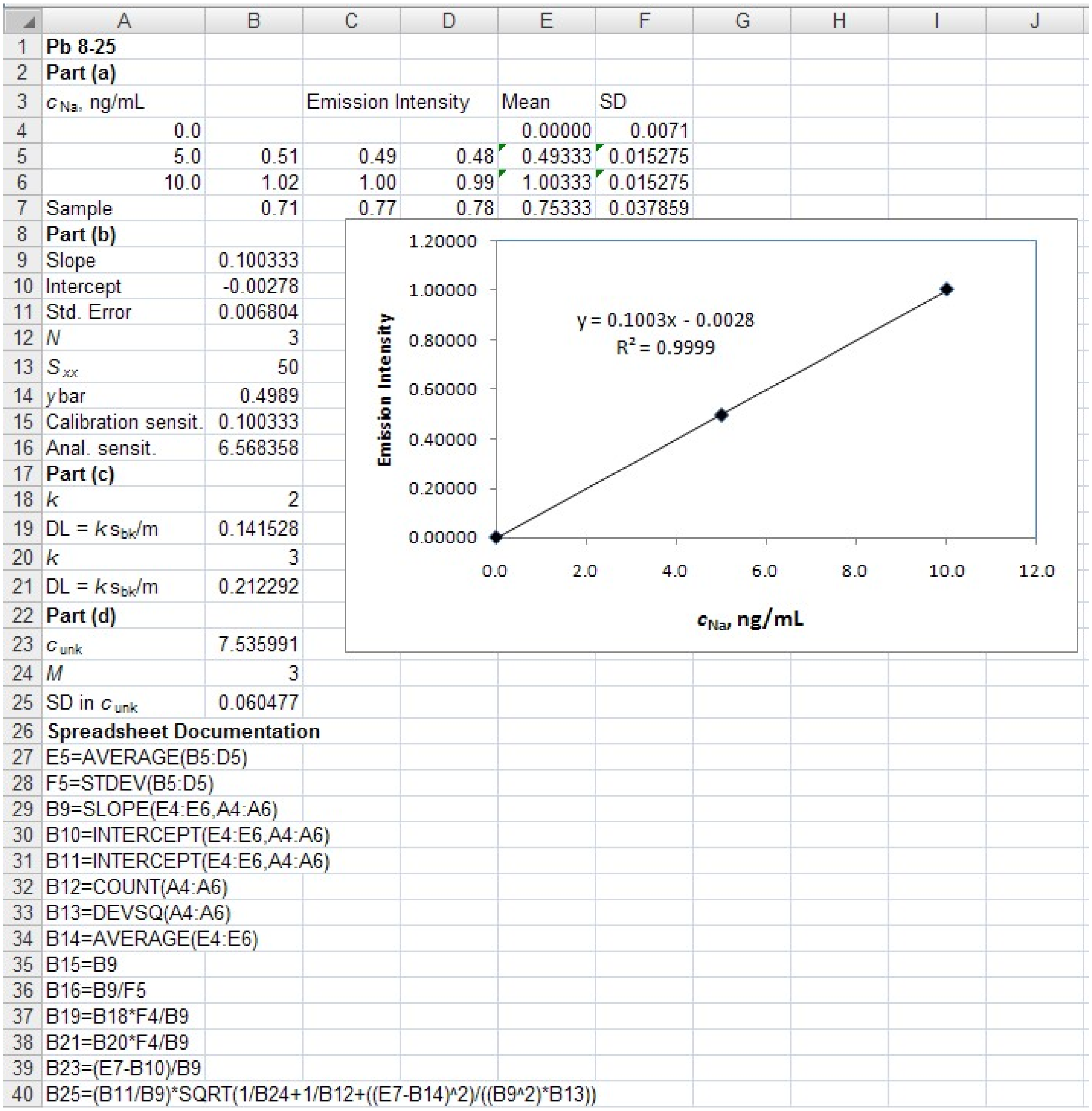
(a) See Spreadsheet

(b) calibration sensitivity = 0.0098; analytical sensitivity = 3.47

(c) For *k* = 3, DL = 1.44 ng/mL. This is a confidence level of 98.3%.

(d) c_{Zn} = 6.629 ± 0.005 ng/mL

8-25.



	A	B	C	D	E	F
1	**Pb 8-25**					
2	**Part (a)**					
3	c_{Na}, ng/mL		Emission Intensity		Mean	SD
4	0.0				0.00000	0.0071
5	5.0	0.51	0.49	0.48	0.49333	0.015275
6	10.0	1.02	1.00	0.99	1.00333	0.015275
7	Sample	0.71	0.77	0.78	0.75333	0.037859
8	**Part (b)**					
9	Slope	0.100333				
10	Intercept	-0.00278				
11	Std. Error	0.006804				
12	*N*	3				
13	S_{xx}	50				
14	*y* bar	0.4989				
15	Calibration sensit.	0.100333				
16	Anal. sensit.	6.568358				
17	**Part (c)**					
18	*k*	2				
19	DL = $k s_{bk}$/m	0.141528				
20	*k*	3				
21	DL = $k s_{bk}$/m	0.212292				
22	**Part (d)**					
23	c_{unk}	7.535991				
24	*M*	3				
25	SD in c_{unk}	0.060477				
26	**Spreadsheet Documentation**					
27	E5=AVERAGE(B5:D5)					
28	F5=STDEV(B5:D5)					
29	B9=SLOPE(E4:E6,A4:A6)					
30	B10=INTERCEPT(E4:E6,A4:A6)					
31	B11=INTERCEPT(E4:E6,A4:A6)					
32	B12=COUNT(A4:A6)					
33	B13=DEVSQ(A4:A6)					
34	B14=AVERAGE(E4:E6)					
35	B15=B9					
36	B16=B9/F5					
37	B19=B18*F4/B9					
38	B21=B20*F4/B9					
39	B23=(E7-B10)/B9					
40	B25=(B11/B9)*SQRT(1/B24+1/B12+((E7-B14)^2)/((B9^2)*B13))					

(a) See Spreadsheet

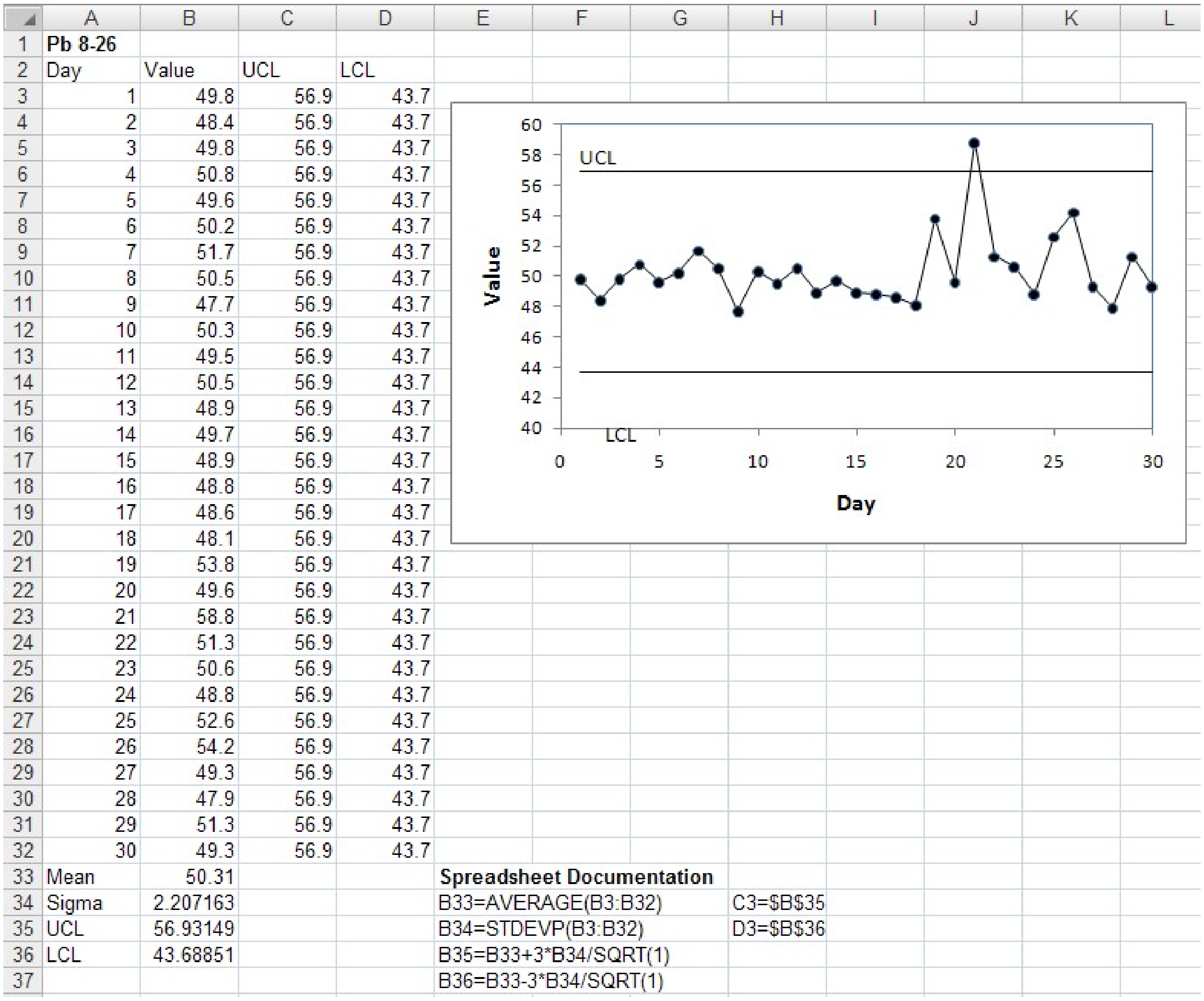
(b) calibration sensitivity = 0.100; analytical sensitivity = 6.57

(c) For *k* = 2, DL = 0.14 ng/mL (92.1% confidence level)

for *k* = 3, DL = 0.21 ng/mL (98.3% confidence level)

(d) c_{Na} = 7.54 ± 0.06 ng/mL

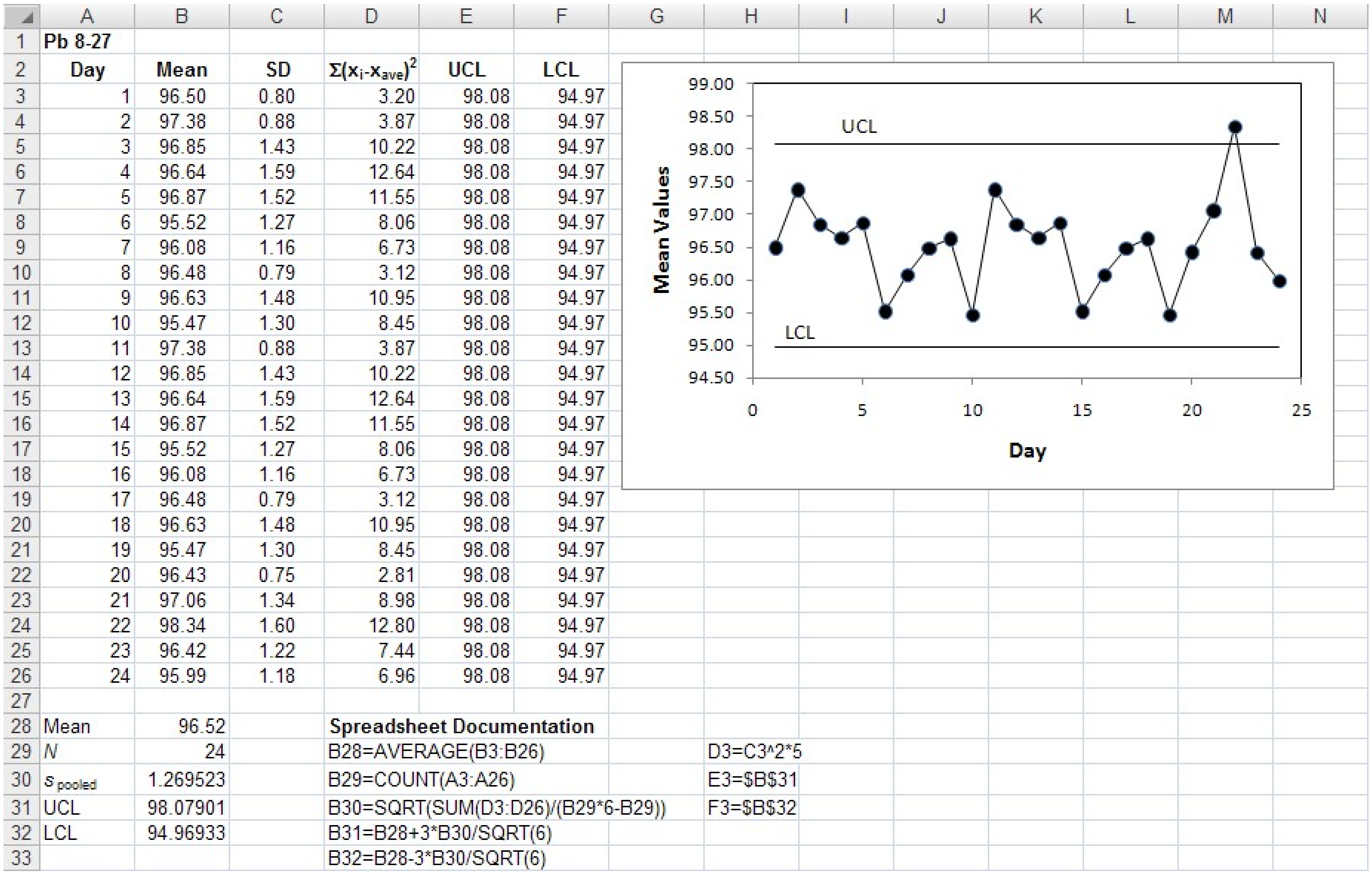
8-26.



	A	B	C	D	E	H
1	**Pb 8-26**					
2	Day	Value	UCL	LCL		
3	1	49.8	56.9	43.7		
4	2	48.4	56.9	43.7		
5	3	49.8	56.9	43.7		
6	4	50.8	56.9	43.7		
7	5	49.6	56.9	43.7		
8	6	50.2	56.9	43.7		
9	7	51.7	56.9	43.7		
10	8	50.5	56.9	43.7		
11	9	47.7	56.9	43.7		
12	10	50.3	56.9	43.7		
13	11	49.5	56.9	43.7		
14	12	50.5	56.9	43.7		
15	13	48.9	56.9	43.7		
16	14	49.7	56.9	43.7		
17	15	48.9	56.9	43.7		
18	16	48.8	56.9	43.7		
19	17	48.6	56.9	43.7		
20	18	48.1	56.9	43.7		
21	19	53.8	56.9	43.7		
22	20	49.6	56.9	43.7		
23	21	58.8	56.9	43.7		
24	22	51.3	56.9	43.7		
25	23	50.6	56.9	43.7		
26	24	48.8	56.9	43.7		
27	25	52.6	56.9	43.7		
28	26	54.2	56.9	43.7		
29	27	49.3	56.9	43.7		
30	28	47.9	56.9	43.7		
31	29	51.3	56.9	43.7		
32	30	49.3	56.9	43.7		
33	Mean	50.31			**Spreadsheet Documentation**	
34	Sigma	2.207163			B33=AVERAGE(B3:B32)	C3=$B$35
35	UCL	56.93149			B34=STDEVP(B3:B32)	D3=$B$36
36	LCL	43.68851			B35=B33+3*B34/SQRT(1)	
37					B36=B33-3*B34/SQRT(1)	

The process went out of control on Day 21.

8-27.



	A	B	C	D	E	F	G	H
1	Pb 8-27							
2	Day	Mean	SD	$\Sigma(x_i\text{-}x_{ave})^2$	UCL	LCL		
3	1	96.50	0.80	3.20	98.08	94.97		
4	2	97.38	0.88	3.87	98.08	94.97		
5	3	96.85	1.43	10.22	98.08	94.97		
6	4	96.64	1.59	12.64	98.08	94.97		
7	5	96.87	1.52	11.55	98.08	94.97		
8	6	95.52	1.27	8.06	98.08	94.97		
9	7	96.08	1.16	6.73	98.08	94.97		
10	8	96.48	0.79	3.12	98.08	94.97		
11	9	96.63	1.48	10.95	98.08	94.97		
12	10	95.47	1.30	8.45	98.08	94.97		
13	11	97.38	0.88	3.87	98.08	94.97		
14	12	96.85	1.43	10.22	98.08	94.97		
15	13	96.64	1.59	12.64	98.08	94.97		
16	14	96.87	1.52	11.55	98.08	94.97		
17	15	95.52	1.27	8.06	98.08	94.97		
18	16	96.08	1.16	6.73	98.08	94.97		
19	17	96.48	0.79	3.12	98.08	94.97		
20	18	96.63	1.48	10.95	98.08	94.97		
21	19	95.47	1.30	8.45	98.08	94.97		
22	20	96.43	0.75	2.81	98.08	94.97		
23	21	97.06	1.34	8.98	98.08	94.97		
24	22	98.34	1.60	12.80	98.08	94.97		
25	23	96.42	1.22	7.44	98.08	94.97		
26	24	95.99	1.18	6.96	98.08	94.97		
27								
28	Mean	96.52		**Spreadsheet Documentation**				
29	*N*	24		B28=AVERAGE(B3:B26)				D3=C3^2*5
30	s_{pooled}	1.269523		B29=COUNT(A3:A26)				E3=$B$31
31	UCL	98.07901		B30=SQRT(SUM(D3:D26)/(B29*6-B29))				F3=$B$32
32	LCL	94.96933		B31=B28+3*B30/SQRT(6)				
33				B32=B28-3*B30/SQRT(6)				

The process went out of control on Day 22.

Chapter 9

9-1. **(a)** A *weak electrolyte* only partially ionizes when dissolved in water. H_2CO_3 is an example of a weak electrolyte.

(b) A *Brønsted-Lowry acid* is a molecule that donates a proton when it encounters a base (proton acceptor). By this definition, NH_4^+ can be a Brønsted-Lowry acid.

(c) The *conjugate acid of a Brønsted-Lowry base* is the potential proton donator formed when a Brønsted-Lowry base accepts a proton. For example, the NH_4^+ is a conjugate acid in the reaction, $NH_3 + \text{proton} \rightleftharpoons NH_4^+$.

(d) *Neutralization*, according to the Brønsted-Lowry concept, occurs when a reaction involving an acid and its conjugate base is combined with a second reaction involving a base and its conjugate acid. Thus,

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In the example above, NH_3 acts as a base with NH_4^+ as its conjugate acid. H_2O acts as an acid with OH^- as its conjugate base.

(e) An *amphiprotic solvent* can act either as an acid or a base depending on the solute. Water is an example of an amphiprotic chemical species.

(f) A *zwitterion* is a chemical species that bears both positive and negative charges. Free amino acids, such as glycine, can exist as zwitterions in solution.

$$NH_2CH_2COOH \rightleftharpoons NH_3^+CH_2COO^-$$

(g) *Autoprotolysis* is the act of self-ionization to produce both a conjugate acid and a conjugate base.

(h) A *strong acid* dissociates completely such that no undissociated molecules are left in aqueous solution. Hydrochloric acid, HCl, is an example of a strong acid.

(i) The *Le Châtelier principle* states that the position of an equilibrium always shifts in such a direction that it relieves the stress. A common ion like sulfate added to a solution containing sparingly soluble $BaSO_4$ is an example

(j) *The common-ion effect* is responsible for the reduced solubility of an ionic precipitate when one of the soluble components reacting to form the precipitate is added to the solution in equilibrium with the precipitate. Chloride ion added to a AgCl solution decreases the solubility of Ag^+ because of the common ion effect.

9-2. **(a)** An *amphiprotic solute* is a chemical species that possesses both acidic and basic properties. The dihydrogen phosphate ion, $H_2PO_4^-$, is an example of an amphiprotic solute.

(b) *A differentiating solvent* reveals different strengths of acids. By this definition, anhydrous acetic acid is a differentiating solvent because perchloric acid dissociates 5000 times more than hydrochloric acid.

(c) A *leveling solvent* shows no difference between strong acids. Perchloric acid and hydrochloric acid ionize completely in water; thus, water is a leveling solvent.

(d) *A mass-action effect* arises when a shift in the chemical equilibrium occurs due to the introduction of one of the participating chemical species (i.e., addition of one of the reactants or products.

9-3. For dilute aqueous solutions, the concentration of water remains constant and is assumed to be independent of the equilibrium. Thus, its concentration is included within the equilibrium constant. For a pure solid, the concentration of the chemical species in the solid phase is constant. As long as some solid exists as a second phase, its effect on the equilibrium is constant and is included within the equilibrium constant.

9-4.

	Acid	Conjugate Base
(a)	HOCl	OCl^-
(b)	H_2O	OH^-
(c)	NH_4^+	NH_3
(d)	HCO_3^-	CO_3^{2-}
(e)	$H_2PO_4^-$	HPO_4^-

9-5.

	Base	Conjugate Acid
(a)	H_2O	H_3O^+
(b)	$HONH_2$	$HONH_3^+$
(c)	H_2O	H_3O^+
(d)	HCO_3^-	H_2CO_3
(e)	PO_4^{3-}	HPO_4^{2-}

9-6. **(a)** $2H_2O \rightleftharpoons H_3O^+ + OH^-$

(b) $2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$

(c) $2CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + CH_3NH^-$

(d) $2CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$

9-7. **(a)** $C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_2^+ + OH^-$

$$K_b = \frac{K_w}{K_a} = \frac{1.00\times10^{-14}}{2.3\times10^{-11}} = \frac{[C_2H_5NH_2^+][OH^-]}{[C_2H_5NH_2]} = 4.3 \times 10^{-4}$$

(b) $HOCl + H_2O \rightleftharpoons OCl^- + H_3O^+$

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]} = 3.0 \times 10^{-8}$$

(c)

$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$

$$K_a = \frac{K_w}{K_b} = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = 2.3 \times 10^{-11}$$

(d) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{7.1 \times 10^{-4}} = \frac{[HNO_2][OH^-]}{[NO_2^-]} = 1.4 \times 10^{-11}$$

(e) $H_3AsO_4 + H_2O \rightleftharpoons H_3O^+ + H_2AsO_4^-$

$H_2AsO_4^- + H_2O \rightleftharpoons H_3O^+ + HAsO_4^{2-}$

$\underline{HAsO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + AsO_4^{3-}}$

$H_3AsO_4 + 3H_2O \rightleftharpoons 3H_3O^+ + AsO_4^{3-}$

$$K_{a1} = \frac{[H_3O^+][H_2AsO_4^-]}{[H_3AsO_4]} \quad K_{a2} = \frac{[H_3O^+][HAsO_4^{2-}]}{[H_2AsO_4^-]} \quad K_{a3} = \frac{[H_3O^+][AsO_4^{3-}]}{[HAsO_4^{2-}]}$$

$$K_{overall} = \frac{[H_3O^+]^3[AsO_4^{3-}]}{[H_3AsO_4]} = K_{a1}K_{a2}K_{a3} = 5.8 \times 10^{-3} \times 1.1 \times 10^{-7} \times 3.2 \times 10^{-12} = 2.0 \times 10^{-21}$$

(f) $C_2O_4^{2-} + 2\,H_2O \rightleftharpoons H_2C_2O_4 + 2OH^-$

This can be broken into $C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$ with a constant K_{b1}

and $HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$ with a constant K_{b2}

$$K_{b1} = \frac{[HC_2O_4^-][OH^-]}{[C_2O_4^{2-}]} = \frac{K_w}{K_{a2}} \quad K_{b2} = \frac{[H_2C_2O_4][OH^-]}{[HC_2O_4^-]} = \frac{K_w}{K_{a1}}$$

$$K_{overall} = K_{b1}K_{b2} = \frac{K_w}{K_{a2}} \times \frac{K_w}{K_{a1}} = \frac{K_w^2}{K_{a2}K_{a1}} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5} \times 5.60 \times 10^{-2}} = 3.3 \times 10^{-9}$$

9-8. **(a)** $CuBr(s) \rightleftharpoons Cu^+ + Br^- \quad K_{sp} = [Cu^+][Br^-]$

(b) $HgClI(s) \rightleftharpoons Hg^{2+} + Cl^- + I^- \quad K_{sp} = [Hg^{2+}][Cl^-][I^-]$

(c) $PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^- \quad K_{sp} = [Pb^{2+}][Cl^-]^2$

(d) $La(IO_3)_3(s) \rightleftharpoons La^{3+} + 3IO_3^- \quad K_{sp} = [La^{3+}][IO_3^-]^3$

(e) $Ag_3AsO_4(s) \rightleftharpoons 3Ag^+ + AsO_4^{3-} \quad K_{sp} = [Ag^+][AsO_4^{3-}]$

9-9. **(a)** $S = [Cu^+] = [Br^-] \quad K_{sp} = [Cu^+][Br^-] = S^2$

(b) $S = [Hg^{2+}] = [Cl^-] = [I^-] \quad K_{sp} = [Hg^{2+}][Cl^-][I^-] = S^3$

(c) $S = [Pb^{2+}] = \frac{1}{2}[Cl^-] \quad K_{sp} = [Pb^{2+}][Cl^-]^2 = (S)(2S)^2 = 4S^3$

(d) $S = [La^{3+}] = \frac{1}{3}[IO_3^-] \quad K_{sp} = [La^{3+}][IO_3^-]^3 = (S)(3S)^3 = 27S^4$

(e) $S = [AsO_4^{3-}] = \frac{1}{3}[Ag^+] \quad K_{sp} = [Ag^+][AsO_4^{3-}] = 3S \times S = 3S^2$

9-10. **(a)** $AgSeCN \rightleftharpoons Ag^+ + SeCN^-$

$[Ag^+] = [SeCN^-] = 2.0 \times 10^{-8}$ M

$K_{sp} = [Ag^+][SeCN^-] = 2.0 \times 10^{-8} \times 2.0 \times 10^{-8} = 4.0 \times 10^{-16}$

(b) $RaSO_4 \rightleftharpoons Ra^{2+} + SO_4^{2-}$

$[Ra^{2+}] = [SO_4^{2-}] = 6.6 \times 10^{-6}$ M

$K_{sp} = [Ra^{2+}][SO_4^{2-}] = (6.6 \times 10^{-6}\ \text{M})^2 = 4.4 \times 10^{-11}$

(c) $Pb(BrO_3)_2 \rightleftharpoons Pb^{2+} + 2BrO_3^-$

$[Pb^{2+}] = 1.7 \times 10^{-1}$ M $[BrO_3^-] = 2 \times 1.7 \times 10^{-1}$ M $= 3.4 \times 10^{-1}$ M

$K_{sp} = [Pb^{2+}]\ BrO_3^-]^2 = 1.7 \times 10^{-1} \times (3.4 \times 10^{-1})^2 = 2.0 \times 10^{-3}$

(d) $Ce(IO_3)_3 \rightleftharpoons Ce^{3+} + 3IO_3^-$

$[Ce^{3+}] = 1.9 \times 10^{-3}$ M $[IO_3^-] = 3 \times 1.9 \times 10^{-3}$ M $= 5.7 \times 10^{-3}$ M

$K_{sp} = [Ce^{3+}][IO_3^-]^3 = 1.9 \times 10^{-3} \times (5.7 \times 10^{-3})^3 = 3.5 \times 10^{-10}$

9-11. **(a)** $K_{sp} = [Ag^+][SeCN^-] = 4.0 \times 10^{-16}$

$K_{sp} = (0.030)[SeCN^-] = 4.0 \times 10^{-16}$

$S = [SeCN^-] = 4.0 \times 10^{-16}/0.030 = 1.3 \times 10^{-14}$ M

(b) $K_{sp} = [Ra^{2+}][SO_4^{2-}] = 4.4 \times 10^{-11}$

$S = [SO_4^{2-}] = 4.4 \times 10^{-11}/ 0.030 = 1.5 \times 10^{-9}$ M

(c) $K_{sp} = [Pb^{2+}][BrO_3^-]^2 = 2.0 \times 10^{-3}$

$$[BrO_3^-] = \sqrt{\frac{2.0 \times 10^{-3}}{0.030}} = 0.258 \text{ M}$$

$$S = \frac{1}{2}[BrO_3^-] = 0.13 \text{ M}$$

(d) $K_{sp} = [Ce^{3+}][IO_3^-]^3 = 3.5 \times 10^{-10}$

$$[IO_3^-] = \sqrt[3]{\frac{3.5 \times 10^{-10}}{0.030}} = 7.047 \times 10^{-4} \text{ M}$$

$$S = \frac{1}{3}[IO_3^-] = 2.3 \times 10^{-4} \text{ M}$$

9-12. **(a)** $K_{sp} = [Ag^+][SeCN^-] = 4.0 \times 10^{-16}$

$S = [Ag^+] = 4.0 \times 10^{-16}/0.030 = 1.3 \times 10^{-14}$ M

(b) $K_{sp} = [Ra^{2+}][SO_4^{2-}] = 4.4 \times 10^{-11}$

$S = [Ra^{2+}] = 4.4 \times 10^{-11}/ 0.030 = 1.5 \times 10^{-9}$ M

(c) $K_{sp} = [Pb^{2+}][BrO_3^-]^2 = 2.0 \times 10^{-3}$

$S = [Pb^{2+}] = 2.0 \times 10^{-3}/(0.030)^2 = 2.2$ M

(d) $K_{sp} = [Ce^{3+}][IO_3^-]^3 = 3.5 \times 10^{-10}$

$S = [Ce^{3+}] = 3.5 \times 10^{-10}/(0.030)^3 = 1.3 \times 10^{-5}$ M

9-13. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

(a) $[CrO_4^{2-}] = \dfrac{1.2 \times 10^{-12}}{(4.13 \times 10^{-3})^2} = 7.04 \times 10^{-8}$ M

(b) $[CrO_4^{2-}] = \dfrac{1.2 \times 10^{-12}}{(9.00 \times 10^{-7})^2} = 1.48$ M

9-14. $Al(OH)_3(s) \rightleftharpoons Al^{3+} + OH^-$ $\quad K_{sp} = 3.0 \times 10^{-34} = [Al^{3+}][OH^-]^3$

(a) Because K_{sp} is very small, we can assume that $[Al^{3+}] = 4.60 \times 10^{-2}$ M with essentially no contribution from the dissolution of $Al(OH)_3$.

$[OH^-]^3 \times 4.60 \times 10^{-2} = 3.0 \times 10^{-34}$

$$[OH^-] = \sqrt[3]{\frac{3.0 \times 10^{-34}}{4.60 \times 10^{-2}}} = 1.9 \times 10^{-11} \text{ M}$$

(b) As in part (a),

$$[OH^-] = \sqrt[3]{\frac{3.0 \times 10^{-34}}{3.50 \times 10^{-7}}} = 9.5 \times 10^{-10} \text{ M}$$

9-15. $Ce^{3+} + 3IO_3^- \rightleftharpoons Ce(IO_3)_3(s)$

$K_{sp} = [Ce^{3+}][IO_3^-]^3 = 3.2 \times 10^{-10}$

(a) 50.00 mL × 0.0450 mmol/ml = 2.25 mmol Ce^{3+}

$$[Ce^{3+}] = \frac{2.25 \text{ mmol}}{(50.00 + 50.00) \text{ mL}} = 0.0225 \text{ M}$$

(b) We mix 2.25 mmol Ce^{3+} with 50.00 mL × 0.045 mmol/mL = 2.25 mmol IO_3^-.

Each mole of IO_3^- reacts with 1/3 mole of Ce^{3+} so 2.25 mmol would consume 1/3 × 2.25 mmol Ce^{3+} or the amount of unreacted Ce^{3+} = 2.25 – 2.25/3 = 1.5 mmol

$$c_{\mathrm{Ce}^{3+}} = \frac{1.50\ \text{mmol}}{100\ \text{mL}} = 0.0150\ \text{M}$$

$[\mathrm{Ce}^{3+}] = 0.0150 + S$ (where S is the solubility).

$[\mathrm{IO_3}^-] = 3S$

$K_{sp} = [\mathrm{Ce}^{3+}][\mathrm{IO_3}^-]^3 = 0.0150 \times 3S^3 = 3.2 \times 10^{-10}$

$$S = \left(\frac{3.2 \times 10^{-10}}{27 \times 1.50 \times 10^{-2}}\right)^{1/3} = 9.2 \times 10^{-4}$$

$[\mathrm{Ce}^{3+}] = 1.50 \times 10^{-2} + 9.2 \times 10^{-4} = 1.6 \times 10^{-2}$ M

(c) Now we have 0.250 mmol $\mathrm{IO_3}^-$ × 50.00 mL = 12.5 mmol. Since 3 × 2.25 mmol = 6.75 mmol would be required to completely react with the Ce^{3+}, we have excess $\mathrm{IO_3}^-$.

$$[\mathrm{IO_3}^-] = \frac{12.5\ \text{mmol} - 6.75\ \text{mmol}}{100\ \text{mL}} + 3S = 0.0575 + 3S$$

$[\mathrm{Ce}^{3+}] = S$

$K_{sp} = S(0.0575 + 3S)^3 = 3.2 \times 10^{-10}$

Lets assume $3S << 0.0575$

$S = [\mathrm{Ce}^{3+}] = 3.2 \times 10^{-10}/(0.0575)^3 = 1.7 \times 10^{-6}$ M

Checking the assumption $3 \times 1.7 \times 10^{-6}$ M $= 5.1 \times 10^{-6}$ which is much smaller than 0.0575.

(d) Now we are mixing 2.25 mmol Ce^{3+} with 50.00 mL × 0.050 mmol/mL = 2.50 mmol $\mathrm{IO_3}^-$. The Ce^{3+} is now in excess so that

amount of Ce^{3+} = 2.25 mmol – 2.5/3 mmol = 1.42 mmol

$$c_{\mathrm{Ce}^{3+}} = \frac{1.42\ \text{mmol}}{100\ \text{mL}} = 0.0142\ \text{M}$$

$[\mathrm{Ce}^{3+}] = 1.42 \times 10^{-2} + S$

$K_{sp} = [\mathrm{Ce}^{3+}][\mathrm{IO_3}^-]^3 = 0.0142 \times 3S^3 = 3.2 \times 10^{-10}$

$$S = \left(\frac{3.2 \times 10^{-10}}{27 \times 1.42 \times 10^{-2}}\right)^{1/3} = 9.42 \times 10^{-4}$$

$[Ce^{3+}] = 1.42 \times 10^{-2} + 9.42 \times 10^{-4} = 1.5 \times 10^{-2}$ M

9-16. $K\text{sp} = [K^+]^2[PdCl_6{}^{2-}] = (2S)^2(S) = 6.0 \times 10^{-6}$

amount K^+ = 50.0 mL × 0.200 mmol/ml = 10 mmol

(a) amount $PdCl_6{}^-$ = 50.0 mL × 0.0800 mmol/mL = 4 mmol

amount excess K^+ = 10 mmol – 2 × 4 mmol = 2 mmol

$$[K^+] = \frac{2 \text{ mmol}}{100 \text{ mL}} + 2S = 0.020 + 2S$$

$$[K^+] = 0.020 + 2\left(\frac{6 \times 10^{-6}}{4 \times 0.020}\right)^{1/3} = 0.02 \text{ M}$$

(b) amount $PdCl_6{}^-$ = 50.0 mL × 0.160 mmol/mL = 8 mmol

amount excess $PdCl_6{}^-$ = 8 mmol – 10 mmol/2 = 3 mmol

$[PdCl_6{}^-]$ = 3 mmol/100 mL + S = 0.030 M + S

$[K^+] = 2S$

$K_{sp} = (2S)^2(0.030 + S) = 6.0 \times 10^{-6}$

Assuming $S << 0.030$, we have $S^2 = 6.0 \times 10^{-6}/(4 \times 0.030)$

$S = 7.1 \times 10^{-3}$ M

$[K^+] = 2S = 0.014$M

(c) amount $PdCl_6{}^-$ = 0.240 mmol/mL × 50.0 mL = 12 mmol

Excess $PdCl_6{}^-$ = 12 mmol – 5 mmol = 7 mmol

$[PdCl_6{}^-]$ = 7 mmol/100 mL + S = 0.07 M + $S \approx 0.07$ M

$K_{sp} = (2S)^2 \times 0.07 = 6.0 \times 10^{-6}$

$S = 4.6 \times 10^{-3}$ M

$[K^+] = 2S = 9.3 \times 10^{-3}$ M

9-17. $CuI(s) \rightleftharpoons Cu^+ + I^-$ $K_{sp} = [Cu^+][I^-] = 1 \times 10^{-12}$

$AgI(s) \rightleftharpoons Ag^+ + I^-$ $K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$

$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$ $K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9} = S(2S)^2 = 4S^3$

$BiI_3(s) \rightleftharpoons Bi^{3+} + 3I^-$ $K_{sp} = [Bi^{3+}][I^-]^3 = 8.1 \times 10^{-19} = S(3S)^3 = 27S^4$

(a) For CuI, $S = [Cu^+] = [I^-] = \sqrt{1 \times 10^{-12}} = 1 \times 10^{-6}$ M

For AgI, $S = [Ag^+] = [I^-] = \sqrt{8.3 \times 10^{-17}} = 9.1 \times 10^{-9}$ M

For PbI_2, $S = \sqrt[3]{\dfrac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3}$ M

For BiI_3 $S = \sqrt[4]{\dfrac{8.1 \times 10^{-19}}{27}} = 1.3 \times 10^{-5}$ M

So, solubilities are in the order $PbI_2 > BiI_3 > CuI > AgI$

(b) For CuI, $S = 1 \times 10^{-12}/0.20 = 5 \times 10^{-12}$ M

For AgI, $S = 8.3 \times 10^{-17}/0.20 = 4.2 \times 10^{-16}$ M

For PbI_2, $S = 7.1 \times 10^{-9}/(0.20)^2 = 1.8 \times 10^{-7}$ M

For BiI_3, $S = 8.1 \times 10^{-19}/(0.20)^3 = 1.0 \times 10^{-16}$ M

So, solubilities are in the order $PbI_2 > CuI > AgI > BiI_3$

(c) For CuI, $S = 1 \times 10^{-12}/0.020 = 5 \times 10^{-11}$ M

For AgI, $S = 8.3 \times 10^{-17}/0.020 = 4.2 \times 10^{-15}$ M

For PbI_2, $S = \dfrac{1}{2}\sqrt{\dfrac{7.1 \times 10^{-9}}{0.020}} = 3.0 \times 10^{-4}$ M

For BiI_3, $S = \frac{1}{3}\sqrt[3]{\frac{8.1 \times 10^{-19}}{0.020}} = 1.1 \times 10^{-6}\ \text{M}$

So solubilities are in the order, $PbI_2 > BiI_3 > CuI > AgI$

9-18. $BiOOH(s) \rightleftharpoons BiO^+ + OH^-$ $K_{sp} = [BiO^+][OH^-] = 4.0 \times 10^{-10}$

$Be(OH)_2(s) \rightleftharpoons Be^{2+} + 2OH^-$ $K_{sp} = [Be^{2+}][OH^-]^2 = 7.0 \times 10^{-22} = S(2S)^2 = 4S^3$

$Tm(OH)_3(s) \rightleftharpoons Tm^{3+} + 3OH^-$ $K_{sp} = [Tm^{3+}][\ OH^-]^3 = 3.0 \times 10^{-24} = S(3S)^3 = 27S^4$

$Hf(OH)_4 \rightleftharpoons Hf^{4+} + 4OH^-$ $K_{sp} = [Hf^{4+}][OH^-]^4 = 4.0 \times 10^{-26} = S(4S)^4 = 256S^5$

(a) For BiOOH, $S = [BiO^+] = [OH^-] = \sqrt{4.0 \times 10^{-10}} = 2.0 \times 10^{-5}\ \text{M}$

For $Be(OH)_2$, $S = [Be^{2+}] = \frac{1}{2}[OH^-] = \sqrt[3]{\frac{7.0 \times 10^{-22}}{4}} = 5.6 \times 10^{-8}\ \text{M}$

For $Tm(OH)_3$ $S = [Tm^{3+}] = \frac{1}{3}[OH^-] = \left(\frac{3.0 \times 10^{-24}}{27}\right)^{1/4} = 5.8 \times 10^{-7}\ \text{M}$

For $Hf(OH)_4$ $S = [Hf^{4+}] = \frac{1}{4}[OH^-] = \left(\frac{4.0 \times 10^{-26}}{256}\right)^{1/5} = 2.7 \times 10^{-6}\ \text{M}$

$Be(OH)_2$ has the lowest molar solubility.

(b) For BiOOH, $S = \frac{4.0 \times 10^{-10}}{0.30} = 1.3 \times 10^{-9}\ \text{M}$

For $Be(OH)_2$, $S = \frac{7.0 \times 10^{-22}}{(0.30)^2} = 7.8 \times 10^{-21}\ \text{M}$

For $Tm(OH)_3$, $S = \frac{3.0 \times 10^{-24}}{(0.30)^3} = 1.1 \times 10^{-22}\ \text{M}$

For $Hf(OH)_4$, $S = \frac{4.0 \times 10^{-26}}{(0.30)^4} = 4.9 \times 10^{-24}\ \text{M}$

$Hf(OH)_4$ has the lowest molar solubility in 0.30 M NaOH.

9-19. At 25ºC, $pK_w = 13.99$, $K_w = 1.023 \times 10^{-14}$. At 75ºC, $pK_w = 12.70$, $K_w = 1.995 \times 10^{-13}$

$[H_3O^+] = [OH^-]$ in pure water. Thus $[H_3O^+] = \sqrt{K_w}$

At 25ºC, $[H_3O^+] = \sqrt{1.023 \times 10^{-14}} = 1.011 \times 10^{-7}\ M$, $pH = -\log[H_3O^+] = 6.99_5 \approx 7.00$

At 75ºC, $[H_3O^+] = \sqrt{1.995 \times 10^{-13}} = 4.467 \times 10^{-7}\ M$, $pH = 6.35$

9-20. **(a)** For benzoic acid, $K_a = 6.28 \times 10^{-5}$. Call benzoic acid HBz and the benzoate anion Bz^-

$$HBz + H_2O \rightleftharpoons Bz^- + H_3O^+$$

$$K_a = \frac{[Bz^-][H_3O^+]}{[HBz]} = 6.28 \times 10^{-5}$$ Mass balance $c_{HBz} = [HBz] + [Bz^-] = 0.0300$

$[Bz^-] = [H_3O^+]$ Thus, $[HBz] = 0.0300 - [Bz^-] = 0.0300 - [H_3O^+]$

$$\frac{[H_3O^+]^2}{0.0300 - [H_3O^+]} = 6.28 \times 10^{-5}$$

Solving the quadratic or solving by iterations gives,

$[H_3O^+] = 1.34 \times 10^{-3}$ M so $[OH^-] = 1.00 \times 10^{-14}/ 1.34 \times 10^{-3} = 7.5 \times 10^{-12}$ M

(b) $HN_3 + H_2O \rightleftharpoons N_3^- + H_3O^+$ $K_a = 2.2 \times 10^{-5}$

$$\frac{[H_3O^+]^2}{0.0600 - [H_3O^+]} = 2.2 \times 10^{-5}$$

$[H_3O^+] = 1.14 \times 10^{-3}$ so $[OH^-] = 1.00 \times 10^{-14}/ 1.14 \times 10^{-3} = 8.8 \times 10^{-12}$

(c)

$$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3{}^+ + OH^-$$

$$K_b = \frac{[C_2H_5NH_3{}^+][OH^-]}{[C_2H_5NH_2]} = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{2.31\times10^{-11}} = 4.33\times10^{-4}$$

$$[OH^-] = [C_2H_5NH_3{}^+] \qquad [C_2H_5NH_2] = 0.100 - [OH^-]$$

$$\frac{[OH^-]^2}{(0.100 - [OH^-])} = 4.33\times10^{-4} \qquad [OH^-]^2 = 4.33\times10^{-4}(0.100 - [OH^-])$$

$$[OH^-]^2 + 4.33\times10^{-4}[OH^-] - 4.33\times10^{-5} = 0$$

$$[OH^-] = -\frac{4.33\times10^{-4} + \sqrt{(4.33\times10^{-4})^2 + 4(4.33\times10^{-5})}}{2} = 6.37\times10^{-3}\,\text{M}$$

$$[H_3O^+] = \frac{1.0\times10^{-14}}{6.37\times10^{-3}} = 1.57\times10^{-12}\,\text{M}$$

(d)

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.58\times10^{-10}} = 6.33\times10^{-5}$$

$$[OH^-] = [(CH_3)_3NH^+] \qquad [(CH_3)_3N] = 0.200\text{ M} - [OH^-]$$

$$\frac{[OH^-]^2}{(0.200 - [OH^-])} = 6.33\times10^{-5} \qquad [OH^-]^2 = 6.33\times10^{-5}(0.200 - [OH^-])$$

$$[OH^-]^2 + 6.33\times10^{-5}[OH^-] - 1.27\times10^{-5} = 0$$

$$[OH^-] = -\frac{6.33\times10^{-5} + \sqrt{(6.33\times10^{-5})^2 + 4(1.27\times10^{-5})}}{2} = 3.53\times10^{-3}\,\text{M}$$

$$[H_3O^+] = \frac{1.0\times10^{-14}}{3.53\times10^{-3}} = 2.83\times10^{-12}\,\text{M}$$

(e)

$Bz^- + H_2O \rightleftharpoons HBz + OH^-$ $\qquad K_b = K_w/K_a = 1.00 \times 10^{-14}/6.28 \times 10^{-5} = 1.60 \times 10^{-10}$

$[OH^-] = [HBz]$ $\qquad [Bz^-] = 0.200 - [OH^-]$

$$\frac{[OH^-]^2}{0.200 - [OH^-]} = 1.60 \times 10^{-10}$$

$[OH^-] = 5.66 \times 10^{-6}$ M $\qquad [H_3O^+] = 1.00 \times 10^{-14}/5.66 \times 10^{-6} = 1.77 \times 10^{-9}$ M

(f) Let HPr be propanoic acid and Pr^- be the anion.

$Pr^- + H_2O \rightleftharpoons HPr + OH^-$ $K_b = K_w/K_a = 1.00 \times 10^{-14}/1.34 \times 10^{-5} = 7.46 \times 10^{-10}$

Proceeding as in part (e) $[OH^-] = 8.01 \times 10^{-6}$ M $[H_3O^+] = 1.25 \times 10^{-9}$ M

(g) $HONH_3^+ + H_2O \rightleftharpoons HONH_2 + H_3O^+$ $K_a = 1.1 \times 10^{-6}$

As in part (b) $\dfrac{[H_3O^+]^2}{0.250 - [H_3O^+]} = 1.1 \times 10^{-6}$

$[H_3O^+] = 5.24 \times 10^{-4}$ M $[OH^-] = 1.91 \times 10^{-11}$ M

(h) $EtNH_3^+ + H_2O \rightleftharpoons EtNH_2 + H_3O^+$ $K_a = 2.31 \times 10^{-11}$

$$\frac{[H_3O^+]^2}{0.0250 - [H_3O^+]} = 2.31 \times 10^{-11}$$

$[H_3O^+] = 7.60 \times 10^{-7}$ M $[OH^-] = 1.32 \times 10^{-8}$ M

Note that these values are close to the concentrations of H_3O^+ and OH^- from the dissociation of water. Correction for water dissociation changes the values only slightly.

9-21. (a)

$$ClCH_2COOH + H_2O \rightleftharpoons ClCH_2COO^- + H_3O^+ \quad K_a = \frac{[ClCH_2COO^-][H_3O^+]}{[ClCH_2COOH]} = 1.36 \times 10^{-3}$$

$[H_3O^+] = [ClCH_2COO^-]$ $[ClCH_2COOH] = 0.200 - [H_3O^+]$

$$\frac{[H_3O^+]^2}{(0.200 - [H_3O^+])} = 1.36 \times 10^{-3} \quad [H_3O^+]^2 = 1.36 \times 10^{-3}(0.200 - [H_3O^+])$$

$$[H_3O^+]^2 + 1.36 \times 10^{-3}[H_3O^+] - 2.72 \times 10^{-4} = 0$$

$$[H_3O^+] = -\frac{1.36 \times 10^{-3} + \sqrt{(1.36 \times 10^{-3})^2 + 4(2.72 \times 10^{-4})}}{2} = 1.58 \times 10^{-2} \text{ M}$$

(b)

$$ClCH_2COO^- + H_2O \rightleftharpoons ClCH_2COOH + OH^-$$

$$K_b = \frac{[ClCH_2COOH][OH^-]}{[ClCH_2COO^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.36 \times 10^{-3}} = 7.35 \times 10^{-12}$$

$$[OH^-] = [ClCH_2COOH] \qquad [ClCH_2COO^-] = 0.200\ M - [OH^-]$$

$$\frac{[OH^-]^2}{(0.200 - [OH^-])} = 7.35 \times 10^{-12} \quad [OH^-]^2 = 7.35 \times 10^{-12}(0.200 - [OH^-])$$

$$[OH^-]^2 + 7.35 \times 10^{-12}[OH^-] - 1.47 \times 10^{-12} = 0$$

$$[OH^-] = 1.21 \times 10^{-6}\ \text{M}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{1.21 \times 10^{-6}} = 8.26 \times 10^{-9}\ \text{M}$$

(c)

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-11}} = 4.35 \times 10^{-4}$$

$$[OH^-] = [CH_3NH_3^+] \qquad [CH_3NH_2] = 0.0200\ \text{M} - [OH^-]$$

Proceeding as in part (b), we find

$[OH^-] = 2.74 \times 10^{-3}$ M $\qquad [H_3O^+] = 1.0 \times 10^{-14}/2.74 \times 10^{-3} = 3.65 \times 10^{-12}$ M

(d)

$$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+ \quad K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = 2.3 \times 10^{-11}$$

$$[H_3O^+] = [CH_3NH_2] \qquad [CH_3NH_3^+] = 0.0200\ \text{M} - [H_3O^+]$$

Proceeding as in part (a), we find

$[H_3O^+] = 6.78 \times 10^{-7}$

(e)

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+ \quad K_a = \frac{[C_6H_5NH_2][H_3O^+]}{[C_6H_5NH_3^+]} = 2.51 \times 10^{-5}$$

$[H_3O^+] = [C_6H_5NH_2]$ $[C_6H_5NH_3^+] = 0.0020\text{ M} - [H_3O^+]$

$$\frac{[H_3O^+]^2}{(0.0020 - [H_3O^+])} = 2.51 \times 10^{-5}$$

Proceeding as in part (d), we find $[H_3O^+] = 2.11 \times 10^{-4}$ M

(f)

$$HIO_3 + H_2O \rightleftharpoons IO_3^- + H_3O^+ \quad K_a = \frac{[IO_3^-][H_3O^+]}{[HIO_3]} = 1.7 \times 10^{-1}$$

$[H_3O^+] = [IO_3^-]$ $[HIO_3] = 0.300\text{ M} - [H_3O^+]$

Proceeding as in part (e), we find $[H_3O^+] = 0.16$ M

9-22. A *buffer solution* resists changes in pH with dilution or with addition of acids or bases. A buffer is composed of a mixture of a weak acid and its conjugate base.

9-23. *Buffer capacity* of a solution is defined as the number of moles of a strong acid (or a strong base) that causes 1.00 L of a buffer to undergo a 1.00-unit change in pH.

9-24.

(a) $\text{pH} = \text{pK}_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.7 \times 10^{-10}) + \log\frac{(0.100\text{M})}{(0.200\text{M})} = 8.943$

(b) $\text{pH} = \text{pK}_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.7 \times 10^{-10}) + \log\frac{(0.050\text{M})}{(0.100\text{M})} = 8.943$

Although the two solutions have identical pH values, the solution in (a) has the greatest buffer capacity, because it has the higher concentration of weak acid and its conjugate base.

9-25. $HOAc + H_2O \rightleftharpoons OAc^- + H_3O^+$ $OAc^- + H_2O \rightleftharpoons HOAc + OH^-$

(a)

$$[\mathrm{OAc^-}] = \frac{8.00\ \mathrm{mmol}}{200\ \mathrm{mL}} = 4 \times 10^{-2}\ \mathrm{M}$$

$$[\mathrm{HOAc}] = 0.100\ \mathrm{M}$$

$$\mathrm{pH} = -\log(1.75 \times 10^{-5}) + \log\frac{4 \times 10^{-2}}{0.100} = 4.359$$

(b)

$$0.175\ \mathrm{M\ HOAc} = \frac{0.175\ \mathrm{mmol}}{\mathrm{mL}} \times 100\ \mathrm{mL} = 17.5\ \mathrm{mmol}$$

$$0.0500\ \mathrm{M\ NaOH} = \frac{0.0500\ \mathrm{mmol}}{\mathrm{mL}} \times 100\ \mathrm{mL} = 5.00\ \mathrm{mmol}$$

$$[\mathrm{HOAc}] = \frac{(17.5 - 5.00)\ \mathrm{mmol}}{200\ \mathrm{mL}} = 6.25 \times 10^{-2}\ \mathrm{M}$$

$$[\mathrm{OAc^-}] = \frac{5\ \ \mathrm{mmol}}{200\ \mathrm{mL}} = 2.50 \times 10^{-2}\ \mathrm{M}$$

$$\mathrm{pH} = -\log(1.75 \times 10^{-5}) + \log\frac{2.50 \times 10^{-2}}{6.25 \times 10^{-2}} = 4.359$$

(c)

$$0.0420\ \mathrm{M\ OAc^-} = \frac{0.042\ \mathrm{mmol}}{\mathrm{mL}} \times 160\ \mathrm{mL} = 6.72\ \mathrm{mmol}$$

$$0.1200\ \mathrm{M\ HCl} = \frac{0.1200\ \mathrm{mmol}}{\mathrm{mL}} \times 40.0\ \mathrm{mL} = 4.80\ \mathrm{mmol}$$

$$[\mathrm{OAc^-}] = \frac{(6.72 - 4.80)\ \mathrm{mmol}}{200\ \mathrm{mL}} = 9.6 \times 10^{-3}\ \mathrm{M}$$

$$[\mathrm{HOAc}] = \frac{4.8\ \mathrm{mmol}}{200\ \mathrm{mL}} = 2.4 \times 10^{-2}\ \mathrm{M}$$

$$\mathrm{pH} = -\log(1.75 \times 10^{-5}) + \log\frac{9.6 \times 10^{-3}}{2.4 \times 10^{-2}} = 4.359$$

The solutions all are buffers with the same pH, but they differ in buffer capacity with **(a)** having the greatest and **(c)** the least.

9-26. **(a)** $C_6H_5NH_3^+/C_6H_5NH_2$ ($pK_a = 4.60$)

(b) The closest is $H_2NNH_3^+/H_2NNH_2$ ($pK_a = 7.98$)

(c) The closest are $C_2H_5NH_3^+$/ $C_2H_5NH_2$ (pK_a = 10.64) and $CH_3NH_3^+/CH_3NH_2$ pK_a = 10.64)

(d) The closest is $HONH_3^+/HONH_2$ (pK_a = 5.96), but H_2CO_3/HCO_3^- is close (pK_a= 6.35)

9-27.

$$\text{pH} = 3.50 = \text{p}K_a + \log\frac{[\text{HCOO}^-]}{[\text{HCOOH}]} = -\log(1.8 \times 10^{-4}) + \log\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$3.50 = 3.74 + \log\frac{[\text{HCOO}^-]}{[\text{HCOOH}]} \qquad \frac{[\text{HCOO}^-]}{[\text{HCOOH}]} = 10^{-0.24} = 0.575$$

$$500 \text{ mL} \times 1.00 \frac{\text{mmol HCOOH}}{\text{mL}} = 500 \text{ mmol}$$

So amount of $HCOO^-$ needed = 0.575 × 500 mmol = 287.5 mmol

287.5 mmol × 10^{-3} mol/mmol = 0.2875 mol $HCOO^-$

Mass HCOONa = 0.2875 mol × 67.997 g/mol = 19.6 g

9-28. Let HGl = glycolic acid

$$\text{pH} = 4.00 = \text{p}K_a + \log\frac{[\text{Gl}^-]}{[\text{HGl}]} = 3.83 + \log\frac{[\text{Gl}^-]}{[\text{HGl}]}$$

$$\log\frac{[\text{Gl}^-]}{[\text{HGl}]} = 4.00 - 3.83 = 0.17$$

$$\frac{[\text{Gl}^-]}{[\text{HGl}]} = 1.479$$

amount of HGl = 400.0 mL × 1.00 M = 400 mmol or 0.400 mol

Need 0.400 × 1.479 = 0.592 mol NaGl

mass of NaGl needed is 0.592 mol × 98.01 g/mol = 58.0 g

9-29. Let HMn = mandelic acid, Mn^- = mandelate anion.

500 mL × 0.300 M NaMn = 150 mmol Mn^-.

For a pH of 3.37 need the ratio of Mn^- to HMn to be

$$\text{pH} = 3.37 = \text{p}K_a + \log\frac{[\text{Mn}^-]}{[\text{HMn}]} = 3.398 + \log\frac{[\text{Mn}^-]}{[\text{HMn}]} \qquad \log\frac{[\text{Mn}^-]}{[\text{HMn}]} = 3.37 - 3.398 = -0.028$$

$$\frac{[\text{Mn}^-]}{[\text{HMn}]} = 0.938$$

$$\frac{\text{mmol Mn}^- - x\text{ mmol HCl}}{x\text{ mmol HCl}} = 0.938$$

$0.938 \times x$ mmol HCl = mmol Mn^- – x mmol HCl

x = mmol Mn^-/1.938 = 150 Mn^-/1.938 = 77.399 mmol HCl

Volume HCl = 77.399 mmol/(0.200 mmol/mL) = 387 mL

9-30. 200.0 mL × 1.00 mmol/mL = 200.0 mmol HGl

pH = 4.00 = pK_a+ log[Gl^-]/[HGl] = 3.83 + log[Gl^-]/[HGl]

log[Gl^-]/[HGl] = 4.00 – 3.83 = 0.17 [Gl^-]/[HGl] = 1.479

$$\frac{\text{mole Gl}^-}{\text{mole HGl}} = 1.479$$

$$\frac{x\text{ mole NaOH}}{(\text{mole HGl} - x\text{ mole NaOH})} = 1.479$$

x mole NaOH = 1.479 × (mole HGl – x mole NaOH)

$$x\text{ mole NaOH} = \frac{1.479 \times (\text{HGl})}{2.479} = \frac{1.479 \times (0.200\text{ mole})}{2.479} = 0.119$$

$$\text{volume NaOH} = 0.119\text{ mole} \times \frac{\text{L}}{2.00\text{ mole}} \times \frac{1000\text{ mL}}{\text{L}} = 59.66\text{ mL}$$

9-31. The statement "A buffer maintains the pH of a solution constant" is partially true and partially false. The change in pH of a buffered solution is relatively small with the addition of a small volume of acid or base as can be seen in Example 9-13, where the pH only increases from 9.07 to 9.11 on adding NaOH and drops from 9.07 to 9.02 on adding HCl. Compared to no buffer, this is essentially constant, but not absolutely constant. Hence, the statement has some truth to it, but is not totally true.

Chapter 10

10-1. **(a)** *Activity*, a_A, is the effective concentration of a chemical species A in solution. The *activity coefficient*, γ_A, is the numerical factor necessary to convert the molar concentration of the chemical species A to activity as shown below:

$a_A = \gamma_A[A]$

(b) The *thermodynamic equilibrium constant* refers to an ideal system within which each chemical species is unaffected by any others. A *concentration equilibrium constant* takes into account the influence exerted by solute species upon one another. The thermodynamic equilibrium constant is numerically constant and independent of ionic strength; the concentration equilibrium constant depends on molar concentrations of reactants and products as well as other chemical species that may not participate in the equilibrium.

10-2. Activity coefficients have the following properties:

1. The activity coefficient depends on the solution ionic strength.

2. In very dilute solutions, the activity coefficient approaches unity.

3. For a given ionic strength, the activity coefficient becomes smaller as the charge of the chemical species increases.

4. At any ionic strength, the activity coefficients are approximately equal for chemical species having the same charge state.

10-3. **(a)** $MgCl_2 + 2NaOH \rightleftharpoons Mg(OH)_2(s) + 2NaCl$

Replacing divalent Mg^{2+} with Na^+ causes the ionic strength to decrease.

(b) $HCl + NaOH \rightleftharpoons H_2O + NaCl$

There is no change in the charge states of the ions present in the solution equilibria. The ionic strength is unchanged.

(c) $HOAc + NaOH \rightleftharpoons H_2O + NaOAc$

The ionic strength will increase because NaOH and NaOAc are totally ionized wheras acetic acid is only partially ionized.

10-4. **(a)** The ionic strength will increase when $FeCl_3$ is added to HCl.

(b) $3NaOH + FeCl_3 \rightleftharpoons Fe(OH)_3(s) + 3NaCl$

Addition of $FeCl_3$ to NaOH replaces a univalent OH^- with univalent Cl^-; thus, the ionic strength is unchanged.

(c) $3AgNO_3 + FeCl_3 \rightleftharpoons Fe(NO_3)_3 + 3\ AgCl(s)$

Addition of $FeCl_3$ replaces the univalent Ag^+ with the trivalent Fe^{3+}; thus, the ionic strength increases.

10-5. Water is a neutral molecule and its activity equals its concentration at all low to moderate ionic strengths. That is, its activity coefficient is unity. In solutions of low to moderate ionic strength, activity coefficients of ions decrease with increasing ionic strength because the ionic atmosphere surrounding the ion causes it to lose some of its chemical effectiveness and its activity is less than its concentration.

10-6. There is no ionic atmosphere surrounding a neutral molecule and so its activity is does not change with increasing ionic strength. Hence, its activity coefficient is essentially unity and its activity is equal to its concentration.

10-7. Multiply charged ions deviate from ideality more than singly charged ions because of the effect of the surrounding ionic atmosphere. The initial slope of the activity coefficient vs square root of ionic strength for Ca^{2+} is steeper than that for K^+ the activity coefficient of Ca^{2+} is more influenced by ionic strength than that for K^+.

10-8. Ammonia (NH_3) is an uncharged molecule and thus its activity coefficient is unity.

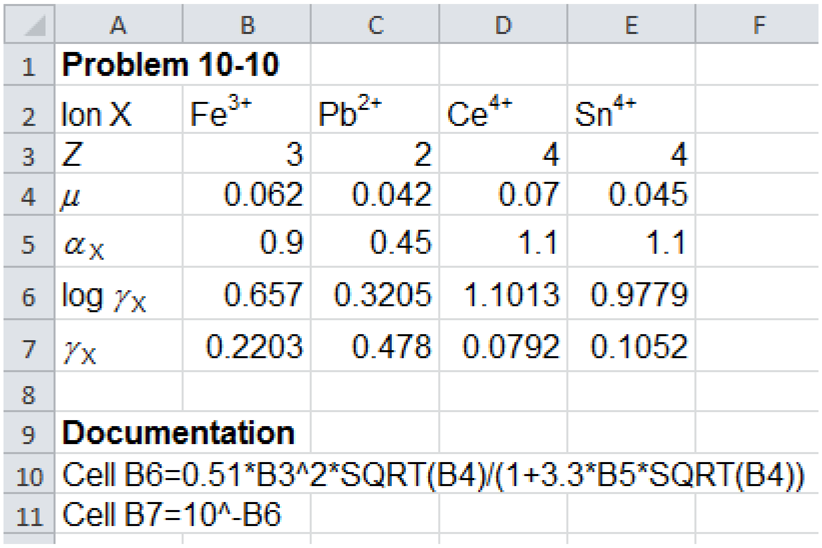
10-9. **(a)** $\mu = ½[0.030 \times 2^2 + 0.030 \times 2^2] = 0.12$

(b) $\mu = ½[0.60 \times 1^2 + 0.30 \times 2^2] = 0.90$

(c) $\mu = ½[0.30 \times 3^2 + 0.90 \times 1^2 + 0.20 \times 2^2 + 0.40 \times 1^2] = 2.4$

(d) $\mu = ½[0.03 \times 3^2 + 0.09 \times 1^2 + 0.06 \times 2^2 + 0.12 \times 1^2] = 0.36$

10-10. $-\log \gamma_X = \dfrac{0.51Z_X^2\sqrt{\mu}}{1 + 3.3\alpha_X\sqrt{\mu}}$ This problem is easiest to work with a spreadsheet.



	A	B	C	D	E	F
1	**Problem 10-10**					
2	Ion X	Fe^{3+}	Pb^{2+}	Ce^{4+}	Sn^{4+}	
3	Z	3	2	4	4	
4	μ	0.062	0.042	0.07	0.045	
5	α_X	0.9	0.45	1.1	1.1	
6	$\log \gamma_X$	0.657	0.3205	1.1013	0.9779	
7	γ_X	0.2203	0.478	0.0792	0.1052	
8						
9	**Documentation**					
10	Cell B6=0.51*B3^2*SQRT(B4)/(1+3.3*B5*SQRT(B4))					
11	Cell B7=10^-B6					

Rounding these results,gives

(a) 0.22 **(b)** 0.48 **(c)** 0.08 **(d)** 0.11

10-11. (a)

$$\mu = 0.05 \quad \gamma_{Fe^{3+}} = 0.24 \quad \mu = 0.10 \quad \gamma_{Fe^{3+}} = 0.18$$

$$\gamma_{Fe^{3+}}(\mu = 0.062) = 0.18 + \frac{0.038}{0.05}\left(0.24 - 0.18\right) = 0.23$$

(b)

$$\mu = 0.01 \quad \gamma_{Pb^{2+}} = 0.665 \quad \mu = 0.05 \quad \gamma_{Pb^{2+}} = 0.45$$

$$\gamma_{Pb^{2+}}(\mu = 0.042) = 0.45 + \frac{0.008}{0.05}\left(0.665 - 0.45\right) = 0.48$$

(c)

$$\mu = 0.05 \quad \gamma_{Ce^{4+}} = 0.10 \quad \mu = 0.10 \quad \gamma_{Ce^{4+}} = 0.063$$

$$\gamma_{Ce^{4+}}(\mu = 0.070) = 0.063 + \frac{0.03}{0.05}\left(0.10 - 0.063\right) = 0.085 \approx 0.08$$

(d)

$$\mu = 0.01 \quad \gamma_{Sn^{4+}} = 0.252 \quad \mu = 0.05 \quad \gamma_{Sn^{4+}} = 0.10$$

$$\gamma_{Sn^{4+}}(\mu = 0.045) = 0.10 + \frac{0.005}{0.04}\left(0.252 - 0.10\right) = 0.12$$

10-12. We must use $-\log \gamma_{\mathrm{X}} = \dfrac{0.51 Z_{\mathrm{X}}^2 \sqrt{\mu}}{1 + 3.3\alpha_{\mathrm{X}}\sqrt{\mu}}$

(a) For Ag^+, $\alpha_{\mathrm{Ag}^+} = 0.25$. At $\mu = 0.08$, $\gamma_{\mathrm{Ag}^+} = 0.7639$; For SCN^-, $\alpha_{\mathrm{SCN}^-} = 0.35$ and $\gamma_{\mathrm{SCN}^-} = 0.7785$ retaining insignificant figures for later calculations.

$$K'_{\mathrm{sp}} = \frac{K_{\mathrm{sp}}}{\gamma_{\mathrm{Ag}^+}\gamma_{\mathrm{SCN}^-}} = \frac{1.1 \times 10^{-12}}{(0.7639)(0.7785)} = 1.8 \times 10^{-12}$$

(b) For Pb^{2+} $\gamma_{\mathrm{Pb}2+} = 0.4042$ For I^-. $\gamma_{\mathrm{I}^-} = 0.7714$

$$K'_{\text{sp}} = \frac{K_{\text{sp}}}{\gamma_{\text{Pb}^{2+}}\gamma_{\text{I}^-}} = \frac{7.9 \times 10^{-9}}{(0.4042)(0.7714)^2} = 3.3 \times 10^{-8}$$

(c) For La^{3+}, $\gamma_{\text{La}3+} = 0.197$. For IO_3^-, $\gamma_{\text{IO}3-} = 0.7785$

$$K'_{\text{sp}} = \frac{K_{sp}}{\gamma_{\text{La}^{3+}}\gamma_{\text{IO}_3^-}} = \frac{1.0 \times 10^{-11}}{(0.197)(0.7785)^3} = 1.1 \times 10^{-10}$$

(d) For Mg^{2+}, $\gamma = 0.4674$; for NH_4^+, $\gamma = 0.7639$; for PO_4^{3-}, $\gamma = 0.1134$

$$K'_{\text{sp}} = \frac{K_{\text{sp}}}{\gamma_{\text{Mg}^{2+}}\gamma_{\text{NH}_4^+}\gamma_{\text{PO}_4^{3-}}} = \frac{3.0 \times 10^{-13}}{(0.4674)(0.7639)(0.1134)} = 7.4 \times 10^{-12}$$

10-13. $\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+} + 2\text{OH}^-$ $K_{\text{sp}} = 3.0 \times 10^{-16}$

(a) $\mu = ½[0.02 \times 1^2 + 0.02 \times 1^2] = 0.02$

Using Equation 10-5,

$$\gamma_{\text{Zn}^{2+}} = 0.5951 \quad \gamma_{\text{OH}^-} = 0.867$$

$$K'_{\text{sp}} = a_{\text{Zn}^{2+}}a^2_{\text{OH}^-} = \gamma_{\text{Zn}^{2+}}[\text{Zn}^{2+}] \times \gamma^2_{\text{OH}^-}[\text{OH}^-]^2$$

$$[\text{Zn}^{2+}][\text{OH}^-]^2 = \frac{3.0 \times 10^{-16}}{\gamma_{\text{Zn}^{2+}}\ \gamma^2_{\text{OH}^-}} = \frac{3.0 \times 10^{-16}}{(0.5951)(0.867)^2} = 6.706 \times 10^{-16}$$

Solubility = $S = [\text{Zn}^{2+}] = ½[\text{OH}^-]$

$S(2S)^2 = 6.706 \times 10^{-16}$

$$S = \left(\frac{6.706 \times 10^{-16}}{4}\right)^{1/3} = 5.5 \times 10^{-6}\ \text{M}$$

(b) $\mu = ½[2 \times 0.03 \times 1^2 + 0.03 \times 2^2] = 0.18$

From Equation 10-5,

$$\gamma_{\text{Zn}^{2+}} = 0.3386 \quad \gamma_{\text{OH}^-} = 0.7158$$

$$K'_{sp} = a_{Zn^{2+}}a^2_{OH^-} = \gamma_{Zn^{2+}}[Zn^{2+}] \times \gamma^2_{OH^-}[OH^-]^2$$

$$[Zn^{2+}][OH^-]^2 = \frac{3.0 \times 10^{-16}}{(0.3386)(0.7158)^2} = 1.729 \times 10^{-15}$$

Solubility = $S = [Zn^{2+}] = ½[OH^-]$

$S(2S)^2 = 1.729 \times 10^{-15}$

$$S = \left(\frac{1.729 \times 10^{-15}}{4}\right)^{\frac{1}{3}} = 7.6 \times 10^{-6} \text{ M}$$

(c)

$$\text{amount of KOH} = \frac{0.250 \text{ mmol}}{\text{mL}} \times 40.0 \text{ mL} = 10.0 \text{ mmol}$$

$$\text{amount of } ZnCl_2 = \frac{0.0250 \text{ mmol}}{\text{mL}} \times 60.0 \text{ mL} = 1.5 \text{ mmol}$$

$$[K^+] = \frac{10 \text{ mmol}}{100.0 \text{ mL}} = 0.10 \text{ M}$$

$$[OH^-] = \frac{\left(10 \text{ mmol} - (2 \times 1.5 \text{ mmol})\right)}{100.0 \text{ mL}} \times = 0.07 \text{ M}$$

$$[Cl^-] = \frac{2 \times 1.5 \text{ mmol}}{100.0 \text{ mL}} = 0.03 \text{ M}$$

$$[Zn^{2+}]=0$$

$\mu = ½[0.10 \times 1^2 + 0.07 \times 1^2 + 2 \times 0.03 \times 1^2] = 0.115$

From Equation 10-5,

$$\gamma_{Zn^{2+}} = 0.3856 \quad \gamma_{OH^-} = 0.7511 \qquad K'_{sp} = a_{Zn^{2+}}a^2_{OH^-} = \gamma_{Zn^{2+}}[Zn^{2+}] \times \gamma^2_{OH^-}[OH^-]^2$$

$$[Zn^{2+}][OH^-]^2 = \frac{3.0 \times 10^{-16}}{\gamma_{Zn^{2+}}\gamma^2_{OH^-}} = \frac{3.0 \times 10^{-16}}{(0.3856)(0.7511)^2} = 1.379 \times 10^{-15}$$

$$\text{Solubility} = S = [Zn^{2+}] \qquad S(0.07)^2 = 1.379 \times 10^{-15}$$

$$S = \left(\frac{1.379 \times 10^{-15}}{(0.07)^2}\right) = 2.8 \times 10^{-13} \text{ M}$$

(d)

$$\text{amount KOH} = \frac{0.100\text{ mmol}}{\text{mL}} \times 20.0\text{ mL} = 2.0\text{ mmol}$$

$$\text{amount ZnCl}_2 = \frac{0.0250\text{ mmol}}{\text{mL}} \times 80.0\text{ mL} = 2.0\text{ mmol}$$

$$[\text{K}^+] = \frac{2\text{ mmol}}{100.0\text{ mL}} = 0.02\text{ M}$$

$$[\text{OH}^-] = 0$$

$$[\text{Cl}^-] = \frac{2 \times 2.0\text{ mmol}}{100.0\text{ mL}} = 0.04\text{ M}$$

$$[\text{Zn}^{2+}] = \frac{2\text{ mmol } - \frac{1}{2}(2\text{ mmol})}{100.0\text{ mL}} = 0.01\text{ M}$$

$$\mu = \frac{1}{2}\left(0.02 \times 1^2 + 0.040 \times 1^2 + 0.01 \times 2^2\right) = 0.05$$

From Table 10-2,

$$\gamma_{\text{Zn}^{2+}} = 0.48 \quad \gamma_{\text{OH}^-} = 0.81$$

$$K'_{\text{sp}} = a_{\text{Zn}^{2+}} a^2_{\text{OH}^-} = \gamma_{\text{Zn}^{2+}}[\text{Zn}^{2+}] \times \gamma^2_{\text{OH}^-}[\text{OH}^-]^2$$

$$[\text{Zn}^{2+}][\text{OH}^-]^2 = \frac{3.0 \times 10^{-16}}{\gamma_{\text{Zn}^{2+}}\gamma^2_{\text{OH}^-}} = \frac{3.0 \times 10^{-16}}{(0.48)(0.81)^2} = 9.53\times10^{-16}$$

$$\text{Solubility} = S = [\text{OH}^-]/2$$

$$(0.01)[\text{OH}^-]^2 = 9.53 \times 10^{-16}$$

$$[\text{OH}^-] = \left(\frac{9.53 \times 10^{-16}}{0.01}\right)^{\frac{1}{2}} = 3.09 \times 10^{-7}\text{ M}$$

$$S = \left(3.09 \times 10^{-7}\text{ M}\right)/2 = 1.5 \times 10^{-7}\text{ M}$$

10-14. $\mu = ½[0.0333 \times 2^2 + 2 \times 0.0333 \times 1^2] = 0.100$ Can use data in Table 10-2.

(a) $\text{AgSCN}(s) \rightleftharpoons \text{Ag}^+ + \text{SCN}^-$

(1) For Ag^+, $\gamma_{\text{Ag}^+} = 0.75$; for SCN^-, $\gamma_{\text{SCN}^-} = 0.76$

$$K'_{sp} = \gamma_{Ag^+}[Ag^+]\gamma_{SCN^-}[SCN^-] = 1.1 \times 10^{-12}$$

$$[Ag^+][SCN^-] = \frac{1.1 \times 10^{-12}}{0.75 \times 0.76} = 1.9298 \times 10^{-12}$$

$S = [Ag^+] = [SCN^-]$

$$S = \sqrt{1.928 \times 10^{-12}} = 1.4 \times 10^{-6}\text{ M}$$

(2) $S = \sqrt{1.1 \times 10^{-12}} = 1.0 \times 10^{-6}$ M

(b)

$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$

(1) $\gamma_{Pb^{2+}} = 0.36 \quad \gamma_{I^-} = 0.75 \quad K'_{sp} = a_{Pb^{2+}}a_{I^-}^2 = \gamma_{Pb^{2+}}[Pb^{2+}] \times (\gamma_{I^-}[I^-])^2$

$$[Pb^{2+}][I^-]^2 = \frac{7.9 \times 10^{-9}}{\gamma_{Pb^{2+}}\gamma_{I^-}{}^2} = \frac{7.9 \times 10^{-9}}{(0.36)(0.75)^2} = 3.90 \times 10^{-8}$$

$$\text{Solubility} = S = [Pb^{2+}] = \frac{1}{2}[I^-]$$

$$S(2S)^2 = 3.90 \times 10^{-8}$$

$$S = \left(\frac{3.90 \times 10^{-8}}{4}\right)^{\frac{1}{3}} = 2.1 \times 10^{-3}\text{ M}$$

(2) $S = \left(\frac{7.9 \times 10^{-9}}{4}\right)^{\frac{1}{3}} = 1.3 \times 10^{-3}$ M

(c) $BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4{}^{2-}$

$\gamma_{Ba^{2+}} = 0.38; \quad \gamma_{SO_4{}^{2-}} = 0.35$

$$[Ba^{2+}][SO_4{}^{2-}] = \frac{1.1 \times 10^{-10}}{\gamma_{Ba^{2+}}\gamma_{SO_4{}^{2-}}} = \frac{1.1 \times 10^{-10}}{(0.38)(0.35)} = 8.3 \times 10^{-10}$$

$$\text{Solubility} = S = [Ba^{2+}] = [SO_4{}^{2-}]$$

$$S^2 = 8.3 \times 10^{-10}$$

$$S = \sqrt{8.3 \times 10^{-10}} = 2.9 \times 10^{-5}\text{ M}$$

(2) $S = \sqrt{1.1 \times 10^{-10}} = 1.0 \times 10^{-5}$ M

(d) $Cd_2Fe(CN)_6(s) \rightleftharpoons 2\ Cd^{2+} + Fe(CN)_6^{4-}$

(1) $\gamma_{Cd^{2+}} = 0.38 \quad \gamma_{Fe(CN)_6^{4-}} = 0.020$

$$[Cd^{2+}]^2[Fe(CN)_6^{4-}] = \frac{3.2\times10^{-17}}{\gamma^2_{Cd^{2+}}\gamma_{Fe(CN)_6^{4-}}} = \frac{3.2\times10^{-17}}{(0.38)^2(0.020)} = 1.108\times10^{-14}$$

$$\text{Solubility} = S = \frac{1}{2}[Cd^{2+}] = [Fe(CN)_6^{4-}]$$

$$(2S)^2S = 1.108\times10^{-14}$$

$$S = \left(\frac{1.108\times10^{-14}}{4}\right)^{\frac{1}{3}} = 1.4\times10^{-5}\ \text{M}$$

(2) $S = (\frac{3.2\times10^{-17}}{4})^{\frac{1}{3}} = 2.0\times10^{-6}\ \text{M}$

10-15. $\mu = ½[0.0167 \times 2^2 + 2 \times 0.0167 \times 1^2] = 0.050$

(a) $AgIO_3(s) \rightleftharpoons Ag^+ + IO_3^-$

(1) $\gamma_{Ag^+} = 0.80 \quad \gamma_{IO_3^-} = 0.82$

$$[Ag^+][IO_3^-] = \frac{3.1\times10^{-8}}{\gamma_{Ag^+}\gamma_{IO_3^-}} = \frac{3.1\times10^{-8}}{(0.80)(0.82)} = 4.7\times10^{-8}$$

$$\text{Solubility} = S = [Ag^+] = [IO_3^-]$$

$$S^2 = 4.7\times10^{-8}$$

$$S = \sqrt{4.7\times10^{-8}} = 2.2\times10^{-4}\ \text{M}$$

(2) $S = \sqrt{3.1\times10^{-8}} = 1.8\times10^{-4}\ \text{M}$

(b) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$

(1) $\gamma_{Mg^{2+}} = 0.52 \quad \gamma_{OH^-} = 0.8$

$$[\mathrm{Mg}^{2+}][\mathrm{OH}^-]^2 = \frac{7.1\times10^{-12}}{\gamma_{\mathrm{Mg}^{2+}}\gamma^2_{\mathrm{OH}^-}} = \frac{7.1\times10^{-12}}{(0.52)(0.81)^2} = 2.081\times10^{-11}$$

$$\text{Solubility} = S = [\mathrm{Mg}^{2+}] = \frac{1}{2}[\mathrm{OH}^-]$$

$$S(2S)^2 = 2.081\times10^{-11}$$

$$S = \left(\frac{2.081\times10^{-11}}{4}\right)^{\frac{1}{3}} = 1.7\times10^{-4}\ \mathrm{M}$$

$$(2)\quad S = \left(\frac{7.1\times10^{-12}}{4}\right)^{\frac{1}{3}} = 1.2\times10^{-4}\ \mathrm{M}$$

(c) $\mathrm{BaSO_4}(s) \rightleftharpoons \mathrm{Ba}^{2+} + \mathrm{SO_4}^{2-}$

$$(1)\quad \gamma_{\mathrm{Ba}^{2+}} = 0.46 \quad \gamma_{\mathrm{SO_4}^{2-}} = 0.44$$

$$[\mathrm{Ba}^{2+}][\mathrm{SO_4}^{2-}] = \frac{1.1\times10^{-10}}{\gamma_{\mathrm{Ba}^{2+}}\gamma_{\mathrm{SO_4}^{2-}}} = \frac{1.1\times10^{-10}}{(0.46)(0.44)} = 5.435\times10^{-10}$$

$$\text{Solubility} = S = [\mathrm{SO_4}^{2-}]$$

$$(0.0167)\times S = 5.435\times10^{-10}$$

$$S = \left(\frac{5.435\times10^{-10}}{0.0167}\right) = 3.3\times10^{-8}\ \mathrm{M}$$

$$(2)\quad S = \left(\frac{1.1\times10^{-10}}{0.0167}\right) = 6.6\times10^{-9}\ \mathrm{M}$$

(d) $\mathrm{La(IO_3)_3}(s) \rightleftharpoons \mathrm{La}^{3+} + 3\mathrm{IO_3}$

$$(1)\quad \gamma_{\mathrm{La}^{3+}} = 0.24 \quad \gamma_{\mathrm{IO_3}^-} = 0.82 \quad K_{\mathrm{sp}} = a_{\mathrm{La}^{3+}}a^3_{\mathrm{IO_3}^-} = \gamma_{\mathrm{La}^{3+}}[\mathrm{La}^{3+}]\times(\gamma_{\mathrm{IO_3}^-}[\mathrm{IO_3}^-])^3$$

$$[\mathrm{La}^{3+}][\mathrm{IO_3}^-]^3 = \frac{1.0\times10^{-11}}{\gamma_{\mathrm{La}^{3+}}\gamma^3_{\mathrm{IO_3}^-}} = \frac{1.0\times10^{-11}}{(0.24)(0.82)^3} = 7.557\times10^{-11}$$

$$\text{Solubility} = S = [\mathrm{La}^{3+}] = \frac{1}{3}[\mathrm{IO_3}^-]$$

$$S(3S)^3 = 7.557 \times 10^{-11}$$

$$S = \left(\frac{7.557 \times 10^{-11}}{27}\right)^{\frac{1}{4}} = 1.3 \times 10^{-3}\ \text{M}$$

$$(2)\quad S = \left(\frac{1.0 \times 10^{-11}}{27}\right)^{\frac{1}{4}} = 7.8 \times 10^{-4}\ \text{M}$$

10-16. (a) $\text{CuCl}(s) \rightleftharpoons \text{Cu}^{+} + \text{Cl}^{-}$

If we assume that Cu^{+} has an effective diameter of 0.3 like similarly charged cations, then

$$(1)\quad \gamma_{\text{Cu}^{+}} = 0.80 \quad \gamma_{\text{Cl}^{-}} = 0.80 \quad K'_{\text{sp}} = a_{\text{Cu}^{+}}a_{\text{Cl}^{-}} = \gamma_{\text{Cu}^{+}}[\text{Cu}^{+}]\times\gamma_{\text{Cl}^{-}}[\text{Cl}^{-}]$$

$$[\text{Cu}^{+}][\text{Cl}^{-}] = \frac{1.9 \times 10^{-7}}{\gamma_{\text{Cu}^{+}}\gamma_{\text{Cl}^{-}}} = \frac{1.9 \times 10^{-7}}{(0.80)(0.80)} = 2.969 \times 10^{-7}$$

$$\text{Solubility} = S = [\text{Cu}^{+}] = [\text{Cl}^{-}]$$

$$S^2 = 2.969 \times 10^{-7}$$

$$S = \sqrt{2.969 \times 10^{-7}} = 5.4 \times 10^{-4}\ \text{M}$$

$$(2)\quad S = \sqrt{1.9 \times 10^{-7}} = 4.4 \times 10^{-4} M$$

$$\text{relative error} = \frac{\left(4.4 \times 10^{-4} - 5.4 \times 10^{-4}\right)}{5.4 \times 10^{-4}} \times 100\% = -19\%$$

(b) $\text{Fe(OH)}_2(s) \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^{-}$

$$(1)\quad \gamma_{\text{Fe}^{2+}} = 0.48 \quad \gamma_{\text{OH}^{-}} = 0.81 \quad K'_{\text{sp}} = a_{\text{Fe}^{2+}}a^2_{\text{OH}^{-}} = \gamma_{\text{Fe}^{2+}}[\text{Fe}^{2+}]\times(\gamma_{\text{OH}^{-}}[\text{OH}^{-}])^2$$

$$[\text{Fe}^{2+}][\text{OH}^{-}]^2 = \frac{4.1 \times 10^{-15}}{\gamma_{\text{Fe}^{2+}}\gamma^2_{\text{OH}^{-}}} = \frac{4.1 \times 10^{-15}}{(0.48)(0.81)^2} = 1.302 \times 10^{-14}$$

$$\text{Solubility} = \text{S} = [\text{Fe}^{2+}] = \frac{1}{2}[\text{OH}^{-}]$$

$$S(2S)^2 = 1.302 \times 10^{-14}$$

$$S = \left(\frac{1.302\times10^{-14}}{4}\right)^{\frac{1}{3}} = 1.5\times10^{-5}\ \text{M}$$

$$(2)\quad S = \left(\frac{4.1\times10^{-15}}{4}\right)^{\frac{1}{3}} = 1.0\times10^{-5}\ \text{M}$$

$$\text{relative error} = \frac{1.0\times10^{-5} - 1.5\times10^{-5}}{1.5\times10^{-5}}\times100\% = -33\%$$

(c) $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

$$(1)\quad \gamma_{Fe^{3+}} = 0.24 \quad \gamma_{OH^-} = 0.81 \quad K'_{sp} = a_{Fe^{3+}}a^3_{OH^-} = \gamma_{Fe^{3+}}[Fe^{3+}]\times(\gamma_{OH^-}[OH^-])^3$$

$$[Fe^{3+}][OH^-]^3 = \frac{2\times10^{-39}}{\gamma_{Fe^{3+}}\gamma^3_{OH^-}} = \frac{2\times10^{-39}}{(0.24)(0.81)^3} = 1.568\times10^{-38}$$ retaining figures until the end

$$\text{Solubility} = S = [Fe^{3+}] = \frac{1}{3}[OH^-]$$

$$S(3S)^3 = 1.568\times10^{-38}$$

$$S = \left(\frac{1.568\times10^{-38}}{27}\right)^{\frac{1}{4}} = 1.55\times10^{-10}\ \text{M}$$

$$(2)\quad S = \left(\frac{2\times10^{-39}}{27}\right)^{\frac{1}{4}} = 9.3\times10^{-11}M$$

$$\text{relative error} = \frac{9.3\times10^{-11} - 1.55\times10^{-10}}{1.55\times10^{-10}}\times100\% = -40\%$$

(d) $La(IO_3)_3(s) \rightleftharpoons La^{3+} + 3IO_3$

$$(1)\quad \gamma_{La^{3+}} = 0.24 \quad \gamma_{IO_3^-} = 0.82 \quad K'_{sp} = a_{La^{3+}}a^3_{IO_3^-} = \gamma_{La^{3+}}[La^{3+}]\times(\gamma_{IO_3^-}[IO_3^-])^3$$

$$[La^{3+}][IO_3^-]^3 = \frac{1.0\times10^{-11}}{\gamma_{La^{3+}}\gamma^3_{IO_3^-}} = \frac{1.0\times10^{-11}}{(0.24)(0.82)^3} = 7.557\times10^{-11}$$

$$\text{Solubility} = S = [La^{3+}] = \frac{1}{3}[IO_3^-]$$

$$S(3S)^3 = 7.557 \times 10^{-11}$$

$$S = \left(\frac{7.557 \times 10^{-11}}{27}\right)^{\frac{1}{4}} = 1.3 \times 10^{-3} \text{ M}$$

$$(2) \quad S = \left(\frac{1.1 \times 10^{-11}}{27}\right)^{\frac{1}{4}} = 8.0 \times 10^{-4} \text{ M}$$

$$\text{relative error} = \frac{8.0 \times 10^{-4} - 1.3 \times 10^{-3}}{1.3 \times 10^{-3}} \times 100\% = -38\%$$

(e) $Ag_3(AsO_4)(s) \rightleftharpoons 3Ag^+ + AsO_4^{3-}$

Since the α_X of AsO_4^{3-} was given as 0.4, the γ value will be like PO_4^{3-}. So,

$$(1) \quad \gamma_{Ag^+} = 0.80 \quad \gamma_{AsO_4^{3-}} = 0.16 \quad K'_{sp} = a^3_{Ag^+} a_{AsO_4^{3-}} = (\gamma_{Ag^+}[Ag^+])^3 \times \gamma_{AsO_4^{3-}}[AsO_4^{3-}]$$

$$[Ag^+]^3[AsO_4^{3-}] = \frac{6 \times 10^{-23}}{\gamma^3_{Ag^+}\gamma_{AsO_4^{3-}}} = \frac{6 \times 10^{-23}}{(0.80)^3(0.16)} = 7.324 \times 10^{-22}$$

$$\text{Solubility} = S = [AsO_3^{4-}] = \frac{1}{3}[Ag^+]$$

$$(3S)^3 S = 7.324 \times 10^{-22}$$

$$S = \left(\frac{7.324 \times 10^{-22}}{27}\right)^{\frac{1}{4}} = 2.3 \times 10^{-6} \text{ M}$$

$$(2) \quad S = \left(\frac{6 \times 10^{-23}}{27}\right)^{\frac{1}{4}} = 1.2 \times 10^{-6} \text{ M}$$

$$\text{relative error} = \frac{1.2 \times 10^{-6} - 2.3 \times 10^{-6}}{2.3 \times 10^{-6}} \times 100\% = -48\%$$

10-17. (a)

In this buffer solution, we assume [HOAc] = c_{HOAc} and $[OAC^-] = c_{NaOAc}$. We also assume that the ionic strength is contributed solely by NaOAc, neglecting H_3O^+ and OH^-.

μ = ½[0.250 × 1^2 + 0.250 × 1^2] = 0.250

$$-\log\gamma_{\mathrm{H_3O^+}} = \frac{(0.51)(1)^2\sqrt{0.250}}{1+(3.3)(0.9)\sqrt{0.250}} = 0.1026 \quad \gamma_{\mathrm{H_3O^+}} = 0.790$$

$$-\log\gamma_{\mathrm{OAc^-}} = \frac{(0.51)(1)^2\sqrt{0.250}}{1+(3.3)(0.425)\sqrt{0.520}} = 0.1499 \quad \gamma_{\mathrm{OAc^-}} = 0.708$$

$$K_{\mathrm{a}} = \frac{\gamma_{\mathrm{H_3O^+}}[\mathrm{H_3O^+}]\gamma_{\mathrm{OAc^-}}[\mathrm{OAc^-}]}{[\mathrm{HOAc}]}$$

$$K'_{\mathrm{a}} = \frac{[\mathrm{H_3O^+}][\mathrm{OAc^-}]}{[\mathrm{HOAc}]} = \frac{K_{\mathrm{a}}}{\gamma_{\mathrm{H_3O^+}}\gamma_{\mathrm{OAc^-}}} = \frac{1.75\times10^{-5}}{0.790\times0.708} = 3.129\times10^{-5}$$

$$[\mathrm{H_3O^+}] = \frac{K'_a[\mathrm{HOAc}]}{[\mathrm{OAc^-}]} = \frac{3.129\times10^{-5}\times0.150}{0.250} = 1.9\times10^{-5}\ \mathrm{M}$$

pH = 4.73

With no activity corrections

$$[\mathrm{H_3O^+}] = \frac{1.75\times10^{-5}\times0.150}{0.250} = 1.05\times10^{-5}\ \mathrm{M}$$

pH = 4.98

$$\text{relative error in }[\mathrm{H_3O^+}] = \frac{1.05\times10^{-5} - 1.9\times10^{-5}}{1.9\times10^{-5}}\times100\% = -45\%$$

(b) In this buffer, we assume that the ionic strength is contributed by only NH_4Cl and that $c_{NH_3} = [NH_3]$ and $c_{NH_4^+} = [NH_4^+]$.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $\quad K_b = K_w/K_a = 1.00\times10^{-14}/5.70\times10^{-10} = 1.75\times10^{-5}$

$\mu = ½[0.100 \times 1^2 + 0.100 \times 1^2] = 0.100$

From Table 10-2, $\gamma_{\mathrm{NH_4^+}} = 0.75$, $\gamma_{\mathrm{OH^-}} = 0.76$

$$K_\mathrm{b} = \frac{a_{\mathrm{NH_4^+}} a_{\mathrm{OH^-}}}{a_{\mathrm{NH_3}}} = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]\gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{OH^-}}}{[\mathrm{NH_3}]} = K'_\mathrm{b}\gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{OH^-}}$$

$$K'_\mathrm{b} = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]} = \frac{K_\mathrm{b}}{\gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{OH^-}}} = \frac{1.75 \times 10^{-5}}{0.75 \times 0.76} = 3.07 \times 10^{-5}$$

$$[\mathrm{OH^-}] = \frac{K'_\mathrm{b}[\mathrm{NH_3}]}{[\mathrm{NH_4^+}]} = \frac{3.07 \times 10^{-5} \times 0.040}{0.100} = 1.2 \times 10^{-5}\ \mathrm{M}$$

$$[\mathrm{H_3O^+}] = \frac{K_\mathrm{w}}{[\mathrm{OH^-}]} = \frac{1.00 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.1 \times 10^{-10}\ \mathrm{M}$$

Assuming activity coefficients are unity,

$$[\mathrm{OH^-}] = \frac{K_\mathrm{b}[\mathrm{NH_3}]}{[\mathrm{NH_4^+}]} = \frac{1.75 \times 10^{-5} \times 0.040}{0.100} = 7.0 \times 10^{-6}\ \mathrm{M}$$

$$[\mathrm{H_3O^+}] = \frac{K_\mathrm{w}}{[\mathrm{OH^-}]} = \frac{1.00 \times 10^{-14}}{7.0 \times 10^{-6}} = 1.4 \times 10^{-9}\ \mathrm{M}$$

$$\text{relative error} = \frac{1.4 \times 10^{-9} - 8.1 \times 10^{-10}}{8.1 \times 10^{-10}} = 73\%$$

(c)

$\mathrm{ClHOAc + H_2O \rightleftharpoons H_3O^+ + ClOAc^-}$ $K_\mathrm{a} = 1.36 \times 10^{-3}$

We assume that the ionic strength is created by NaClHOAc = 0.050, [ClHOAc] = 0.020 M, and [ClOAc$^-$] = 0.050 M

Hence, $\gamma_{\mathrm{H_3O^+}} = 0.85$, $\gamma_{\mathrm{ClOAc^-}} = 0.81$

$$K'_a = \frac{[H_3O^+][ClOAc^-]}{[ClHOAc]} = \frac{K_a}{\gamma_{H_3O^+}\gamma_{ClOAc^-}} = \frac{1.36 \times 10^{-3}}{0.85 \times 0.81} = 1.975 \times 10^{-3}$$

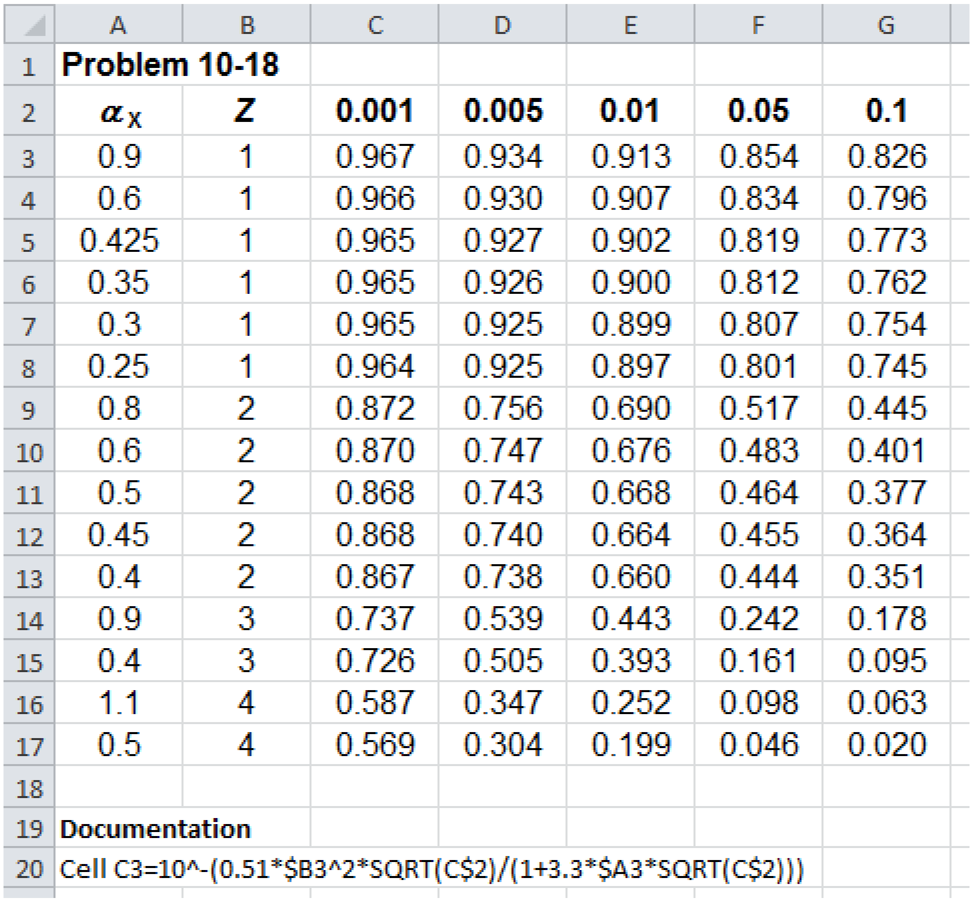
$$[H_3O^+] = \frac{1.975 \times 10^{-3} \times [ClHOAc]}{[ClOAc^-]} = \frac{1.975 \times 10^{-3} \times 0.020}{0.050} = 7.9 \times 10^{-4}\ M$$

With no activity corrections,

$$[H_3O^+] = \frac{1.36 \times 10^{-3} \times 0.020}{0.050} = 5.4 \times 10^{-4}\ M$$

$$\text{relative error} = \frac{5.4 \times 10^{-4} - 7.9 \times 10^{-4}}{7.9 \times 10^{-4}} \times 100\% = 31.6\%$$

10-18.



	A	B	C	D	E	F	G
1	**Problem 10-18**						
2	α_X	**Z**	**0.001**	**0.005**	**0.01**	**0.05**	**0.1**
3	0.9	1	0.967	0.934	0.913	0.854	0.826
4	0.6	1	0.966	0.930	0.907	0.834	0.796
5	0.425	1	0.965	0.927	0.902	0.819	0.773
6	0.35	1	0.965	0.926	0.900	0.812	0.762
7	0.3	1	0.965	0.925	0.899	0.807	0.754
8	0.25	1	0.964	0.925	0.897	0.801	0.745
9	0.8	2	0.872	0.756	0.690	0.517	0.445
10	0.6	2	0.870	0.747	0.676	0.483	0.401
11	0.5	2	0.868	0.743	0.668	0.464	0.377
12	0.45	2	0.868	0.740	0.664	0.455	0.364
13	0.4	2	0.867	0.738	0.660	0.444	0.351
14	0.9	3	0.737	0.539	0.443	0.242	0.178
15	0.4	3	0.726	0.505	0.393	0.161	0.095
16	1.1	4	0.587	0.347	0.252	0.098	0.063
17	0.5	4	0.569	0.304	0.199	0.046	0.020
18							
19	**Documentation**						
20	Cell C3=10^-(0.51*$B3^2*SQRT(C$2)/(1+3.3*$A3*SQRT(C$2)))						

Chapter 11

11-1. The overall dissociation constant for H_2S is

$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_1K_2$$

In a solution saturated with the gas, $[H_2S]$ is constant, therefore

$$[S^{2-}] = \frac{[H_2S]}{[H_3O^+]^2}K_1K_2 \qquad \text{or } [S^{2-}] = \frac{K}{[H_3O^+]^2}$$

11-2. To simplify equilibrium calculations, we sometimes assume that the concentrations of one or more species are negligible and can be approximated as 0.00 M. In a sum or difference assuming a concentration is 0.00 M leads to an appropriate result. In contrast, if we were to simplify and equilibrium constant expression by assuming on or more concentrations are zero, we would be multiplying or dividing by 0.00, which would render the expression meaningless.

11-3. Let us take the case of 0.100 M acetic acid (HOAc). We usually write the mass balance as a concentration balance. That is

$c_{HOAc} = 0.100 = [HOAc] + [OAc^-]$

Since the concentrations are moles/L, we can write

Initial moles HOAc/L = equilibrium moles HOAc/L + equilibrium moles OAc^-/L

Since everything is in the same volume of solution, this becomes

Initial no. moles HOAc = equilibrium no. moles of HOAc + equilibrium no. moles OAc^-

If we divide these quantities by the molecular mass, we obtain, after rearranging:

Initial mass HOAC = equil. mass HOAC + mass OAc^- × $\mathcal{M}_{HOAc}/\mathcal{M}_{OAc-}$

11-4. A charge-balance equation is derived by relating the concentration of cations and anions

no. mol/L positive charge = no. mol/L negative charge

For a doubly charged ion, such as Ba^{2+}, the concentration of charge for each mole is twice the molar *concentration* of the Ba^{2+}. That is,

mol/L positive charge = $2[Ba^{2+}]$

Thus, the molar concentration of all multiply charged species is always multiplied by the charge in a charge-balance equation.

11-5. **(a)** $0.20 = [HF] + [F^-]$

(b) For $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$, we write

$0.35 = [NH_3] + [NH_4]^+$

(c) $0.10 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

(d) $0.20 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

$[Na^+] = 2c_{\mathrm{Na2HPO4}} = 0.40$ M

(e) $0.0500 + 0.100 = [HClO_2] + [ClO_2^-]$

$[Na^+] = c_{\mathrm{NaClO2}} = 0.100$ M

(f) $[F^-] + [HF] = 0.12 + 2[Ca^{2+}]$

$[Na^+] = 0.12$ M

(g) $0.100 = [Na^+] = [OH^-] + 2\,[Zn(OH)_4^{2-}]$

(h) $[Ag^+] = 2([C_2O_4^{2-}] + [HC_2O_4^-] + [H_2CO_4])$

(i) $[Pb^{2+}] = ½([Cl^-]\,)$

11-6. **(a)** $[H_3O^+] = [F^-] + [OH^-]$

(b) $[H_3O^+] + [NH_4^+] = [OH^-]$

(c) $[H_3O^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$

(d) $[Na^+] + [H_3O^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$

(e) $[Na^+] + [H_3O^+] = [OH^-] + [ClO_2^-]$

(f) $[Na^+] + [H_3O^+] + 2[Ca^{2+}] = [OH^-] + [F^-]$

(g) $2[Zn^{2+}] + [Na^+] + [H_3O^+] = =[Zn(OH)_4^{2-}] + [OH^-]$

(h) $[Ag^+] + [H_3O^+] = 2[C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-]$

(i) $2[Pb^{2+}] + [H_3O^+] = [Cl^-] + [OH^-]$

11-7. Following the systematic procedure, using part (a)

Step 1 $SrC_2O_4(s) \rightleftharpoons Sr^{2+} + C_2O_4^{2-}$

$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$

$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$

Step 2 S = solubility = $[Sr^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [\ H_2C_2O_4]$

Step 3 $[Sr^{2+}][C_2O_4^{2-}] = K_{sp} = 5 \times 10^{-8}$ (1)

$$\frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = K_1 = 5.6 \times 10^{-2} \quad (2)$$

$$\frac{[H_3O^+][C_2O_4^-]}{[HC_2O_4^-]} = K_2 = 5.42 \times 10^{-5} \quad (3)$$

Step 4 $[Sr^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [\ H_2C_2O_4]$ (4)

$[H_3O^+] = 1.0 \times 10^{-6}$ M

Step 5 No charge balance because an unknown buffer is maintaining the pH.

Step 6 Unknowns are $[Sr^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, $[H_2C_2O_4]$

Step 7 No approximations needed, because we have 4 equations and 4 unkowns.

Step 8 Substituting $[H_3O^+] = 1.0 \times 10^{-6}$ M into equation (3) and rearranging gives

$$[HC_2O_4^-] = \frac{1 \times 10^{-6}[C_2O_4^-]}{5.42 \times 10^{-5}} = 1.845 \times 10^{-2}[C_2O_4^-]$$

Substituting this relationship and $[H_3O^+] = 1.0 \times 10^{-6}$ M into equation (2) and rearranging gives

$$[H_2C_2O_4] = \frac{1 \times 10^{-6} \times 1.845 \times 10^{-2}[C_2O_4^-]}{5.6 \times 10^{-2}} = 3.295 \times 10^{-7}[C_2O_4^-]$$

Substituting these last two relationships in to equation (4) gives

$$[Sr^{2+}] = [C_2O_4^{2-}] + 1.845 \times 10^{-2}[C_2O_4^{2-}] + 3.295 \times 10^{-7}[C_2O_4^{2-}] = 1.0185[C_2O_4^{2-}]$$

Substituting this last relationship into equation (1) gives

$$K_{sp} = \frac{[Sr^{2+}][Sr^{2+}]}{1.0185} = 5 \times 10^{-8}$$

$$[Sr^{2+}] = (5 \times 10^{-8} \times 1.0185)^{1/2} = 2.26 \times 10^{-4}$$

$$S = [Sr^{2+}] = 2.3 \times 10^{-4}\ \text{M}$$

Substituting other values for $[H_3O^+]$ gives the following:

	$[H_3O^+]$	S, M
(a)	1.00×10^{-6}	2.3×10^{-4}
(b)	1.00×10^{-7}	2.2×10^{-4}
(c)	1.00×10^{-9}	2.2×10^{-4}
(d)	1.00×10^{-11}	2.2×10^{-4}

11-8. Proceeding as in Problem 11-7, we write

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ $K_{sp} = 1.1 \times 10^{-10}$

$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ $K_2 = 1.02 \times 10^{-2}$

$S = [Ba^{2+}]$

$$[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10} \qquad (1)$$

$$\frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = 1.02 \times 10^{-2} \qquad (2)$$

Mass balance requires that

$$[Ba^{2+}] = [SO_4^{2-}] + [HSO_4^-] \qquad (3)$$

The unknowns are $[Ba^{2+}]$, $[SO_4^{2-}]$, and $[HSO_4^-]$

We have 3 equations and 3 unknowns so no approximations are needed.

Substituting eqation (2) into (3) gives

$$[Ba^{2+}] = [SO_4^{2-}] + \frac{[H_3O^+][SO_4^{2-}]}{1.02 \times 10^{-2}} = [SO_4^{2-}]\left(1 + \frac{[H_3O^+]}{1.02 \times 10^{-2}}\right)$$

Substituting equation (1) to eliminate $[SO_4^{2-}]$, gives

$$[Ba^{2+}] = \frac{1.1 \times 10^{-10}}{[Ba^{2+}]} \times \left(1 + \frac{[H_3O^+]}{1.02 \times 10^{-2}}\right) = \frac{1.1 \times 10^{-10}}{[Ba^{2+}]} \times \left(1 + 98.0[H_3O^+]\right)$$

$$S = [Ba^{2+}] = \sqrt{1.1 \times 10^{-10}\left(1 + 98.0[H_3O^+]\right)} = \sqrt{1.1 \times 10^{-10} + 1.078 \times 10^{-8}[H_3O^+]}$$

Using the different values of $[H_3O^+]$

	$[H_3O^+]$	**S, M**
(a)	3.5	1.9×10^{-4}
(b)	0.5	7.4×10^{-5}
(c)	0.08	3.1×10^{-5}
(d)	0.100	3.4×10^{-5}

11-9. The derivation that follows applies to problems 9-11.

$MS(s) \rightleftharpoons M^{2+} + S^{2-}$ K_{sp}

$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$ $K_1 = 9.6 \times 10^{-8}$

$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$ $K_2 = 1.3 \times 10^{-14}$

Overall $H_2S + 2H_2O \rightleftharpoons 2H_3O^+ + S^{2-}$ $K_1K_2 = 1.25 \times 10^{-21}$

S = solubility = $[M^{2+}]$

$$[M^{2+}][S^{2-}] = K_{sp} \qquad (1)$$

$$\frac{[H_3O^+][HS^-]}{[H_2S]} = K_2 = 1.3 \times 10^{-14} \qquad (2)$$

$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_1K_2 = 1.25 \times 10^{-21} \qquad (3)$$

Mass balance is:

$$[M^{2+}] = [S^{2-}] + [HS^-] + [H_2S] \qquad (4)$$

Substituting equation (2) and (3) into (4), gives:

$$[M^{2+}] = [S^{2-}] + \frac{[H_3O^+][S^{2-}]}{K_2} + \frac{[H_3O^+]^2[S^{2-}]}{K_1K_2} = [S^{2-}]\left(1 + \frac{[H_3O^+]}{K_2} + \frac{[H_3O^+]^2}{K_1K_2}\right) \qquad (5)$$

Substituting equation (1) into (5), gives

$$[M^{2+}] = \frac{K_{sp}}{[M^{2+}]}\left(1 + \frac{[H_3O^+]}{K_2} + \frac{[H_3O^+]^2}{K_1K_2}\right)$$

$$[M^{2+}] = \sqrt{K_{sp}\left(1 + \frac{[H_3O^+]}{1.3 \times 10^{-14}} + \frac{[H_3O^+]^2}{1.25 \times 10^{-21}}\right)} \qquad (6)$$

(a) Substituting $K_{sp} = 3 \times 10^{-28}$ and $[H_3O^+] = 3.0 \times 10^{-1}$ into equation (6), gives

$$[M^{2+}] = \text{ solubility} = \sqrt{3\times10^{-28}\left(1+\frac{0.30}{1.3\ \times\ 10^{-14}}\ +\ \frac{(0.30)^2}{1.25\ \times\ 10^{-21}}\right)} = 1.5 \times 10^{-4}\text{ M}$$

(b) Using the same K_{sp}, but $[H_3O^+] = 3.0 \times 10^{-4}$, gives

$[M^{2+}]$ = solubility = 1.5×10^{-7} M

11-10. For CuS, $K_{sp} = 8 \times 10^{-37}$

(a) For $[H_3O^+] = 2.0 \times 10^{-1}$,

$[M^{2+}]$ = solubility = 5.1×10^{-9} M

(b) For $[H_3O^+] = 2.0 \times 10^{-4}$

$[M^{2+}]$ = solubility = 5.1×10^{-12} M

11-11. For MnS(pink), $K_{sp} = 3.0 \times 10^{-11}$

(a) For $[H_3O^+] = 3.00 \times 10^{-5}$

$[M^{2+}]$ = solubility = 4.7 M

(b) For $[H_3O^+] = 3.00 \times 10^{-7}$

$[M^{2+}]$ = solubility = 5.3×10^{-2} M

11-12. Proceeding as in Problem 11-9, we find

$$[Zn^{2+}] = \sqrt{K_{sp}\left(1+\frac{[H_3O^+]}{K_2}\ +\ \frac{[H_3O^+]^2}{K_1K_2}\right)}$$

For $ZnCO_3$, $K_{sp} = 1.0 \times 10^{-10}$. For H_2CO_3, $K_1 = 4.45 \times 10^{-7}$, and $K_2 = 4.69 \times 10^{-11}$

$$[Zn^{2+}] = \sqrt{1\ \times\ 10^{-10}\left(1\ +\ \frac{[H_3O^+]}{4.69\ \times\ 10^{-11}}\ +\ \frac{[H_3O^+]^2}{4.45\ \times\ 10^{-7}\ \times\ 4.69\ \times\ 10^{-11}}\right)}$$

For pH = 7.00, $[H_3O^+] = 1.00 \times 10^{-7}$

$[Zn^{2+}] = 5.1 \times 10^{-4}$ M

11-13. $Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$ $\qquad K_{sp} = [Ag^+]^2[CO_3^{2-}] = 8.1 \times 10^{-12}$ (1)

$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ $\qquad K_1 = \dfrac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7}$ (2)

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ $\qquad K_2 = \dfrac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$ (3)

$H_2CO_3 + 2H_2O \rightleftharpoons 2H_3O^+ + CO_3^{2-}$ $\qquad K_1K_2 = \dfrac{[H_3O^+]^2[CO_3^{2-}]}{[H_2CO_3]} = 2.087 \times 10^{-17}$ (4)

Solubility = $[Ag^+]/2$

pH = 7.50, $[H_3O^+] = 3.16 \times 10^{-8}$

Mass balance:

$$\frac{[Ag^+]}{2} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \qquad (5)$$

$$[H_3O^+] = 3.16 \times 10^{-8} \qquad (6)$$

Substituting equations (3), (4) and (6) into (5) gives,

$$\frac{[Ag^+]}{2} = [CO_3^{2-}]\left(1 + \frac{3.16 \times 10^{-8}}{4.69 \times 10^{-11}} + \frac{\left(3.16 \times 10^{-8}\right)^2}{2.087 \times 10^{-17}}\right)$$

Substituting equation (1) into this expression gives,

$$\frac{[Ag^+]}{2} = \frac{K_{sp}}{[Ag^+]^2}\left(1 + \frac{3.16 \times 10^{-8}}{4.69 \times 10^{-11}} + \frac{\left(3.16 \times 10^{-8}\right)^2}{2.087 \times 10^{-17}}\right)$$

$$[Ag^+]^3 = 2 \times 8.1 \times 10^{-12}\left(1 + \frac{3.16 \times 10^{-8}}{4.69 \times 10^{-11}} + \frac{\left(3.16 \times 10^{-8}\right)^2}{2.087 \times 10^{-17}}\right)$$

$[Ag^+] = 2.27 \times 10^{-3}$ M

$S = [Ag^+]/2 = 1.1 \times 10^{-3}$ M

11-14. $[Cu^{2+}][OH^-]^2 = 4.8 \times 10^{-20}$ $[Mn^{2+}][OH^-]^2 = 2 \times 10^{-13}$

(a) $Cu(OH)_2$ precipitates first

(b) Cu^{2+} begins to precipitate when

$$[OH^-] = \sqrt{\frac{4.8 \times 10^{-20}}{0.05}} = 9.8 \times 10^{-10} \text{ M}$$

(c) Mn^{2+} begins to precipitate when

$$[OH^-] = \sqrt{\frac{2 \times 10^{-13}}{0.04}} = 2.24 \times 10^{-6} \text{ M}$$

$[Cu^{2+}] = 4.8 \times 10^{-20}/(2.24 \times 10^{-6})^2 = 9.6 \times 10^{-9}$ M

11-15. $Ba(IO_3)_2 \rightleftharpoons Ba^{2+} + 2IO_3^-$ $K_{sp} = 1.57 \times 10^{-9}$

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ $K_{sp} = 1.3 \times 10^{-10}$

To initiate precipitation of $Ba(IO_3)_2$

$[Ba^{2+}] = 1.57 \times 10^{-9}/(0.050)^2 = 6.3 \times 10^{-7}$

To initiate precipitation of $BaSO_4$

$[Ba^{2+}] = 1.3 \times 10^{-10}/(0.040) = 3.2 \times 10^{-9}$ M

(a) $BaSO_4$ precipitates first

(b) $[Ba^{2+}] = 3.2 \times 10^{-9}$ M

(c) When $[Ba^{2+}] = 6.3 \times 10^{-7}$ M

$[SO_4^{2-}] = 1.1 \times 10^{-10}/(6.3 \times 10^{-7}) = 1.7 \times 10^{-4}$ M

11-16. (a) $[Ag^+] = K_{sp}/[I^-] = 8.3 \times 10^{-17}/(1.0 \times 10^{-6}) = 8.3 \times 10^{-11}$ M

(b) $[Ag^+] = K_{sp}/[SCN–] = 1.1 \times 10^{-12}/(0.080) = 1.375 \times 10^{-11}$ M $\approx 1.4 \times 10^{-11}$ M

(c) $[I^-]$ when $[Ag^+] = 1.375 \times 10^{-11}$ M

$[I^-] = 8.3 \times 10^{-17}/(1.375 \times 10^{-11}) = 6.0 \times 10^{-6}$ M

$[SCN^-]/[I^-] = 0.080/(6.0 \times 10^{-6}) = 1.3 \times 10^4$

(d) $[I^-] = 8.3 \times 10^{-17}/(1.0 \times 10^{-3}) = 8.3 \times 10^{-14}$ M

$[SCN^-] = 1.1 \times 10^{-12}/(1.0 \times 10^{-3}) = 1.1 \times 10^{-9}$ M

$[SCN^-]/[I^-] = 1.1 \times 10^{-9}/(8.3 \times 10^{-14}) = 1.3 \times 10^4$

Note that this ratio is independent of $[Ag^+]$ as long as some $AgSCN_{(s)}$ is present.

11-17. (a) $[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$ $[Sr^{2+}][SO_4^{2-}] = 3.2 \times 10^{-7}$

$BaSO_4$ precipitation is complete when

$[SO_4^{2-}] = 1.1 \times 10^{-10}/(1.0 \times 10^{-6}) = 1.1 \times 10^{-4}$ M

$SrSO_4$ begins to precipitate when

$[SO_4^{2-}] = 3.2 \times 10^{-7}/(0.040) = 8.0 \times 10^{-6}$ M

$SrSO_4$ begins to precipitate before the Ba^{2+} concentration is reduced to 1.0×10^{-6} M

(b) $[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$ $[Ag^+]^2[SO_4^{2-}] = 1.6\times10^{-5}$

$BaSO_4$ precipitation is complete when $[SO_4^{2-}] = 1.1 \times 10^{-4}$ M

Ag_2SO_4 begins to precipitate when

$[SO_4^{2-}] = 1.6 \times 10^{-5}/(0.030)^2 = 0.0177$ M

Ag_2SO_4 does not precipitate before the Ba^{2+} concentration is reduced to 1.0×10^{-6} M

(c) Be^{3+} precipitates when $[OH^-] = (7.0 \times 10^{-22}/0.030)^{1/2} = 1.5 \times 10^{-10}$ M

Hf^{4+} precipitates when $[OH^-] = (4.0 \times 10^{-26}/0.020)^{1/4} = 1.2 \times 10^{-6}$ M

Be precipitation complete when $[OH^-] = (7.0 \times 10^{-22}/1.0 \times 10^{-6})^{1/2} = 2.6 \times 10^{-8}$ M

$Hf(OH)_4$ does not precipitate before the Be^{3+} concentration is reduced to 1.0×10^{-6} M.

(d) In^{3+} precipitates when $[IO_3^-] = (3.3 \times 10^{-11}/0.30)^{1/3} = 4.8 \times 10^{-4}$ M

Tl^+ precipitates when $[IO_3^-] = 3.1 \times 10^{-6}/(0.10) = 3.1 \times 10^{-5}$ M

Tl^+ precipitation complete when $[IO_3^-] = 3.1 \times 10^{-6}/1.0 \times 10^{-6} = 3.1$ M

$In(IO_3)_3$ begins to precipitate before the Tl^+ concentration is reduced to 1.0×10^{-6} M.

11-18. $AgBr \rightleftharpoons Ag^+ + Br^- \qquad K_{sp} = 5.0\times10^{-13} = [Ag^+][Br^-] \qquad (1)$

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^- \qquad \beta_2 = 1.3\times10^{21} = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} \qquad (2)$$

It is readily shown that $CN^- + H_2O \rightleftharpoons HCN + OH^-$ can be neglected in this problem so that only the two equilibria shown above need to be considered.

Solubility = $[Br^-]$

Mass balance requires that

$[Br^-] = [Ag^+] + [Ag(CN)_2^-] \qquad (3)$

$0.200 = [CN^-] + 2[Ag(CN)_2^-] \qquad (4)$

We now have 4 equations and 4 unknowns.

Because β_2 is very large, let us assume that

$[CN^-] << 2[Ag(CN)_2^-]$ and $[Ag^+] << [Ag(CN)_2^-]$

(4) becomes $[Ag(CN)_2^-] = 0.200/2 = 0.100$

and (3) becomes $[Br^-] = [Ag(CN)_2^-] = 0.100$

To check the assumptions, we calculate $[Ag^+]$ by substituting into (1)

$[Ag^+] = 5.0 \times 10^{-13}/0.100 \cong 5 \times 10^{-12}$ $(5 \times 10^{-12} <<$

0.100)

To obtain $[CN^-]$ we substitute into (2) and rearrange

$$[CN^-] = \sqrt{\frac{0.100}{(1 \times 10^{-11})(1.3 \times 10^{21})}} = 2.8 \times 10^{-6} \qquad (2.8 \times 10^{-6} << 0.100)$$

Thus, the two assumptions are valid and

Solubility = $[Br^-]$ = 0.100 M

$$\text{mass AgBr/200 mL} = 0.100 \frac{\text{mmol}}{\text{mL}} \times 200 \text{ mL} \times \frac{0.1877 \text{ g}}{\text{mmol}}$$

$$= 3.754 \text{ g}$$

11-19. $CuCl_{(s)} \rightleftharpoons Cu^+ + Cl^-$ $K_{sp} = [Cu^+][Cl^-] = 1.9 \times 10^{-7}$ (1)

$Cu^+ + 2Cl^- \rightleftharpoons CuCl_2^-$ $\beta_2 = \dfrac{[CuCl_2^-]}{[Cu^+][Cl^-]^2} = 7.9 \times 10^4$ (2)

It is convenient to multiply (1) by (2) to give

$$\frac{[CuCl_2^-]}{[Cl^-]} = 1.9 \times 10^{-7} \times 7.9 \times 10^4 = 1.50 \times 10^{-2} \qquad (3)$$

From a charge balance consideration, we can write (if we assume $[H_3O^+] = [OH^-]$)

$$[Cu^+] + [Na^+] = [Cl^-] + [CuCl_2^-] \qquad (4)$$

By rearranging (1) and (3) and substituting into (4) we obtain

$$[Cl^-] = [Na^+] + \frac{1.9 \times 10^{-7}}{[Cl^-]} - 1.50 \times 10^{-2}[Cl^-]$$

which rearranges to the quadratic

$$0 = 1.015[Cl^-]^2 - [Na^+][Cl^-] - 1.9 \times 10^{-7} \qquad (5)$$

By using $[Na^+]$ = the NaCl analytical concentration, (5) can be solved to give the following $[Cl^-]$

(a) 4.93 M **(b)** 0.493 M **(c)** 0.0493 M

(d) 0.00493 M **(e)** 7.44×10^{-4} M

Note that the equilibrium $[Cl^-]$ concentration is *larger* than the NaCl analytical concentration for part (e). The reason for this apparent anomaly is that the dissolution of CuCl to give Cu^+ and Cl^- contributes significantly to the equilibrium $[Cl^-]$ at the lower NaCl analytical concentrations

The solubility of CuCl can be obtained from the calculated $[Cl^-]$ and the expression

$$S = [Cu^+] + [CuCl_2^-] = \frac{1.9 \times 10^{-7}}{[Cl^-]} + 1.50 \times 10^{-2}[Cl^-]$$

Solution of this equation for each of the $[Cl^-]$ gives

(a) 7.4×10^{-2} M **(b)** 7.4×10^{-3} M **(c)** 7.4×10^{-4} M

(d) 1.1×10^{-4} M **(e)** 2.7×10^{-4} M

11-20. $CaSO_{4(s)} \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad K_{sp} = [Ca^{2+}][SO_4^{2-}] = 2.6 \times 10^{-5}$ (1)

$$CaSO_{4(aq)} \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad K_d = \frac{[Ca^{2+}][SO_4^{-}]}{[CaSO_4]_{aq}} = 5.2 \times 10^{-3} \qquad (2)$$

$$CaSO_{4(s)} \rightleftharpoons CaSO_{4(aq)} \qquad (3)$$

The mass balance gives

$$[Ca^{2+}] = [SO_4^{2-}] \qquad (4)$$

We have 3 equations and 3 unknowns ($[Ca^{2+}]$, $[SO_4^{2-}]$, and $[CaSO_4]_{aq}$

To solve we divide (1) by (2) to give

$$[CaSO_4]_{aq} = K_{sp}/K_d = (2.6 \times 10^{-5})/(5.2 \times 10^{-3}) = 5.0 \times 10^{-3}$$

Note that this is the equilibrium constant expression for (3) and indicates that the concentration of un-ionized $CaSO_4$ is always the same in a saturated solution of $CaSO_4$.

Substituting (4) into (1) gives

$$[Ca^{2+}] = (2.6 \times 10^{-5})^{1/2} = 5.1 \times 10^{-3}\ \text{M}$$

and since $S = [CaSO_4]_{aq} + [Ca^{2+}]$, we obtain

$$S = 5.0 \times 10^{-3} + 5.1 \times 10^{-3} = 1.01 \times 10^{-2}\ \text{M}$$

$$\%CaSO_{4(aq)} = (5.0 \times 10^{-3}/1.01 \times 10^{-2}) \times 100\% = 49\%$$

(b) Here $[CaSO_4]_{aq}$ is again equal to 5.0×10^{-3} and the mass balance gives

$$[SO_4^{2-}] = 0.0100 + [Ca^{2+}] \qquad (5)$$

Substituting (1) into (5) and rearranging gives

$$0 = [SO_4^{2-}]^2 - 0.0100[SO_4^{2-}] - K_{sp}$$

which may be solved using the quadratic equation to give

$$[SO_4^{2-}] = 0.0121 \qquad \text{and} \qquad [Ca^{2+}] = 2.14 \times 10^{-3}$$

$$S = 5.0 \times 10^{-3} + 2.14 \times 10^{-3} = 7.14 \times 10^{-3}\ \text{M}$$

$$\%CaSO_{4(aq)} = (5.0 \times 10^{-3}/7.14 \times 10^{-3}) \times 100\% = 70\%$$

11-21. $Tl_2S(s) \rightleftharpoons 2Tl^+ + S^{2-}$ $K_{sp} = 6.0 \times 10^{-22} = [Tl^+]^2[S^{2-}]$

$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$ $K_1 = 9.6 \times 10^{-8}$

$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$ $K_2 = 1.3 \times 10^{-14}$

$S = [Tl^+]/2$

Mass balance

$[Tl^+]/2 = [S^{2-}] + [HS^-] + [H_2S]$

$$\frac{[Tl^+]}{2} = [S^{2-}] + \frac{[H_3O^+][S^{2-}]}{K_2} + \frac{[H_3O^+]^2[S^{2-}]}{K_1K_2} = [S^{2-}]\left(1+\frac{[H_3O^+]}{K_2}+\frac{[H_3O^+]^2}{K_1K_2}\right)$$

Substituting the K_{sp} into this equation gives:

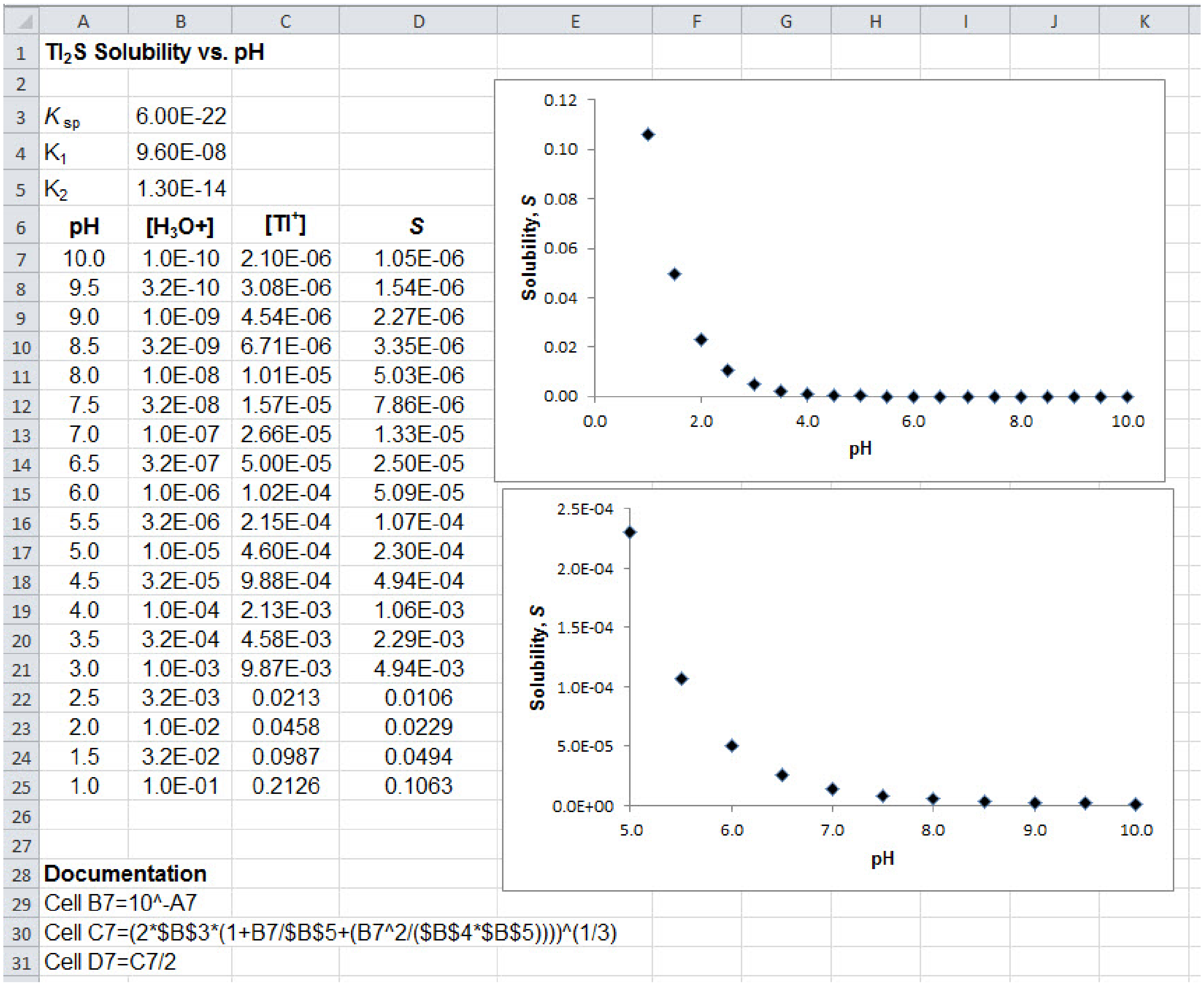
$$\frac{[Tl^+]}{2} = \frac{K_{sp}}{[Tl^+]^2}\left(1+\frac{[H_3O^+]}{K_2}+\frac{[H_3O^+]^2}{K_1K_2}\right) = \frac{6.0\times 10^{-22}}{[Tl^+]^2}\left(1+\frac{[H_3O^+]}{K_2}+\frac{[H_3O^+]^2}{K_1K_2}\right)$$

$$[Tl^+]^3 = 2\times 6.0\times 10^{-22}\left(1+\frac{[H_3O^+]}{K_2}+\frac{[H_3O^+]^2}{K_1K_2}\right)$$

$$[Tl^+] = \left\{2\times 6.0\times 10^{-22}\left(1+\frac{[H_3O^+]}{K_2}+\frac{[H_3O^+]^2}{K_1K_2}\right)\right\}^{1/3}$$

$S = [Tl^+]/2$

The spreadsheet is shown on the next page. The upper chart is for all the data and the lower expands the region from pH 5.0 to 10.0.



Tl_2S Solubility vs. pH

K_{sp}	6.00E-22
K_1	9.60E-08
K_2	1.30E-14

pH	$[H_3O+]$	$[Tl^+]$	*S*
10.0	1.0E-10	2.10E-06	1.05E-06
9.5	3.2E-10	3.08E-06	1.54E-06
9.0	1.0E-09	4.54E-06	2.27E-06
8.5	3.2E-09	6.71E-06	3.35E-06
8.0	1.0E-08	1.01E-05	5.03E-06
7.5	3.2E-08	1.57E-05	7.86E-06
7.0	1.0E-07	2.66E-05	1.33E-05
6.5	3.2E-07	5.00E-05	2.50E-05
6.0	1.0E-06	1.02E-04	5.09E-05
5.5	3.2E-06	2.15E-04	1.07E-04
5.0	1.0E-05	4.60E-04	2.30E-04
4.5	3.2E-05	9.88E-04	4.94E-04
4.0	1.0E-04	2.13E-03	1.06E-03
3.5	3.2E-04	4.58E-03	2.29E-03
3.0	1.0E-03	9.87E-03	4.94E-03
2.5	3.2E-03	0.0213	0.0106
2.0	1.0E-02	0.0458	0.0229
1.5	3.2E-02	0.0987	0.0494
1.0	1.0E-01	0.2126	0.1063

Documentation

Cell B7=10^-A7

Cell C7=(2*$B$3*(1+B7/$B$5+(B7^2/($B$4*$B$5))))^(1/3)

Cell D7=C7/2

Chapter 12

12-1. **(a)** A *colloidal precipitate* consists of solid particles with dimensions that are less than 10^{-4} cm. A *crystalline precipitate* consists of solid particles with dimensions that at least 10^{-4} cm or greater. As a result, crystalline precipitates settle rapidly, whereas colloidal precipitates remain suspended in solution unless caused to agglomerate.

(b) In *gravimetric precipitation*, the analyte is converted to a sparing soluble precipitate, which is then filtered, washed free of impurities, and then converted into a product of known composition by suitable heat treatment. In *gravimetric volatilization*, the analyte is separated from other sample constituents by converting it to a gas of known composition.

(c) *Precipitation* is the process by which a solid phase forms and is carried out of solution when the solubility product of a chemical species is exceeded. *Coprecipitation* is a process in which normally soluble compounds are carried out of solution during precipitate formation.

(d) *Coagulation*, or agglomeration, is the process by which colloidal particles coalesce to form larger aggregates. *Peptization* refers to the process by which a coagulated colloid reverts to its original dispersed state. Heating, stirring and adding an electrolyte can coagulate colloidal suspensions. Washing the coagulated colloid with water often removes sufficient electrolyte to permit the re-establishment of repulsive forces that favor return to the colloidal state.

(e) *Occlusion* is a type of coprecipitation in which a compound is trapped within a pocket formed during rapid crystal formation. *Mixed-crystal formation* is also a type of coprecipitation in which a contaminant ion replaces an ion in the crystal lattice.

(f) *Nucleation* is a process in which a minimum number of atoms, ions or molecules associate to give a stable solid. *Particle growth* is a process by which growth continues on existing nuclei. Precipitation by nucleation results in a large number of small particles. Precipitation by particle growth results in a smaller number of large particles.

12-2. **(a)** *Digestion* is a process in which a precipitate is heated in the presence of the solution from which it was formed (the *mother liquor*). Digestion improves the purity and filterability of the precipitate.

(b) *Adsorption* is the process by which ions are retained on the surface of a solid.

(c) In *reprecipitation*, the filtered solid precipitate is redissolved and reprecipitated. Because the concentration of the impurity in the new solution is lower, the second precipitate contains less coprecipitated impurity.

(d) *Precipitation from homogeneous solution* is a technique by which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excess does not occur and the resultant solid product is better suited for analysis than precipitate formed by direct addition of precipitating reagent.

(e) The *counter-ion layer* describes a layer of solution containing sufficient excess negative ions that surrounds a charged particle. This counter-ion layer balances the surface charge on the particle.

(f) *Mother liquor* is the solution from which a precipitate is formed.

(g) *Supersaturation* describes an unstable state in which a solution contains higher solute concentration than a saturated solution. Supersaturation is relieved by precipitation of excess solute.

12-3. A *chelating agent* is an organic compound that contains two or more electron-donor groups located in such a configuration that five- or six-membered rings are formed when the donor groups complex a cation.

12-4. *Relative supersaturation* can be regulated through control of reagent concentration, temperature and the rate at which reagents are combined.

12-5. **(a)** There is positive charge on the surface of the coagulated colloidal particles.

(b) The positive charge arises from adsorbed Ag^+ ions.

(c) NO_3^- ions make up the counter-ion layer.

12-6. $CH_3CSNH_4 + H_2O \rightleftharpoons CH_3CONH_2 + H_2S$

The slow hydrolysis of thioacetamide can be used to generate a source of hydrogen sulfide gas. Hydrogen sulfide gas is then involved in the equilibria below:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$$
$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$$

12-7. In *peptization*, a coagulated colloid returns to its original dispersed state because of a decrease in the electrolyte concentration of the solution contacting the precipitate. Peptization can be avoided by washing the coagulated colloid with an electrolyte solution instead of pure water.

12-8. Chloroplatinic acid, H_2PtCl_6, forms the precipitate K_2PtCl_6 when mixed with K^+ but does not form analogous precipitates with Li^+ and Na^+. Thus, chloroplatinic acid can be used to separate K^+ from a mixture containing Li^+ and Na^+.

12-9. **(a)** mass SO_2 = mass $BaSO_4$ × $\dfrac{\mathcal{M}_{SO_2}}{\mathcal{M}_{BaSO_4}}$

(b) mass Mg = mass $Mg_2P_2O_7$ × $\dfrac{2\ \mathcal{M}_{Mg}}{\mathcal{M}_{Mg_2P_2O_7}}$

(c) mass In = mass In_2O_3 × $\dfrac{2\mathcal{M}_{In}}{\mathcal{M}_{In_2O_3}}$

(d) mass K = mass K_2PtCl_6 × $\dfrac{2\mathcal{M}_{K}}{\mathcal{M}_{K_2PtCl_6}}$

(e) mass CuO = mass $Cu_2(SCN)_2$ × $\dfrac{2\mathcal{M}_{CuO}}{\mathcal{M}_{Cu_2(SCN)_2}}$

(f) mass $MnCl_2$ = mass Mn_3O_4 × $\dfrac{3\mathcal{M}_{MnCl_2}}{\mathcal{M}_{Mn_3O_4}}$

(g) mass Pb_3O_4 = mass PbO_2 × $\dfrac{\mathcal{M}_{Pb_3O_4}}{3\mathcal{M}_{PbO_2}}$

(h) mass $U_2P_2O_{11}$ = mass P_2O_5 × $\dfrac{\mathcal{M}_{U_2P_2O_{11}}}{\mathcal{M}_{P_2O_5}}$

(i) masss $Na_2B_4O_7$•$10H_2O$ = mass B_2O_3 × $\dfrac{\mathcal{M}_{Na_2B_4O_7 \cdot 10H_2O}}{2\mathcal{M}_{B_2O_3}}$

(j) mass Na_2O = mass $NaZn(UO_2)_3(C_2H_3O_2)_9$•$6H_2O$ × $\dfrac{\mathcal{M}_{Na_2O}}{2\mathcal{M}_{NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O}}$

12-10. $\mathcal{M}_{AgCl}$ = 143.32 g/mol $\mathcal{M}_{KCl}$ = 74.55 g/mol

$$\frac{0.2912\text{ g AgCl} \times \left(\dfrac{1\text{ mol AgCl}}{143.32\text{ g}}\right) \times \left(\dfrac{1\text{ mol KCl}}{1\text{ mol AgCl}}\right) \times \left(\dfrac{74.55\text{ g KCl}}{\text{mol}}\right)}{0.2500\text{ g impure sample}} \times 100\% = 60.59\%$$

12-11. $\mathcal{M}_{\text{Al2O3}} = 101.96$ g/mol $\mathcal{M}_{\text{NH4Al(SO4)2}} = 237.03$ g/mol

(a)

$$0.2001\text{ g Al}_2\text{O}_3 \times \frac{1\text{ mol Al}_2\text{O}_3}{101.96\text{ g Al}_2\text{O}_3} \times \frac{2\text{ mol NH}_4\text{Al(SO}_4)_2}{\text{mol Al}_2\text{O}_3} = 3.925 \times 10^{-3}\text{ mol NH}_4\text{Al(SO}_4)_2$$

$$\frac{3.925 \times 10^{-3}\text{mol NH}_4\text{Al(SO}_4)_2 \times \dfrac{237.03\text{ g NH}_4\text{Al(SO}_4)_2}{\text{mol NH}_4\text{Al(SO}_4)_2}}{1.200\text{ g}} \times 100\% = 77.5\%$$

(b)

$$\frac{0.2001\text{ g Al}_2\text{O}_3}{1.200\text{ g impure sample}} \times 100\% = 16.7\%$$

(c)

$$\text{no. mol Al} = \text{ no. mol NH}_4\text{Al(SO}_4)_2 = 3.925 \times 10^{-3}\text{ mol}$$

$$\frac{3.925 \times 10^{-3}\text{ mol Al} \times \dfrac{26.982\text{ g Al}}{\text{mol}}}{1.200\text{ g impure sample}} \times 100\% = 8.83\%\text{ Al}$$

12-12.

$$0.650\text{ g CuSO}_4\text{•5H}_2\text{O} \times \frac{1\text{ mol CuSO}_4\text{•5H}_2\text{O}}{249.67\text{ g CuSO}_4\text{•5H}_2\text{O}} \times \frac{1\text{ mol Cu(IO}_3)_2}{1\text{ mol CuSO}_4\text{•5H}_2\text{O}}$$

$$\times \frac{413.35\text{ g Cu(IO}_3)_2}{1\text{ mol Cu(IO}_3)_2} = 1.076\text{ g Cu(IO}_3)_2$$

12-13.

$$0.2750\text{ g CuSO}_4\text{•5H}_2\text{O} \times \frac{1\text{ mol CuSO}_4\text{•5H}_2\text{O}}{249.67\text{ g CuSO}_4\text{•5H}_2\text{O}} \times \frac{1\text{ mol Cu(IO}_3)_2}{1\text{ mol CuSO}_4\text{•5H}_2\text{O}}$$

$$\times \frac{2\text{ mol KIO}_3}{1\text{ mol Cu(IO}_3)_2} \times \frac{214\text{ g KIO}_3}{1\text{ mol KIO}_3} = 0.471\text{ g KIO}_3$$

12-14.

$$\text{mass AgI} = 0.512\text{ g} \times \frac{20.1\text{ g}}{100\text{ g}} \times \frac{1\text{ mol AlI}_3}{407.69\text{ g}} \times \frac{3\text{ mol AgI}}{\text{mol AlI}_3} \times \frac{234.77\text{ g AgI}}{\text{mol AgI}} = 0.178\text{ g}$$

12-15. 1 g U is produces

$$1\text{ g U}\times\frac{1\text{ mol U}}{238.03\text{ g}}\times\frac{634.0\text{ g }Na_2U_2O_7}{\text{mol}}\times\frac{1\text{ mol }Na_2U_2O_7}{2\text{ mol U}}=1.33\text{ g }Na_2U_2O_7$$

$$1\text{ g U}\times\frac{1\text{ mol U}}{238.03\text{ g}}\times\frac{714.0\text{ g }(UO_2)_2P_2O_7}{\text{mol}}\times\frac{1}{2}=1.50\text{ g }(UO_2)_2P_2O_7$$

$$1\times\frac{1}{238.03}\times 753.9\times\frac{1}{2}=1.58\text{ g }V_2O_5{\bullet}2UO_2$$

Thus, $V_2O_5{\bullet}2UO_2$ produces the greatest mass.

12-16. $Al_2(CO_3)_3 + 6HCl \rightleftharpoons 3CO_2 + 3H_2O + 2AlCl_3$

$$0.0515\text{ g }CO_2\times\frac{1\text{ mol }CO_2}{60.0\text{ g }CO_2}\times\frac{1\text{ mol }Al_2(CO_3)_3}{3\text{ mol }CO_2}\times\frac{2\text{ mol Al}}{1\text{ mol }Al_2(CO_3)_3}\times\frac{26.98\text{ g Al}}{\text{mol Al}}$$
$$=0.01543\text{ g Al}$$
$$\frac{0.01543\text{ g Al}}{0.8102\text{ g impure sample}}\times 100\%=1.90\%\text{ Al}$$

12-17. $CdS + 2O_2 \rightleftharpoons CdSO_4$

$$\text{no. mol CdS}=\text{no. mol }CdSO_4=0.125\text{ g }CdSO_4\times\frac{1\text{ mol }CdSO_4}{208.47\text{ g}}\times\frac{1\text{ mol CdS}}{1\text{ mol }CdSO_4}$$
$$=5.996\times10^{-4}\text{ mol}$$

The number moles H_2S is equal to number moles CdS

$$\text{mass }H_2S=5.996\times10^{-4}\text{ mol}\times\frac{34.08\text{ g }H_2S}{1\text{ mole }H_2S}=2.04\times10^{-2}\text{ g}$$
$$\frac{2.04\times10^{-2}\text{ g }H_2S}{80.0\text{ g impure sample}}\times100\%=0.026\%\text{ }H_2S$$

12-18. $$\frac{0.6006\text{ g }BaCO_3\times\frac{1\text{ mol }BaCO_3}{197.34\text{ g}}\times\frac{1\text{ mol C}}{1\text{ mol }BaCO_3}\times\frac{12.011\text{ g C}}{1\text{ mol C}}}{0.2121\text{ g sample}}\times100\%=17.23\%\text{ C}$$

12-19.

$$\frac{0.2513\text{ g AgCl}\times\dfrac{1\text{ mol AgCl}}{143.37\text{ g}}\times\dfrac{1\text{ mol C}_{14}\text{H}_9\text{Cl}_5}{5\text{ mol AgCl}}\times\dfrac{354.72\text{ g C}_{14}\text{H}_9\text{Cl}_5}{1\text{ mol C}_{14}\text{H}_9\text{Cl}_5}}{7.000\text{ g sample}}\times 100\%$$

$$= 1.776\%\ \text{C}_{14}\text{H}_9\text{Cl}_5$$

12-20.

$$\frac{\left(\begin{array}{l}0.5718\text{ g Hg}_5(\text{IO}_6)_2\times\dfrac{1\text{ mol Hg}_5(\text{IO}_6)_2}{1448.75\text{ g Hg}_5(\text{IO}_6)_2}\times\dfrac{5\text{ mol Hg}^{2+}}{1\text{ mol Hg}_5(\text{IO}_6)_2}\\ \times\dfrac{1\text{ mol Hg}_2\text{Cl}_2}{2\text{ mol Hg}^{2+}}\times\dfrac{472.18\text{ g Hg}_2\text{Cl}_2}{1\text{ mol Hg}_2\text{Cl}_2}\end{array}\right)}{1.0451\text{ g sample}}\times 100\% = 44.58\%\ \text{Hg}_2\text{Cl}_2$$

12-21. $\mathcal{M}_{\text{Ba(IO3)2}}$ = 487.13 g/mol $\mathcal{M}_{\text{KI}}$ = 166.00g/mol

$$\frac{0.0538\text{ g Ba(IO}_3)_2\times\left(\dfrac{1\text{ mol Ba(IO}_3)_2}{487.13\text{ g}}\right)\times\left(\dfrac{2\text{ mol KI}}{1\text{ mol Ba(IO}_3)_2}\right)\times\left(\dfrac{166.00\text{ g KI}}{\text{mol}}\right)}{1.59\text{ g impure sample}}\times 100\% = 2.31\%\text{ KI}$$

12-22. $\mathcal{M}_{\text{NH3}}$ = 17.0306 g/mol $\mathcal{M}_{\text{Pt}}$ = 195.08 g/mol

$$\frac{0.4693\text{ g Pt}\times\left(\dfrac{1\text{ mol Pt}}{195.08\text{ g}}\right)\times\left(\dfrac{2\text{ mol NH}_3}{1\text{ mol Pt}}\right)\times\left(\dfrac{17.0306\text{ g NH}_3}{\text{mol}}\right)}{0.2115\text{ g impure sample}}\times 100\% = 38.74\%\ \text{NH}_3$$

12-23. $\mathcal{M}_{\text{MnO2}}$ = 86.94 g/mol $\mathcal{M}_{\text{AlCl3}}$ = 133.34 g/mol

$$\frac{\left(\begin{array}{l}(0.6447\text{ g}-0.3521\text{ g MnO}_2)\times\left(\dfrac{1\text{ mol MnO}_2}{86.94\text{ g}}\right)\times\left(\dfrac{2\text{ mol Cl}}{1\text{ mol MnO}_2}\right)\\ \times\left(\dfrac{1\text{ mol AlCl}_3}{3\text{ mol Cl}}\right)\times\left(\dfrac{133.34\text{ g AlCl}_3}{\text{mol}}\right)\end{array}\right)}{1.1402\text{ g impure sample}}\times 100\% = 26.24\%\ \text{AlCl}_3$$

12-24. $\mathcal{M}_{\text{BaSO4}}$ = 233.39 g/mol $\mathcal{M}_{\text{SO42-}}$ = 96.064 g/mol

Let S_w = mass of sample in grams

$$0.200\text{ g BaSO}_4 \times \frac{1\text{ mol BaSO}_4}{233.39\text{ g}} \times \frac{1\text{ mol SO}_4{}^{2-}}{1\text{ mol BaSO}_4} = 8.57 \times 10^{-4}\text{ mol SO}_4{}^{2-}$$

$$\frac{8.57 \times 10^{-4}\text{ mol SO}_4{}^{2-} \times \dfrac{96.064\text{ g SO}_4{}^{2-}}{\text{mol}}}{S_\text{w}\text{ g sample}} = 100\% = 20\%\text{ SO}_4{}^{2-}$$

$$S_\text{w} = \frac{8.57 \times 10^{-4}\text{ mol SO}_4{}^{2-} \times \dfrac{96.064\text{ g SO}_4{}^{2-}}{\text{mol}} \times 100\%}{20\%} = 0.412\text{ g sample}$$

The maximum precipitate mass expected given this sample mass is

$$0.412\text{ g sample} \times \frac{55\text{ g SO}_4{}^{2-}}{100\text{ g sample}} \times \frac{1\text{ mol SO}_4{}^{2-}}{96.064\text{ g}} \times \frac{1\text{ mol BaSO}_4}{1\text{ g SO}_4{}^{2-}} \times \frac{233.39\text{ g BaSO}_4}{1\text{ mol}}$$

$$=0.550\text{ g BaSO}_4$$

12-25. Let S_w = mass of sample in grams.

The higher percentage of Ni in the alloy sample is selected because this corresponds to maximum amount expected precipitate

$\mathcal{M}_{\text{NiDMG}}$ = 288.92 g/mol $\mathcal{M}_{\text{Ni}}$ = 58.693 g/mol

$$0.175\text{ g Ni(HC}_4\text{H}_6\text{O}_2\text{N}_2)_2 \times \frac{1\text{ mol Ni(HC}_4\text{H}_6\text{O}_2\text{N}_2)_2}{288.92\text{ g}} \times \frac{1\text{ mol Ni}}{1\text{ mol Ni(HC}_4\text{H}_6\text{O}_2\text{N}_2)_2}$$

$$= 6.06 \times 10^{-4}\text{ mol Ni}$$

$$\frac{6.06 \times 10^{-4}\text{mol Ni} \times \dfrac{58.693\text{ g Ni}}{\text{mol}}}{S_\text{w}\text{ g sample}} = 100\% = 35\%\text{ Ni}$$

$$S_\text{w} = \frac{6.06 \times 10^{-4}\text{ mol Ni} \times \dfrac{58.693\text{ g Ni}}{\text{mol}} \times 100\%}{35\%} = 0.102\text{ g sample}$$

12-26. Let S_w = mass of sample in grams.

(a) $\mathcal{M}_{\text{AgCl}}$ = 143.32 g/mol $\mathcal{M}_{\text{ZrCl4}}$ = 233.03 g/mol

$$\frac{0.400\text{ g AgCl} \times \frac{1\text{ mol AgCl}}{143.32\text{ g}} \times \frac{1\text{ mol ZrCl}_4}{4\text{ mol AgCl}} \times \frac{233.03\text{ g ZrCl}_4}{1\text{ mol}}}{S_\text{w}\text{ g sample}} \times 100\% = 68\%\text{ ZrCl}_4$$

$$S_w = \frac{1.62 \times 10^{-1}\text{g ZrCl}_4 \times 100\%}{68\%} = 0.239\text{ g sample}$$

(b)

$$0.239\text{ g sample} \times \frac{84\text{ g ZrCl}_4}{100\text{ g sample}} \times \frac{1\text{ mole ZrCl}_4}{233.03\text{ g}} \times \frac{4\text{ mole AgCl}}{1\text{ mole ZrCl}_4} \times \frac{143.32\text{ g AgCl}}{1\text{ mole}} = 0.494\text{ g AgCl}$$

(c)

$$\%\text{ ZrCl}_4 = \frac{1.62 \times 10^{-1} g\text{ ZrCl}_4 \times 100\%}{S_\text{w}} = 40\%$$

$$S_w = \frac{1.62 \times 10^{-1}\text{g ZrCl}_4 \times 100\%}{40\%} = 0.406\text{ g sample}$$

12-27. $\mathcal{M}_{\text{NaBr}} = 102.894$ g/mol $\mathcal{M}_{\text{KBr}} = 119.002$ g/mol $\mathcal{M}_{\text{AgBr}} = 187.772$ g/mol

$0.8720\text{ g sample} = x\text{ g NaBr} + y\text{ g KBr}$

$$\text{g AgBr from NaBr} = x\text{ g NaBr} \times \frac{1\text{ mol NaBr}}{102.894\text{ g}} \times \frac{1\text{ mol AgBr}}{1\text{ mol NaBr}} \times \frac{187.772\text{ g AgBr}}{1\text{ mole}} = 1.823\,x\text{ g AgBr}$$

$$\text{g AgBr from KBr} = y\text{ g KBr} \times \frac{1\text{ mol KBr}}{119.002\text{ g}} \times \frac{1\text{ mol AgBr}}{1\text{ mol KBr}} \times \frac{187.772\text{ g AgBr}}{1\text{ mol}} = 1.578\,y\text{ g AgBr}$$

$1.505\text{ g AgBr} = 1.823\,(x\text{ g NaBr}) + 1.578\,(y\text{ g KBr})$

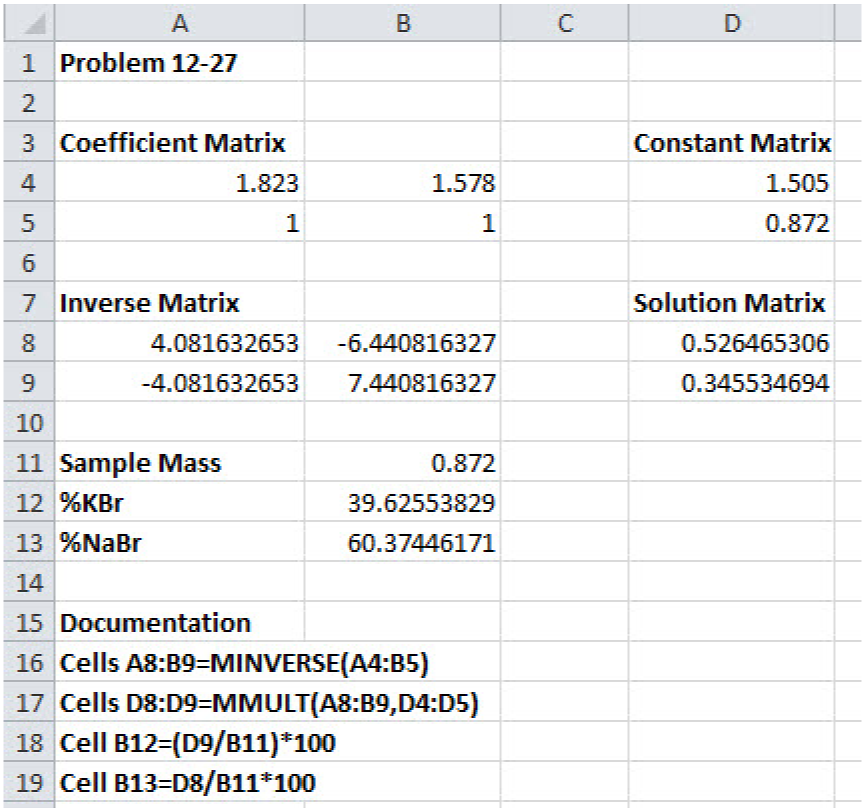
So, we have 2equations and 2 unknowns,

$x + y = 0.8720$

$1.823x + 1.578y = 1.505.$

These are solved by the a matrix method in the spreadsheet on the next page.

We would report %KBr = 39.6 and %NaBr = 60.4



	A	B	C	D
1	**Problem 12-27**			
2				
3	**Coefficient Matrix**			**Constant Matrix**
4	1.823	1.578		1.505
5	1	1		0.872
6				
7	**Inverse Matrix**			**Solution Matrix**
8	4.081632653	-6.440816327		0.526465306
9	-4.081632653	7.440816327		0.345534694
10				
11	**Sample Mass**	0.872		
12	**%KBr**	39.62553829		
13	**%NaBr**	60.37446171		
14				
15	**Documentation**			
16	**Cells A8:B9=MINVERSE(A4:B5)**			
17	**Cells D8:D9=MMULT(A8:B9,D4:D5)**			
18	**Cell B12=(D9/B11)*100**			
19	**Cell B13=D8/B11*100**			

12-28. $\mathcal{M}_{\text{AgCl}} = 143.32$ g/mol $\mathcal{M}_{\text{AgI}} = 234.77$ g/mol

$$0.4430\text{ g} = x\text{ g AgCl} + y\text{ g AgI}$$

$$\text{g AgCl} = x\text{ g AgCl} + \left(y\text{ g AgI} \times \frac{1\text{ mol AgI}}{234.77\text{ g}} \times \frac{1\text{ mol AgCl}}{1\text{ mol AgI}} \times \frac{143.32\text{ g AgCl}}{1\text{ mol}} \right) = 0.3181\text{ g}$$

$$0.3181 = x\text{ g AgCl} + 0.6104698\, y\text{ g AgI}$$

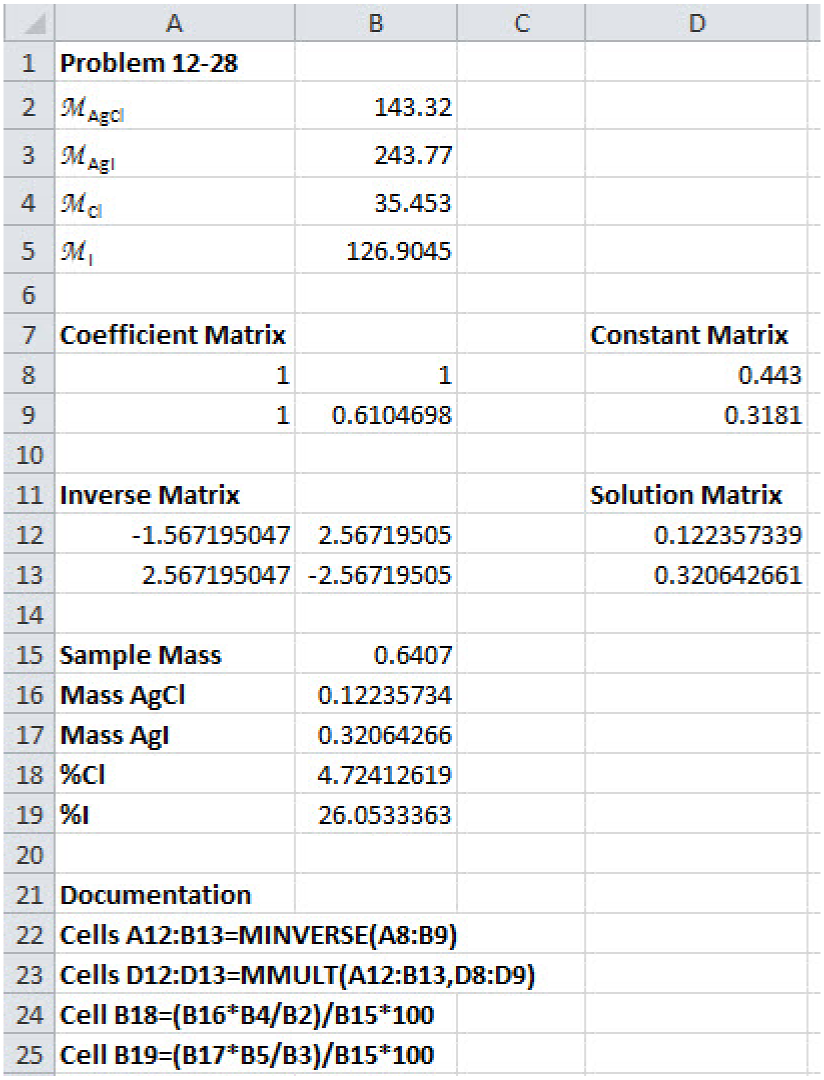
Here again, we have 2 equations and 2 unknowns,

$x + y = 0.4430$

$x + 0.6104698y = 0.3181$

The spreadsheet is shown on the next page

We would report %Cl = 4.72 and %I = 27.05



	A	B	C	D
1	**Problem 12-28**			
2	$\mathcal{M}_{AgCl}$	143.32		
3	$\mathcal{M}_{AgI}$	243.77		
4	$\mathcal{M}_{Cl}$	35.453		
5	$\mathcal{M}_{I}$	126.9045		
6				
7	**Coefficient Matrix**			**Constant Matrix**
8	1	1		0.443
9	1	0.6104698		0.3181
10				
11	**Inverse Matrix**			**Solution Matrix**
12	-1.567195047	2.56719505		0.122357339
13	2.567195047	-2.56719505		0.320642661
14				
15	**Sample Mass**	0.6407		
16	**Mass AgCl**	0.12235734		
17	**Mass AgI**	0.32064266		
18	**%Cl**	4.72412619		
19	**%I**	26.0533363		
20				
21	**Documentation**			
22	**Cells A12:B13=MINVERSE(A8:B9)**			
23	**Cells D12:D13=MMULT(A12:B13,D8:D9)**			
24	**Cell B18=(B16*B4/B2)/B15*100**			
25	**Cell B19=(B17*B5/B3)/B15*100**			

12-29.

$\mathcal{M}_{PbMoO_4} = 367.14$ g/mol $\qquad \mathcal{M}_{P_2O_5} = 141.94$ g/mol

$$\text{amount PbMoO}_4 = 0.2922 \text{ g PbMoO}_4 \times \frac{1 \text{ mol PbMoO}_4}{367.14 \text{ g}} = 7.9588 \times 10^{-4} \text{ mol}$$

$$\frac{\left(7.9588 \times 10^{-4} \text{ mol PbMoO}_4 \times \dfrac{1 \text{ mol P}}{12 \text{ mole PbMoO}_4} \times \dfrac{1 \text{ mol P}_2\text{O}_5}{2 \text{ mol P}} \times \dfrac{141.94 \text{ g P}_2\text{O}_5}{1 \text{ mol}}\right)}{0.2091 \text{ g sample}} \times 100\%$$

$= 2.251\ \%\ P_2O_5$

12-30.

$$\mathcal{M}_{\mathrm{CO_2}} = 44.010\ \mathrm{g/mol} \quad \mathcal{M}_{\mathrm{MgCO_3}} = 84.31\ \mathrm{g/mol} \quad \mathcal{M}_{K_2CO_3} = 138.21\ \mathrm{g/mol}$$

$$\mathrm{mol\ CO_2 = mol\ MgCO_3 + mol\ K_2CO_3}$$

$$= \left(2.300\ \mathrm{g\ sample} \times \frac{38\ \mathrm{g\ MgCO_3}}{100\ \mathrm{g\ sample}} \times \frac{1\ \mathrm{mol\ MgCO_3}}{84.31\ \mathrm{g}}\right) +$$

$$\left(2.300\ \mathrm{g\ sample} \times \frac{42\ \mathrm{g\ K_2CO_3}}{100\ \mathrm{g\ sample}} \times \frac{1\ \mathrm{mol\ K_2CO_3}}{138.21\ \mathrm{g}}\right)$$

$$\mathrm{amount\ CO_2} = 0.0104 + 6.989 \times 10^{-3} = 0.01736\ \mathrm{mol}$$

$$\mathrm{mass\ CO_2} = 0.01736\ \mathrm{mole} \times \frac{44.010\ \mathrm{g\ CO_2}}{1\ \mathrm{mole}} = 0.764\ \mathrm{g}$$

12-31.

$$\mathcal{M}_{Mg_2P_2O_7} = 222.55\ \mathrm{g/mol} \quad \mathcal{M}_{NaCl} = 58.44\ \mathrm{g/mol} \quad \mathcal{M}_{MgCl_2 \bullet 6H_2O} = 203.32\ \mathrm{g/mol}$$

$$0.1796\ \mathrm{g\ Mg_2P_2O_7} \times \frac{1\ \mathrm{mol\ Mg_2P_2O_7}}{222.55\ \mathrm{g}} \times \frac{2\ \mathrm{mol\ MgCl_2 \bullet 6H_2O}}{1\ \mathrm{mol\ Mg_2P_2O_7}} =$$

$$1.61402 \times 10^{-3}\ \mathrm{mol\ MgCl_2 \bullet 6H_2O}$$

$$0.5923\ \mathrm{g\ AgCl} \times \frac{1\ \mathrm{mol\ AgCl}}{143.32\ \mathrm{g}} = 4.13268 \times 10^{-3}\ \mathrm{mol\ AgCl}$$

$$1.61402 \times 10^{-3}\ \mathrm{mol\ MgCl_2 \bullet 6H_2O} \times \frac{2\ \mathrm{mole\ AgCl}}{1\ \mathrm{mol\ MgCl_2 \bullet 6H_2O}} = 3.22804 \times 10^{-3}\ \mathrm{mol\ AgCl}$$

$$(4.13268 \times 10^{-3} - 3.228 \times 10^{-3})\ \mathrm{mol\ AgCl} \times \frac{1\ \mathrm{mol\ NaCl}}{1\ \mathrm{mol\ AgCl}} = 9.0464 \times 10^{-4}\ \mathrm{mol\ NaCl}$$

$$\frac{1.61402 \times 10^{-3}\ \mathrm{mol\ MgCl_2 \bullet 6H_2O} \times \frac{203.32\ \mathrm{g\ MgCl_2 \bullet 6H_2O}}{1\ \mathrm{mol}} \times \frac{500.0\ \mathrm{mL}}{50.0\ \mathrm{mL}}}{6.881\ \mathrm{g\ sample}} \times 100\%$$

$$= 47.69\%\ \mathrm{MgCl_2 \bullet 6H_2O}$$

$$\frac{9.0464 \times 10^{-4}\ \mathrm{mol\ NaCl} \times \frac{58.44\ \mathrm{g\ NaCl}}{1\ \mathrm{mol}} \times \frac{500.0\ \mathrm{mL}}{50.0\ \mathrm{mL}}}{6.881\ \mathrm{g\ sample}} \times 100\% = 7.68\%\ \mathrm{NaCl}$$

12-32.

$$\mathcal{M}_{\mathrm{BaCl_2 \bullet 2H_2O}} = 244.26 \text{ g/mol} \quad \mathcal{M}_{\mathrm{NaIO_3}} = 197.89 \text{ g/mol} \quad \mathcal{M}_{\mathrm{Ba(IO_3)_2}} = 487.13 \text{ g/mol}$$

$$0.200 \text{ g BaCl}_2 \bullet 2\text{H}_2\text{O} \times \frac{1 \text{ mol BaCl}_2 \bullet 2\text{H}_2\text{O}}{244.26 \text{ g}} \times \frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaCl}_2 \bullet 2\text{H}_2\text{O}}$$

$$= 8.188 \times 10^{-4} \text{ mol Ba}^{2+}$$

$$0.300 \text{ g NaIO}_3 \times \frac{1 \text{ mol NaIO}_3}{197.89 \text{ g}} \times \frac{1 \text{ mol IO}_3^-}{1 \text{ mol NaIO}_3} = 1.516 \times 10^{-3} \text{ mol IO}_3^-$$

Because IO_3^- is the limiting reagent,

(a)

$$\text{amount Ba(IO}_3)_2 = \frac{1.516 \times 10^{-3} \text{ mol}}{2} = 7.580 \times 10^{-4} \text{ mol}$$

$$\text{mass Ba(IO}_3)_2 = 7.580 \times 10^{-4} \text{ mol} \times \frac{487.13 \text{ g Ba(IO}_3)_2}{1 \text{ mol}} = 0.369 \text{ g Ba(IO}_3)_2$$

(b)

$$\text{amount BaCl}_2\bullet 2\text{H}_2\text{O remaining} = \left((8.188 \times 10^{-4}) - (7.580 \times 10^{-4})\right) \text{mol} = 6.080 \times 10^{-5} \text{ mol}$$

$$\text{mass BaCl}_2 \bullet 2\text{H}_2\text{O} = 6.08 \times 10^{-5} \text{ mol BaCl}_2 \bullet 2\text{H}_2\text{O} \times \frac{244.26 \text{ g BaCl}_2 \bullet 2\text{H}_2\text{O}}{1 \text{ mol}}$$

$$= 0.0149 \text{ g}$$

12-33.

$$\mathcal{M}_{AgNO_3} = 169.873 \text{ g/mol} \quad \mathcal{M}_{Ag_2CrO_4} = 331.730 \text{ g/mol} \quad \mathcal{M}_{K_2CrO_4} = 194.190 \text{ g/mol}$$

$$0.500 \text{ g AgNO}_3 \times \frac{1 \text{ mol AgNO}_3}{169.873 \text{ g}} \times \frac{1 \text{ mol Ag}_2\text{CrO}_4}{2 \text{ mol AgNO}_3} \times \frac{331.730 \text{ g Ag}_2\text{CrO}_4}{1 \text{ mol}}$$

$$= 0.4882 \text{ g Ag}_2\text{CrO}_4$$

$$0.300 \text{ g K}_2\text{CrO}_4 \times \frac{1 \text{ mol K}_2\text{CrO}_4}{194.190 \text{ g}} \times \frac{1 \text{ mol Ag}_2\text{CrO}_4}{1 \text{ mol K}_2\text{CrO}_4} \times \frac{331.730 \text{ g Ag}_2\text{CrO}_4}{1 \text{ mol}}$$

$$= 0.5125 \text{ g Ag}_2\text{CrO}_4$$

Because Ag^+ is the limiting reagent,

(a) mass Ag_2CrO_4 = 0.488 g

(b)

$$\text{amount } K_2CrO_4 \text{ remaining} = \left((1.545 \times 10^{-3}) - (1.472 \times 10^{-3})\right) \text{mol} = 7.331 \times 10^{-5} \text{ mol}$$

$$\text{mass } K_2CrO_4 = 7.331 \times 10^{-5} \text{ mol } K_2CrO_4 \times \frac{194.190 \text{ g } K_2CrO_4}{1 \text{ mol}} = 0.0142 \text{ g}$$

Chapter 13

13-1. **(a)** The *millimole* is the amount of an elementary species, such as an atom, an ion, a molecule, or an electron. A millimole contains

$$6.02\times10^{23}\,\frac{\text{particles}}{\cancel{\text{mol}}}\times\frac{\cancel{\text{mol}}}{1000\text{ mmol}}=6.02\times10^{20}\,\frac{\text{particles}}{\text{mmol}}$$

(b) A *titration* involves measuring the quantity of a reagent of known concentration required to react with a measured quantity of sample of an unknown concentration. The concentration of the sample is then determined from the quantities of reagent and sample, the concentration of the reagent, and the stoichiometry of the reaction.

(c) The *stoichiometric ratio* is the molar ratio of two chemical species that appear in a balanced chemical equation.

(d) *Titration error* is the error encountered in titrimetry that arises from the difference between the amount of reagent required to give a detectable end point and the theoretical amount for reaching the equivalence point.

13-2. amount A (mmol) = $\text{volume (mL)}\times c_{\text{A}}\,\text{(mmol A / mL)}$

$$\text{amount A (mmol)} = \frac{\text{mass A(g)}}{\text{millimolar mass A(g/mmol)}}$$

13-3. **(a)** The *equivalence point* in a titration is that point at which sufficient titrant has been added so that stoichiometrically equivalent amounts of analyte and titrant are present. The *end point* in a titration is the point at which an observable physical change signals the equivalence point.

(b) A *primary standard* is a highly purified substance that serves as the basis for a titrimetric method. It is used either (i) to prepare a standard solution directly by mass or (ii) to standardize a solution to be used in a titration.

A *secondary standard* is material or solution whose concentration is determined from the stoichiometry of its reaction with a primary standard material. Secondary standards are employed when a reagent is not available in primary standard quality. For example, solid sodium hydroxide is hygroscopic and cannot be used to prepare a standard solution directly. A secondary standard solution of the reagent is readily prepared, however, by standardizing a solution of sodium hydroxide against a primary standard reagent such as potassium hydrogen phthalate.

13-4. For a dilute aqueous solution, 1 L = 1000 mL = 1000g. So,

$$\frac{1\text{ mg}}{\text{L}} = \frac{10^{-3}\text{ g solute}}{1000\text{ g solution}} = \frac{1\text{ g solute}}{1{,}000{,}000\text{ g solution}} = 1\text{ ppm}$$

13-5. **(a)** $\frac{1\text{ mol H}_2\text{NNH}_2}{2\text{ mol I}_2}$

(b) $\frac{5\text{ mol H}_2\text{O}_2}{2\text{ mol MnO}_4^-}$

(c) $\frac{1\text{ mole Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}}{2\text{ moles H}^+}$

(d) $\frac{2\text{ moles S}}{3\text{ moles KIO}_3}$

13-6. **(a)** $2.00\ \cancel{\text{L}} \times 2.76 \times 10^{-3}\ \frac{\cancel{\text{mol}}}{\cancel{\text{L}}} \times \frac{1000\text{ mmol}}{\cancel{\text{mol}}} = 5.52\text{ mmol}$

(b) $250.0\ \cancel{\text{mL}} \times 0.0423\ \dfrac{\text{mmol}}{\cancel{\text{mL}}} = 10.575\text{ mmol}$

(c)

$$\frac{2.97\ \cancel{\text{g CuSO}_4}}{10^6\ \cancel{\text{g solution}}} \times \frac{1\ \cancel{\text{g solution}}}{\cancel{\text{mL}}} \times \frac{1\text{ mmol}}{0.1596\ \cancel{\text{g CuSO}_4}} \times 500.0\ \cancel{\text{mL}} = 9.305 \times 10^{-3}\text{ mmol}$$

(d) $2.50\ \cancel{\text{L}} \times 0.352\ \dfrac{\cancel{\text{mol}}}{\cancel{\text{L}}} \times \dfrac{1000\text{ mmol}}{\cancel{\text{mol}}} = 880\text{ mmol}$

13-7. **(a)** $2.95\ \cancel{\text{mL}} \times \dfrac{0.0789\text{ mmol}}{\cancel{\text{mL}}} = 0.233\text{ mmol}$

(b) $0.2011\ \cancel{\text{L}} \times \dfrac{0.0564\ \cancel{\text{mol}}}{\cancel{\text{L}}} \times \dfrac{1000\text{ mmol}}{\cancel{\text{mol}}} = 11.34\text{ mmol}$

(c)

$$\frac{47.5\ \cancel{\text{g Mg(NO}_3)_2}}{10^6\ \cancel{\text{g soln}}} \times \frac{1000\ \cancel{\text{g soln}}}{\cancel{\text{L}}} \times \frac{1\ \cancel{\text{mol}}}{148.31\ \cancel{\text{g Mg(NO}_3)_2}} \times 2.56\ \cancel{\text{L}} \times \frac{1000\text{ mmol}}{\cancel{\text{mol}}} = 0.820\text{ mmol}$$

(d) $79.8\ \cancel{\text{mL}} \times \dfrac{0.1379\text{ mmol}}{\cancel{\text{mL}}} = 11.00\text{ mmol}$

13-8. **(a)**

$$26.0\ \cancel{\text{mL}} \times \frac{0.250\ \cancel{\text{mmol sucrose}}}{\cancel{\text{mL}}} \times \frac{0.342\ \cancel{\text{g}}}{\cancel{\text{mmol sucrose}}} \times \frac{1000\text{ mg}}{\cancel{\text{g}}} = 2.22 \times 10^3\text{ mg}$$

(b) $2.92\ \cancel{\text{L}} \times \dfrac{5.23 \times 10^{-4}\ \cancel{\text{mol H}_2\text{O}_2}}{\cancel{\text{L}}} \times \dfrac{34.02\ \cancel{\text{g}}}{\text{mol}\ \cancel{\text{H}_2\text{O}_2}} \times \dfrac{1000\text{ mg}}{\cancel{\text{g}}} = 51.95\text{ mg}$

(c) $\dfrac{5.76\text{ mg Pb(NO}_3)_2}{\cancel{\text{L}}} \times \dfrac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times 673\ \cancel{\text{mL}} = 3.88\text{ mg}$ (1 ppm = 1 mg/L)

(d) $6.75\ \cancel{\text{mL}} \times \dfrac{0.0426\ \cancel{\text{mmol KNO}_3}}{\cancel{\text{mL}}} \times \dfrac{101.10\ \text{mg}}{\cancel{\text{mmol KNO}_3}} = 29.07\ \text{mg}$

13-9. **(a)** $450.0\ \cancel{\text{mL}} \times \dfrac{0.0986\ \cancel{\text{mol H}_2\text{O}_2}}{\cancel{\text{L}}} \times \dfrac{34.02\ \text{g}}{\cancel{\text{mol H}_2\text{O}_2}} \times \dfrac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} = 1.51\ \text{g}$

(b) $26.4\ \cancel{\text{mL}} \times \dfrac{9.36 \times 10^{-4}\ \cancel{\text{mol}}}{\cancel{\text{L}}} \times \dfrac{122.1\ \text{g}}{\cancel{\text{mol}}} \times \dfrac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} = 3.02 \times 10^{-3}\ \text{g}$

(c) $2.50\ \cancel{\text{L}} \times \dfrac{23.4\ \cancel{\text{mg}}}{\cancel{\text{L}}} \times \dfrac{1\ \text{g}}{1000\ \cancel{\text{mg}}} = 0.0585\ \text{g}$ (1 ppm = 1 mg/L)

(d) $21.7\ \cancel{\text{mL}} \times \dfrac{0.0214\ \cancel{\text{mol}}}{\cancel{\text{L}}} \times \dfrac{167.0\ \text{g}}{\cancel{\text{mol}}} \times \dfrac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} = 0.0776\ \text{g}$

13-10.

$$\frac{50.0\ \cancel{\text{g NaOH}}}{100\ \cancel{\text{g soln}}} \times \frac{1.52\ \cancel{\text{g soln}}}{\cancel{\text{mL}}} \times \frac{1\ \text{mol NaOH}}{39.997\ \cancel{\text{g NaOH}}} \times \frac{1000\ \cancel{\text{mL}}}{\text{L}} = 19.0\ \frac{\text{mol NaOH}}{\text{L}} = 19.0\ \text{M}$$

13-11. $\dfrac{20.0\ \cancel{\text{g KCl}}}{100\ \cancel{\text{g soln}}} \times \dfrac{1.13\ \cancel{\text{g soln}}}{\text{mL}} \times \dfrac{1\ \text{mmol KCl}}{0.07455\ \cancel{\text{g KCl}}} = 3.03\ \dfrac{\text{mmol KCl}}{\text{mL}} = 3.03\ \text{M}$

13-12. **(a)**

$$0.0750\ \text{M AgNO}_3 = \frac{0.0750\ \text{mole AgNO}_3}{\cancel{\text{L}}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times 500\ \cancel{\text{mL}} = 0.0375\ \text{mole AgNO}_3$$

$$0.0375\ \cancel{\text{mole AgNO}_3} \times \frac{169.87\ \text{g AgNO}_3}{\cancel{\text{mole AgNO}_3}} = 6.37\ \text{g AgNO}_3$$

Dissolve 6.37 g AgNO_3 in water and dilute to 500 mL.

(b) $0.325\ \text{M HCl} = \dfrac{0.325\ \text{mole HCl}}{\cancel{\text{L}}} \times 2.00\ \cancel{\text{L}} = 0.650\ \text{mole HCl}$

$$0.650\text{ mole HCl} \times \frac{1\text{ L}}{6.00\text{ mole HCl}} = 0.108\text{ L}$$

Dilute 108 mL of the 6 M HCl with enough water to make 2.00 L total volume

(c) $$0.0900\text{ M K}^+ = \frac{0.0900\text{ mole K}^+}{\cancel{\text{L}}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times 750\ \cancel{\text{mL}} = 0.0675\text{ mole K}^+$$

$$0.0675\text{ mole K}^+ \times \frac{1\text{ mole K}_4\text{Fe(CN)}_6}{4\text{ moles K}^+} \times \frac{368.35\text{ g K}_4\text{Fe(CN)}_6}{\text{mole}} = 6.22\text{ g K}_4\text{Fe(CN)}_6$$

Dissolve 6.22 g $K_4Fe(CN)_6$ in water and dilute to 750 mL.

(d)

$$2.00\%\text{ (w/v) BaCl}_2 = \frac{2.00\ \cancel{\text{g BaCl}_2}}{100\ \cancel{\text{mL}}} \times \frac{\text{mole BaCl}_2}{208.23\ \cancel{\text{g BaCl}_2}} \times 600\ \cancel{\text{mL}} = 0.0576\text{ mole BaCl}_2$$

$$0.0576\ \cancel{\text{mole BaCl}_2} \times \frac{1\text{ L}}{0.500\ \cancel{\text{mole BaCl}_2}} = 0.115\text{ L}$$

Dilute 115 mL of 0.500M $BaCl_2$ in enough water to yield 600 mL total volume.

(e) $$0.120\text{ M HClO}_4 = \frac{0.120\text{ mole HClO}_4}{\cancel{\text{L}}} \times 2.00\ \cancel{\text{L}} = 0.240\text{ mole HClO}_4$$

$$\text{Commercial reagent} = \frac{1.60 \times 10^3\ \cancel{\text{g}}}{\text{L}} \times \frac{60\text{ g }\cancel{\text{HClO}_4}}{100\ \cancel{\text{g}}} \times \frac{\text{mole HClO}_4}{100.5\ \cancel{\text{g HClO}_4}} = \frac{9.55\text{ mole HClO}_4}{\text{L}}$$

$$\text{vol. reagent} = 0.240\ \cancel{\text{mole HClO}_4} \times \frac{\text{L}}{9.55\ \cancel{\text{mole HClO}_4}} = 0.025\text{ L}$$

Dilute 25 mL $HClO_4$ reagent in enough water to yield 2.00 L.

(f) $60.0\text{ ppm Na}^+ = \frac{60\text{ mg Na}^+}{\cancel{\text{L}}} \times 9.00\ \cancel{\text{L}} = 5.40\times10^2\text{mg Na}^+$

$$5.4\times10^2\ \cancel{\text{mg Na}^+} \times \frac{1\ \cancel{\text{g}}}{1000\ \cancel{\text{mg}}} \times \frac{\cancel{\text{mole Na}^+}}{22.99\ \cancel{\text{g Na}^+}} \times \frac{\cancel{\text{mole Na}_2\text{SO}_4}}{2\ \cancel{\text{moles Na}^+}} \times \frac{142.0\text{ g Na}_2\text{SO}_4}{\cancel{\text{mole Na}_2\text{SO}_4}} = 1.67\text{ g Na}_2\text{SO}_4$$

Dissolve 1.67 g Na_2SO_4 in water and bring to 9.00 L total volume.

13-13. (a) $1.00\ \cancel{\text{L}} \times \frac{0.150\ \cancel{\text{mol}}}{\cancel{\text{L}}} \times \frac{158.03\text{ g}}{\cancel{\text{mol}}} = 23.70\text{ g}$

Dissolve 23.70 g $KMnO_4$ in water and dilute to 1.00 L total volume.

(b) 2.50 L of 0.500 M $HClO_4$ contains $2.50\ \cancel{\text{L}} \times \frac{0.500\text{ mol}}{\cancel{\text{L}}} = 1.25\text{ mol}$

Need to take a volume of $\frac{1.25\ \cancel{\text{mol}}}{9.00\ \cancel{\text{mol}}/\text{L}} = 0.139\text{ L}$

Take 139 mL of concentrated (9.00 M) reagent and dilute to 2.50 L.

(c)

$$400\ \cancel{\text{mL}} \times \frac{0.0500\ \cancel{\text{mol I}^-}}{\cancel{\text{L}}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{1\ \cancel{\text{mol MgI}_2}}{2\ \cancel{\text{mol I}^-}} \times \frac{278.11\text{ g}}{\cancel{\text{mol MgI}_2}} = 2.78\text{ g}$$

Dissolve 2.78 g MgI_2 in water and bring to 400 mL total volume.

(d)

$$200\ \cancel{\text{mL}} \times \frac{1.00\ \cancel{\text{g CuSO}_4}}{100\ \cancel{\text{mL}}} \times \frac{1\ \cancel{\text{mol}}}{159.61\ \cancel{\text{g CuSO}_4}} \times \frac{1\ \cancel{\text{L}}}{0.218\ \cancel{\text{mol}}} \times \frac{1000\text{ mL}}{1\ \cancel{\text{L}}} = 57.5\text{ mL}$$

Take 57.5 mL of the 0.218 M solution and dilute to a volume of 200 mL.

(e) In 1.50 L of 0.215 M NaOH, there are

$$\frac{0.215\text{ mole NaOH}}{\text{L}} \times 1.50\text{ L} = 0.3225\text{ mole NaOH}$$

The commercial reagent is $\frac{1.525 \times 10^3\ \cancel{g}}{L} \times \frac{50\ \cancel{g\ NaOH}}{100\ \cancel{g}} \times \frac{mole}{40.00\ \cancel{g\ NaOH}} = 19.06\ M$

$$\text{Thus, volume} = 0.3225\ \cancel{mole\ NaOH} \times \frac{L}{19.06\ \cancel{mole\ NaOH}} = 0.0169\ L$$

Take 16.9 mL of the concentrated reagent and dilute to 1.50 L.

(f) $12\ ppm\ K^+ = \frac{12\ mg\ K^+}{\cancel{L}} \times 1.50\ \cancel{L} = 18\ mg\ K^+$

$$18\ \cancel{mg} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{\cancel{mole\ K^+}}{39.10\ \cancel{g}} \times \frac{\cancel{mole\ K_4Fe(CN)_6}}{4\ \cancel{mole\ K^+}} \times \frac{368.3\ g}{mole\ \cancel{K_4Fe(CN)_6}}$$

$= 0.0424\ g\ K_4Fe(CN)_6$

Dissolve 42.4 mg $K_4Fe(CN)_6$ in water and dilute to 1.50 L.

13-14. $\mathcal{M}_{HgO} = 216.59\ \frac{g}{mole}$

$$HgO(s) + 4Br^- + H_2O \rightleftharpoons HgBr_4^{2-} + 2OH^-$$

$$\frac{0.4008\ g\ HgO \times \frac{1\ mole\ HgO}{216.59\ g\ HgO} \times \frac{2\ mole\ OH^-}{mole\ HgO} \times \frac{1\ mole\ HClO_4}{1\ mole\ OH^-} \times \frac{1000\ mmol\ HClO_4}{mole}}{43.75\ mL}$$

$= 0.08459\ M\ HClO_4$

13-15. $\mathcal{M}_{Na_2CO_3} = 105.99\ \frac{g}{mole}$

$$CO_3^{2-} + 2H^+ \rightleftharpoons H_2O + CO_2(g)$$

$$\frac{0.4723\ \cancel{g\ Na_2CO_3} \times \frac{1\ \cancel{mole\ Na_2CO_3}}{105.99\ \cancel{g\ Na_2CO_3}} \times \frac{2\ \cancel{mole\ H^+}}{\cancel{mole\ Na_2CO_3}} \times \frac{1\ \cancel{mole\ H_2SO_4}}{2\ \cancel{mole\ H^+}} \times \frac{1000\ mmol}{\cancel{mole\ H_2SO_4}}}{34.78\ mL}$$

$$= 0.1281\ \text{M}$$

13-16. $\mathcal{M}_{\text{Na}_2\text{SO}_4} = 142.04\ \dfrac{\text{g}}{\text{mole}}$

$$\frac{0.5002\ \cancel{\text{g}} \times \dfrac{96.4\ \cancel{\text{g Na}_2\text{SO}_4}}{100\ \cancel{\text{g}}} \times \dfrac{1\ \cancel{\text{mole Na}_2\text{SO}_4}}{142.04\ \cancel{\text{g Na}_2\text{SO}_4}} \times \dfrac{1\ \cancel{\text{mole BaCl}_2}}{1\ \cancel{\text{mole Na}_2\text{SO}_4}} \times \dfrac{1000\ \text{mmol}}{\cancel{\text{mole BaCl}_2}}}{48.63\ \text{mL}}$$

$$= 0.0698\ \text{M}$$

13-17. $\dfrac{V_{\text{HClO}_4}}{V_{\text{NaOH}}} = \dfrac{26.93\ \text{mL HClO}_4}{25.00\ \text{mL NaOH}} = 1.0772\ \dfrac{\text{mL HClO}_4}{\text{mL NaOH}}$

The volume of HClO_4 needed to titrate 0.4126 g of Na_2CO_3 is

$$40.00\ \text{mL HClO}_4 - 9.20\ \text{mL NaOH} \times \frac{1.0772\ \text{mL HClO}_4}{\text{mL NaOH}} = 30.09\ \text{mL}$$

Thus, $\dfrac{0.4126\ \cancel{\text{g Na}_2\text{CO}_3}}{30.09\ \text{mL HClO}_4} \times \dfrac{1\ \cancel{\text{mmol Na}_2\text{CO}_3}}{0.10588\ \cancel{\text{g Na}_2\text{CO}_3}} \times \dfrac{2\ \text{mmol HClO}_4}{\cancel{\text{mmol Na}_2\text{CO}_3}} = 0.2590\ \text{M HClO}_4$

and $c_{\text{NaOH}} = c_{\text{HClO}_4} \times \dfrac{V_{\text{HClO}_4}}{V_{\text{NaOH}}}$

$$= \frac{0.2590\ \cancel{\text{mmol HClO}_4}}{\cancel{\text{mL HClO}_4}} \times \frac{1.0772\ \cancel{\text{mL HClO}_4}}{\text{mL NaOH}} \times \frac{1\ \text{mmol NaOH}}{\cancel{\text{mmol HClO}_4}} = 0.2790\ \text{M}$$

13-18.

$$\frac{50.00\ \cancel{\text{mL Na}_2\text{C}_2\text{O}_4} \times \dfrac{0.04715\ \cancel{\text{mmol Na}_2\text{C}_2\text{O}_4}}{\cancel{\text{mL Na}_2\text{C}_2\text{O}_4}} \times \dfrac{2\ \text{mmol KMnO}_4}{5\ \cancel{\text{mmol Na}_2\text{C}_2\text{O}_4}}}{39.25\ \text{mL}} = 0.02403\ \text{M}$$

13-19. Each mole of KIO_3 consumes 6 moles of $\text{S}_2\text{O}_3^{2-}$

$$\frac{0.1142\ \cancel{\text{g KIO}_3} \times \dfrac{1\ \cancel{\text{mol KIO}_3}}{214.001\ \cancel{\text{g KIO}_3}} \times \dfrac{1000\ \text{mmol Na}_2\text{SO}_3}{\cancel{\text{mol}}\ \text{Na}_2\text{SO}_3} \times \dfrac{6\ \cancel{\text{mol Na}_2\text{SO}_3}}{\cancel{\text{mol KIO}_3}}}{27.95\ \text{mL Na}_2\text{SO}_3}$$

$= 0.1146\ \text{M Na}_2\text{SO}_3$

13-20. total mmol NaOH = 25.00 mL × 0.00873 mmol/mL = 0.21825

mmol HCl added = 15.17 mL × 0.01102 mmol/mL = 0.16717

mmol NaOH consumed by analyte = 0.21825 – 0.16717 =0.05108

$$\frac{0.05108\ \cancel{\text{mmol NaOH}} \times \dfrac{1\ \cancel{\text{mmol H}_2\text{SO}_4}}{2\ \cancel{\text{mmol NaOH}}} \times \dfrac{1\ \cancel{\text{mmol S}}}{1\ \cancel{\text{mmol H}_2\text{SO}_4}} \times \dfrac{0.03207\ \text{g S}}{\cancel{\text{mmol S}}}}{4.912\ \text{g sample}} \times 10^6\ \text{ppm}$$

= 166.7 ppm S

13-21. $\text{No. mmol Fe}^{2+} = 25.00\ \text{mL} \times \dfrac{0.002517\ \text{mmol Cr}_2\text{O}_7^{2-}}{\text{mL}} \times \dfrac{6\ \text{mmol Fe}^{2+}}{\text{mmol Cr}_2\text{O}_7^{2-}} = 0.37755$

= no. mmol analyte Fe^{2+} + no. mmol Fe^{2+} back titrated

No. mmol analyte Fe^{2+} = 0.37755 – 8.53 × 0.00949 M = 0.2966

$$\frac{0.2966\ \cancel{\text{mmol Fe}}}{100\ \cancel{\text{mL}}} \times \frac{0.055845\ \cancel{\text{g}}}{\cancel{\text{mmol Fe}}} \times \frac{1\ \cancel{\text{mL}}}{\cancel{\text{g}}} \times 10^6\ \text{ppm} = 165.6\ \text{ppm Fe}$$

13-22. Amount Ag^+ added = $= 40.00\ \cancel{\text{mL}} \times \dfrac{0.05871\ \text{mmol}}{\cancel{\text{mL}}} = 2.348\ \text{mmol}$

Amount Ag^+ required for Ag_3AsO_4 = 2.348 mmol –9.63 mL × 0.1000 M = 1.385 mmol

$$\frac{1.3854\ \cancel{\text{mmol Ag}^+} \times \dfrac{1\ \cancel{\text{mmol As}}}{3\ \cancel{\text{mmol Ag}}} \times \dfrac{1\ \cancel{\text{mmol As}_2\text{O}_3}}{2\ \cancel{\text{mmol As}}} \times \dfrac{0.197841\ \text{g As}_2\text{O}_3}{\cancel{\text{mmol As}_2\text{O}_3}}}{1.203\ \text{g}} \times 100\%$$

$= 3.797\ \%\ \text{As}_2\text{O}_3$

13-23. $$\frac{37.31\text{ mL Hg}^{2+} \times \dfrac{0.009372\text{ mmol Hg}^{2+}}{\text{mL Hg}^{2+}} \times \dfrac{4\text{ mmol}}{\text{mmol Hg}^{2+}} \times \dfrac{0.07612\text{ g}}{\text{mmol}}}{1.455\text{ g}} \times 100\%$$

$= 7.317\ \%\ (NH_2)_2CS$

13-24. **(a)**

molarity of $Ba(OH)_2 =$

$$\frac{0.1215\text{ g }C_6H_5COOH \times \dfrac{1\text{ mole }C_6H_5COOH}{122.12\text{ g}} \times \dfrac{1\text{ mole Ba(OH)}_2}{2\text{ mole }C_6H_5COOH} \times \dfrac{1000\text{ mmol}}{\text{mole}}}{43.25\text{ mL}}$$

$= 0.01150\text{ M Ba(OH)}_2$

(b)

$$s_y = (1.150\times10^{-2}\text{ M}) \times \sqrt{\left(\frac{0.0003}{0.1215}\right)^2 + \left(\frac{0.02}{43.25}\right)^2} = 2.9\times10^{-5}\text{ M}$$

Hence, the molarity of $Ba(OH)_2$ can be written 0.01150 ± 0.00003 M

(c) A mass measurement error of – 0.3 mg would make the molarity actually

$$\frac{(0.1215 - 0.0003)\text{ g }C_6H_5COOH \times \dfrac{1\text{ mole }C_6H_5COOH}{122.12\text{ g}} \times \dfrac{1\text{ mole Ba(OH)}_2}{2\text{ mole }C_6H_5COOH} \times \dfrac{1000\text{ mmol}}{\text{mole}}}{43.25\text{ mL}}$$

$= 0.01147\text{ M Ba(OH)}_2$

The error E is then

$$E = (0.1147 - 0.1150)\text{ M} = -3 \times 10^{-5}\text{ M}$$

The relative error, E_r is

$$E_r = \frac{\left(-3.0 \times 10^{-5}\text{ M}\right)}{1.150 \times 10^{-2}\text{ M}} = -3.0 \times 10^{-3}\text{ or } -3\text{ ppt}$$

13-25. Total amount KOH = 40.00 mL × 0.04672 mmol/mL = 1.8688 mmol

KOH reacting with H_2SO_4

$$= 3.41\ \cancel{\text{mL } H_2SO_4} \times \frac{0.05042\ \cancel{\text{mmol } H_2SO_4}}{\cancel{\text{mL } H_2SO_4}} \times \frac{2\text{ mmol KOH}}{\cancel{\text{mmol } H_2SO_4}} = 0.34386\text{ mmol}$$

$$\text{mass EtOAc} = (1.8688 - 0.34386)\ \cancel{\text{mmol KOH}} \times \frac{1\ \cancel{\text{mmol EtOAc}}}{\cancel{\text{mmol KOH}}} \times \frac{0.08811\text{ g}}{\cancel{\text{mmol EtOAc}}}$$

= 0.13436 g in the 20.00-mL portion. In the entire 100.00-mL there are

5 × 0.13326 g or 0.6718 g.

13-26. (a)

For sample 1, the w/v percentage HOAc is given by

$$\frac{\dfrac{0.1475\text{ mmol Ba(OH)}_2}{\text{mL}} \times 43.17\text{ mL} \times \dfrac{2\text{ mmol HOAc}}{1\text{ mmol Ba(OH)}_2} \times \dfrac{60.05\text{ g HOAc}}{1000\text{ mmol}}}{50.00\text{ mL}} \times 100\%$$

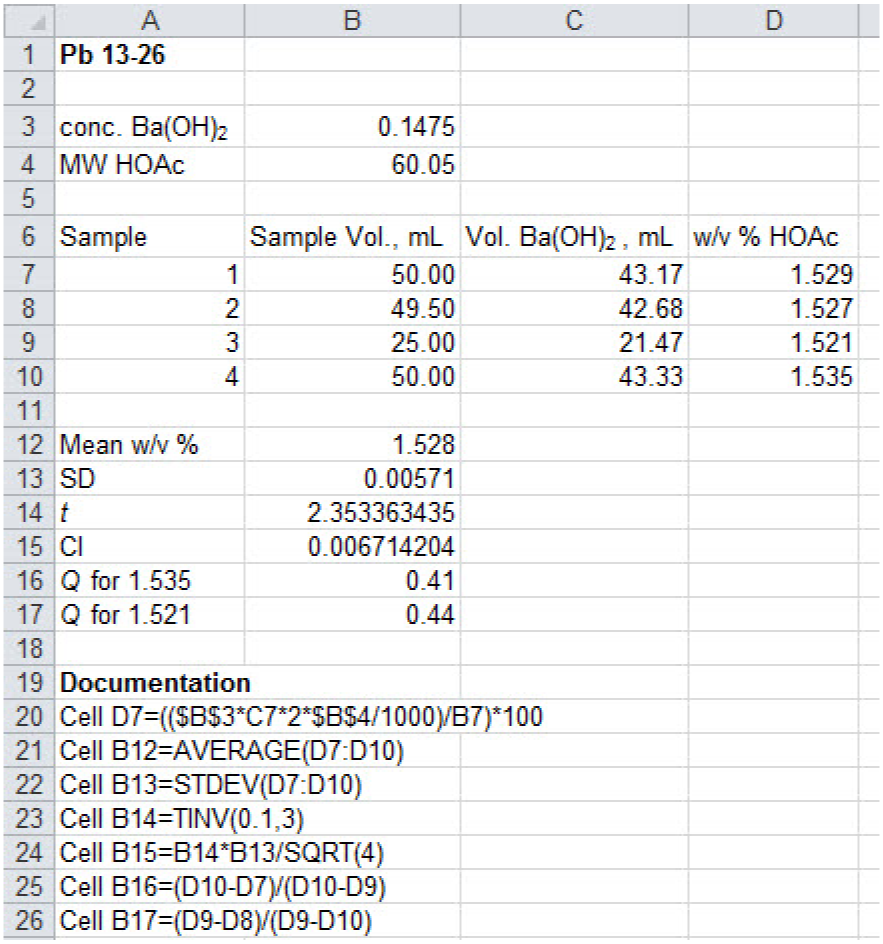
= 1.529% HOAC

Similar calculations for samples 2-4 give the results shown in the spreadsheet that follows.

(b) See the spreadsheet

(c) See the spreadsheet. The 90% CI = 1.528 ± 0.007

(d) The values of 1.535 and 1.521 can be considered for rejection. The Q values are calculated in the spreadsheet. Since both results are less than $Q_{\text{crit}} = 0.765$, neither value should be rejected.



	A	B	C	D
1	**Pb 13-26**			
2				
3	conc. $Ba(OH)_2$	0.1475		
4	MW HOAc	60.05		
5				
6	Sample	Sample Vol., mL	Vol. $Ba(OH)_2$, mL	w/v % HOAc
7	1	50.00	43.17	1.529
8	2	49.50	42.68	1.527
9	3	25.00	21.47	1.521
10	4	50.00	43.33	1.535
11				
12	Mean w/v %	1.528		
13	SD	0.00571		
14	*t*	2.353363435		
15	CI	0.006714204		
16	Q for 1.535	0.41		
17	Q for 1.521	0.44		
18				
19	**Documentation**			
20	Cell D7=(($B$3*C7*2*$B$4/1000)/B7)*100			
21	Cell B12=AVERAGE(D7:D10)			
22	Cell B13=STDEV(D7:D10)			
23	Cell B14=TINV(0.1,3)			
24	Cell B15=B14*B13/SQRT(4)			
25	Cell B16=(D10-D7)/(D10-D9)			
26	Cell B17=(D9-D8)/(D9-D10)			

13-27. (a) $$\frac{0.3147\ \cancel{\text{g Na}_2\text{C}_2\text{O}_4}}{0.1340\ \cancel{\text{g Na}_2\text{C}_2\text{O}_4}\ /\ \cancel{\text{mmol Na}_2\text{C}_2\text{O}_4}} \times \frac{2\text{ mmol KMnO}_4}{5\ \cancel{\text{mmol Na}_2\text{C}_2\text{O}_4}} = 0.9394\text{ mmol KMnO}_4$$

$$\frac{0.9394\text{ mmol KMnO}_4}{31.67\text{ mL}} = 0.02966\text{ M KMnO}_4$$

(b) $$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$$

26.75 mL $KMnO_4$ × 0.02966 M = 0.7934 mmol $KMnO_4$. Each mmol $KMnO_4$ consumes 5 mmol Fe^{2+}. So

mmol Fe^{2+} = 5 × 0.7934 = 3.967

$$\frac{3.967 \text{ mmol Fe}^{2+} \times \dfrac{1 \text{ mmol Fe}_2\text{O}_3}{2 \text{ mmol Fe}^{2+}} \times \dfrac{0.15969 \text{ g Fe}_2\text{O}_3}{\text{mmol Fe}_2\text{O}_3}}{0.6656 \text{ g}} \times 100\% = 47.59\%$$

13-28. (a)

$$\text{weight molarity Ag}^+ = \frac{0.1527 \cancel{\text{ g AgNO}_3} \times \dfrac{1 \cancel{\text{ mmol AgNO}_3}}{0.16987 \cancel{\text{ g}}} \times \dfrac{1 \text{ mmol Ag}^+}{1 \cancel{\text{ mmol AgNO}_3}}}{502.3 \text{ g}}$$

$$= 1.7896 \times 10^{-3} \text{ mmol/g}$$

(b)

Reaction $\text{Ag}^+ + \text{SCN}^- \rightleftharpoons \text{AgSCN}(s)$ Each mole of Ag^+ consumes 1 mole of SCN^-

$24.615 \text{ g AgNO}_3 \times 1.7896 \times 10^{-3} \text{ mmol/g} = 0.04405 \text{ mmol AgNO}_3$ or KSCN

$$\text{weight molarity KSCN} = \frac{0.04405 \text{ mmol KSCN}}{25.171 \text{ g}} = 1.750 \times 10^{-3} \text{ mmol/g}$$

(c) Total amount of AgNO_3 added = $20.102 \text{ g} \times 1.7896 \times 10^{-3} \text{ mmol/g} = 0.03597$ mmol

Excess $\text{AgNO}_3 = 7.543 \text{ g} \times 1.750 \times 10^{-3} \text{ mmol/g} = 0.01320$ mmol

Amount AgNO_3 used for analyte = 0.03597 – 0.01320 = 0.02277 mmol

There are 2 moles Ag^+ used for each mole of BaCl_2 in the $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)$ reaction

$$\text{mmol BaCl}_2\bullet 2\text{H}_2\text{O} = 0.02277 \cancel{\text{ mmol AgNO}_3} \times \frac{1 \text{ mmol BaCl}_2\cdot 2\text{H}_2\text{O}}{2 \cancel{\text{ mmol AgNO}_3}} = 0.011385$$

$$\frac{0.011385 \text{ mmol BaCl}_2\cdot 2\text{H}_2\text{O}}{0.7120 \text{ g}} \times \frac{0.24428 \text{ g BaCl}_2\cdot 2\text{H}_2\text{O}}{\text{mmol BaCl}_2\cdot 2\text{H}_2\text{O}} \times 100\% = 0.3906\ \%$$

13-29. (a) $c = \dfrac{7.48 \text{ g} \times \dfrac{1 \text{ mol}}{277.85 \text{ g}}}{2.000 \text{ L}} = 1.35 \times 10^{-2} \text{ M}$

(b) $[\text{Mg}^{2+}] = 1.35 \times 10^{-2}$ M

(c) There are 3 moles of Cl^- for each mole of $\text{KCl}\bullet\text{MgCl}_2\bullet6\text{H}_2\text{O}$. Hence,

$[\text{Cl}^-] = 3 \times 1.346 \times 10^{-2} = 4.038 \times 10^{-2}$ M

(d) $\dfrac{7.48\text{ g}}{2.00\text{ L}} \times \dfrac{1\text{ L}}{1000\text{ mL}} \times 100\% = 0.374\%$ (w/v)

(e)

$$\frac{1.346 \times 10^{-2}\ \cancel{\text{mmol KCl·MgCl}_2}}{\cancel{\text{mL}}} \times \frac{3\text{ mmol Cl}^-}{\cancel{\text{mmol KCl·MgCl}_2}} \times 25.00\ \cancel{\text{mL}} = 1.0095\text{ mmol Cl}^-$$

(f)

$$\frac{1.346 \times 10^{-2}\text{ mmol KCl·MgCl}_2}{\text{mL}} \times \frac{1\text{ mmol K}^+}{\text{mmol KCl·MgCl}_2} \times \frac{39.10\text{ mg}}{\text{mmol K}^+} \times \frac{1000\text{ mL}}{\text{L}} = \frac{526\text{ mg K}^+}{\text{L}}$$

$= 526$ ppm K^+

13-30. **(a)** $$c_{\text{K}_3\text{Fe(CN)}_6} = \frac{367\text{ mg} \times \dfrac{1\text{ mmol}}{329.2\text{ mg}}}{750.0\text{ mL}} = 1.49 \times 10^{-3}\text{ M}$$

(b) $[\text{K}^+] = 3 \times 1.49 \times 10^{-3} = 4.46 \times 10^{-3}$ M

(c) $[\text{Fe(CN)}_6^{3-}] = c_{\text{K}_3\text{Fe(CN)}_6} = 1.49 \times 10^{-3}$ M

(d) $$\frac{367\ \cancel{\text{mg K}_3\text{Fe(CN)}_6}}{750\text{ mL}} \times \frac{1\text{ g}}{\cancel{1000\text{ mg}}} \times 100\% = 4.89 \times 10^{-2}\%\ (\text{m/v})$$

(e) $$\frac{1.49 \times 10^{-3}\ \cancel{\text{mmol K}_3\text{Fe(CN)}_6}}{\cancel{\text{mL}}} \times \frac{3\text{ mmol K}^+}{\cancel{\text{mmol K}_3\text{Fe(CN)}_6}} \times 50\ \cancel{\text{mL}} = 0.224\text{ mmol K}^+$$

(f) The molar mass of $\text{Fe(CN)}_6^{3-} = 212.0$ g/mol

$$\frac{1.49 \times 10^{-3}\text{ mol}}{\text{L}} \times \frac{212.0\text{ g}}{\text{mol}} \times \frac{1\text{ L}}{1000\text{ g}} \times 10^6\text{ ppm} = 316\text{ ppm}$$

Chapter 14

14-1. The eye has limited sensitivity. To see the color change requires a roughly tenfold excess of one or the other form of the indicator. This change corresponds to a pH range of the indicator pK_a ± 1 pH unit, a total range of 2 pH units.

14-2. End-point sharpness is influenced by completeness of the reaction between the analyte and titrant and the concentrations of the analyte and titrant.

14-3. **(a)** The initial pH of the NH_3 solution will be less than that for the solution containing NaOH. With the first addition of titrant, the pH of the NH_3 solution will decrease rapidly and then level off and become nearly constant throughout the middle part of the titration. In contrast, additions of standard acid to the NaOH solution will cause the pH of the NaOH solution to decrease gradually and nearly linearly until the equivalence point is approached. The equivalence point pH for the NH_3 solution will be well below 7, whereas for the NaOH solution it will be exactly 7.

(b) Beyond the equivalence point, the pH is determined by the excess titrant. Thus, the curves become identical in this region.

14-4. The standard reagents in neutralization titrations are generally strong acids or strong bases because the reactions with this type of titrant are more complete than with those of their weaker counterparts. Sharper end points are the end result of this difference.

14-5. The variables are temperature, ionic strength, and the presence of organic solvents and colloidal particles.

14-6. The sharper end point will be observed with the solute having the larger $K_{b.}$

(a) For NaOCl, $K_b = \dfrac{1.00 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7}$

For hydroxylamine $K_b = \dfrac{1.00 \times 10^{-14}}{1.1 \times 10^{-6}} = 9.1 \times 10^{-9}$ Thus, NaOCl

(b) For NH_3, $K_b = \dfrac{1.00 \times 10^{-14}}{5.7 \times 10^{-10}} = 1.75 \times 10^{-5}$

For sodium phenolate, $K_b = \dfrac{1.00 \times 10^{-14}}{1.00 \times 10^{-10}} = 1.00 \times 10^{-4}$ sodium phenolate

(c) For hydroxylamine $K_b = 9.1 \times 10^{-9}$ (part a)

For methyl amine, $K_b = \dfrac{1.00 \times 10^{-14}}{2.3 \times 10^{-11}} = 4.3 \times 10^{-4}$ Thus, methyl amine

(d) For hydrazine $K_b = \dfrac{1.00 \times 10^{-14}}{1.05 \times 10^{-8}} = 9.5 \times 10^{-7}$

For NaCN, $K_b = \dfrac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-3}$ NaCN

14-7. The sharper end point will be observed with the solute having the larger K_a.

(a) For nitrous acid $K_a = 7.1\times10^{-4}$

For iodic acid $K_a = 1.7\times10^{-1}$ Thus, iodic acid

(b) For anilinium $K_a = 2.51\times10^{-5}$

For benzoic acid $K_a = 6.28\times10^{-5}$ benzoic acid

(c) For hypochlorous acid $K_a = 3.0\times10^{-8}$

For pyruvic acid $K_a = 3.2\times10^{-3}$ Thus, pyruvic acid

(d) For salicylic acid $K_a = 1.06\times10^{-3}$

For acetic acid $K_a = 1.75\times10^{-5}$ salicylic acid

14-8. $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$ $\qquad \dfrac{[H_3O^+][In^-]}{[HIn]} = K_a$

For bromthyol blue, pK_a = 7.10 (Table 14-1)

K_a = antilog(–7.10) = 7.94×10^{-8}

$[HIn]/[In^-] = 1.29$

Substituting these values into the equilibrium expression and rearranging gives

$[H_3O^+] = 7.94 \times 10^{-8} \times 1.29 = 1.025 \times 10^{-7}$

$pH = -\log(1.025 \times 10^{-7}) = 6.99$

14-9. $InH^+ + H_2O \rightleftharpoons In + H_3O^+$ $\qquad \dfrac{[H_3O^+][In]}{[InH^+]} = K_a$

For methyl orange, pK_a = 3.46 (Table 14-1)

K_a = antilog(–3.46) = 3.47×10^{-4}

$[InH^+]/[In] = 1.84$

Substituting these values into the equilibrium expression and rearranging gives

$[H_3O^+] = 3.47 \times 10^{-4} \times 1.84 = 6.385 \times 10^{-4}$

$pH = -\log(6.385 \times 10^{-4}) = 3.19$

14-10. $[H_3O^+] = \sqrt{K_w}$ and $pH = -\log(K_w)^{1/2} = -½ \log K_w$

At 0°C, $pH = -½ \log(1.14 \times 10^{-15}) = 7.47$

At 50°C, $pH = -½ \log(5.47 \times 10^{-14}) = 6.63$

At 100°C, $pH = -½ \log(4.9 \times 10^{-13}) = 6.16$

14-11. At 0°C, $pK_w = -\log(1.14\times10^{-15}) = 14.94$

At 50°C, $pK_w = -\log(5.47\times10^{-14}) = 13.26$

At 100°C, $pK_w = -\log(4.9\times10^{-13}) = 12.31$

14-12. $pK_w = pH + pOH$; $pOH = -\log[OH^-] = -\log(1.00\times10^{-2}) = 2.00$

(a) $pH = pK_w - pOH = 4.94 - 2.00 = 12.94$

(b) $pH = 13.26 - 2.00 = 11.26$

(c) $pH = 12.31 - 2.00 = 10.31$

14-13. $$\frac{3.00\ \cancel{\text{g HCl}}}{100\ \cancel{\text{g}}} \times \frac{1.015\ \cancel{\text{g}}}{\text{mL}} \times \frac{1\ \text{mmol HCl}}{0.03646\ \cancel{\text{g HCl}}} = 0.835\ \text{M}$$

$[H_3O^+] = 0.835$ M; $pH = -\log 0.835 = 0.078$

14-14. $$\frac{2.00\ \cancel{\text{g NaOH}}}{100\ \cancel{\text{g}}} \times \frac{1.022\ \cancel{\text{g}}}{\text{mL}} \times \frac{1\ \text{mmol NaOH}}{0.04000\ \cancel{\text{g NaOH}}} = 0.511\ \text{M}$$

$[OH^-] = 0.511$ M; $pH = 14.00 - (-\log 0.511) = 13.71$

14-15. The solution is so dilute that we must take into account the contribution of water to $[OH^-]$ which is equal to $[H_3O^+]$. Thus,

$$[OH^-] = 2.00\times10^{-8} + [H_3O^+] = 2.00\times10^{-8} + \frac{1.00\times10^{-14}}{[OH^-]}$$

$$[OH^-]^2 - 2.00\times10^{-8}[OH^-] - 1.00\times10^{-14} = 0$$

Solving the quadratic equation yields, $[OH^-] = 1.105\times10^{-7}$ M

$pOH = -\log 1.105\times10^{-7} = 6.957$; $pH = 14.00 - 6.957 = 7.04$

14-16. The solution is so dilute that we must take into account the contribution of water to $[H_3O^+]$ which is equal to $[OH^-]$. Thus,

$$[H_3O^+] = 2.00\times10^{-8} + [OH^-] = 2.00\times10^{-8} + \frac{1.00\times10^{-14}}{[H_3O^+]}$$

$$[H_3O^+]^2 - 2.00\times10^{-8}[H_3O^+] - 1.00\times10^{-14} = 0$$

$[H_3O^+] = 1.105 \times 10^{-7}$ M; pH = $-\log 1.105 \times 10^{-7} = 6.96$

14-17. amount of $Mg(OH)_2$ taken = $\dfrac{0.093\ \text{g}\ \cancel{Mg(OH)_2}}{0.05832\ \text{g}\ \cancel{Mg(OH)_2}\ /\ \text{mmol}}$ = 1.595 mmol

(a) $c_{HCl} = (75.0 \times 0.0500 - 1.595 \times 2)/75.0 = 7.467 \times 10^{-3}$ M

$[H_3O^+] = 7.467 \times 10^{-3}$; pH = $-\log(7.467 \times 10^{-3}) = 2.13$

(b) $c_{HCl} = 100.0 \times 0.0500 - 1.595 \times 2)/100.0 = 0.0181$ M

pH = $-\log(0.0181) = 1.74$

(c) $15.0 \times 0.050 = 0.750$ mmol HCl added. Solid $Mg(OH)_2$ remains and

$$[Mg^{2+}] = 0.750\ \text{mmol HCl} \times \frac{1\ \text{mmol}\ Mg^{2+}}{2\ \text{mmol HCl}} \times \frac{1}{15.0\ \text{mL}} = 0.0250\ \text{M}$$

$K_{sp} = 7.1 \times 10^{-12} = [Mg^{2+}][OH^-]^2$

$$[OH^-] = \sqrt{\frac{7.1 \times 10^{-12}}{0.0250}} = 1.68 \times 10^{-5}\ \text{M}$$

pH = $14.00 - (-\log(1.68 \times 10^{-5})) = 9.22$

(d) Since $Mg(OH)_2$ is fairly insoluble, the Mg^{2+} essentially all comes from the added $MgCl_2$, and $[Mg^{2+}] = 0.0500$ M

$$[OH^-] = \sqrt{\frac{7.1 \times 10^{-12}}{0.0500}} = 1.19 \times 10^{-5}\ \text{M}$$

pH = $14.00 - (-\log(1.19 \times 10^{-5})) = 9.08$

14-18. In each part, (20.0 mL HCl × 0.1750 mmol HCl/mL) = 3.50 mmol HCl is taken

(a) $c_{HCl} = [H_3O^+] = \dfrac{3.50\ \text{mmol HCl}}{(20.0+25.0)\text{mL}} = 0.0778$ M

pH = $-\log 0.0778 = 1.11$

(b) Same as in part (a); pH =1.11

(c) $c_{\text{HCl}} = (3.50 – 25.0 \times 0.132)/(20.0 + 25.0) = 4.444\times10^{–3}$ M

$[H_3O^+] = 4.444\times10^{–3}$ M; pH = –log $4.444\times10^{–3}$ = 2.35

(d) As in part (c), $c_{\text{HCl}} = 4.444\times10^{–3}$ M and pH = 2.35

(The presence of NH_4^+ will not alter the pH significantly.)

(e) $c_{\text{NaOH}} = (25.0 \times 0.232 – 3.50)/(45.0) = 5.11 \times 10^{–2}$ M

pOH = – log($5.11 \times 10^{–2}$) = 1.29 pH = 14 – 1.29 = 12.71

14-19. (a) $[H_3O^+]$ = 0.0500 M; pH = –log(0.0500) = 1.30

(b) $\mu = ½ \{(0.0500)(+1)^2 + (0.0500)(–1)^2\} = 0.0500$

$\gamma_{H_3O^+}$ = 0.85 **(Table 10-2)**

$a_{H_3O^+} = 0.85 \times 0.0500 = 0.0425$

pH = –log(0.0425) = 1.37

14-20. (a) $[OH^–] = 2 \times 0.0167 = 0.0334$ M

pH = 14 – (–log(0.0334)) = 12.52

(b) $\mu = ½ \{(0.0167)(+2)^2 + (0.0334)(–1)^2\} = 0.050$

$\gamma_{OH^–}$ = 0.81 **(Table 10-2)**

$a_{OH^–} = 0.81 \times 0.0334 = 0.0271$

$a_{OH^–} \times a_{H_3O^+} = 1.00 \times 10^{–14}$

$a_{H_3O^+} = 1.00 \times 10^{–14}/0.0271 = 3.69\times10^{–13}$

pH = –log($3.69 \times 10^{–13}$) = 12.43

14-21. $HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$ $\quad K_a = \dfrac{[H_3O^+][OCl^-]}{[HOCl]} = 3.0 \times 10^{-8}$

$[H_3O^+] = [OCl^-]$ and $[HOCl] = c_{HOCl} - [H_3O^+]$

$[H_3O^+]^2/(c_{HOCl} - [H_3O^+]) = 3.0 \times 10^{-8}$

rearranging gives: $[H_3O^+]^2 + 3 \times 10^{-8}[H_3O^+] - c_{HOCl} \times 3.0 \times 10^{-8} = 0$

	c_{HOCl}	$[H_3O^+]$	pH
(a)	0.100	5.476×10^{-5}	4.26
(b)	0.0100	1.731×10^{-5}	4.76
(c)	1.00×10^{-4}	1.717×10^{-6}	5.76

14-22. $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$ $K_b = \dfrac{K_w}{K_a} = \dfrac{[HOCl][OH^-]}{[OCl^-]} = \dfrac{1.00 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.33 \times 10^{-7}$

$[HOCl] = [OH^-]$ and $[OCl^-] = c_{NaOCl} - [OH^-]$

$[OH^-]^2/(c_{NaOCl} - [OH^-]) = 3.33 \times 10^{-7}$

rearranging gives $[OH^-]^2 + 3.33 \times 10^{-7}[OH^-] - c_{NaOCl} \times 3.33 \times 10^{-7} = 0$

	c_{NaOCl}	$[OH^-]$	pOH	pH
(a)	0.100	1.823×10^{-4}	3.74	10.26
(b)	0.0100	5.754×10^{-5}	4.24	9.76
(c)	1.00×10^{-4}	5.606×10^{-6}	5.25	8.75

14-23. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $\quad K_b = \dfrac{1.00 \times 10^{-14}}{5.7 \times 10^{-10}} = 1.75 \times 10^{-5}$

$[NH_4^+] = [OH^-]$ and $[NH_3] = c_{NH_3} - [OH^-]$

$[OH^-]^2/(c_{NH_3} - [OH^-]) = 1.75 \times 10^{-5}$

rearranging gives: $[OH^-]^2 + 1.75 \times 10^{-5}[OH^-] - c_{NH_3} \times 1.75 \times 10^{-5} = 0$

	c_{NH_3}	**[OH⁻]**	**pOH**	**pH**
(a)	0.100	1.314×10^{-3}	2.88	11.12
(b)	0.0100	4.097×10^{-4}	3.39	10.62
(c)	1.00×10^{-4}	3.399×10^{-5}	4.47	9.53

14-24. $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $\qquad K_a = 5.7 \times 10^{-10}$

$[H_3O^+] = [NH_3]$ and $[NH_4^+] = c_{NH_4^+} - [H_3O^+]$

$[H_3O^+]^2/(c_{NH_4^+} - [H_3O^+]) = 5.7 \times 10^{-10}$

rearranging gives: $[H_3O^+]^2 + 5.7 \times 10^{-10}[H_3O^+] - c_{NH_4^+} \times 5.7 \times 10^{-10} = 0$

	$c_{NH_4^+}$	$[H_3O^+]$	pH
(a)	0.100	7.550×10^{-6}	5.12
(b)	0.0100	2.387×10^{-6}	5.62
(c)	1.00×10^{-4}	1.385×10^{-7}	6.62

14-25. $C_5H_{11}N + H_2O \rightleftharpoons C_5H_{11}NH^+ + OH^-$ $\qquad K_b = \dfrac{1.00 \times 10^{-14}}{7.5 \times 10^{-12}} = 1.333 \times 10^{-3}$

$[C_5H_{11}NH^+] = [OH^-]$ and $[C_5H_{11}N] = c_{C_5H_{11}N} - [OH^-]$

$[OH^-]^2/(c_{C_5H_{11}N} - [OH^-]) = 1.333 \times 10^{-3}$

rearranging gives: $[OH^-]^2 + 1.333 \times 10^{-3}[OH^-] - c_{C_5H_{11}N} \times 1.333 \times 10^{-3} = 0$

	$c_{C_5H_{11}N}$	**[OH⁻]**	**pOH**	**pH**
(a)	0.100	1.090×10^{-2}	1.96	12.04
(b)	0.0100	3.045×10^{-3}	2.52	11.48
(c)	1.00×10^{-4}	9.345×10^{-5}	4.03	9.97

14-26. $HSfm + H_2O \rightleftharpoons H_3O^+ Sfm^-$ $K_a = 1.03 \times 10^{-1}$

$[H_3O^+] = [Sfm^-]$ and $[HSfm] = c_{HSfm} - [H_3O^+]$

$[H_3O^+]^2/(c_{HSfm} - [H_3O^+]) = 1.03 \times 10^{-1}$

rearranging gives: $[H_3O^+]^2 + 1.03 \times 10^{-1}[H_3O^+] - c_{HIO_3} \times 1.03 \times 10^{-1} = 0$

	c_{HSfm}	$[H_3O^+]$	**pH**
(a)	0.100	6.23×10^{-2}	1.21
(b)	0.0100	9.18×10^{-3}	2.04
(c)	1.00×10^{-4}	9.90×10^{-5}	4.00

14-27. (a)

$$c_{HA} = 36.5 \text{ g HA} \times \frac{1 \text{ mmol HA}}{0.090079 \text{ g HA}} \times \frac{1}{500 \text{ mL soln}} = 0.8104 \text{ M HA}$$

$HL + H_2O \rightleftharpoons H_3O^+ + L^-$ $K_a = 1.38 \times 10^{-4}$

$[H_3O^+] = [L^-]$ and $[HL] = 0.8104 - [H_3O^+]$

$[H_3O^+]^2/(0.8104 - [H_3O^+]) = 1.38 \times 10^{-4}$

rearranging and solving the quadratic gives: $[H_3O^+] = 0.0105$ and pH = 1.98

(b) $c_{HA} = 0.8104\times25.0/250.0 = 0.08104$ M HL

Proceeding as in part (a) we obtain: $[H_3O^+] = 3.28 \times 10^{-3}$ and pH = 2.48

(c) $c_{HA} = 0.08104 \times 10.0/1000.0 = 8.104\times10^{-4}$ M HL

Proceeding as in part (a) we obtain: $[H_3O^+] = 2.72 \times 10^{-4}$ and pH = 3.56

14-28. **(a)**

$$c_{\text{HPc}} = 2.13\text{ g HPc} \times \frac{1\text{ mmol HPc}}{0.22911\text{ g HPc}} \times \frac{1}{100\text{ mL soln}} = 0.09297\text{ M HPc}$$

$\text{HPc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Pc}^-$ $\quad K_a = 0.43$

$[\text{H}_3\text{O}^+] = [\text{Pc}^-]$ and $[\text{HPc}] = 0.09297 - [\text{H}_3\text{O}^+]$

$[\text{H}_3\text{O}^+]^2/(0.09297 - [\text{H}_3\text{O}^+]) = 0.43$

rearranging and solving the quadratic gives: $[\text{H}_3\text{O}^+] = 0.0786$ and pH = 1.10

(b) $c_{\text{HPc}} = 0.09297 \times 10.0/100.0 = 0.009297$ M HPc

Proceeding as in part (a) we obtain: $[\text{H}_3\text{O}^+] = 9.10 \times 10^{-3}$ and pH = 2.04

(c) $c_{\text{HA}} = 0.009297 \times 10.0/1000.0 = 9.297 \times 10^{-5}$ M HPc

Proceeding as in part (a) we obtain: $[\text{H}_3\text{O}^+] = 9.29 \times 10^{-5}$ and pH = 4.03

14-29. amount HFm taken = $20.00\ \cancel{\text{mL}} \times \dfrac{0.1750\text{ mmol}}{\cancel{\text{mL}}} = 3.50\text{ mmol}$

(a) $\text{HFm} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Fm}^-$ $\quad K_a = 1.80 \times 10^{-4}$

$c_{\text{HFm}} = 3.50/45.0 = 7.78 \times 10^{-2}$ M

$[\text{H}_3\text{O}^+] = [\text{Fm}^-]$ and $[\text{HFm}] = 0.0778 - [\text{H}_3\text{O}^+]$

$[\text{H}_3\text{O}^+]^2/(0.0778 - [\text{H}_3\text{O}^+]) = 1.80\times10^{-4}$

rearranging and solving the quadratic gives: $[\text{H}_3\text{O}^+] = 3.65\times10^{-3}$ and pH = 2.44

(b) amount NaOH added = 25.0 × 0.140 = 3.50 mmol

Since all the formic acid has been neutralized, we are left with a solution of NaFm.

$\text{Fm}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HFm}$ $\quad K_b = 1.00 \times 10^{-14}/(1.80 \times 10^{-4}) = 5.56 \times 10^{-11}$

c_{Fm^-} = 3.00/45.0 = 7.78×10^{-2} M

$[\text{OH}^-] = [\text{HFm}]$ and $[\text{Fm}^-] \quad 0.0778 - [\text{OH}^-]$

$[\text{OH}^-]^2/(0.0778 - [\text{OH}^-]) = 5.56 \times 10^{-11}$

rearranging and solving the quadratic gives: $[\text{OH}^-] = 2.08 \times 10^{-6}$ and pH = 8.32

(c) amount NaOH added = 25.0 × 0.200 = 5.00 mmol

therefore, we have an excess of NaOH; the pH is determined by the excess $[\text{OH}^-]$.

$[\text{OH}^-] = (5.00 - 3.50)/45.0 = 3.333 \times 10^{-2}$ M

pH = 14 – pOH = 12.52

(d) amount NaFm added = 25.0 × 0.200 = 5.00 mmol

[HFm] = 3.50/45.0 = 0.0778

$[\text{Fm}^-] = 5.00/45.00 = 0.1111$

$[\text{H}_3\text{O}^+] \times 0.1111/0.0778 = 1.80 \times 10^{-4}$

$[\text{H}_3\text{O}^+] = 1.260 \times 10^{-4}$ and pH = 3.90

14-30. amount NH_3 taken = $40.0\ \cancel{\text{mL}} \times \dfrac{0.1250\ \text{mmol}}{\cancel{\text{mL}}}$ = 5.00 mmol

(a) $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{NH}_4^+$ $\qquad K_b = \dfrac{1.00 \times 10^{-14}}{5.7 \times 10^{-10}} = 1.75 \times 10^{-5}$

$c_{\text{NH}_3} = 5.00/60.0 = 8.333 \times 10^{-2}$ M

$[\text{NH}_4^+] = [\text{OH}^-]$ and $[\text{NH}_3] = 0.0833 - [\text{OH}^-]$

$[\text{OH}^-]^2/(0.0833 - [\text{OH}^-]) = 1.75 \times 10^{-5}$

rearranging and solving the quadratic gives: $[\text{OH}^-] = 1.20 \times 10^{-3}$ and pH = 11.08

(b) amount HCl added = 20.0 × 0.250 = 5.00 mmol

The NH_3 is just neutralized and we are left with a solution of NH_4Cl.

$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $K_a = 5.7 \times 10^{-10}$

$c_{NH_4^+} = 5.00/60.0 = 8.33 \times 10^{-2}$

$[H_3O^+] = [NH_3]$ and $[NH_4^+] = 0.0833 - [H_3O^+]$

$[H_3O^+]^2/(0.0833 - [H_3O^+]) = 5.7 \times 10^{-10}$

rearranging and solving the quadratic gives: $[H_3O^+] = 6.89 \times 10^{-6}$ and pH = 5.16

(c) amount HCl added = 20.0 × 0.300 = 6.00 mmol

We have an excess of HCl which determines the pH.

$[H_3O^+] = (6.00 - 5.00)/60.0 = 1.67 \times 10^{-2}$ M

pH = 1.78

(d) amount NH_4Cl added = 20.0 × 0.200 = 4.00 mmol

$[NH_3] = 5.00/60.0 = 0.0833$ $[NH_4^+] = 4.00/60.0 = 0.0667$

$[H_3O^+] \times 0.0.0833/0.0667 = 5.70 \times 10^{-10}$

$[H_3O^+] = 4.56 \times 10^{-10}$ and pH = 9.34

(e) amount HCl added = 20.0 × 0.100 = 2.00 mmol

$[NH_3] = (5.00 - 2.00)/60.0 = 0.0500$ $[NH_4^+] = 2.00/60.0 = 0.0333$

$[H_3O^+] \times 0.0.050/0.0333 = 5.70 \times 10^{-10}$

$[H_3O^+] = 3.80 \times 10^{-10}$ pH = 9.42

14-31. **(a)** $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $K_a = 5.70 \times 10^{-10} = \dfrac{[H_3O^+][NH_3]}{[NH_4^+]}$

$[NH_3] = 0.0300$ M and $[NH_4^+] = 0.0500$ M

$[H_3O^+] = 5.70 \times 10^{-10} \times 0.0500/0.0300 = 9.50 \times 10^{-10}$ M

$[OH^-] = 1.00 \times 10^{-14}/9.50 \times 10^{-10} = 1.05 \times 10^{-5}$ M

pH = $-\log(9.50 \times 10^{-10}) = 9.02$

(b) $\mu = ½\,\{(0.0500)(+1)^2 + (0.0500)(-1)^2\} = 0.0500$

From Table 10-2 $\gamma_{NH_4^+} = 0.80$ and $\gamma_{NH_3} = 1.0$

$$a_{H_3O^+} = \frac{K_a \gamma_{NH_4^+}[NH_4^+]}{\gamma_{NH_3}[NH_3]} = \frac{5.70 \times 10^{-5} \times 0.80 \times 0.0500}{1.00 \times 0.0300} = 7.60 \times 10^{-10}$$

pH = $-\log(7.60 \times 10^{-10}) = 9.12$

14-32. In each part of this problem, a buffer solution of a weak acid, HA, and its conjugate base, NaA, is formed. In each case, we initially assume that $[H_3O^+]$ and $[OH^-]$ are much smaller than the molar concentration of the acid and conjugate base so that $[A^-] \cong c_{NaA}$ and $[HA] \cong c_{HA}$. These assumptions then lead to the following:

$$[H_3O^+] = \frac{K_a c_{HA}}{c_{NaA}}$$

(a) $c_{HA} = 7.85\ \cancel{\text{g HA}} \times \dfrac{1 \text{ mol HA}}{90.08\ \cancel{\text{g HA}}} \times \dfrac{1}{1.00 \text{ L soln}} = 0.0871$ M

$$c_{NaA} = 10.09\ \cancel{\text{g HA}} \times \frac{1 \text{ mol NaA}}{112.06\ \cancel{\text{g NaA}}} \times \frac{1}{1.00 \text{ L soln}} = 0.0900 \text{ M}$$

$$[H_3O^+] = 1.38 \times 10^{-4} \times \frac{0.0871}{0.0900} = 1.34 \times 10^{-4} \text{ M}$$

Note that $[H_3O^+]$ (and $[OH^-]$) << c_{HA} (and c_{NaA}) as assumed. Therefore

pH = 3.87

(b) $c_{HA} = 0.0630$ M and $c_{NaA} = 0.0210$ M

$[H_3O^+] = 1.75{\times}10^{-5} \times 0.0630/0.0210 = 5.25 \times 10^{-5}$

$pH = -\log(5.25 \times 10^{-5}) = 4.28$

(c) Original amount HA = $3.00\ \cancel{g} \times \dfrac{\text{mmol HA}}{0.13812\ \cancel{g}}$ = 21.72 mmol HA

Original amount NaOH = $50.0\ \cancel{mL} \times \dfrac{0.1130\text{ mmol HA}}{\cancel{mL}}$ = 5.65 mmol NaOH

$c_{HA} = (21.72 - 5.65)/500 = 3.214 \times 10^{-2}$ M

$c_{NaA} = 5.65/500 = 1.130 \times 10^{-2}$ M

estimated $[H_3O^+]_{est} = 1.06 \times 10^{-3} \times 3.214 \times 10^{-2}/(1.130 \times 10^{-2}) = 3.015 \times 10^{-3}$ M

Note, that $[H_3O^+]_{est}$ is not << c_{HA} (and c_{NaA}) as assumed. Therefore

$[A^-] = 1.130 \times 10^{-2} + [H_3O^+] - [OH^-]$

$[HA] = 3.214 \times 10^{-2} - [H_3O^+] + [OH^-]$

Since $K_a = 1.06 \times 10^{-3}$, the solution should be acidic and so $[OH^-] << [H_3O^+]$

Substituting into the dissociation-constant expression gives

$$\frac{[H_3O^+]\left(1.130 \times 10^{-2} + [H_3O^+]\right)}{3.214 \times 10^{-2} - [H_3O^+]} = 1.06 \times 10^{-3}$$

Rearranging gives

$[H_3O^+]^2 + 1.236 \times 10^{-2}\ [H_3O^+] - 3.407 \times 10^{-5} = 0$

$[H_3O^+] = 2.321 \times 10^{-3}$ M and pH = 2.63

(d) Here we must again proceed as in part (c). This leads to

$$\frac{[H_3O^+]\left(0.100 + [H_3O^+]\right)}{0.0100 - [H_3O^+]} = 4.3 \times 10^{-1}$$

$[H_3O^+]^2 + 0.53\ [H_3O^+] - 4.3{\times}10^{-3} = 0$

$[H_3O^+] = 7.99 \times 10^{-3}$ M and pH = 2.10

14-33. In each of the parts of this problem, we are dealing with a weak base B and its conjugate acid BHCl or $(BH)_2SO_4$. The pH determining equilibrium can then be written as

$$BH^+ + H_2O \rightleftharpoons H_3O^+ + B$$

The equilibrium concentration of BH^+ and B are given by

$$[BH^+] = c_{BHCl} + [OH^-] - [H_3O^+] \qquad (1)$$

$$[B] = c_B - [OH^-] + [H_3O^+] \qquad (2)$$

In many cases $[OH^-]$ and $[H_3O^+]$ will be much smaller than c_B and c_{BHCl} and $[BH^+] \approx c_{BHCl}$ and $[B] \approx c_B$ so that

$$[H_3O^+] = K_a \times \frac{c_{BHCl}}{c_B} \qquad (3)$$

(a) Amount $NH_4^+ = 3.30\ \cancel{g\ (NH_4)_2SO_4} \times \frac{1\ \cancel{mmol\ (NH_4)_2SO_4}}{0.13214\ \cancel{g\ (NH_4)_2SO_4}} \times \frac{2\ mmol\ NH_4^+}{\cancel{mmol\ (NH_4)_2SO_4}}$

$= 49.95$ mmol

Amount NaOH = 125.0 mL × 0.1011 mmol/mL = 12.64 mmol

$$c_{NH_3} = 12.64\ \cancel{mmol\ NaOH} \times \frac{1\ mmol\ NH_3}{\cancel{mmol\ NaOH}} \times \frac{1}{500.0\ mL} = 2.528 \times 10^{-2}\ M$$

$$c_{NH_4^+} = (49.95 - 12.64)\ mmol\ NH_4^+ \times \frac{1}{500.0\ mL} = 7.462 \times 10^{-2}\ M$$

Substituting these relationships in equation (3) gives

$$[H_3O^+] = K_a \times \frac{c_{BHCl}}{c_B} = 5.70 \times 10^{-10} \times 7.462 \times 10^{-2} / (2.528 \times 10^{-2}) = 1.682 \times 10^{-9}\ M$$

$$[OH^-] = 1.00 \times 10^{-14} / 1.682 \times 10^{-9} = 5.95 \times 10^{-6}\ M$$

Note, $[H_3O^+]$ and $[OH^-]$ are small compared to c_{NH_3} and $c_{NH_4^+}$ so our assumption is valid.

pH = $-\log(1.682 \times 10^{-9}) = 8.77$

(b) Substituting into equation (3) gives

$[H_3O^+] = 7.5 \times 10^{-12} \times 0.010/0.120 = 6.25 \times 10^{-13}$ M

$[OH^-] = 1.00 \times 10^{-14}/6.25 \times 10^{-13} = 1.60 \times 10^{-2}$ M

Again our assumption is valid and

pH = $-\log(6.25 \times 10^{-13}) = 12.20$

(c) $c_B = 0.050$ M and $c_{BHCl} = 0.167$ M

$[H_3O^+] = 2.31 \times 10^{-11} \times 0.167/0.050 = 7.715 \times 10^{-11}$ M

$[OH^-] = 1.00 \times 10^{-14}/7.715 \times 10^{-11} = 1.30 \times 10^{-4}$ M

The assumption is valid and

pH = $-\log(7.715 \times 10^{-11}) = 10.11$

(d) Original amount B $= 2.32 \ \cancel{\text{g B}} \times \dfrac{1 \text{ mmol}}{0.09313 \ \cancel{\text{g B}}} = 24.91$ mmol $= 24.91$ mmol

Amount HCl = 100 mL × 0.0200 mmol/mL = 2.00 mmol

$c_B = (24.91 - 2.00)/250.0 = 9.164 \times 10^{-2}$ M

$c_{BH^+} = 2.00/250.0 = 8.00 \times 10^{-3}$ M

$[H_3O^+] = 2.51 \times 10^{-5} \times 8.00 \times 10^{-3}/(9.164 \times 10^{-2}) = 2.191 \times 10^{-6}$ M

$[OH^-] = 1.00 \times 10^{-14}/2.191 \times 10^{-6} = 4.56 \times 10^{-9}$ M

Our assumptions are valid, so

pH = $-\log(2.191 \times 10^{-6}) = 5.66$

14-34. (a) 0.00

(b) $[H_3O^+]$ changes to 0.00500 M from 0.0500 M

$\Delta pH = -\log(0.00500) - [-\log(0.0500)] = 2.301 - 1.301 = 1.000$

(c) pH diluted solution = $14.000 - [-\log(0.00500)] = 11.699$

pH undiluted solution = $14.000 - [-\log(0.0500)] = 12.699$

$\Delta pH = 11.699 - 12.699 = -1.000$

(d) In order to get a better picture of the pH change with dilution, we will dispense with the usual approximations and write

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.75\times10^{-5}$$

$[H_3O^+]^2 + 1.75 \times 10^{-5}[H_3O^+] - 0.0500 \times 1.75 \times 10^{-5} = 0$

Solving the quadratic or using successive approximations, gives

$[H_3O^+] = 9.267 \times 10^{-4}$ M and $pH = -\log(9.267 \times 10^{-4}) = 3.033$

For the diluted solution, the quadratic becomes

$[H_3O^+]^2 + 1.75 \times 10^{-5} - 0.00500 \times 1.75 \times 10^{-5} = 0$

$[H_3O^+] = 2.872 \times 10^{-4}$ M and pH = 3.542

$\Delta pH = 3.033 - 3.542 = -0.509$

(e) $OAc^- + H_2O \rightleftharpoons HOAc + OH$

$$K_b = \frac{[HOAc][OH^-]}{[OAc^-]} = \frac{1.00\times10^{-14}}{1.75\times10^{-5}} = 5.71 \times 10^{-10}$$

Here we can use an approximation because K_b is very small. For the undiluted sample:

$$\frac{[OH^-]^2}{0.0500} = 5.71 \times 10^{-10}$$

$[OH^-] = (5.71 \times 10^{-10} \times 0.0500)^{1/2} = 5.343 \times 10^{-6}$ M

pH = 14.00 – [–log(5.343 × 10^{-6})] = 8.728

For the diluted sample

$[OH^-] = (5.71 \times 10^{-10} \times 0.00500)^{1/2} = 1.690 \times 10^{-6}$ M

pH = 14.00 – [–log(1.690 × 10^{-6})] = 8.228

ΔpH = 8.228 – 8.728 = –0.500

(f) Here we must avoid the approximate solution because it will not reveal the small pH change resulting from dilution. Thus, we write

$[HOAc] = c_{HOAc} + [OH^-] - [H_3O^+] \approx c_{HOAc} - [H_3O^+]$ since the solution is acidic

$[OAc^-] = c_{NaOAc} - [OH^-] + [H_3O^+] \approx c_{NaOAc} + [H_3O^+]$

$$K_a = 1.75 \times 10^{-5} = \frac{[H_3O^+]\left(0.0500 + [H_3O^+]\right)}{0.0500 - [H_3O^+]}$$

$[H_3O^+]^2 + 5.0018 \times 10^{-2}[H_3O^+] - 8.75 \times 10^{-7} = 0$

$[H_3O^+] = 1.749 \times 10^{-5}$ and pH = 4.757

Proceeding in the same way we obtain for the diluted sample

$$1.75 \times 10^{-5} = \frac{[H_3O^+]\left(0.00500 + [H_3O^+]\right)}{0.00500 - [H_3O^+]}$$

$[H_3O^+]^2 + 5.0175 \times 10^{-3}[H_3O^+] - 8.75 \times 10^{-8} = 0$

$[H_3O^+] = 1.738 \times 10^{-5}$ and pH = 4.760

ΔpH = 4.760 – 4.757 = 0.003

Note the very small pH change that occurs on diluting this buffer solution.

(g) Proceeding as in part (f) a 10-fold dilution of this solution results in a pH change that is less than 1 in the third decimal place. Thus for all practical purposes,

$\Delta pH = 0.000$

Note a more concentrated buffer compared to part (f) gives an even smaller pH change.

14-35. (a) After addition of acid, $[H_3O^+] = 1 \text{ mmol}/100 \text{ mL} = 0.0100 \text{ M}$ and pH = 2.00

Since original pH = 7.00

$\Delta pH = 2.00 - 7.00 = -5.00$

(b) After addition of acid

$c_{HCl} = (100 \times 0.0500 + 1.00)/100 = 0.0600 \text{ M}$

$\Delta pH = -\log(0.0600) - [-\log(0.0500)] = 1.222 - 1.301 = -0.079$

(c) After addition of acid,

$c_{NaOH} = (100 \times 0.0500 - 1.00)/100 = 0.0400 \text{ M}$

$[OH^-] = 0.0400 \text{ M}$ and $pH = 14.00 - [-\log(0.0400)] = 12.602$

From Problem 14-34 (c), original pH = 12.699

$\Delta pH = -0.097$

(d) From Solution 14-34 (d), original pH = 3.033

Upon adding 1 mmol HCl to the 0.0500 M HOAc, we produce a mixture that is 0.0500 M in HOAc and 1.00/100 = 0.0100 M in HCl. The pH of this solution is approximately that of a 0.0100 M HCl solution, or 2.00. Thus

$\Delta pH = 2.000 - 3.033 = -1.033$

(If the contribution of the dissociation of HOAc to the pH is taken into account, a pH of 1.996 is obtained and ΔpH = −1.037 is obtained.)

(e) From Solution 14-34 (e), original pH = 8.728

Upon adding 1.00 mmol HCl we form a buffer having the composition

$c_{\text{HOAc}} = 1.00/100 = 0.0100$

$c_{\text{NaOAc}} = (0.0500 \times 100 – 1.00)/100 = 0.0400$

$[\text{H}_3\text{O}^+] = 1.75 \times 10^{–5} \times 0.0100/0.0400 = 4.575 \times 10^{–6}$ M

$\text{pH} = –\log(4.575 \times 10^{–6}) = 5.359$

$\Delta\text{pH} = 5.359 – 8.728 = –3.369$

(f) From Solution 14-34 (f), original pH = 4.757

With the addition of 1.00 mmol of HCl we have a buffer whose concentrations are

$c_{\text{HOAc}} = 0.0500 + 1.00/100 = 0.0600$ M

$c_{\text{NaOAc}} = 0.0500 – 1.00/100 = 0.0400$ M

Proceeding as in part (e), we obtain

$[\text{H}_3\text{O}^+] = 2.625 \times 10^{–5}$ M and pH = 4.581

$\Delta\text{pH} = 4.581 – 4.757 = –0.176$

Note again the very small pH change as compared to unbuffered solutions.

(g) For the original solution

$[\text{H}_3\text{O}^+] = 1.75 \times 10^{–5} \times 0.500/0.500 = 1.75 \times 10^{–5}$ M

$\text{pH} = –\log(1.75 \times 10^{–5}) = 4.757$

After addition of 1.00 mmol HCl

$c_{\text{HOAc}} = 0.500 + 1.00/100 = 0.510$ M

c_{NaOAc} = 0.500 – 1.00/100 = 0.490 M

Proceeding as in part (e), we obtain

$[\mathrm{H_3O^+}] = 1.75 \times 10^{-5} \times 0.510/0.490 = 1.821 \times 10^{-5}$ M

pH = –log(1.821×10^{-5}) = 4.740

ΔpH = 4.740 – 4.757 = –0.017

Note that the more concentrated buffer is even more effective in resisting pH changes.

14-36. **(a)** c_{NaOH} = 1.00/100 = 0.0100 = $[\mathrm{OH^-}]$

pH = 14.00 – [–log(0.0100)] = 12.00

Original pH = 7.00 and ΔpH = 12.00 – 7.00 = 5.00

(b) Original pH = 1.301 [see Problem 14-34 (b)]

After addition of base, c_{HCl} = (100 × 0.0500 – 1.00)/100 = 0.0400 M

ΔpH = –log(0.0400) – 1.301 = 1.398 – 1.30 = 0.097

(c) Original pH = 12.699 [see Problem 14.34 (c)]

After addition of base, c_{NaOH} = (100 × 0.0500 + 1.00)/100 = 0.0600 M

pH = 14.00 – [–log(0.0600)] = 12.778

ΔpH = 12.778 – 12.69 = 0.079

(d) Original pH = 3.033 [see Problem 14-34 (d)]

Addition of strong base gives a buffer of HOAc and NaOAc

c_{NaOAc} = 1.00 mmol/100 = 0.0100 M

c_{HOAc} = 0.0500 – 1.00/100 = 0.0400 M

Proceeding as in Solution 14-35 (e) we obtain

$[\mathrm{H_3O^+}] = 1.75 \times 10^{-5} \times 0.0400/0.0100 = 7.00 \times 10^{-5}$ M

$\text{pH} = -\log(7.00 \times 10^{-5}) = 4.155$

$\Delta\text{pH} = 4.155 - 3.033 = 1.122$

Note rather large change in pH since there was no buffer until after the base was added.

(e) Original pH = 8.728 [see Problem 14.34 (e)]

We have a mixture of NaOAc and NaOH and the pH is determined by the excess NaOH

$c_{\text{NaOH}} = 1.00 \text{ mmol}/100 = 0.0100 \text{ M}$

$\text{pH} = 14.00 - [-\log(0.0100)] = 12.00$

$\Delta\text{pH} = 12.00 - 8.728 = 3.272$

Note again the large change in pH.

(f) Original pH = 4.757 [see Problem 14-34 (f)]

$c_{\text{NaOAc}} = 0.0500 + 1.00/100 = 0.0600 \text{ M}$

$c_{\text{HOAc}} = 0.0500 - 1.00/100 = 0.0400 \text{ M}$

Proceeding as in Solution 14.35 (e) we obtain

$[\text{H}_3\text{O}^+] = 1.167 \times 10^{-5} \text{ M}$ and $\text{pH} = 4.933$

$\Delta\text{pH} = 4.933 - 4.757 = 0.176$

Note that the pH change is relatively small with this buffer solution.

(g) Original pH = 4.757 [see Problem 14-34 (f)]

$c_{\text{HOAc}} = 0.500 - 1.00/100 = 0.490 \text{ M}$

$c_{\text{NaOAc}} = 0.500 + 1.00/100 = 0.510 \text{ M}$

$[\text{H}_3\text{O}^+] = 1.75 \times 10^{-5} \times 0.400/0.510 = 1.681 \times 10^{-5} \text{ M}$

$\text{pH} = -\log(1.681 \times 10^{-5}) = 4.774$

$\Delta\text{pH} = 4.774 - 4.757 = 0.017$

Note here the extremely small pH change with this more concentrated buffer solution.

14-37. For lactic acid, $K_a = 1.38 \times 10^{-4} = [H_3O^+][L^-]/[HL]$

Throughout this problem we will base calculations on Equations 9-25 and 9-26

$[L^-] = c_{NaL} + [H_3O^+] - [OH^-] \approx c_{NaL} + [H_3O^+]$

$[HL] = c_{HL} - [H_3O^+] - [OH^-] \approx c_{HL} - [H_3O^+]$

$$\frac{[H_3O^+]\left(c_{NaL} + [H_3O^+]\right)}{c_{HL} - [H_3O^+]} = 1.38 \times 10^{-4}$$

This equation rearranges to

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0800)[H_3O^+] - 1.38 \times 10^{-4} \times c_{HL} = 0$

(a) Before addition of acid

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0800)[H_3O^+] - 1.38 \times 10^{-4} \times 0.0200 = 0$

$[H_3O^+] = 3.443 \times 10^{-5}$ and pH = 4.46

Upon adding 0.500 mmol of strong acid

$c_{HL} = (100 \times 0.0200 + 0.500)/100 = 0.0250$ M

$c_{NaL} = (100 \times 0.0800 - 0.500)/100 = 0.0750$ M

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0750)[H_3O^+] - 1.38 \times 10^{-4} \times 0.0250 = 0$

$[H_3O^+] = 4.589 \times 10^{-5}$ and pH = 4.338

$\Delta pH = 4.338 - 4.463 = -0.125$

(b) Before addition of acid

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0200)[H_3O^+] - 1.38 \times 10^{-4} \times 0.0800 = 0$

$[H_3O^+] = 5.341 \times 10^{-5}$ and pH = 3.272

After adding acid

c_{HL} = (100 × 0.0800 + 0.500)/100 = 0.0850 M

c_{NaL} = (100 × 0.0200 – 0.500)/100 = 0.0150 M

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0150)[H_3O^+] - 1.38 \times 10^{-4} \times 0.0850 = 0$

$[H_3O^+] = 7.388 \times 10^{-4}$ and pH = 3.131

ΔpH = 3.131 – 3.272 = –0.141

(c) Before addition of acid

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0500)[H_3O^+] - 1.38 \times 10^{-4} \times 0.0500 = 0$

$[H_3O^+] = 1.372 \times 10^{-4}$ and pH = 3.863

After adding acid

c_{HL} = (100 × 0.0500 + 0.500)/100 = 0.0550 M

c_{NaL} = (100 × 0.0500 – 0.500)/100 = 0.0450 M

$[H_3O^+]^2 + (1.38 \times 10^{-4} + 0.0450)[H_3O^+] - 1.38 \times 10^{-4} \times 0.0550 = 0$

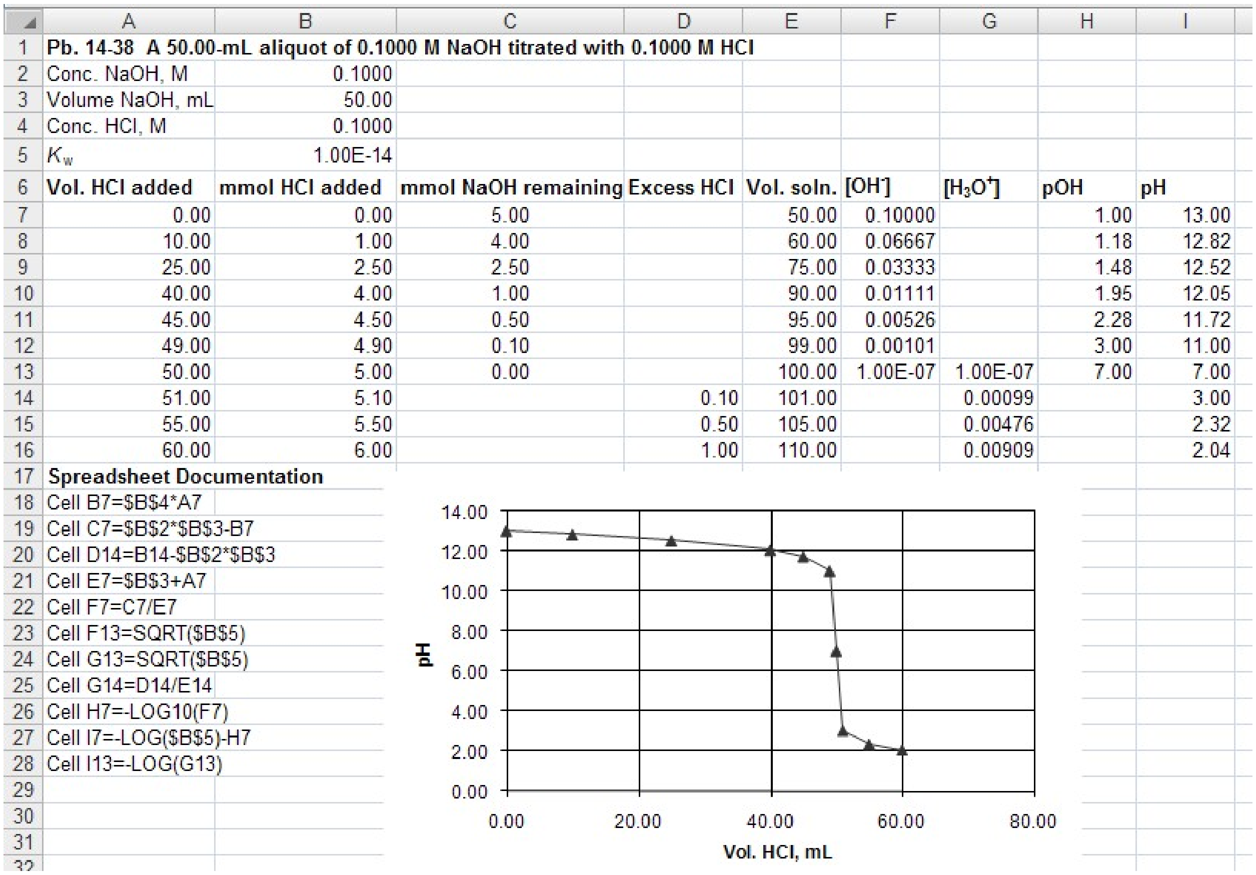
$[H_3O^+] = 1.675 \times 10^{-4}$ and pH = 3.776

ΔpH = 3.776 – 3.863 = –0.087

Note very small change in pH when concentrations of HL and NaL are equal to start.

14-38. Before the equivalence point (50.00 mL), we calculate the number of mmol NaOH remaining from the original number of mmol of NaOH present minus the number of mmol of HCl added. The $[OH^-]$ is then obtained from the number of mmol of NaOH remaining divided by the total solution volume. The pOH and pH are then calculated from $[OH^-]$. At the equivalence point, the solution is neutral and the pOH and pH are obtained from $\sqrt{K_w}$. After the equivalence point, we calculate the excess HCl from the number of mmol of HCl added minus the number of mmol of NaOH originally present.

The number of mmol of HCl in excess divided by the total volume gives the concentration of H_3O^+ and from this the pH. The spreadsheet shows the resulting pH values after each increment of added NaOH. The plot is an XY (Scatter) plot of pH vs. Vol. HCl.



	A	B	C	D	E	F	G	H	I
1	**Pb. 14-38 A 50.00-mL aliquot of 0.1000 M NaOH titrated with 0.1000 M HCl**								
2	Conc. NaOH, M	0.1000							
3	Volume NaOH, mL	50.00							
4	Conc. HCl, M	0.1000							
5	K_w	1.00E-14							
6	**Vol. HCl added**	**mmol HCl added**	**mmol NaOH remaining**	**Excess HCl**	**Vol. soln.**	**$[OH^-]$**	**$[H_3O^+]$**	**pOH**	**pH**
7	0.00	0.00	5.00		50.00	0.10000		1.00	13.00
8	10.00	1.00	4.00		60.00	0.06667		1.18	12.82
9	25.00	2.50	2.50		75.00	0.03333		1.48	12.52
10	40.00	4.00	1.00		90.00	0.01111		1.95	12.05
11	45.00	4.50	0.50		95.00	0.00526		2.28	11.72
12	49.00	4.90	0.10		99.00	0.00101		3.00	11.00
13	50.00	5.00	0.00		100.00	1.00E-07	1.00E-07	7.00	7.00
14	51.00	5.10		0.10	101.00		0.00099		3.00
15	55.00	5.50		0.50	105.00		0.00476		2.32
16	60.00	6.00		1.00	110.00		0.00909		2.04
17	**Spreadsheet Documentation**								
18	Cell B7=\$B\$4*A7								
19	Cell C7=\$B\$2*\$B\$3-B7								
20	Cell D14=B14-\$B\$2*\$B\$3								
21	Cell E7=\$B\$3+A7								
22	Cell F7=C7/E7								
23	Cell F13=SQRT(\$B\$5)								
24	Cell G13=SQRT(\$B\$5)								
25	Cell G14=D14/E14								
26	Cell H7=-LOG10(F7)								
27	Cell I7=-LOG(\$B\$5)-H7								
28	Cell I13=-LOG(G13)								

14-39. The end point will occur when 25.00 mL of titrant have been added. Let us calculate pH when 24.95 and 25.05 mL of reagent have been added.

$$c_{A^-} \approx \frac{\text{amount KOH added}}{\text{total volume soln}} = \frac{24.95 \times 0.1000 \text{ mmol KOH}}{74.95 \text{ mL soln}} = \frac{2.495}{74.95} = 0.03329 \text{ M}$$

$$c_{HA} \approx [HA] = \frac{\text{original amount HA} - \text{amount KOH added}}{\text{total volume soln}}$$

$$= \frac{(50.00 \times 0.0500 - 24.95 \times 0.1000) \text{ mmol HA}}{74.95 \text{ mL soln}}$$

$$= \frac{2.500 - 2.495}{74.95} = \frac{0.005}{74.95} = 6.67 \times 10^{-5} \text{ M}$$

Substituting into Equation 9-29

$$[\mathrm{H_3O^+}] = K_a \frac{c_{\mathrm{HA}}}{c_{\mathrm{A^-}}} = \frac{1.80 \times 10^{-4} \times 6.67 \times 10^{-5}}{0.03329} = 3.607 \times 10^{-7} \text{ M}$$

$$\mathrm{pH} = -\log(3.607 \times 10^{-7}) = 6.44$$

At 25.05 mL KOH

$$c_{\mathrm{KOH}} = [\mathrm{OH^-}] = \frac{\text{amount KOH added} - \text{initial amount HA}}{\text{total volume soln}}$$

$$= \frac{25.05 \times 0.1000 - 50.00 \times 0.05000}{75.05 \text{ mL soln}} = 6.66 \times 10^{-5} \text{ M}$$

$$\mathrm{pH} = 14.00 - [-\log(6.66 \times 10^{-5})] = 9.82$$

Thus, the indicator should change color in the range of pH 6.5 to 9.8. Cresol purple (range 7.6 to 9.2, Table 14-1) would be quite suitable.

14-40. (See Solution 14-39) Let us calculate the pH when 49.95 and 50.05 mL of $HClO_4$ have been added.

At 49.95 mL $HClO_4$

$B = C_2H_5NH_2$ $BH^+ = C_2H_5NH_3^+$

$$c_{\mathrm{BH^+}} = \frac{\text{no. mmol HClO}_4}{\text{total volume soln}} = \frac{49.95 \times 0.10000}{99.95} = \frac{4.995}{99.95} \approx [\mathrm{BH^+}]$$

$$c_{\mathrm{B}} = \frac{(50.00 \times 0.1000 - 49.95 \times 0.1000)}{99.95} = \frac{0.00500}{99.95} \approx [\mathrm{B}]$$

$$\frac{[H_3O^+][B]}{[BH^+]} = 2.31 \times 10^{-11} = \frac{[H_3O^+](0.00500/\cancel{99.95})}{4.995/\cancel{99.95}}$$

$[H_3O^+] = 2.31 \times 10^{-11} \times 4.995/0.00500) = 2.308 \times 10^{-8}$ M

pH = $-\log(2.308 \times 10^{-8}) = 7.64$

At 50.05 mL $HClO_4$

$$c_{HClO_4} = \frac{(50.05 \times 0.1000 - 50.00 \times 0.1000)}{100.05} = 4.998 \times 10^{-5} = [H_3O^+]$$

pH = $-\log(4.998 \times 10^{-5}) = 4.30$

The indicator should change color in the pH range of 7.64 to 4.30. Bromocresol purple would be suitable.

Problems 14-41 through 14-43. We will set up spreadsheets that will solve a quadratic equation to determine $[H_3O^+]$ or $[OH^-]$, as needed. While approximate solutions are appropriate for many of the calculations, the approach taken represents a more general solution and is somewhat easier to incorporate in a spreadsheet. As an example consider the titration of a weak acid with a strong base. Here c_a and V_i represent initial concentration and initial volume.

Before the equivalence point:

$$[HA] = \frac{(c_{\text{i HA}}V_{\text{i HA}} - c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} - [H_3O^+]$$

and

$$[OH^-] = \frac{(c_{\text{i NaOH}}V_{\text{NaOH}} - c_{\text{i HA}}V_{\text{i HA}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} + [HA]$$

Substituting these expressions into the equilibrium expression for [HA] and rearranging gives

$$[H_3O^+]^2 + \left(\frac{(c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} + K_a\right)[H_3O^+] - \frac{K_a(c_{\text{i HA}}V_{\text{i HA}} - c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} = 0$$

From which $[H_3O^+]$ is directly determined.

At and after the equivalence point:

$$[A^-] = \frac{(c_{\text{i HA}}V_{\text{HA}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} - [HA]$$

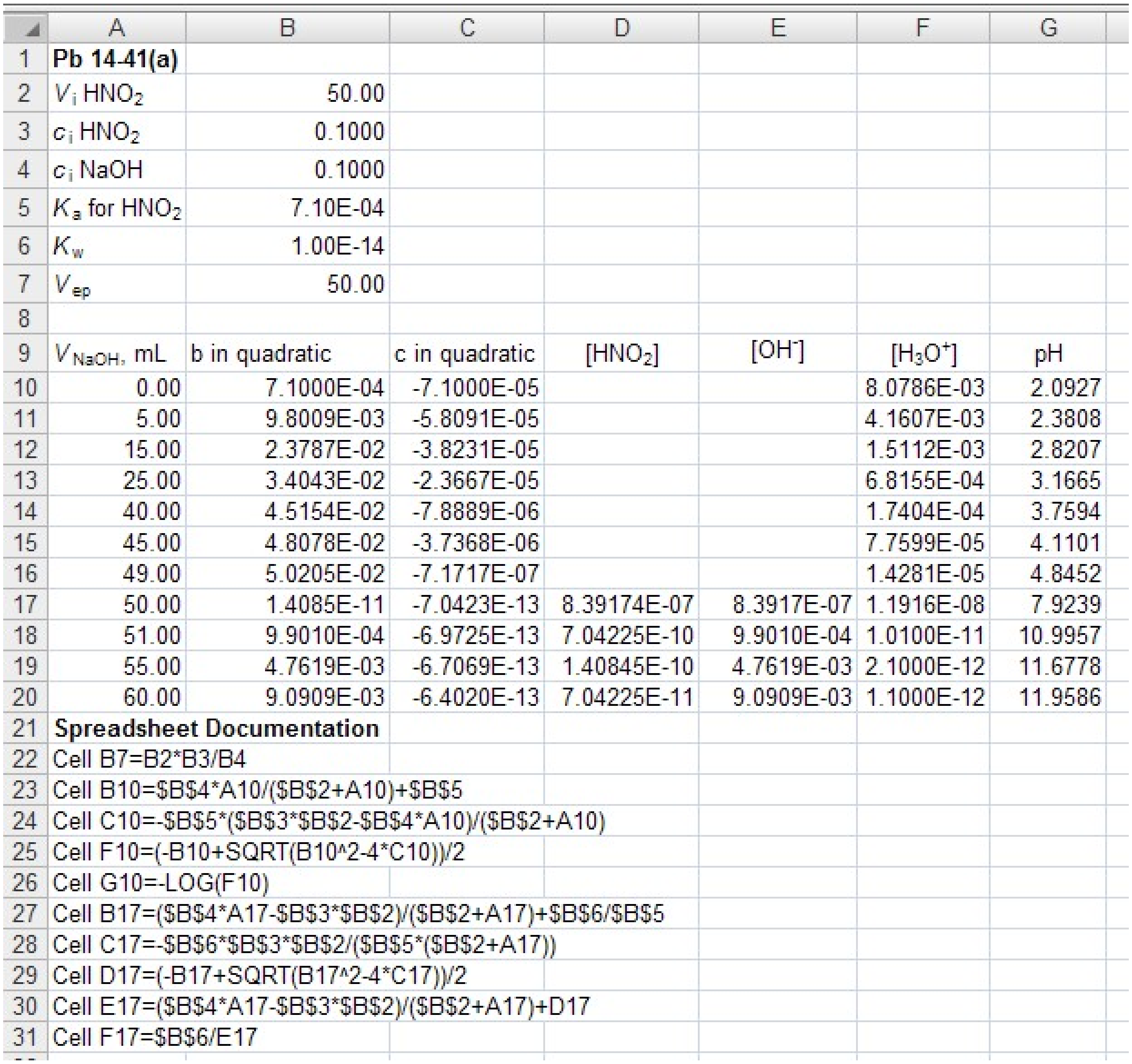
$$[OH^-] = \frac{(c_{\text{i NaOH}}V_{\text{NaOH}} - c_{\text{i HA}}V_{\text{i HA}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} + [HA]$$

Substituting these expressions into the equilibrium expression for $[A^-]$ and rearranging gives

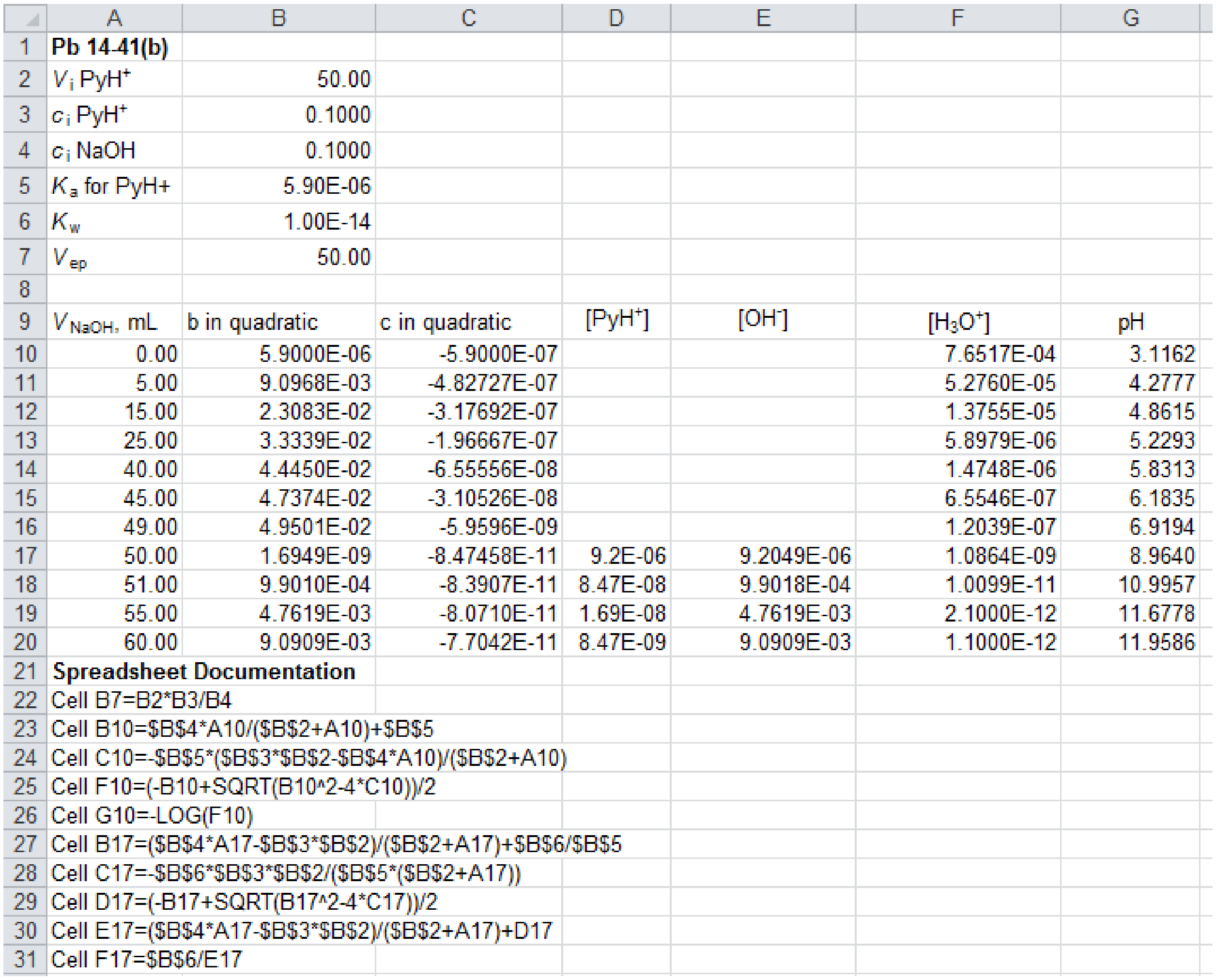
$$[HA]^2 + \left(\frac{(c_{\text{i NaOH}}V_{\text{NaOH}} - c_{\text{i HA}}V_{\text{i HA}})}{(V_{\text{i HA}} + V_{\text{NaOH}})} + \frac{K_w}{K_a}\right)[HA] - \frac{K_w\,(c_{\text{i HA}}V_{\text{HA}})}{K_a\,(V_{\text{i HA}} + V_{\text{NaOH}})} = 0$$

From which [HA] can be determined and $[OH^-]$ and $[H_3O^+]$ subsequently calculated. A similar approach is taken for the titration of a weak base with a strong acid.

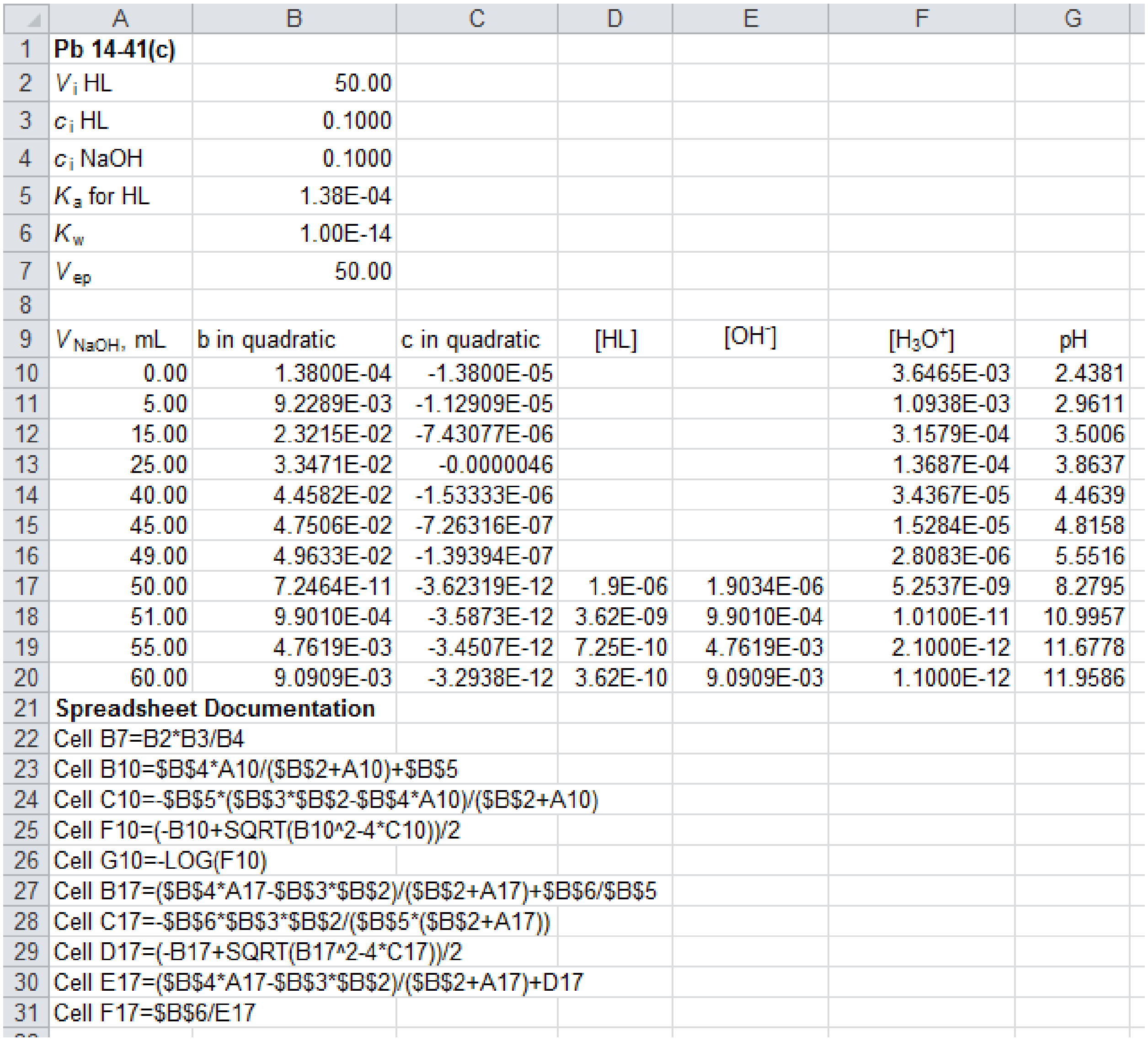
14-41.



	A	B	C	D	E	F	G
1	**Pb 14-41(a)**						
2	V_i HNO_2	50.00					
3	c_i HNO_2	0.1000					
4	c_i NaOH	0.1000					
5	K_a for HNO_2	7.10E-04					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{NaOH}, mL	b in quadratic	c in quadratic	$[HNO_2]$	$[OH^-]$	$[H_3O^+]$	pH
10	0.00	7.1000E-04	-7.1000E-05			8.0786E-03	2.0927
11	5.00	9.8009E-03	-5.8091E-05			4.1607E-03	2.3808
12	15.00	2.3787E-02	-3.8231E-05			1.5112E-03	2.8207
13	25.00	3.4043E-02	-2.3667E-05			6.8155E-04	3.1665
14	40.00	4.5154E-02	-7.8889E-06			1.7404E-04	3.7594
15	45.00	4.8078E-02	-3.7368E-06			7.7599E-05	4.1101
16	49.00	5.0205E-02	-7.1717E-07			1.4281E-05	4.8452
17	50.00	1.4085E-11	-7.0423E-13	8.39174E-07	8.3917E-07	1.1916E-08	7.9239
18	51.00	9.9010E-04	-6.9725E-13	7.04225E-10	9.9010E-04	1.0100E-11	10.9957
19	55.00	4.7619E-03	-6.7069E-13	1.40845E-10	4.7619E-03	2.1000E-12	11.6778
20	60.00	9.0909E-03	-6.4020E-13	7.04225E-11	9.0909E-03	1.1000E-12	11.9586
21	**Spreadsheet Documentation**						
22	Cell B7=B2*B3/B4						
23	Cell B10=$B$4*A10/($B$2+A10)+$B$5						
24	Cell C10=-$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)						
25	Cell F10=(-B10+SQRT(B10^2-4*C10))/2						
26	Cell G10=-LOG(F10)						
27	Cell B17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+$B$6/$B$5						
28	Cell C17=-$B$6*$B$3*$B$2/($B$5*($B$2+A17))						
29	Cell D17=(-B17+SQRT(B17^2-4*C17))/2						
30	Cell E17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+D17						
31	Cell F17=$B$6/E17						



	A	B	C	D	E	F	G
1	**Pb 14-41(b)**						
2	V_i PyH$^+$	50.00					
3	c_i PyH$^+$	0.1000					
4	c_i NaOH	0.1000					
5	K_a for PyH+	5.90E-06					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{NaOH}, mL	b in quadratic	c in quadratic	[PyH$^+$]	[OH$^-$]	[H$_3$O$^+$]	pH
10	0.00	5.9000E-06	-5.9000E-07			7.6517E-04	3.1162
11	5.00	9.0968E-03	-4.82727E-07			5.2760E-05	4.2777
12	15.00	2.3083E-02	-3.17692E-07			1.3755E-05	4.8615
13	25.00	3.3339E-02	-1.96667E-07			5.8979E-06	5.2293
14	40.00	4.4450E-02	-6.55556E-08			1.4748E-06	5.8313
15	45.00	4.7374E-02	-3.10526E-08			6.5546E-07	6.1835
16	49.00	4.9501E-02	-5.9596E-09			1.2039E-07	6.9194
17	50.00	1.6949E-09	-8.47458E-11	9.2E-06	9.2049E-06	1.0864E-09	8.9640
18	51.00	9.9010E-04	-8.3907E-11	8.47E-08	9.9018E-04	1.0099E-11	10.9957
19	55.00	4.7619E-03	-8.0710E-11	1.69E-08	4.7619E-03	2.1000E-12	11.6778
20	60.00	9.0909E-03	-7.7042E-11	8.47E-09	9.0909E-03	1.1000E-12	11.9586
21	**Spreadsheet Documentation**						
22	Cell B7=B2*B3/B4						
23	Cell B10=$B$4*A10/($B$2+A10)+$B$5						
24	Cell C10=-$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)						
25	Cell F10=(-B10+SQRT(B10^2-4*C10))/2						
26	Cell G10=-LOG(F10)						
27	Cell B17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+$B$6/$B$5						
28	Cell C17=-$B$6*$B$3*$B$2/($B$5*($B$2+A17))						
29	Cell D17=(-B17+SQRT(B17^2-4*C17))/2						
30	Cell E17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+D17						
31	Cell F17=$B$6/E17						



	A	B	C	D	E	F	G
1	**Pb 14-41(c)**						
2	V_i HL	50.00					
3	c_i HL	0.1000					
4	c_i NaOH	0.1000					
5	K_a for HL	1.38E-04					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{NaOH}, mL	b in quadratic	c in quadratic	[HL]	$[OH^-]$	$[H_3O^+]$	pH
10	0.00	1.3800E-04	-1.3800E-05			3.6465E-03	2.4381
11	5.00	9.2289E-03	-1.12909E-05			1.0938E-03	2.9611
12	15.00	2.3215E-02	-7.43077E-06			3.1579E-04	3.5006
13	25.00	3.3471E-02	-0.0000046			1.3687E-04	3.8637
14	40.00	4.4582E-02	-1.53333E-06			3.4367E-05	4.4639
15	45.00	4.7506E-02	-7.26316E-07			1.5284E-05	4.8158
16	49.00	4.9633E-02	-1.39394E-07			2.8083E-06	5.5516
17	50.00	7.2464E-11	-3.62319E-12	1.9E-06	1.9034E-06	5.2537E-09	8.2795
18	51.00	9.9010E-04	-3.5873E-12	3.62E-09	9.9010E-04	1.0100E-11	10.9957
19	55.00	4.7619E-03	-3.4507E-12	7.25E-10	4.7619E-03	2.1000E-12	11.6778
20	60.00	9.0909E-03	-3.2938E-12	3.62E-10	9.0909E-03	1.1000E-12	11.9586
21	**Spreadsheet Documentation**						
22	Cell B7=B2*B3/B4						
23	Cell B10=$B$4*A10/($B$2+A10)+$B$5						
24	Cell C10=-$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)						
25	Cell F10=(-B10+SQRT(B10^2-4*C10))/2						
26	Cell G10=-LOG(F10)						
27	Cell B17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+$B$6/$B$5						
28	Cell C17=-$B$6*$B$3*$B$2/($B$5*($B$2+A17))						
29	Cell D17=(-B17+SQRT(B17^2-4*C17))/2						
30	Cell E17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+D17						
31	Cell F17=$B$6/E17						

14-42. Considerations similar to those in Problem 14-41 lead to the following quadratic equation for titrating a weak base with HCl**.**

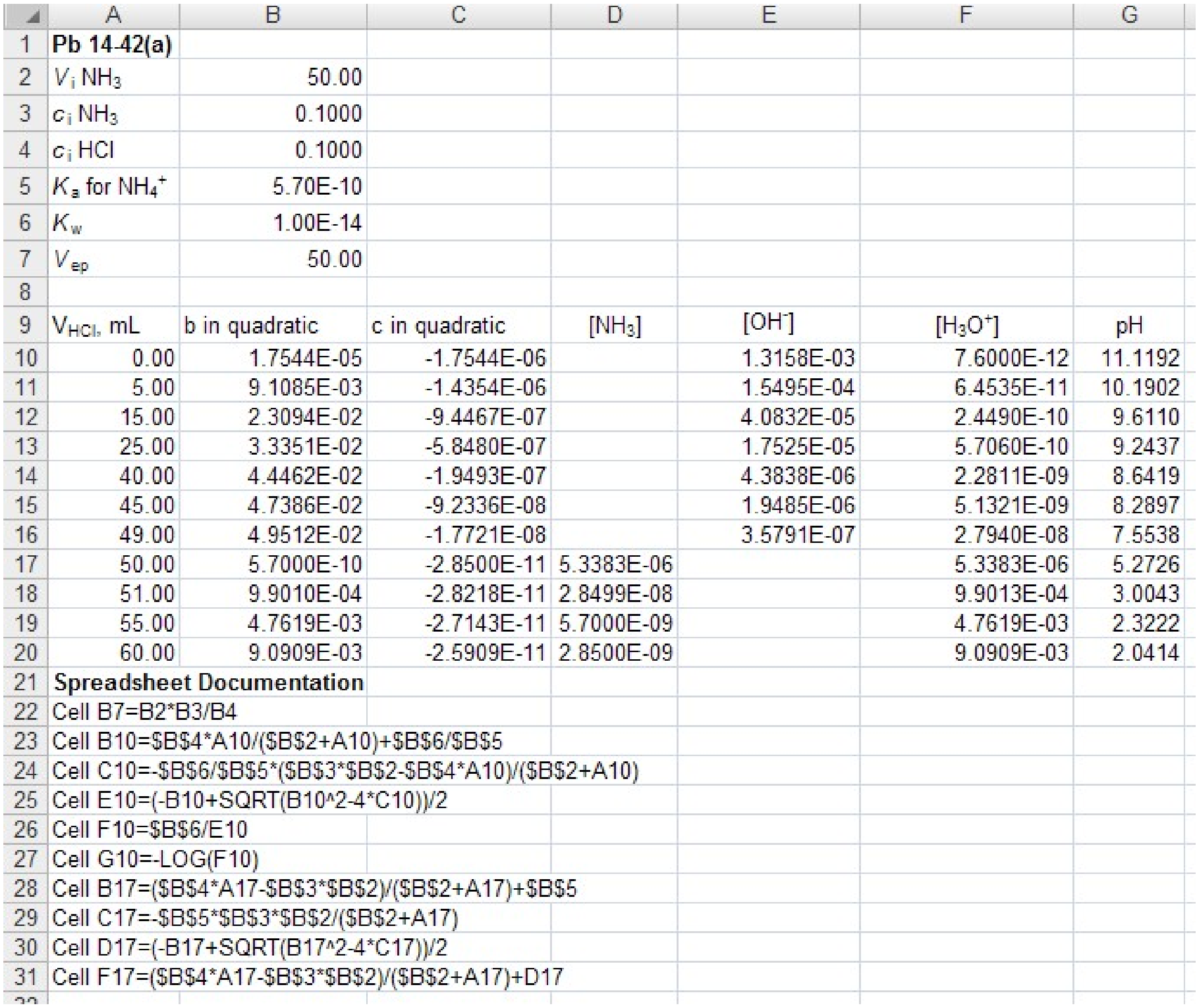
Before the equivalence point

$$[\mathrm{OH^-}]^2 + \left(\frac{\left(c_{\mathrm{i\,HCl}}V_{\mathrm{HCl}}\right)}{\left(V_{\mathrm{i\,NH_3}} + V_{\mathrm{HCl}}\right)} + \frac{K_\mathrm{w}}{K_\mathrm{a}}\right)[\mathrm{OH^-}] - \frac{\dfrac{K_\mathrm{w}}{K_\mathrm{a}} \times \left(c_{\mathrm{i\,NH_3}}V_{\mathrm{i\,NH_3}} - c_{\mathrm{i\,HCl}}V_{\mathrm{HCl}}\right)}{\left(V_{\mathrm{i\,NH_3}} + V_{\mathrm{HCl}}\right)} = 0$$

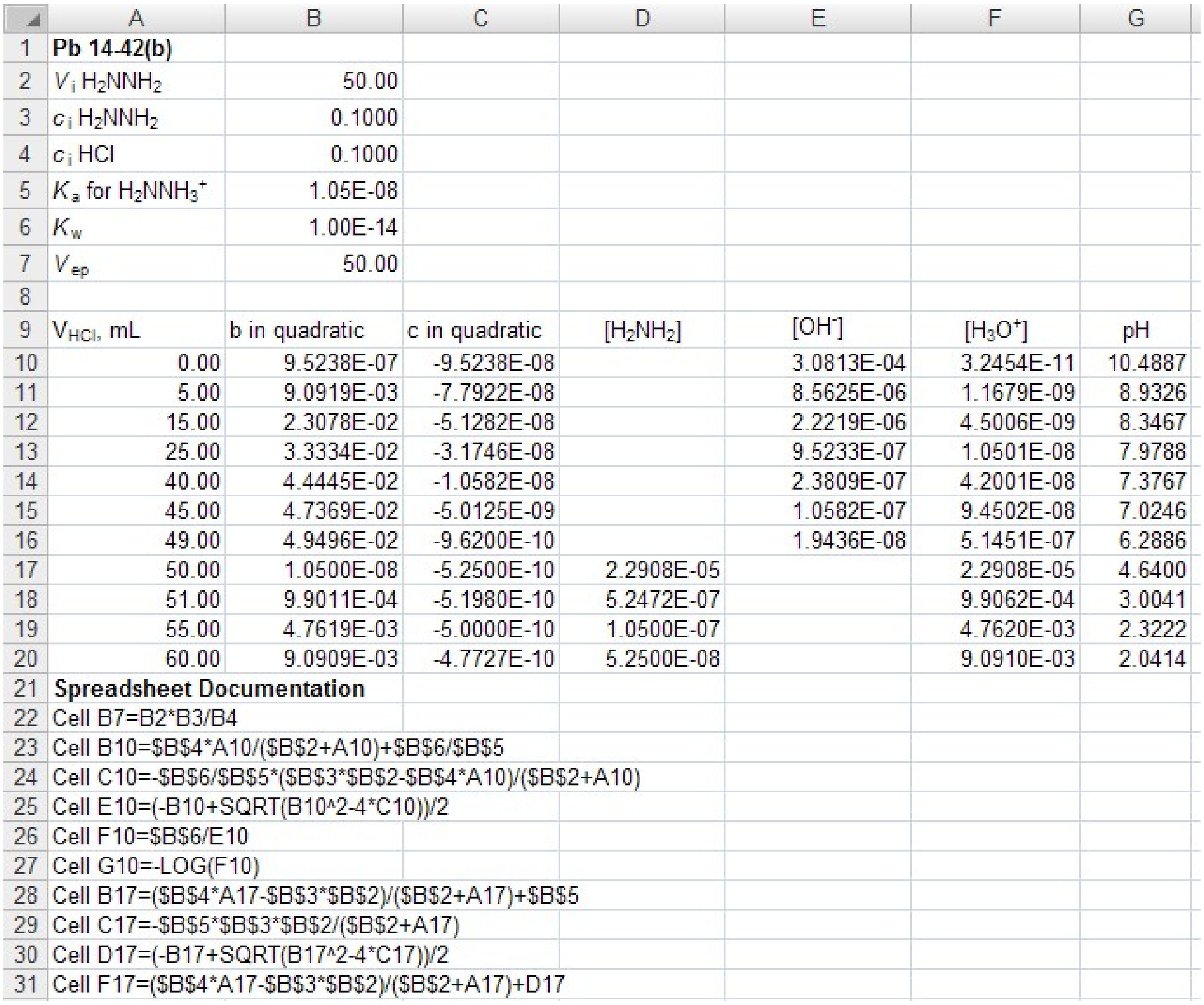
At and after the equivalence point

$$[\mathrm{NH_3}]^2 + \left(\frac{(c_{\mathrm{i\,HCl}}V_{\mathrm{HCl}} - c_{\mathrm{i\,NH_3}}V_{\mathrm{i\,NH_3}}}{V_{\mathrm{HCl}} + V_{\mathrm{i\,NH_3}}} + K_\mathrm{a}\right)[\mathrm{NH_3}] - K_\mathrm{a}\left(\frac{c_{\mathrm{i\,NH_3}}V_{\mathrm{i\,NH_3}}}{V_{\mathrm{i\,NH_3}} + V_{\mathrm{HCl}}}\right) = 0$$

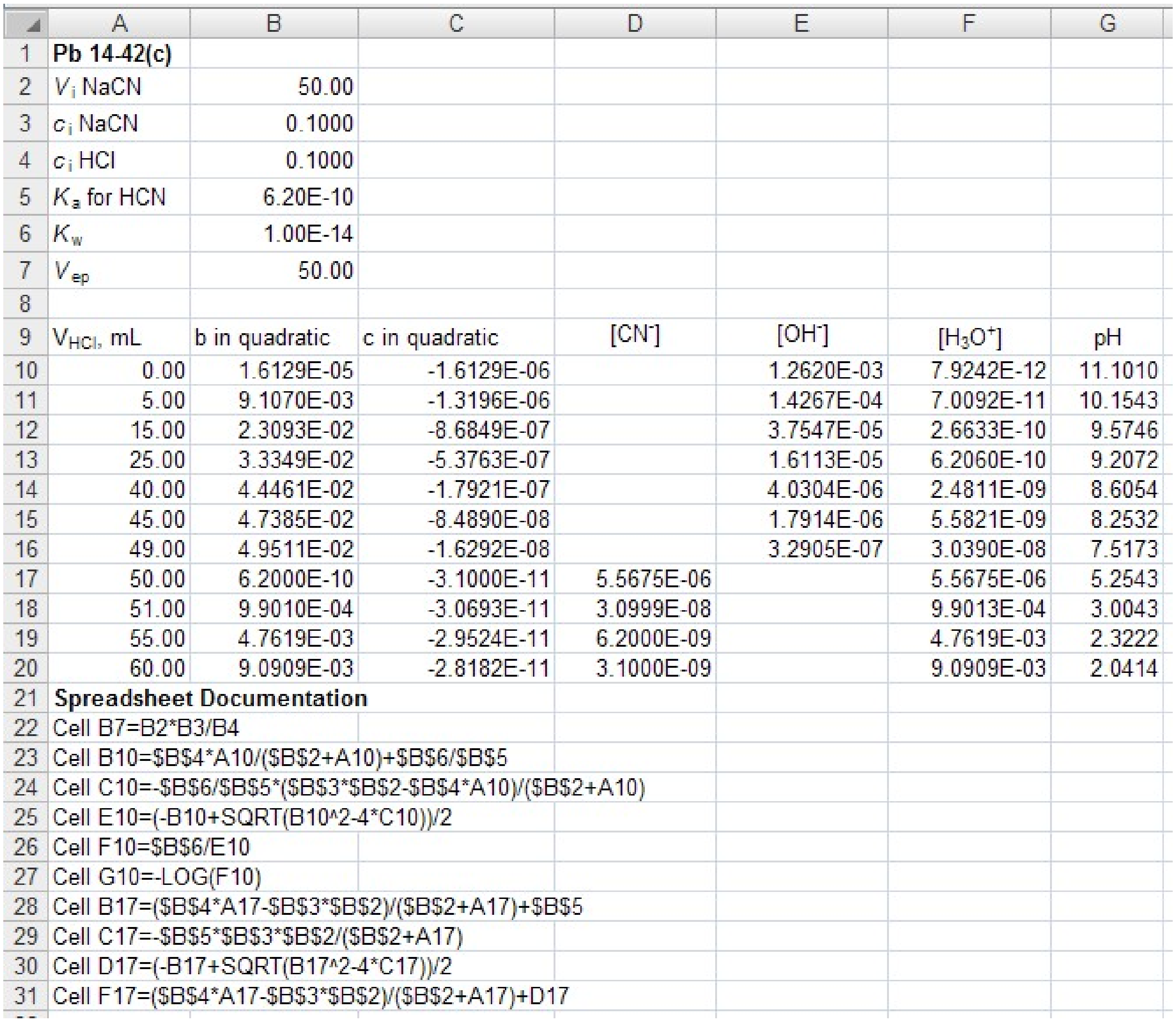
The ammonia concentration can then be used to calculate $[\mathrm{OH^-}]$ and $[\mathrm{H_3O^+}]$.



	A	B	C	D	E	F	G
1	**Pb 14-42(a)**						
2	V_i NH$_3$	50.00					
3	c_i NH$_3$	0.1000					
4	c_i HCl	0.1000					
5	K_a for NH$_4^+$	5.70E-10					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{HCl}, mL	b in quadratic	c in quadratic	[NH$_3$]	[OH$^-$]	[H$_3$O$^+$]	pH
10	0.00	1.7544E-05	-1.7544E-06		1.3158E-03	7.6000E-12	11.1192
11	5.00	9.1085E-03	-1.4354E-06		1.5495E-04	6.4535E-11	10.1902
12	15.00	2.3094E-02	-9.4467E-07		4.0832E-05	2.4490E-10	9.6110
13	25.00	3.3351E-02	-5.8480E-07		1.7525E-05	5.7060E-10	9.2437
14	40.00	4.4462E-02	-1.9493E-07		4.3838E-06	2.2811E-09	8.6419
15	45.00	4.7386E-02	-9.2336E-08		1.9485E-06	5.1321E-09	8.2897
16	49.00	4.9512E-02	-1.7721E-08		3.5791E-07	2.7940E-08	7.5538
17	50.00	5.7000E-10	-2.8500E-11	5.3383E-06		5.3383E-06	5.2726
18	51.00	9.9010E-04	-2.8218E-11	2.8499E-08		9.9013E-04	3.0043
19	55.00	4.7619E-03	-2.7143E-11	5.7000E-09		4.7619E-03	2.3222
20	60.00	9.0909E-03	-2.5909E-11	2.8500E-09		9.0909E-03	2.0414
21	**Spreadsheet Documentation**						
22	Cell B7=B2*B3/B4						
23	Cell B10=$B$4*A10/($B$2+A10)+$B$6/$B$5						
24	Cell C10=-$B$6/$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)						
25	Cell E10=(-B10+SQRT(B10^2-4*C10))/2						
26	Cell F10=$B$6/E10						
27	Cell G10=-LOG(F10)						
28	Cell B17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+$B$5						
29	Cell C17=-$B$5*$B$3*$B$2/($B$2+A17)						
30	Cell D17=(-B17+SQRT(B17^2-4*C17))/2						
31	Cell F17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+D17						

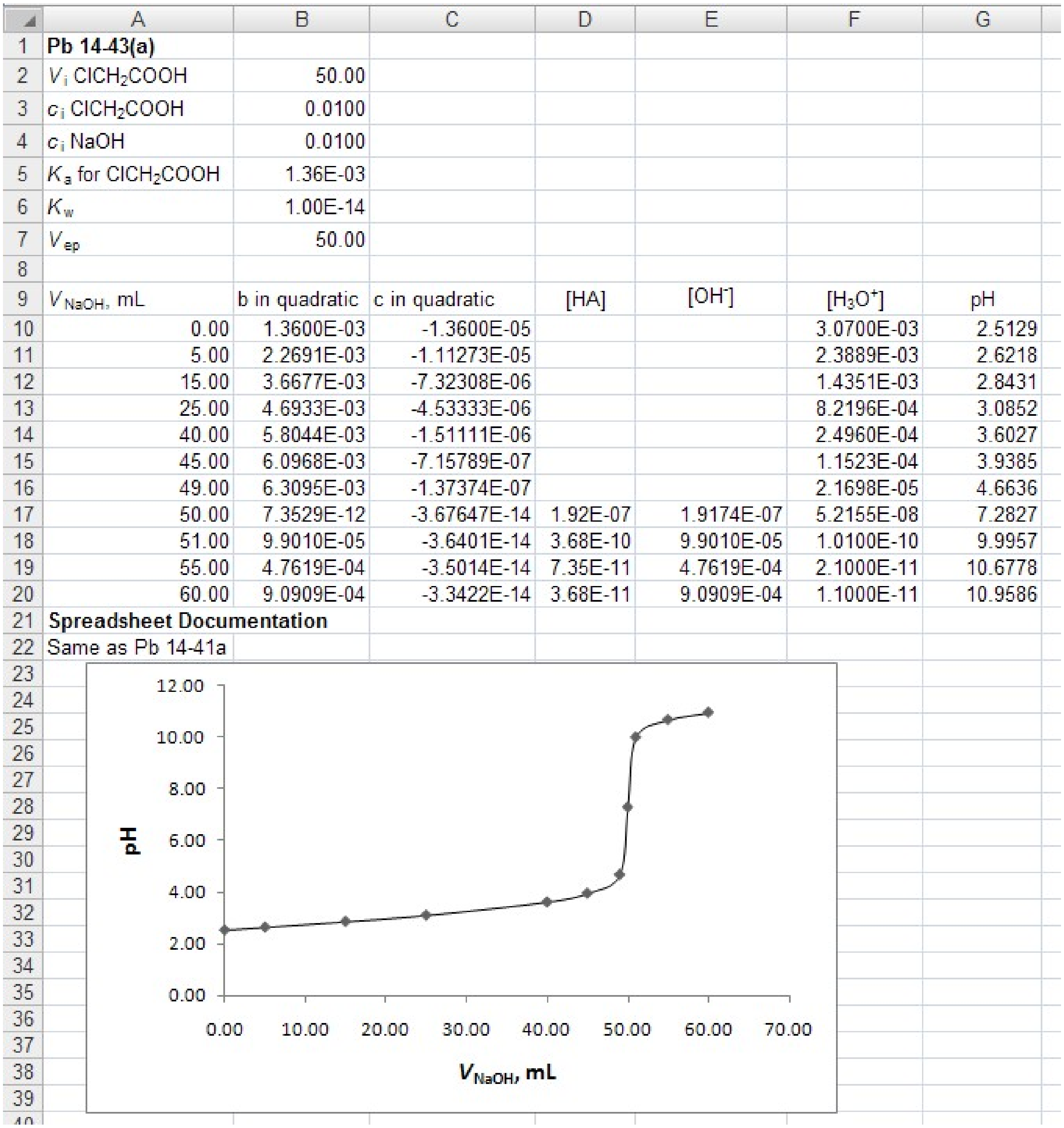


	A	B	C	D	E	F	G
1	**Pb 14-42(b)**						
2	V_i H_2NNH_2	50.00					
3	c_i H_2NNH_2	0.1000					
4	c_i HCl	0.1000					
5	K_a for $H_2NNH_3^+$	1.05E-08					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{HCl}, mL	b in quadratic	c in quadratic	[H_2NH_2]	[OH^-]	[H_3O^+]	pH
10	0.00	9.5238E-07	-9.5238E-08		3.0813E-04	3.2454E-11	10.4887
11	5.00	9.0919E-03	-7.7922E-08		8.5625E-06	1.1679E-09	8.9326
12	15.00	2.3078E-02	-5.1282E-08		2.2219E-06	4.5006E-09	8.3467
13	25.00	3.3334E-02	-3.1746E-08		9.5233E-07	1.0501E-08	7.9788
14	40.00	4.4445E-02	-1.0582E-08		2.3809E-07	4.2001E-08	7.3767
15	45.00	4.7369E-02	-5.0125E-09		1.0582E-07	9.4502E-08	7.0246
16	49.00	4.9496E-02	-9.6200E-10		1.9436E-08	5.1451E-07	6.2886
17	50.00	1.0500E-08	-5.2500E-10	2.2908E-05		2.2908E-05	4.6400
18	51.00	9.9011E-04	-5.1980E-10	5.2472E-07		9.9062E-04	3.0041
19	55.00	4.7619E-03	-5.0000E-10	1.0500E-07		4.7620E-03	2.3222
20	60.00	9.0909E-03	-4.7727E-10	5.2500E-08		9.0910E-03	2.0414
21	**Spreadsheet Documentation**						
22	Cell B7=B2*B3/B4						
23	Cell B10=$B$4*A10/($B$2+A10)+$B$6/$B$5						
24	Cell C10=-$B$6/$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)						
25	Cell E10=(-B10+SQRT(B10^2-4*C10))/2						
26	Cell F10=$B$6/E10						
27	Cell G10=-LOG(F10)						
28	Cell B17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+$B$5						
29	Cell C17=-$B$5*$B$3*$B$2/($B$2+A17)						
30	Cell D17=(-B17+SQRT(B17^2-4*C17))/2						
31	Cell F17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+D17						



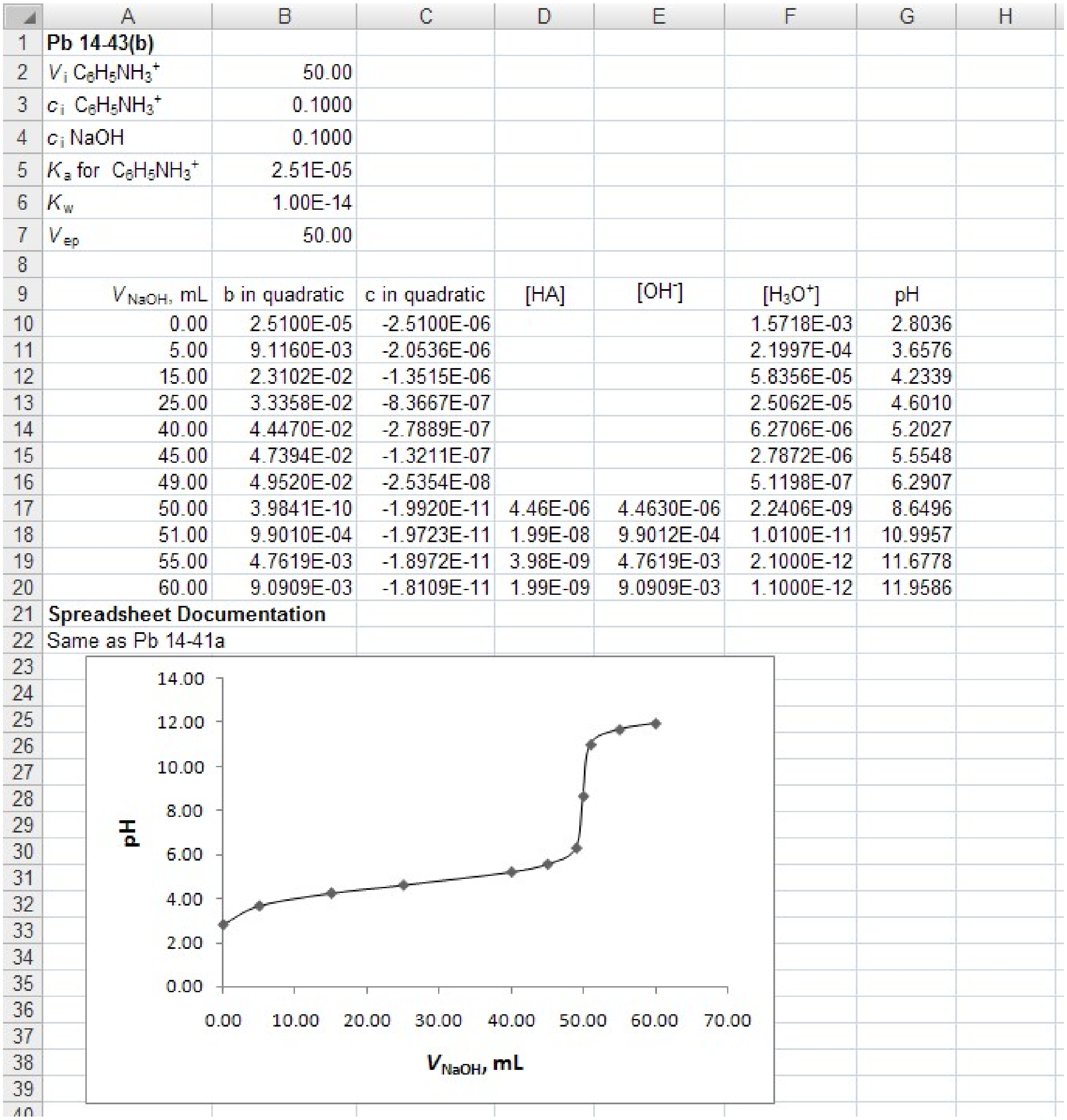
	A	B	C	D	E	F	G
1	**Pb 14-42(c)**						
2	V_i NaCN	50.00					
3	c_i NaCN	0.1000					
4	c_i HCl	0.1000					
5	K_a for HCN	6.20E-10					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{HCl}, mL	b in quadratic	c in quadratic	$[CN^-]$	$[OH^-]$	$[H_3O^+]$	pH
10	0.00	1.6129E-05	-1.6129E-06		1.2620E-03	7.9242E-12	11.1010
11	5.00	9.1070E-03	-1.3196E-06		1.4267E-04	7.0092E-11	10.1543
12	15.00	2.3093E-02	-8.6849E-07		3.7547E-05	2.6633E-10	9.5746
13	25.00	3.3349E-02	-5.3763E-07		1.6113E-05	6.2060E-10	9.2072
14	40.00	4.4461E-02	-1.7921E-07		4.0304E-06	2.4811E-09	8.6054
15	45.00	4.7385E-02	-8.4890E-08		1.7914E-06	5.5821E-09	8.2532
16	49.00	4.9511E-02	-1.6292E-08		3.2905E-07	3.0390E-08	7.5173
17	50.00	6.2000E-10	-3.1000E-11	5.5675E-06		5.5675E-06	5.2543
18	51.00	9.9010E-04	-3.0693E-11	3.0999E-08		9.9013E-04	3.0043
19	55.00	4.7619E-03	-2.9524E-11	6.2000E-09		4.7619E-03	2.3222
20	60.00	9.0909E-03	-2.8182E-11	3.1000E-09		9.0909E-03	2.0414
21	**Spreadsheet Documentation**						
22	Cell B7=B2*B3/B4						
23	Cell B10=$B$4*A10/($B$2+A10)+$B$6/$B$5						
24	Cell C10=-$B$6/$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)						
25	Cell E10=(-B10+SQRT(B10^2-4*C10))/2						
26	Cell F10=$B$6/E10						
27	Cell G10=-LOG(F10)						
28	Cell B17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+$B$5						
29	Cell C17=-$B$5*$B$3*$B$2/($B$2+A17)						
30	Cell D17=(-B17+SQRT(B17^2-4*C17))/2						
31	Cell F17=($B$4*A17-$B$3*$B$2)/($B$2+A17)+D17						

14-43 (a) This titration of a weak acid with strong base follows the same basic spreadsheet as Pb 14-41 with the concentrations changed. A Scatter plot of pH vs. volume of NaOH is produced from the data.



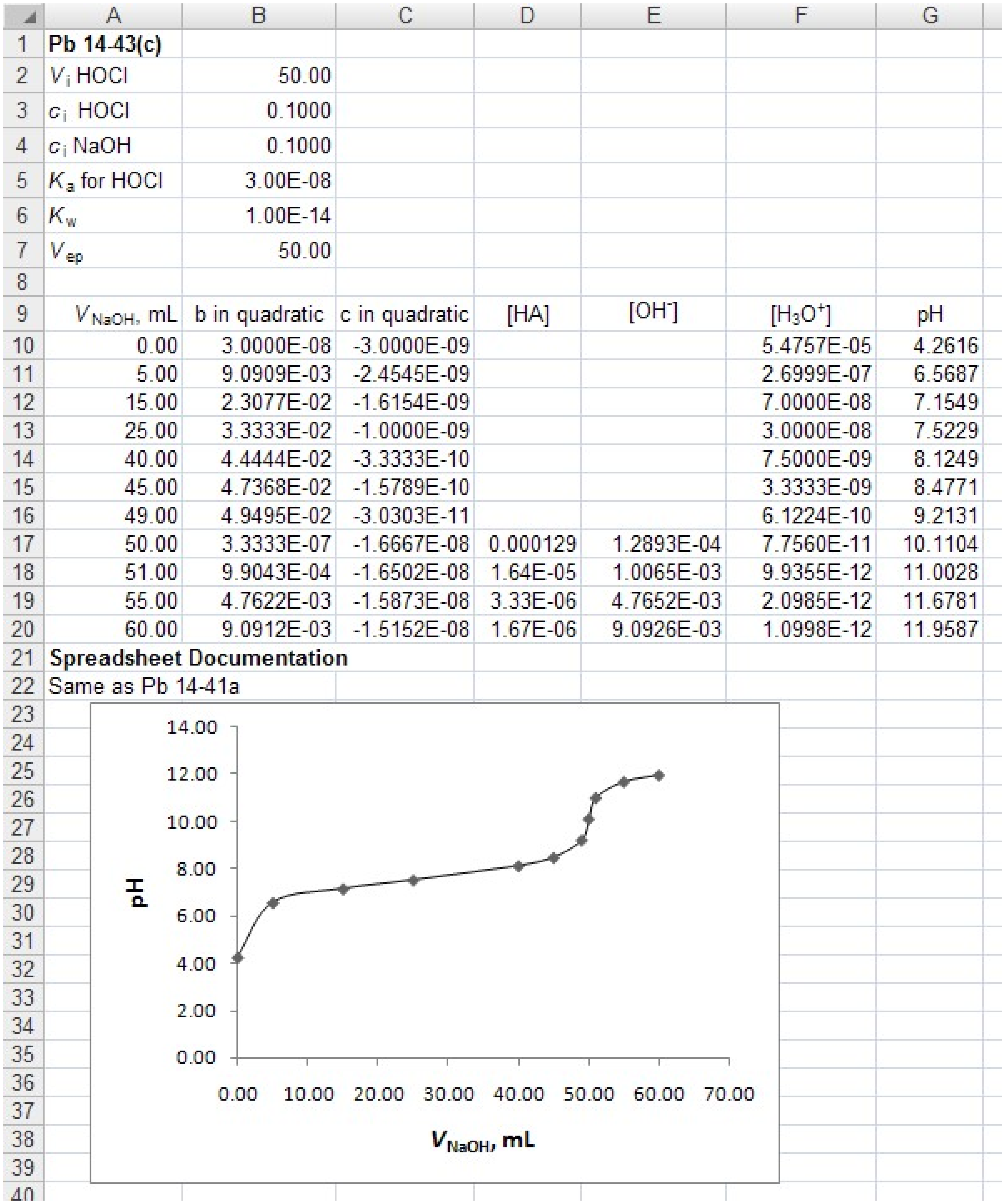
	A	B	C	D	E	F	G
1	**Pb 14-43(a)**						
2	V_i ClCH$_2$COOH	50.00					
3	c_i ClCH$_2$COOH	0.0100					
4	c_i NaOH	0.0100					
5	K_a for ClCH$_2$COOH	1.36E-03					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{NaOH}, mL	b in quadratic	c in quadratic	[HA]	[OH$^-$]	[H$_3$O$^+$]	pH
10	0.00	1.3600E-03	-1.3600E-05			3.0700E-03	2.5129
11	5.00	2.2691E-03	-1.11273E-05			2.3889E-03	2.6218
12	15.00	3.6677E-03	-7.32308E-06			1.4351E-03	2.8431
13	25.00	4.6933E-03	-4.53333E-06			8.2196E-04	3.0852
14	40.00	5.8044E-03	-1.51111E-06			2.4960E-04	3.6027
15	45.00	6.0968E-03	-7.15789E-07			1.1523E-04	3.9385
16	49.00	6.3095E-03	-1.37374E-07			2.1698E-05	4.6636
17	50.00	7.3529E-12	-3.67647E-14	1.92E-07	1.9174E-07	5.2155E-08	7.2827
18	51.00	9.9010E-05	-3.6401E-14	3.68E-10	9.9010E-05	1.0100E-10	9.9957
19	55.00	4.7619E-04	-3.5014E-14	7.35E-11	4.7619E-04	2.1000E-11	10.6778
20	60.00	9.0909E-04	-3.3422E-14	3.68E-11	9.0909E-04	1.1000E-11	10.9586
21	**Spreadsheet Documentation**						
22	Same as Pb 14-41a						

(b) This titration also follows the same procedure as that in part (a).



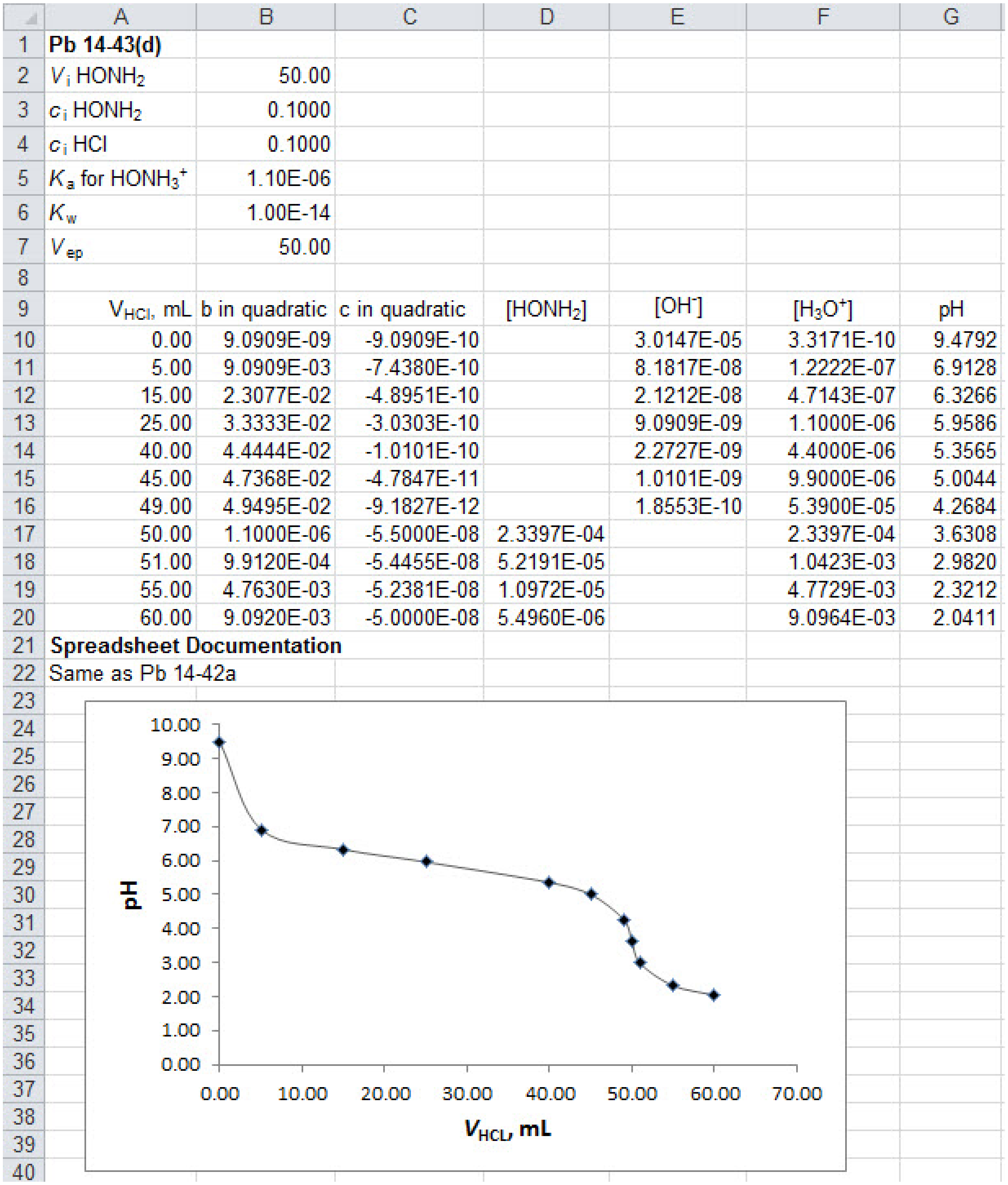
	A	B	C	D	E	F	G	H
1	**Pb 14-43(b)**							
2	V_i $C_6H_5NH_3^+$	50.00						
3	c_i $C_6H_5NH_3^+$	0.1000						
4	c_i NaOH	0.1000						
5	K_a for $C_6H_5NH_3^+$	2.51E-05						
6	K_w	1.00E-14						
7	V_{ep}	50.00						
8								
9	V_{NaOH}, mL	b in quadratic	c in quadratic	[HA]	$[OH^-]$	$[H_3O^+]$	pH	
10	0.00	2.5100E-05	-2.5100E-06			1.5718E-03	2.8036	
11	5.00	9.1160E-03	-2.0536E-06			2.1997E-04	3.6576	
12	15.00	2.3102E-02	-1.3515E-06			5.8356E-05	4.2339	
13	25.00	3.3358E-02	-8.3667E-07			2.5062E-05	4.6010	
14	40.00	4.4470E-02	-2.7889E-07			6.2706E-06	5.2027	
15	45.00	4.7394E-02	-1.3211E-07			2.7872E-06	5.5548	
16	49.00	4.9520E-02	-2.5354E-08			5.1198E-07	6.2907	
17	50.00	3.9841E-10	-1.9920E-11	4.46E-06	4.4630E-06	2.2406E-09	8.6496	
18	51.00	9.9010E-04	-1.9723E-11	1.99E-08	9.9012E-04	1.0100E-11	10.9957	
19	55.00	4.7619E-03	-1.8972E-11	3.98E-09	4.7619E-03	2.1000E-12	11.6778	
20	60.00	9.0909E-03	-1.8109E-11	1.99E-09	9.0909E-03	1.1000E-12	11.9586	
21	**Spreadsheet Documentation**							
22	Same as Pb 14-41a							

(c)



	A	B	C	D	E	F	G
1	**Pb 14-43(c)**						
2	V_i HOCl	50.00					
3	c_i HOCl	0.1000					
4	c_i NaOH	0.1000					
5	K_a for HOCl	3.00E-08					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{NaOH}, mL	b in quadratic	c in quadratic	[HA]	$[OH^-]$	$[H_3O^+]$	pH
10	0.00	3.0000E-08	-3.0000E-09			5.4757E-05	4.2616
11	5.00	9.0909E-03	-2.4545E-09			2.6999E-07	6.5687
12	15.00	2.3077E-02	-1.6154E-09			7.0000E-08	7.1549
13	25.00	3.3333E-02	-1.0000E-09			3.0000E-08	7.5229
14	40.00	4.4444E-02	-3.3333E-10			7.5000E-09	8.1249
15	45.00	4.7368E-02	-1.5789E-10			3.3333E-09	8.4771
16	49.00	4.9495E-02	-3.0303E-11			6.1224E-10	9.2131
17	50.00	3.3333E-07	-1.6667E-08	0.000129	1.2893E-04	7.7560E-11	10.1104
18	51.00	9.9043E-04	-1.6502E-08	1.64E-05	1.0065E-03	9.9355E-12	11.0028
19	55.00	4.7622E-03	-1.5873E-08	3.33E-06	4.7652E-03	2.0985E-12	11.6781
20	60.00	9.0912E-03	-1.5152E-08	1.67E-06	9.0926E-03	1.0998E-12	11.9587
21	**Spreadsheet Documentation**						
22	Same as Pb 14-41a						

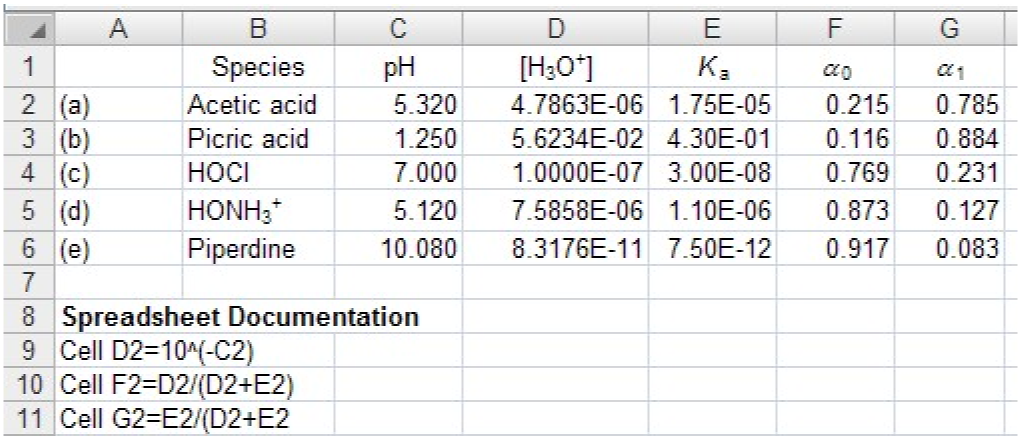
(d) This is a titration of a weak base with HCl and so follows the format of Pb 14-42. A Scatter plot is produced.



	A	B	C	D	E	F	G
1	**Pb 14-43(d)**						
2	V_i HONH$_2$	50.00					
3	c_i HONH$_2$	0.1000					
4	c_i HCl	0.1000					
5	K_a for HONH$_3^+$	1.10E-06					
6	K_w	1.00E-14					
7	V_{ep}	50.00					
8							
9	V_{HCl}, mL	b in quadratic	c in quadratic	[HONH$_2$]	[OH$^-$]	[H$_3$O$^+$]	pH
10	0.00	9.0909E-09	-9.0909E-10		3.0147E-05	3.3171E-10	9.4792
11	5.00	9.0909E-03	-7.4380E-10		8.1817E-08	1.2222E-07	6.9128
12	15.00	2.3077E-02	-4.8951E-10		2.1212E-08	4.7143E-07	6.3266
13	25.00	3.3333E-02	-3.0303E-10		9.0909E-09	1.1000E-06	5.9586
14	40.00	4.4444E-02	-1.0101E-10		2.2727E-09	4.4000E-06	5.3565
15	45.00	4.7368E-02	-4.7847E-11		1.0101E-09	9.9000E-06	5.0044
16	49.00	4.9495E-02	-9.1827E-12		1.8553E-10	5.3900E-05	4.2684
17	50.00	1.1000E-06	-5.5000E-08	2.3397E-04		2.3397E-04	3.6308
18	51.00	9.9120E-04	-5.4455E-08	5.2191E-05		1.0423E-03	2.9820
19	55.00	4.7630E-03	-5.2381E-08	1.0972E-05		4.7729E-03	2.3212
20	60.00	9.0920E-03	-5.0000E-08	5.4960E-06		9.0964E-03	2.0411
21	**Spreadsheet Documentation**						
22	Same as Pb 14-42a						

14-44. Here, we make use of Equations 9-36 And 9-37:

$$\alpha_0 = \frac{[H_3O^+]}{[H_3O^+] + K_a} \qquad \alpha_1 = \frac{K_a}{[H_3O^+] + K_a}$$



	A	B	C	D	E	F	G
1		Species	pH	$[H_3O^+]$	K_a	α_0	α_1
2	(a)	Acetic acid	5.320	4.7863E-06	1.75E-05	0.215	0.785
3	(b)	Picric acid	1.250	5.6234E-02	4.30E-01	0.116	0.884
4	(c)	HOCl	7.000	1.0000E-07	3.00E-08	0.769	0.231
5	(d)	$HONH_3^+$	5.120	7.5858E-06	1.10E-06	0.873	0.127
6	(e)	Piperdine	10.080	8.3176E-11	7.50E-12	0.917	0.083
7							
8	**Spreadsheet Documentation**						
9	Cell D2=10^(-C2)						
10	Cell F2=D2/(D2+E2)						
11	Cell G2=E2/(D2+E2						

14-45. $[H_3O^+] = 3.38 \times 10^{-12}$ M. For $CH_3NH_3^+$, Equation 9-37 takes the form,

$$\alpha_1 = \frac{[CH_3NH_2]}{c_T} = \frac{K_a}{[H_3O^+] + K_a} = \frac{2.3 \times 10^{-11}}{3.38 \times 10^{-12} + 2.3 \times 10^{-11}} = 0.872$$

$[CH_3NH_2] = 0.872 \times 0.120 = 0.105$ M

14-46. For **a** pH of 3.200, $[H_3O^+] = 10^{-3.200} = 6.310 \times 10^{-4}$ M. For formic acid $K_a = 1.80 \times 10^{-4}$

$$\alpha_0 = \frac{6.310 \times 10^{-4}}{6.310 \times 10^{-4} + 1.80 \times 10^{-4}} = 0.778$$

$$\frac{[HCOOH]}{c_T} = \frac{[HCOOH]}{0.0850} = \alpha_0$$

$[HCOOH] = \alpha_0 \times c_T = 0.778 \times 0.0850 = 6.61 \times 10^{-2}$ M

14-47. For lactic acid, $K_a = 1.38 \times 10^{-4}$

$$\alpha_0 = \frac{[H_3O^+]}{K_a + [H_3O^+]} = \frac{[H_3O^+]}{1.38 \times 10^{-4} + [H_3O^+]}$$

$$\alpha_0 = 0.640 = \frac{[\text{HA}]}{c_\text{T}} = \frac{[\text{HA}}{0.120}$$

$[\text{HA}] = 0.640 \times 0.120 = 0.0768$ M

$\alpha_1 = 1.000 - 0.640 = 0.360$

$[\text{A}^-] = \alpha_1 \times 0.120 = (1.000 - 0.640) \times 0.120 = 0.0432$ M

$[\text{H}_3\text{O}^+] = K_\text{a} \times c_\text{HA}/c_{\text{A}^-} = 1.38 \times 10^{-4} \times 0.640/(1 - 0.640) = 2.453 \times 10^{-4}$ M

$\text{pH} = -\log(2.453 \times 10^{-4}) = 3.61$

The remaining entries in the table are obtained in a similar manner. Bolded entries are the missing data points.

Acid	**c_T**	**pH**	**[HA]**	**[A$^-$]**	**α_0**	**α_1**
Lactic	0.120	**3.61**	**0.0768**	**0.0432**	0.640	**0.360**
Iodic	0.200	**1.28**	**0.0470**	**0.153**	**0.235**	0.765
Butanoic	**0.162**	5.00	0.644	**0.0979**	**0.397**	**0.604**
HOCl	0.280	7.00	**0.215**	**0.0646**	**0.769**	**0.231**
Nitrous	**0.179**	3.30	**0.0739**	0.105	0.413	0.587
HCN	**0.366**	**9.39**	0.145	0.221	**0.396**	**0.604**
Sulfamic	0.250	1.20	**0.095**	**0.155**	**0.380**	**0.620**

Chapter 15

15-1. Not only is NaHA a proton donor, it is also the conjugate base of the parent acid H_2A.

$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-}$

$HA^- + H_2O \rightleftharpoons H_2A + OH^-$

Solutions of acid salts can be acidic or alkaline, depending on which of the above equilibria predominates. In order to calculate the pH of solutions of this type, it is necessary to take both equilibria into account.

15-2. The first term arises from the dissociation of HA^- to give H_3O^+ and A^{2-}. The second term arises from HA^- reacting in water to give H_2A and OH^-. The equation makes intuitive sense because H_3O^+ is formed by reaction that gives A^{2-}, while it is depleted by reaction to give H_2A and OH^-.

15-3. In Equation 15-15, the only concentration term is c_{NaHA}. Thus, the equation is only applicable to a solution in which the only species affecting pH is the acid salt NaHA.

15-4. The species HPO_4^{2-} is such a weak acid ($K_{a3} = 4.5 \times 10^{-13}$) that the change in pH in the vicinity of the third equivalence point is too small to be observable.

15-5. **(a)** $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $K_a = 5.70 \times 10^{-10}$

$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$ $K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$

Since the K's are essentially identical, the solution should be approximately neutral

(b) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ Solution will be basic

(c) Neither K^+ nor NO_3^- reacts with H_2O. Solution will be neutral

(d) $HC_2O_4^- + H_2O \rightleftharpoons C_2O_4^{2-} + H_3O^+$ $K_{a2} = 5.42 \times 10^{-5}$

$HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$ $K_{b2} = \dfrac{1.00 \times 10^{-14}}{5.60 \times 10^{-2}} = 1.79 \times 10^{-13}$

Solution will be acidic since $K_{a2} >> K_{b2}$.

(e) $C_2O_4^{2-} + H_2O \leftrightarrows HC_2O_4^- + OH^-$ $K_b = \dfrac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.84 \times 10^{-10}$

Solution will be basic

(f) $HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$ $K_{a3} = 4.5 \times 10^{-13}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ $K_{b2} = \dfrac{1.00 \times 10^{-14}}{6.32 \times 10^{-8}} = 1.58 \times 10^{-7}$

Solution will be basic

(g) $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ $K_{a2} = 6.32 \times 10^{-8}$

$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$ $K_{b3} = \dfrac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.4 \times 10^{-12}$

Solution will be acidic

(h) $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$ $K_{b1} = \dfrac{1.00 \times 10^{-14}}{4.5 \times 10^{-13}} = 2.2 \times 10^{-2}$

Solution will be basic

15-6. We can approximate the $[H_3O^+]$ at the first equivalence point by Equation 15-16. Thus,

$$[H_3O^+] = \sqrt{5.8 \times 10^{-3} \times 1.1 \times 10^{-7}} = 2.53 \times 10^{-5}$$

$$\text{pH} = -\log(2.53 \times 10^{-5}) = 4.60$$

Bromocresol green would be a satisfactory indicator.

15-7. Let us assume that $c_{\text{Na}_2\text{HAsO}_4} = 0.033$ M at the equivalence point. Also, $K_{a2} = 1.1 \times 10^{-7}$ and $K_{a3} = 3.2 \times 10^{-12}$. Substituting into Equation 15-15 gives

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{3.2 \times 10^{-12} \times 0.033 + 1 \times 10^{-14}}{1 + 0.033/(1.1 \times 10^{-7})}} = 6.2 \times 10^{-10}$$

$$\text{pH} = -\log(6.2 \times 10^{-10}) = 9.2$$

Phenolphthalein would be a suitable indicator.

15-8. Curve *A* in figure 15-4 is the titration curve for H_3PO_4. Note that one end point occurs at about pH 4.5 and a second at about pH 9.5. Thus, H_3PO_4 would be determined by titration with bromocresol green as an indicator (pH 3.8 to 5.4). A titration to the second end point with phenolphthalein would give the number of millimoles of NaH_2PO_4 plus twice the number of millimoles of H_3PO_4. Thus, the concentration of NaH_2PO_4 is obtained from the difference in volume for the two titrations.

15-9. **(a)**To obtain the approximate equivalence point pH, we employ Equation 15-16

$$[\text{H}_3\text{O}^+] = \sqrt{K_{a1}K_{a2}} = \sqrt{4.2 \times 10^{-7} \times 4.69 \times 10^{-11}} = 4.4 \times 10^{-9}$$

$$\text{pH} = 8.4$$

Cresol purple (7.6 to 9.2) would be suitable.

(b) $P^{2-} + H_2O \rightleftharpoons HP^- + OH^- \qquad K_{b1} =$

$$\frac{[\text{OH}^-][\text{HP}^-]}{[\text{P}^{2-}]} = \frac{1.00 \times 10^{-14}}{3.91 \times 10^{-6}} = 2.56 \times 10^{-9}$$

$[OH^-] = [HP^-]$ and we assume $[P^{2-}] = 0.05 - [OH^-] \cong 0.05$

$[OH^-] = (0.05 \times 2.56 \times 10^{-9})^{1/2} = 1.13 \times 10^{-5}$ M

pH = 14.00 – [–log(1.13×10^{-5})] = 9.05

Phenolphthalein (8.3 to 10)

(c) As in part (b)

$[OH^-] = (0.05 \times 1.00 \times 10^{-14}/4.31 \times 10^{-5})^{1/2} = 3.41 \times 10^{-6}$ M

pH = 14.00 – [–log(3.41×10^{-6})] = 8.53

Cresol purple (7.6 to 9.2)

(d) Here we are able to use equation 15-16

$[H_3O^+] = (1.42 \times 10^{-7} \times 1.18 \times 10^{-10})^{1/2} = 4.09 \times 10^{-9}$ M

pH = –log(4.09×10^{-9}) = 8.39

Cresol purple (7.6 to 9.2)

(e) $NH_3C_2H_4NH_3^{2+} + H_2O \rightleftharpoons NH_3C_2H_4NH_2^{+} + H_3O^+ \quad K_{a1} = 1.42 \times 10^{-7}$

$[H_3O^+] = (0.05 \times 1.42 \times 10^{-7})^{1/2} = 8.43 \times 10^{-5}$ M

pH = –log(8.43×10^{-5}) = 4.07

Bromocresol green (3.8 to 5.4)

(f) Substituting into Equation 15-15 gives

$$[H_3O^+] = \sqrt{\frac{0.05 \times 6.6 \times 10^{-8} + 1.0 \times 10^{-14}}{1 + 0.05/(1.23 \times 10^{-2})}} = 2.55 \times 10^{-5}$$

pH = –log(2.55×10^{-5}) = 4.59

Bromocresol green (3.8 to 5.4)

(g) Proceeding as in part (b) we obtain pH = 9.94

Phenolphthalein (8.5 to 10.0)

15-10. (a) $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$ $K_{a1} = 7.11 \times 10^{-3}$

$$\frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{[H_3O^+]^2}{0.040 - [H_3O^+]} = 7.11 \times 10^{-3}$$

$[H_3O^+]^2 + 7.11 \times 10^{-3}[H_3O^+] - 0.040 \times 7.11 \times 10^{-3} = 0$

Solving by the quadratic formula or by successive approximations, gives

$[H_3O^+] = 1.37 \times 10^{-2}$ M pH = $-\log(1.37 \times 10^{-2}) = 1.86$

(b) Proceeding as in part (a) we have pH = 1.57

(c) pH = 1.64

(d) pH = 1.77

(e) pH = 4.21

(f) $NH_2C_2H_4NH_2 + H_2O \rightleftharpoons NH_3C_2H_4NH_2^+ + OH^-$ $K_{b1} = \dfrac{1.00 \times 10^{-14}}{1.18 \times 10^{-10}} = 8.47 \times 10^{-5}$

$$\frac{[OH^-]^2}{0.0400} = 8.47 \times 10^{-5}$$

$[OH^-] = (0.0400 \times 8.47 \times 10^{-5})^{1/2} = 1.84 \times 10^{-3}$ M

pH = $14.00 - [-\log(1.84 \times 10^{-3})] = 11.26$

15-11. Throughout this problem, we will use Equation 15-15 or one of its simplificationws.

(a) $$[H_3O^+] = \sqrt{\frac{0.0400 \times 6.32 \times 10^{-8}}{1 + 0.0400/(7.11 \times 10^{-3})}} = 1.95 \times 10^{-5}$$

pH = $-\log(1.95 \times 10^{-5}) = 4.71$

(**b)** as in part (a), we obtain pH =2.95

(c) pH = 4.28

(d) pH = 4.60

(e) pH = 9.80

(f) pH = 8.39

15-12. (a) $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$ $K_{b1} = \frac{K_w}{K_{a3}} = \frac{1.00 \times 10^{-14}}{4.5 \times 10^{-13}} = 2.2. \times 10^{-2}$

$$\frac{[OH^-]^2}{0.040 - [OH^-]} = 2.22 \times 10^{-2}$$

$[OH^-]^2 + 2.22 \times 10^{-2}[OH^-] - 8.88 \times 10^{-4} = 0$

Solving gives $[OH^-] = 2.07 \times 10^{-2}$ M

$\text{pH} = 14.00 - [-\log(2.07 \times 10^{-2})] = 12.32$

(b) $C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$ $K_{b1} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.84 \times 10^{-10}$

$[OH^-] = \sqrt{0.040 \times 1.84 \times 10^{-10}} = 2.72 \times 10^{-6}$ M

pH = 8.43

(c) Proceeding as in part (b), we obtain pH = 9.70.

(d) As in part (b), we obtain, pH = 9.89

(e) Proceeding as in part (a), gives pH = 12.58

(f) $NH_3C_2H_4NH_3^{2+} + H_2O \rightleftharpoons NH_3C_2H_4NH_2^{+} + H_3O^+$ $K_{a1} = 1.42\times10^{-7}$

$[H_3O^+] = (0.0400 \times 1.42 \times 10^{-7})^{1/2} = 7.54 \times 10^{-5}$ M and pH = 4.12

15-13. (a) $H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ $K_{a1} = 7.11 \times 10^{-3}$

$$7.11\times10^{-3} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(0.0200 + [H_3O^+])[H_3O^+]}{0.0500 - [H_3O^+]}$$

$[H_3O^+]^2 + (0.0200 + 7.11 \times 10^{-3})[H_3O^+] - (7.11 \times 10^{-3})(0.0500) = 0$

$[H_3O^+] = 9.67 \times 10^{-3}$ M and pH = 2.01

(b) $H_2AsO_4^- + H_2O \rightleftharpoons HAsO_4^{2-} + H_3O^+ \qquad K_{a2} = 1.1 \times 10^{-7}$

$$1.1\times10^{-7} = \frac{[H_3O^+][HAsO_4^{2-}]}{[H_2AsO_4^-]} = \frac{(0.0500 + [H_3O^+])[H_3O^+]}{0.0300 - [H_3O^+]} \cong \frac{(0.0500)[H_3O^+]}{0.0300}$$

$[H_3O^+] = 6.66 \times 10^{-8}$ M and pH = 7.18

(c) Proceeding as in part (b), we obtain $[H_3O^+] = 2.34 \times 10^{-11}$ and pH = 10.63

(d) $H_3PO_4 + HPO_4^{2-} \rightarrow 2H_2PO_4$

For each milliliter of solution, 0.0200 mmol Na_2HPO_4 reacts with 0.0200 mmol H_3PO_4 to give 0.0400 mmol NaH_2PO_4 and to leave 0.0200 mmol H_3PO_4. Thus, we have a buffer that is 0.0200 M in H_3PO_4 and 0.0400 M in NaH_2PO_4.

Proceeding as in part (a) we obtain $[H_3O^+] = 2.82 \times 10^{-3}$ M and pH = 2.55

(e) Proceeding as in part (a) we obtain $[H_3O^+] = 8.66 \times 10^{-3}$ M and pH = 2.06

15-14. (a) Proceeding as in Problem 15-12(a), $[H_3O^+] = 3.77 \times 10^{-3}$ M and pH = 2.42

(b) Proceeding as in 15-12(b), $[H_3O^+] = 3.10 \times 10^{-8}$ Mand pH = 7.51

(c) $HOC_2H_4NH_3^+ + H_2O \rightleftharpoons HOC_2H_4NH_2 + H_3O^+ \quad K_a = 3.18 \times 10^{-10}$

Proceeding as in 15-12(b) we obtain $[H_3O^+] = 3.73 \times 10^{-10}$ M and pH = 9.43

(d) $H_2C_2O_4 + C_2O_4^{2-} \rightarrow 2HC_2O_4^-$

For each milliliter of solution, 0.0240 mmol H_2HPO_4 reacts with 0.0240 mmol $C_2O_4^{2-}$ to give 0.0480 mmol $HC_2O_4^-$ and to leave 0.0120 mmol $C_2O_4^{2-}$. Thus, we have a buffer that is 0.0480 M in $HC_2O_4^-$ and 0.0120 M in $C_2O_4^{2-}$.

Proceeding as in 15-12(a), we obtain $[H_3O^+] = 2.17 \times 10^{-4}$ M and pH = 3.66

(e) Proceeding as in 15-12(b), we obtain $[H_3O^+] = 2.17 \times 10^{-4}$ and pH = 3.66

15-15. (a) $(NO_2)_3C_6H_2OH + H_2O \rightleftharpoons (NO_2)_3C_6H_2O^- + H_3O^+ \quad K_a = 0.43$

$$0.43 = \frac{[H_3O^+][(NO_2)_3C_6H_2O^-]}{[(NO_2)_3C_6H_2OH]} = \frac{(0.0100 + x)x}{0.0200 - x}$$

Rearranging gives $x^2 + (0.0100 + 0.43)x - (0.43)(0.0200) = 0$

solving the quadratic, gives $x = 1.87\times10^{-2}$

The total $[H_3O^+] = 0.0100 + x = 0.0287$ M and pH = 1.54

(b) Proceeding as in part (a), we obtain $[H_3O^+] = 1.013 \times 10^{-2}$ M and pH = 1.99

(c) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad K_{b1} = \frac{1.00 \times 10^{-14}}{4.69 \times 10^{-11}} = 2.13 \times 10^{-4}$

$$2.13 \times 10^{-4} = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = \frac{(0.0100 + x)x}{0.100 - x}$$

Rearranging gives $0 = x^2 + (0.0100 + 2.13 \times 10^{-4})x - (2.13 \times 10^{-4})(0.100)$

and solving the quadratic gives $x = 1.78 \times 10^{-3}$

The total $[OH^-] = 0.0100 + x = 0.0118$ M and pH = 12.07

(d) Proceeding as in part (c), we obtain$[OH^-] = 1.017 \times 10^{-2}$ M and pH = 12.01

15-16. (a) Proceeding as in 15-14(a), we obtain $[H_3O^+] = 1.287 \times 10^{-2}$ M and pH = 1.89

(b) Recognizing that the first proton of H_2SO_4 completely dissociates we obtain

$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+ \qquad K_{a2} = 1.02 \times 10^{-2}$

$$1.02 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.0100 + 0.0150 + x)x}{0.0150 - x}$$

Rearranging gives $x^2 + (0.0250 + 1.02 \times 10^{-2})x - (1.02 \times 10^{-2})(0.0150) = 0$

Solving the quadratic, gives $x = 3.91 \times 10^{-3}$

The total $[H_3O^+] = 0.0250 + x = 0.0289$ M and pH = 1.54

(c) Proceeding as in 15-14(c) we obtain $[OH^-] = 0.0382$ M and pH = 12.58

(d) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ $\quad K_{b1} = \dfrac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$

CH_3COO^- is such a weak base that it makes no significant contribution to $[OH^-]$

Therefore,$[OH^-] = 0.010$ M and pH = 12.00

15-17. (a) Let's compare the ratio $[H_2SO_3]/[HSO_3^-]$ with that of $[SO_3^{2-}]/[HSO_3^-]$ at $[H_3O^+] = 1.00 \times 10^{-6}$. The larger ratio is the predominant acid/base pair.

$$\frac{[H_2SO_3]}{[HSO_3^-]} = \frac{[H_3O^+]}{K_{a1}} = \frac{1.00 \times 10^{-6}}{1.23 \times 10^{-2}} = 8.1 \times 10^{-5}$$

$$\frac{[SO_3^{2-}]}{[HSO_3^-]} = \frac{K_{a2}}{[H_3O^+]} = \frac{6.6 \times 10^{-8}}{1.00 \times 10^{-6}} = 0.066$$

Clearly the predominant pair is SO_3^{2-}/HSO_3^- and its acid/base ratio is

1/0.066 = 15.2

(b) Substituting $[H_3O^+] = 1.00 \times 10^{-6}$ into the expressions for K_{a1}, K_{a2} and K_{a3} yields

$$\frac{[H_2Cit^-]}{[H_3Cit]} = 745 \qquad \frac{[HCit^{2-}]}{[H_2Cit^-]} = 17.3 \qquad \frac{[Cit^{3-}]}{[HCit^{2-}]} = 0.40$$

The large size of the first two ratios and the small size of the third indicate the $HCit^{2-}$ is a predominant species in this solution. To compare $[Cit^{3-}]$ and $[H_2Cit^-]$ we invert the second ratio. Then

$[H_2Cit^-]/[HCit^{2-}] = 1/17.3 = 0.058$

Thus, the predominant acid/base system involves $[\mathrm{Cit}^{3-}]$ and $[\mathrm{HCit}^{2-}]$ and their acid/base ratio is

$[\mathrm{HCit}^{2-}]/[\mathrm{Cit}^{3-}] = 1/0.40 = 2.5$

(c) Proceeding as in part (a), we obtain $[\mathrm{HM}^-]/[\mathrm{M}^{2-}] = 0.498$

(d) Proceeding as in part (a), we obtain $[\mathrm{HT}^-]/[\mathrm{T}^{2-}] = 0.0232$.

15-18. (a) Proceeding as in Problem 15-16(a) with $[\mathrm{H_3O^+}] = 1.00 \times 10^{-9}$ we obtain

$[\mathrm{H_2S}]/[\mathrm{HS^-}] = 0.010$

(b) Formulating the three species as $\mathrm{BH_2}^{2+}$, BH^+ and B, where B is the symbol for $\mathrm{NH_2C_2H_5NH_2}$.

$$\frac{[\mathrm{H_3O^+}][\mathrm{BH^+}]}{[\mathrm{BH_2^{2+}}]} = K_{a1} = 1.42 \times 10^{-7} \text{ and } \frac{[\mathrm{H_3O^+}][\mathrm{B}]}{[\mathrm{BH^+}]} = K_{a2} = 1.18 \times 10^{-10}$$

$$[\mathrm{BH_2}^{2+}]/[\mathrm{BH}^+] = \frac{1.00 \times 10^{-9}}{1.42 \times 10^{-7}} = 0.0070$$

$$[\mathrm{B}]/[\mathrm{BH}^+] = \frac{1.18 \times 10^{-10}}{1.00 \times 10^{-9}} = 0.118$$

$[\mathrm{BH_2}^{2+}]$ is $<$ [B] and $[\mathrm{BH}^+]/[\mathrm{B}] = 1.00/0.118 = 8.5$

(c) Proceeding as in Problem 15-16(b) we find

$[\mathrm{H_2AsO_4}^-]/[\mathrm{HAsO_4}^{2-}] = 9.1 \times 10^{-3}$

(d) Proceeding as in Problem 15-16(a) we find

$[\mathrm{HCO_3}^-]/[\mathrm{CO_3}^{2-}] = 21$

15-19. pH = 7.30; $[\mathrm{H_3O^+}]$ = antilog (–7.30) = 5.012×10^{-8} M

$K_{a2} = [\mathrm{H_3O^+}][\mathrm{HPO_4}^{2-}]/[\mathrm{H_2PO_4}^-] = 6.32 \times 10^{-8}$

$[\mathrm{HPO_4}^{2-}]/[\mathrm{H_2PO_4}^-] = 6.32 \times 10^{-8}/(5.012 \times 10^{-8}) = 1.261$

$HPO_4^{2-} + H_3PO_4 \rightarrow 2H_2PO_4$

amount H_3PO_4 present = 500 mL × 0.160 M = 80.0 mmol

amount $H_2PO_4^-$ in the buffer = 2 × 80.0 mmol = 160.0 mmol

amount HPO_4^{2-} needed for the buffer = 1.261 × 160.0 mmol = 201.8 mmol

Thus, we need 80.0 mmol of Na_2HPO_4 to react with the H_3PO_4 and an additional 201.8 mmol to provide the needed concentration of HPO_4^{2-} or 281.8 mmol.

mass $Na_2HPO_4 \bullet 2H_2O$ = 281.8 mmol × 0.17799 g/mmol = 50.2 g

15-20. pH = 5.75; $[H_3O^+]$ = antilog (–5.75) = 1.778×10^{-6}

$K_{a2} = [H_3O^+][P^{2-}]/[HP^-] = 3.91 \times 10^{-6}$

$[P^{2-}]/[HP^-] = 3.91 \times 10^{-6}/(1.778 \times 10^{-6}) = 2.199$

$P^{2-} + H_2P \rightarrow 2HP^-$

amount H_2P present = 750 mL × 0.0500 M = 37.5 mmol

amount HP^- in the buffer = 2 × 37.5 mmol = 75.0 mmol

amount P^{2-} needed in the buffer = 2.199 × 75.0 mmol = 164.9 mmol

Thus, we need 37.5 + 164.9 = 202.4 mmol of K_2P.

mass K_2P = 202.4 mmol × 0.24232 g/mmol = 49.0 g

15-21. amount NaH_2PO_4 = 40.0 × 0.200 = 8.00 mmol

(a) no. mmol H_3PO_4 formed = no. mmol HCl added = 60.0 × 0.100 = 6.00

$c_{H_3PO_4}$ = 6.00/100 = 0.0600 M

$c_{NaH_2PO_4}$ = (8.00 – 6.00)/100 = 0.0200

Proceeding as in Problem 15-12(a), we obtain pH = 1.95

(b) $c_{\mathrm{Na_2HPO_4}}$ = 6.00/100 = 0.0600 M

$c_{\mathrm{NaH_2PO_4}}$ = (8.00 – 6.00)/100 = 0.0200 M

Proceeding as in Problem 15-12(b), using K_2 gives pH = 7.68

15-22. amount KHP = 100 mL × 0.150 M = 15.0 mmol

(a) amount P^{-} = 100 mL × 0.0800 M = 8.00 mmol

amount KHP = 15.0 – 8.00 = 7.00 mmol

$c_{\mathrm{HP^-}}$ = 7.00/200 = 0.0350 M; $c_{\mathrm{P^{2-}}}$ = 8.00/200 = 0.0400 M

Proceeding as in Problem 15-12(b), we obtain pH = 5.47

(b) $c_{\mathrm{H_2P}}$ = 8.00/200 = 0.0400 M; $c_{\mathrm{HP^-}}$ = (15.00 – 8.00)/200 = 0.0350 M

Proceeding as in Problem 15-12(a), we obtain pH = 2.92

15-23. pH = 9.45; $[H_3O^+]$ = antilog (–9.45) = 3.548×10^{-10}

$K_{a2} = [H_3O^+][CO_3^{2-}]/[HCO_3^-] = 4.69 \times 10^{-11}$

$[CO_3^{2-}]/[HCO_3^-] = 4.69 \times 10^{-11}/(3.5428 \times 10^{-10}) = 0.1322$

Let V_{HCl} = volume 0.200 M HCl in mL and $V_{\mathrm{Na_2CO_3}}$ = volume 0.300 M Na_2CO_3 in mL

Since the solutions are dilute, the volumes will be additive

$V_{\mathrm{HCl}} + V_{\mathrm{Na_2CO_3}}$ = 1000 mL

Assume

$[CO_3^{2-}] \approx c_{\mathrm{Na_2CO_3}} = (V_{\mathrm{Na_2CO_3}} \times 0.300 - V_{\mathrm{HCl}} \times 0.200)/1000$

$[HCO_3^-] \approx c_{\mathrm{HCO_3^-}} = V_{\mathrm{HCl}} \times 0.200/1000$

Substituting these relationships into the ratio $[CO_3^{2-}]/[HCO_3^-]$ gives

$$\frac{0.300\ V_{\mathrm{Na_2CO_3}} - 0.200 V_{\mathrm{HCl}}}{0.200 V_{\mathrm{HCl}}} = 0.1322$$

$$0.300 V_{\mathrm{Na_2CO_3}} - 0.200 V_{\mathrm{HCl}} = 0.02644 V_{\mathrm{HCl}}$$

$$0.300(1000 - V_{\mathrm{HCl}}) - 0.200 V_{\mathrm{HCl}} = 0.02644 V_{\mathrm{HCl}}$$

$$V_{\mathrm{HCl}} = 300/0.52644 = 570\ \mathrm{mL}$$

$$V_{\mathrm{Na_2CO_3}} = 1000 - 570 = 430\ \mathrm{mL}$$

Thus, mix 430 mL of 0.300 M Na_2CO_3 with 570 mL of 0.200 M HCl

15-24. $[H_3O^+][HPO_4^{2-}]/[H_2PO_4^-] = 6.32 \times 10^{-8}$

$$\frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H_2PO_4^-}]} = \frac{6.32 \times 10^{-8}}{1.00 \times 10^{-7}} = 0.632 \qquad (1)$$

Let $V_{\mathrm{H_3PO_4}}$ and V_{NaOH} be the volume in milliliters of the two reagents. Then

$$V_{\mathrm{H_3PO_4}} + V_{\mathrm{NaOH}} = 1000\ \mathrm{mL} \qquad (2)$$

From mass-balance considerations we may write that in the 1000 mL

$$\text{amount NaH}_2\text{PO}_4 + \text{amount Na}_2\text{HPO}_4 = 0.200 \times V_{\mathrm{H_3PO_4}}\ \text{mmol} \qquad (3)$$

$$\text{amount NaH}_2\text{PO}_4 + 2 \times \text{amount Na}_2\text{HPO}_4 = 0.160 \times V_{\mathrm{NaOH}}\ \text{mmol} \qquad (4)$$

Equation (1) can be rewritten

$$\frac{\text{no. mmol Na}_2\text{HPO}_4/1000}{\text{no. mmol NaH}_2\text{PO}_4/1000} = \frac{\text{no. mmol Na}_2\text{HPO}_4}{\text{no. mmol NaH}_2\text{PO}_4} = 0.632 \qquad (5)$$

Thus, we have four equations, (2), (3), (4) and (5), and four unknowns: $V_{\mathrm{H_3PO_4}}$, V_{NaOH}, no. mmol NaH_2PO_4 and no. mmol Na_2HPO_4. Subtracting Equation (3) from (4) yields

$$\text{no. mmol Na}_2\text{HPO}_4 = 0.160\ V_{\mathrm{NaOH}} - 0.200\ V_{\mathrm{H_3PO_4}} \qquad (6)$$

Substituting Equation (6) into (3) gives no. mmo NaH_2PO_4 + 0.160 V_{NaOH} – 0.200 $V_{H_3PO_4}$ = 0.200 $V_{H_3PO_4}$

no. mmo NaH_2PO_4 = –0.160 V_{NaOH} + 0.400 $V_{H_3PO_4}$ (7)

Substituting Equations (6) and (7) into (5) gives

$$\frac{0.160V_{NaOH} - 0.200V_{H_3PO_4}}{0.400V_{H_3PO_4} - 0.160V_{NaOH}} = 0.632$$

This equation rearranges to

$0.2611\ V_{NaOH} = 0.4528\ V_{H_3PO_4}$

Substituting Equation (2) gives

$0.2611\ (1000 - V_{H_3PO_4}) = 0.4528\ V_{H_3PO_4}$

$V_{H_3PO_4}$ = 261.1/0.7139 = 366 mL and V_{NaOH} = 1000 – 366 = 634 mL

Thus, mix 366 mL H_3PO_4 with 634 mL NaOH

15-25. $[H_3O^+][HAsO_4^{2-}]/[H_2AsO_4^-] = 1.1 \times 10^{-7}$

$[HAsO_4^{2-}]/[H_2AsO_4^-] = 1.1 \times 10^{-7}/(1.00 \times 10^{-6}) = 0.11$ (1)

As in Problem 15-23 we now develop four independent equations that allow calculation of V_{HCl}, $V_{Na_3AsO_4}$, no. mmol of $HAsO_4^{2-}$ and no. mmol of $H_2AsO_4^-$.

$V_{Na_3AsO_4} + V_{HCl}$ = 1000 mL (2)

no. mmol NaH_2AsO_4 + no. mmol Na_2HAsO_4 = 0.500 $V_{Na_3AsO_4}$ (3)

2 × no. mmol NaH_2AsO_4 + no. mmol Na_2HAsO_4 = 0.400 V_{HCl} (4)

no. mmol Na_2HAsO_4 / no. mmol NaH_2AsO_4 = 0.11

Proceeding as in Problem 15-23 we solve equations (2), (3), (4) and (5) and conclude that 704 mL of 0.400 M HCl should be mixed with 296 mL of 0.500 M Na_3AsO_4.

15-26. **(a)** For Na_2M, $K_1 = 1.3 \times 10^{-2}$ and $K_2 = 5.9 \times 10^{-7}$. This initial pH is high and two equally spaced end points will be encountered. Thus, curve C.

(b) Curve A

(c) Curve C for the reasons given in part (a).

15-27. (a) Titrations with NaOH of a solution containing a mixture of two weak acids HA_1 and HA_2. HA_1 is present in a greater concentration and has a dissociation constant that is larger by a factor of about 10^4.

(b) Titration of a typical monoprotic weak acid.

(c) Titration of a mixture of a weak base, such as Na_2CO_3, and an acid salt, such as $NaHCO_3$.

15-28. For the titration of a mixture of H_3PO_4 and $H_2PO_4^-$, the volume to the first end point would have to be smaller than one half the total volume to the second end point because in the titration from the first to second end points both analytes are titrated, whereas to the first end point only the H_3PO_4 is titrated.

15-29. For this problem**,** we set up spreadsheets that will solve a quadratic equation to determine $[H_3O^+]$ or $[OH^-]$, as needed (See approach taken for Problems 14-41 through 43). While approximate solutions are appropriate for many of the calculations, the approach taken represents a more general solution and is somewhat easier to incorporate in a spreadsheet. As an example consider the titration of a weak diprotic acid with a strong base.

Before the 1st equivalence point:

$$[H_2A] = \frac{\left(c_{\mathrm{i\,H_2A}}V_{\mathrm{i\,H_2A}} - c_{\mathrm{i\,NaOH}}V_{\mathrm{NaOH}}\right)}{\left(V_{\mathrm{i\,H_2A}} + V_{\mathrm{NaOH}}\right)} - [H_3O^+]$$

and
$$[HA^-] = \frac{(c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} + [H_3O^+]$$

Substituting these expressions into the equilibrium expression for H_2A and rearranging gives

$$[H_3O^+]^2 + \left(\frac{(c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} + K_{a1}\right)[H_3O^+] - \frac{K_{a1}(c_{\text{i H}_2\text{A}}V_{\text{i H}_2\text{A}} - c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} = 0$$

From which $[H_3O^+]$ is directly determined.

At the 1st equivalence point we use Equation 15-13

$$[H_3O^+] = \sqrt{\frac{K_{a2}c_{\text{iH}_2\text{A}}V_{\text{iH}_2\text{A}}/(V_{\text{iH}_2\text{A}} + V_{\text{NaOH}}) + K_w}{1 + c_{\text{iH}_2\text{A}}V_{\text{iH}_2\text{A}}/(K_{a1}(V_{\text{iH}_2\text{A}} + V_{\text{NaOH}}))}}$$

After the 1st and before the 2nd equivalence point:

$$[HA^-] = \frac{(2 \times c_{\text{i H}_2\text{A}}V_{\text{i H}_2\text{A}} - c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} - [H_3O^+]$$

and
$$[A^{2-}] = \frac{(c_{\text{i NaOH}}V_{\text{NaOH}} - c_{\text{iH}_2\text{A}}V_{\text{iH}_2\text{A}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} + [H_3O^+]$$

Substituting these expressions into the equilibrium expression for HA^- and rearranging gives

$$[H_3O^+]^2 + \left(\frac{(c_{\text{i NaOH}}V_{\text{NaOH}} - c_{\text{iH}_2\text{A}}V_{\text{iH}_2\text{A}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} + K_{a2}\right)[H_3O^+] - \frac{K_{a2}(2 \times c_{\text{i H}_2\text{A}}V_{\text{i H}_2\text{A}} - c_{\text{i NaOH}}V_{\text{NaOH}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} = 0$$

From which $[H_3O^+]$ is directly determined.

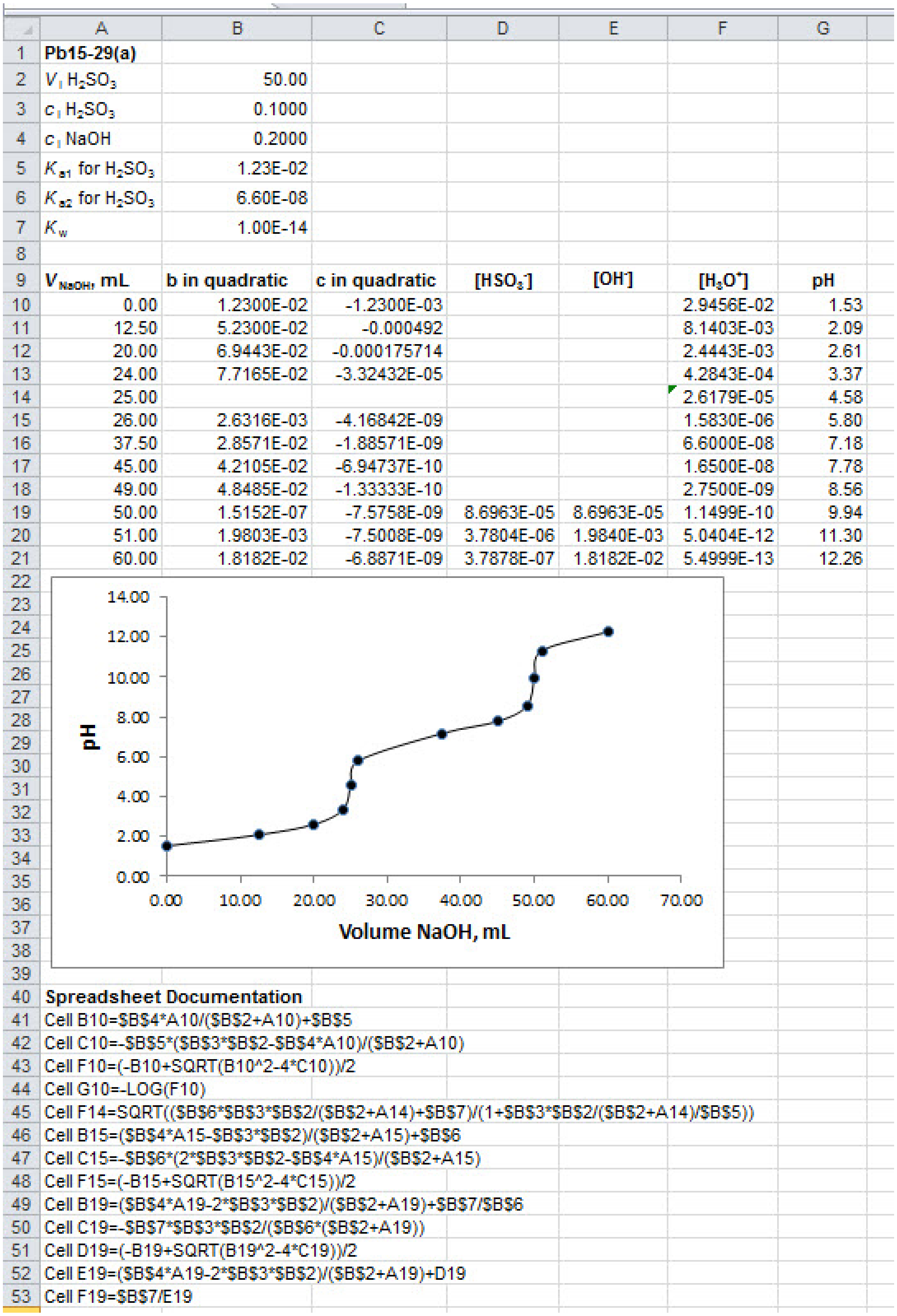
At and after the 2nd equivalence point:
$$[A^{2-}] = \frac{(c_{\text{i H}_2\text{A}}V_{\text{H}_2\text{A}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} - [HA^-]$$

and
$$[OH^-] = \frac{(c_{\text{i NaOH}}V_{\text{NaOH}} - 2 \times c_{\text{i H}_2\text{A}}V_{\text{i H}_2\text{A}})}{(V_{\text{i H}_2\text{A}} + V_{\text{NaOH}})} + [HA^-]$$

Substituting these expressions into the equilibrium expression for A^{2-} and rearranging gives

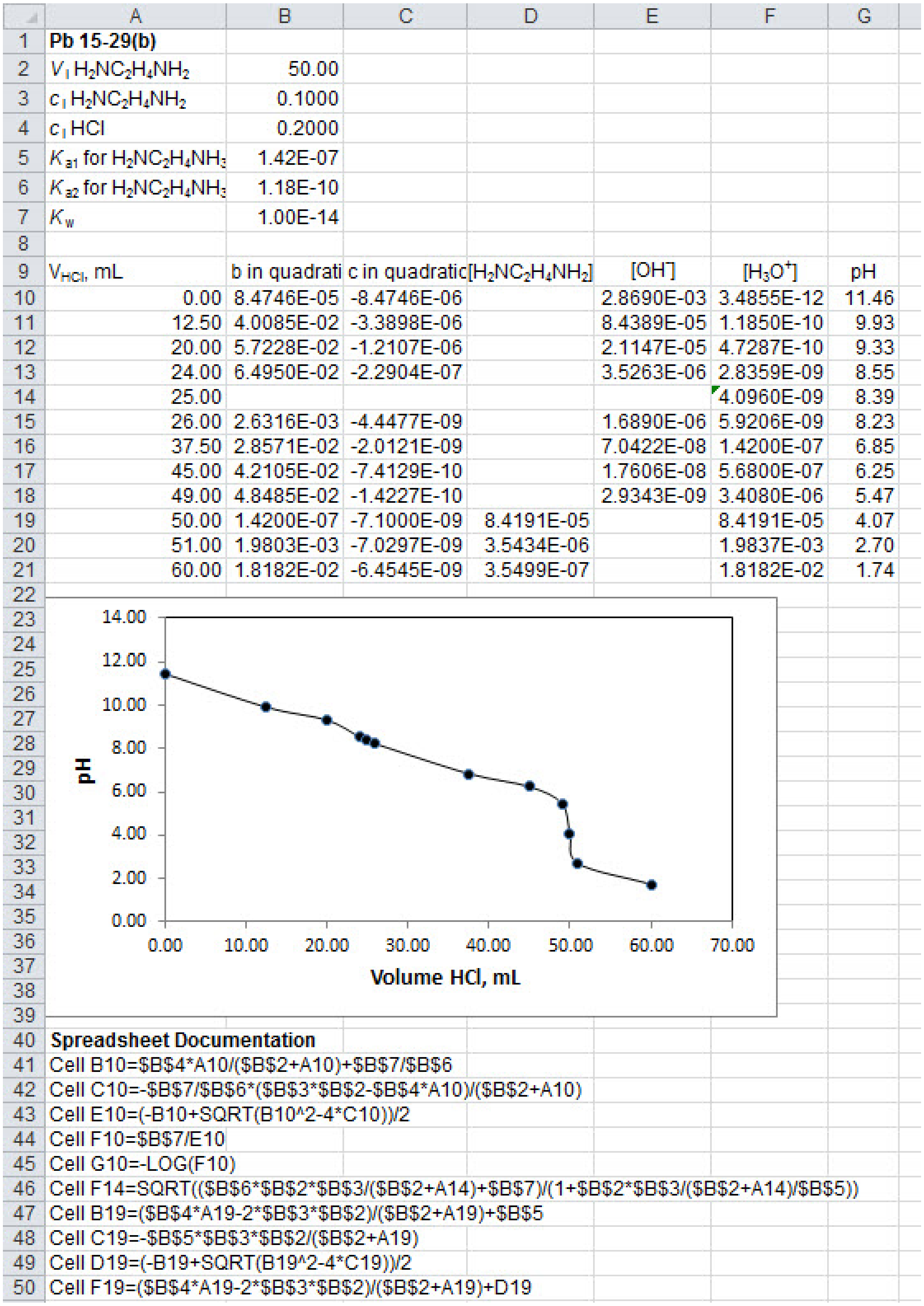
$$[\mathrm{HA}^-]^2 + \left(\frac{\left(c_{\mathrm{i\,NaOH}}V_{\mathrm{NaOH}} - 2 \times c_{\mathrm{i\,H_2A}}V_{\mathrm{i\,H_2A}}\right)}{\left(V_{\mathrm{i\,H_2A}} + V_{\mathrm{NaOH}}\right)} + \frac{K_\mathrm{w}}{K_{\mathrm{a2}}}\right)[\mathrm{HA}^-] - \frac{K_\mathrm{w}\left(c_{\mathrm{i\,H_2A}}V_{\mathrm{iH_2A}}\right)}{K_{\mathrm{a2}}\left(V_{\mathrm{i\,H_2A}} + V_{\mathrm{NaOH}}\right)} = 0$$

From which $[\mathrm{HA}^-]$ can be determined and $[\mathrm{OH}^-]$ and $[\mathrm{H_3O^+}]$ subsequently calculated. A similar approach is taken for the titration of a weak base with a strong acid.



	A	B	C	D	E	F	G
1	**Pb15-29(a)**						
2	V_i H_2SO_3	50.00					
3	c_i H_2SO_3	0.1000					
4	c_i NaOH	0.2000					
5	K_{a1} for H_2SO_3	1.23E-02					
6	K_{a2} for H_2SO_3	6.60E-08					
7	K_w	1.00E-14					
8							
9	**V_{NaOH}, mL**	**b in quadratic**	**c in quadratic**	**[HSO_3^-]**	**[OH^-]**	**[H_3O^+]**	**pH**
10	0.00	1.2300E-02	-1.2300E-03			2.9456E-02	1.53
11	12.50	5.2300E-02	-0.000492			8.1403E-03	2.09
12	20.00	6.9443E-02	-0.000175714			2.4443E-03	2.61
13	24.00	7.7165E-02	-3.32432E-05			4.2843E-04	3.37
14	25.00					2.6179E-05	4.58
15	26.00	2.6316E-03	-4.16842E-09			1.5830E-06	5.80
16	37.50	2.8571E-02	-1.88571E-09			6.6000E-08	7.18
17	45.00	4.2105E-02	-6.94737E-10			1.6500E-08	7.78
18	49.00	4.8485E-02	-1.33333E-10			2.7500E-09	8.56
19	50.00	1.5152E-07	-7.5758E-09	8.6963E-05	8.6963E-05	1.1499E-10	9.94
20	51.00	1.9803E-03	-7.5008E-09	3.7804E-06	1.9840E-03	5.0404E-12	11.30
21	60.00	1.8182E-02	-6.8871E-09	3.7878E-07	1.8182E-02	5.4999E-13	12.26

	A
40	**Spreadsheet Documentation**
41	`Cell B10=$B$4*A10/($B$2+A10)+$B$5`
42	`Cell C10=-$B$5*($B$3*$B$2-$B$4*A10)/($B$2+A10)`
43	`Cell F10=(-B10+SQRT(B10^2-4*C10))/2`
44	`Cell G10=-LOG(F10)`
45	`Cell F14=SQRT(($B$6*$B$3*$B$2/($B$2+A14)+$B$7)/(1+$B$3*$B$2/($B$2+A14)/$B$5))`
46	`Cell B15=($B$4*A15-$B$3*$B$2)/($B$2+A15)+$B$6`
47	`Cell C15=-$B$6*(2*$B$3*$B$2-$B$4*A15)/($B$2+A15)`
48	`Cell F15=(-B15+SQRT(B15^2-4*C15))/2`
49	`Cell B19=($B$4*A19-2*$B$3*$B$2)/($B$2+A19)+$B$7/$B$6`
50	`Cell C19=-$B$7*$B$3*$B$2/($B$6*($B$2+A19))`
51	`Cell D19=(-B19+SQRT(B19^2-4*C19))/2`
52	`Cell E19=($B$4*A19-2*$B$3*$B$2)/($B$2+A19)+D19`
53	`Cell F19=$B$7/E19`



	A	B	C	D	E	F	G
1	**Pb 15-29(b)**						
2	V_I $H_2NC_2H_4NH_2$	50.00					
3	c_I $H_2NC_2H_4NH_2$	0.1000					
4	c_I HCl	0.2000					
5	K_{a1} for $H_2NC_2H_4NH_3$	1.42E-07					
6	K_{a2} for $H_2NC_2H_4NH_3$	1.18E-10					
7	K_w	1.00E-14					
8							
9	V_{HCl}, mL	b in quadrati	c in quadratic	$[H_2NC_2H_4NH_2]$	$[OH^-]$	$[H_3O^+]$	pH
10	0.00	8.4746E-05	-8.4746E-06		2.8690E-03	3.4855E-12	11.46
11	12.50	4.0085E-02	-3.3898E-06		8.4389E-05	1.1850E-10	9.93
12	20.00	5.7228E-02	-1.2107E-06		2.1147E-05	4.7287E-10	9.33
13	24.00	6.4950E-02	-2.2904E-07		3.5263E-06	2.8359E-09	8.55
14	25.00					4.0960E-09	8.39
15	26.00	2.6316E-03	-4.4477E-09		1.6890E-06	5.9206E-09	8.23
16	37.50	2.8571E-02	-2.0121E-09		7.0422E-08	1.4200E-07	6.85
17	45.00	4.2105E-02	-7.4129E-10		1.7606E-08	5.6800E-07	6.25
18	49.00	4.8485E-02	-1.4227E-10		2.9343E-09	3.4080E-06	5.47
19	50.00	1.4200E-07	-7.1000E-09	8.4191E-05		8.4191E-05	4.07
20	51.00	1.9803E-03	-7.0297E-09	3.5434E-06		1.9837E-03	2.70
21	60.00	1.8182E-02	-6.4545E-09	3.5499E-07		1.8182E-02	1.74

Spreadsheet Documentation

Cell B10=\$B\$4*A10/(\$B\$2+A10)+\$B\$7/\$B\$6

Cell C10=-\$B\$7/\$B\$6*(\$B\$3*\$B\$2-\$B\$4*A10)/(\$B\$2+A10)

Cell E10=(-B10+SQRT(B10^2-4*C10))/2

Cell F10=\$B\$7/E10

Cell G10=-LOG(F10)

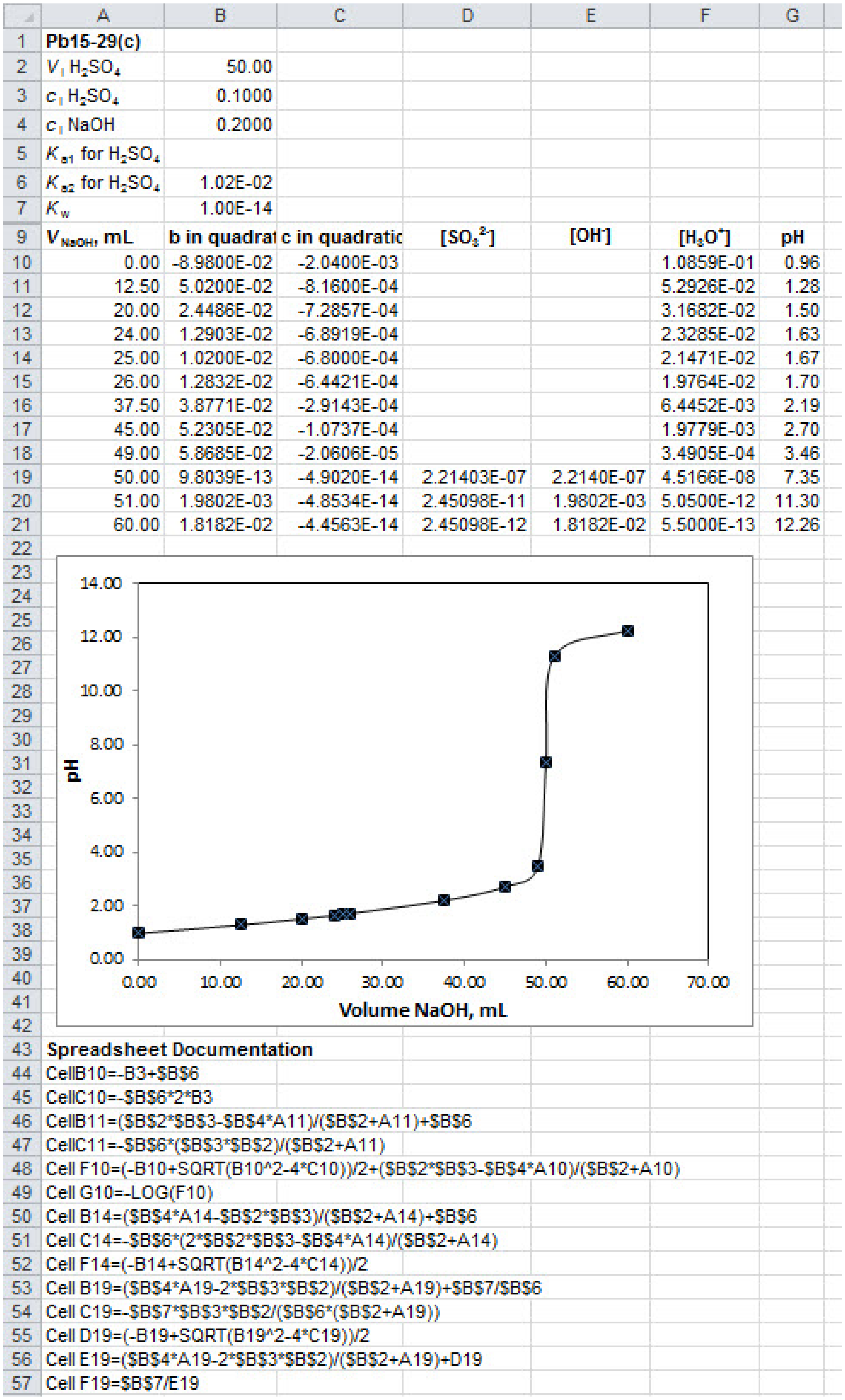
Cell F14=SQRT((\$B\$6*\$B\$2*\$B\$3/(\$B\$2+A14)+\$B\$7)/(1+\$B\$2*\$B\$3/(\$B\$2+A14)/\$B\$5))

Cell B19=(\$B\$4*A19-2*\$B\$3*\$B\$2)/(\$B\$2+A19)+\$B\$5

Cell C19=-\$B\$5*\$B\$3*\$B\$2/(\$B\$2+A19)

Cell D19=(-B19+SQRT(B19^2-4*C19))/2

Cell F19=(\$B\$4*A19-2*\$B\$3*\$B\$2)/(\$B\$2+A19)+D19



	A	B	C	D	E	F	G
1	**Pb15-29(c)**						
2	V_i H_2SO_4	50.00					
3	c_i H_2SO_4	0.1000					
4	c_i NaOH	0.2000					
5	K_{a1} for H_2SO_4						
6	K_{a2} for H_2SO_4	1.02E-02					
7	K_w	1.00E-14					
9	**V_{NaOH}, mL**	**b in quadrat**	**c in quadratic**	**$[SO_3^{2-}]$**	**$[OH^-]$**	**$[H_3O^+]$**	**pH**
10	0.00	-8.9800E-02	-2.0400E-03			1.0859E-01	0.96
11	12.50	5.0200E-02	-8.1600E-04			5.2926E-02	1.28
12	20.00	2.4486E-02	-7.2857E-04			3.1682E-02	1.50
13	24.00	1.2903E-02	-6.8919E-04			2.3285E-02	1.63
14	25.00	1.0200E-02	-6.8000E-04			2.1471E-02	1.67
15	26.00	1.2832E-02	-6.4421E-04			1.9764E-02	1.70
16	37.50	3.8771E-02	-2.9143E-04			6.4452E-03	2.19
17	45.00	5.2305E-02	-1.0737E-04			1.9779E-03	2.70
18	49.00	5.8685E-02	-2.0606E-05			3.4905E-04	3.46
19	50.00	9.8039E-13	-4.9020E-14	2.21403E-07	2.2140E-07	4.5166E-08	7.35
20	51.00	1.9802E-03	-4.8534E-14	2.45098E-11	1.9802E-03	5.0500E-12	11.30
21	60.00	1.8182E-02	-4.4563E-14	2.45098E-12	1.8182E-02	5.5000E-13	12.26

43 **Spreadsheet Documentation**
44 CellB10=-B3+$B$6
45 CellC10=-$B$6*2*B3
46 CellB11=($B$2*$B$3-$B$4*A11)/($B$2+A11)+$B$6
47 CellC11=-$B$6*($B$3*$B$2)/($B$2+A11)
48 Cell F10=(-B10+SQRT(B10^2-4*C10))/2+($B$2*$B$3-$B$4*A10)/($B$2+A10)
49 Cell G10=-LOG(F10)
50 Cell B14=($B$4*A14-$B$2*$B$3)/($B$2+A14)+$B$6
51 Cell C14=-$B$6*(2*$B$2*$B$3-$B$4*A14)/($B$2+A14)
52 Cell F14=(-B14+SQRT(B14^2-4*C14))/2
53 Cell B19=($B$4*A19-2*$B$3*$B$2)/($B$2+A19)+$B$7/$B$6
54 Cell C19=-$B$7*$B$3*$B$2/($B$6*($B$2+A19))
55 Cell D19=(-B19+SQRT(B19^2-4*C19))/2
56 Cell E19=($B$4*A19-2*$B$3*$B$2)/($B$2+A19)+D19
57 Cell F19=$B$7/E19

15-30. For **Problems 15-30 and 15-31** we set up spreadsheets that will solve a quadratic equation to determine [H_3O^+] or [OH^-], as needed (See approach taken for Problems 14-41 through 43). As an example consider the titration of a volume of a mixture (V_{iMix}) of a strong (SA) and weak (HA) acid with a strong base (B).

Before the 1st equivalence point:

$$[\text{HA}] \;=\; \frac{\left(c_{\text{i HA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} - [\text{A}^-]$$

and

$$[\text{H}_3\text{O}^+] \;=\; \frac{\left(V_{\text{iMix}}c_{\text{SA}} - c_{\text{iB}}V_{\text{B}}\right)}{\left(V_{\text{iMix}} + V_{\text{B}}\right)} + [\text{A}^-]$$

Substituting these expressions into the equilibrium expression for HA and rearranging gives

$$[\text{A}^-]^2 + \left(\frac{\left(V_{\text{iMix}}c_{\text{SA}} - c_{\text{iB}}V_{\text{B}}\right)}{\left(V_{\text{iMix}} + V_{\text{B}}\right)} + K_{\text{a}}\right)[\text{A}^-] + \frac{-K_{\text{a}}\left(c_{\text{i HA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} = 0$$

From which [A^-] is determined and [H_3O^+] can be calculated.

From the 1st equivalence to before the 2nd equivalence point:

$$[\text{HA}] \;=\; \frac{\left(c_{\text{i HA}}V_{\text{i Mix}} - \left(c_{\text{iB}}V_{\text{B}} - V_{\text{iMix}}c_{\text{iSA}}\right)\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} - [\text{H}_3\text{O}^+]$$

and

$$[\text{A}^-] = \frac{\left(c_{\text{i B}}V_{\text{B}} - c_{\text{iSA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} + [\text{H}_3\text{O}^+]$$

Substituting these expressions into the equilibrium expression for HA and rearranging gives

$$[\text{H}_3\text{O}^+]^2 + \left(\frac{\left(c_{\text{i B}}V_{\text{B}} - c_{\text{iSA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} + K_{\text{a}}\right)[\text{H}_3\text{O}^+] + \frac{-K_{\text{a}}\left(c_{\text{i HA}}V_{\text{i Mix}} - \left(c_{\text{iB}}V_{\text{B}} - V_{\text{iMix}}c_{\text{iSA}}\right)\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} = 0$$

From which [H_3O^+] is directly determined by solving the quadratic.

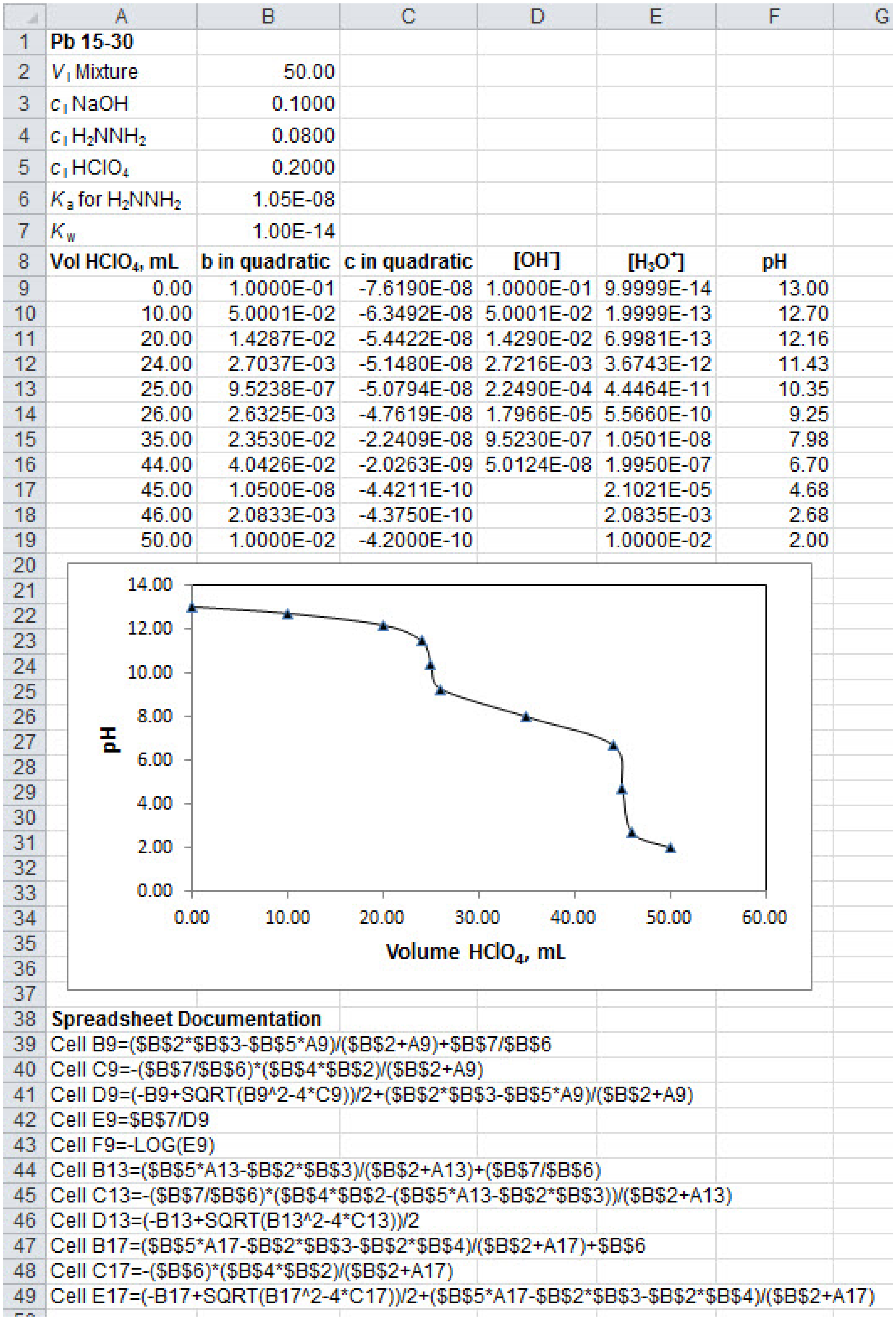
At and after the 2nd equivalence point: $[\text{A}^-] = \dfrac{\left(c_{\text{i HA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} - [\text{HA}]$

and $[\text{OH}^-] = \dfrac{\left(c_{\text{i B}}V_{\text{B}} - c_{\text{i HA}}V_{\text{iMix}} - c_{\text{iSA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} + [\text{HA}]$

Substituting these expressions into the equilibrium expression for A⁻ and rearranging gives

$$[\text{HA}]^2 + \left(\frac{\left(c_{\text{i B}}V_{\text{B}} - c_{\text{i HA}}V_{\text{iMix}} - c_{\text{iSA}}V_{\text{iMix}}\right)}{\left(V_{\text{i Mix}} + V_{\text{B}}\right)} + \frac{K_{\text{w}}}{K_{\text{a}}}\right)[\text{HA}] + \frac{-K_{\text{w}}\left(c_{\text{i HA}}V_{\text{iMix}}\right)}{K_{\text{a}}\left(V_{\text{i Mix}} + V_{\text{B}}\right)} = 0$$

From which [HA] can be determined by solving the quadratic. Having [HA], allows $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ to be calculated. A similar approach is taken for the titration of a mixture of a strong and weak base with a strong acid.



A	B	C	D	E	F
Pb 15-30					
V_i Mixture	50.00				
c_i NaOH	0.1000				
c_i H_2NNH_2	0.0800				
c_i $HClO_4$	0.2000				
K_a for H_2NNH_2	1.05E-08				
K_w	1.00E-14				
Vol $HClO_4$, mL	**b in quadratic**	**c in quadratic**	**$[OH^-]$**	**$[H_3O^+]$**	**pH**
0.00	1.0000E-01	-7.6190E-08	1.0000E-01	9.9999E-14	13.00
10.00	5.0001E-02	-6.3492E-08	5.0001E-02	1.9999E-13	12.70
20.00	1.4287E-02	-5.4422E-08	1.4290E-02	6.9981E-13	12.16
24.00	2.7037E-03	-5.1480E-08	2.7216E-03	3.6743E-12	11.43
25.00	9.5238E-07	-5.0794E-08	2.2490E-04	4.4464E-11	10.35
26.00	2.6325E-03	-4.7619E-08	1.7966E-05	5.5660E-10	9.25
35.00	2.3530E-02	-2.2409E-08	9.5230E-07	1.0501E-08	7.98
44.00	4.0426E-02	-2.0263E-09	5.0124E-08	1.9950E-07	6.70
45.00	1.0500E-08	-4.4211E-10		2.1021E-05	4.68
46.00	2.0833E-03	-4.3750E-10		2.0835E-03	2.68
50.00	1.0000E-02	-4.2000E-10		1.0000E-02	2.00

Spreadsheet Documentation

Cell B9=($B$2*$B$3-$B$5*A9)/($B$2+A9)+$B$7/$B$6

Cell C9=-($B$7/$B$6)*($B$4*$B$2)/($B$2+A9)

Cell D9=(-B9+SQRT(B9^2-4*C9))/2+($B$2*$B$3-$B$5*A9)/($B$2+A9)

Cell E9=$B$7/D9

Cell F9=-LOG(E9)

Cell B13=($B$5*A13-$B$2*$B$3)/($B$2+A13)+($B$7/$B$6)

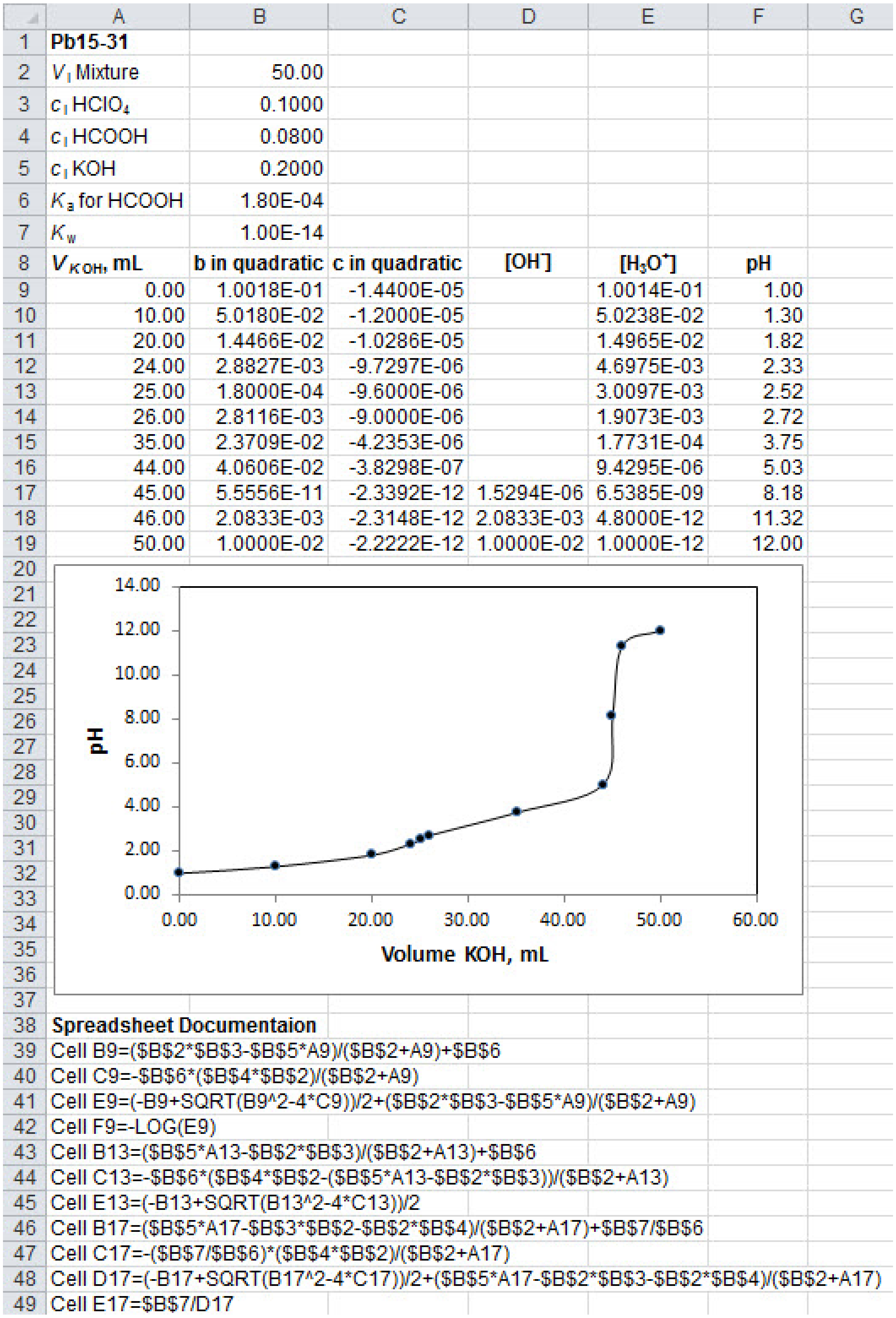
Cell C13=-($B$7/$B$6)*($B$4*$B$2-($B$5*A13-$B$2*$B$3))/($B$2+A13)

Cell D13=(-B13+SQRT(B13^2-4*C13))/2

Cell B17=($B$5*A17-$B$2*$B$3-$B$2*$B$4)/($B$2+A17)+$B$6

Cell C17=-($B$6)*($B$4*$B$2)/($B$2+A17)

Cell E17=(-B17+SQRT(B17^2-4*C17))/2+($B$5*A17-$B$2*$B$3-$B$2*$B$4)/($B$2+A17)



	A	B	C	D	E	F	G
1	**Pb15-31**						
2	V_i Mixture	50.00					
3	c_i $HClO_4$	0.1000					
4	c_i HCOOH	0.0800					
5	c_i KOH	0.2000					
6	K_a for HCOOH	1.80E-04					
7	K_w	1.00E-14					
8	**V_{KOH}, mL**	**b in quadratic**	**c in quadratic**	**$[OH^-]$**	**$[H_3O^+]$**	**pH**	
9	0.00	1.0018E-01	-1.4400E-05		1.0014E-01	1.00	
10	10.00	5.0180E-02	-1.2000E-05		5.0238E-02	1.30	
11	20.00	1.4466E-02	-1.0286E-05		1.4965E-02	1.82	
12	24.00	2.8827E-03	-9.7297E-06		4.6975E-03	2.33	
13	25.00	1.8000E-04	-9.6000E-06		3.0097E-03	2.52	
14	26.00	2.8116E-03	-9.0000E-06		1.9073E-03	2.72	
15	35.00	2.3709E-02	-4.2353E-06		1.7731E-04	3.75	
16	44.00	4.0606E-02	-3.8298E-07		9.4295E-06	5.03	
17	45.00	5.5556E-11	-2.3392E-12	1.5294E-06	6.5385E-09	8.18	
18	46.00	2.0833E-03	-2.3148E-12	2.0833E-03	4.8000E-12	11.32	
19	50.00	1.0000E-02	-2.2222E-12	1.0000E-02	1.0000E-12	12.00	

Spreadsheet Documentaion

Cell B9=($B$2*$B$3-$B$5*A9)/($B$2+A9)+$B$6

Cell C9=-$B$6*($B$4*$B$2)/($B$2+A9)

Cell E9=(-B9+SQRT(B9^2-4*C9))/2+($B$2*$B$3-$B$5*A9)/($B$2+A9)

Cell F9=-LOG(E9)

Cell B13=($B$5*A13-$B$2*$B$3)/($B$2+A13)+$B$6

Cell C13=-$B$6*($B$4*$B$2-($B$5*A13-$B$2*$B$3))/($B$2+A13)

Cell E13=(-B13+SQRT(B13^2-4*C13))/2

Cell B17=($B$5*A17-$B$3*$B$2-$B$2*$B$4)/($B$2+A17)+$B$7/$B$6

Cell C17=-($B$7/$B$6)*($B$4*$B$2)/($B$2+A17)

Cell D17=(-B17+SQRT(B17^2-4*C17))/2+($B$5*A17-$B$2*$B$3-$B$2*$B$4)/($B$2+A17)

Cell E17=$B$7/D17

15-32. **(a)** $2H_2AsO_4^- \rightleftharpoons H_3AsO_4 + HAsO_4^{2-}$

$$K_{a1} = \frac{[H_3O^+][H_2AsO_4^-]}{[H_3AsO_4]} = 5.8 \times 10^{-3} \qquad (1)$$

$$K_{a2} = \frac{[H_3O^+][HAsO_4^{2-}]}{[H_2AsO_4^-]} = 1.1 \times 10^{-7} \qquad (2)$$

$$K_{a3} = \frac{[H_3O^+][AsO_4^{3-}]}{[HAsO_4^{2-}]} = 3.2 \times 10^{-12} \qquad (3)$$

Dividing Equation (2) by Equation (1) leads to

$$\frac{K_{a2}}{K_{a1}} = \frac{[H_3AsO_4][HAsO_4^{2-}]}{[H_2AsO_4^-]^2} = 1.9 \times 10^{-5}$$

which is the desired equilibrium constant expression.

(b) $2HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H_2AsO_4^-$

Here we divide Equation (3) by Equation (2)

$$\frac{K_{a3}}{K_{a2}} = \frac{[AsO_4^{3-}][H_2AsO_4^-]}{[HAsO_4^{2-}]^2} = 2.9 \times 10^{-5}$$

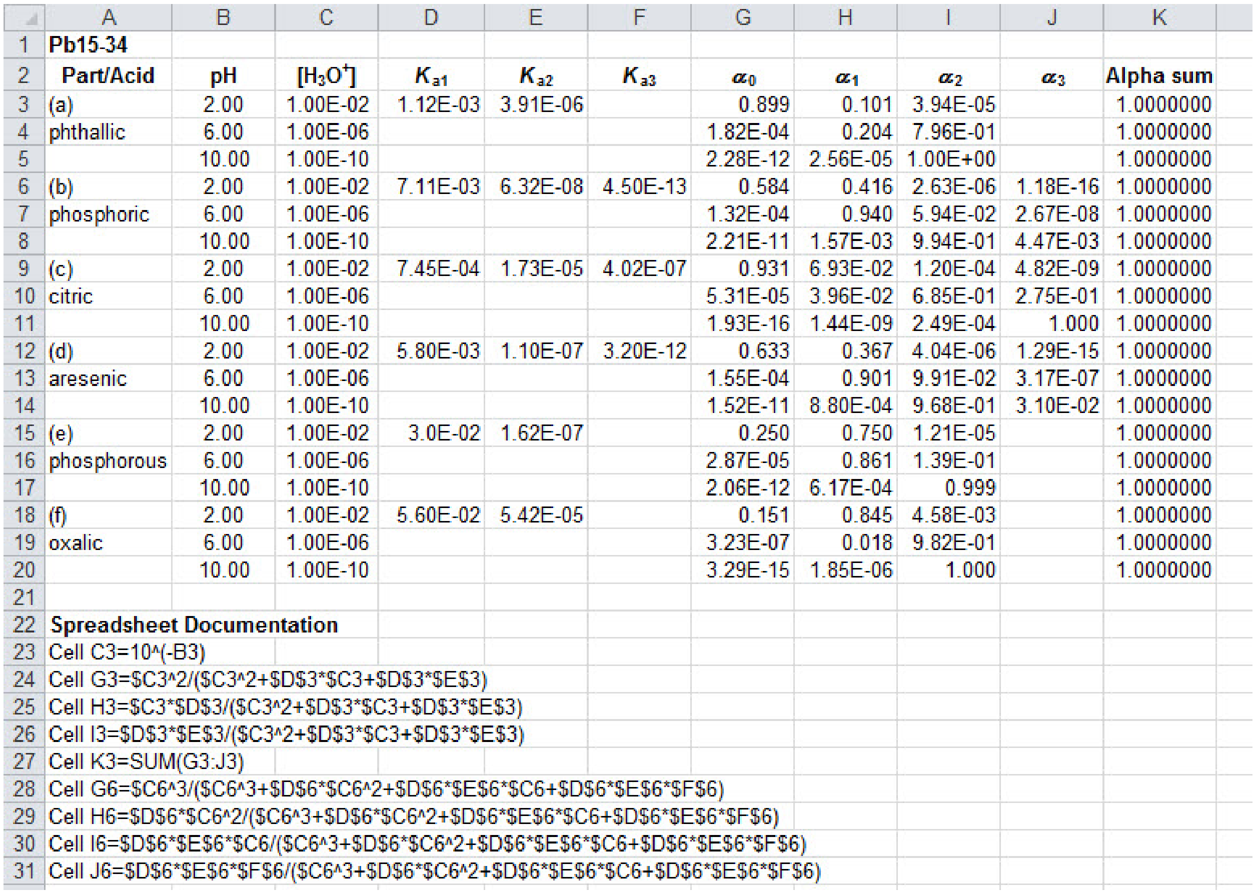
15-33. $HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$ $\qquad K_{HOAc} = 1.75 \times 10^{-5}$

$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $\qquad K_{NH_4^+} = 5.70 \times 10^{-10}$

Subtracting the first reaction from the second and rearranging gives

$NH_4^+ + OAc^- \rightleftharpoons NH_3 + HOAc$ $\qquad K = K_{NH_4^+}/K_{HOAc}$

$$\frac{[NH_3][HOAc]}{[NH_4^+][OAc^-]} = \frac{5.70 \times 10^{-10}}{1.75 \times 10^{-5}} = 3.26 \times 10^{-5}$$



	A	B	C	D	E	F	G	H	I	J	K
1	**Pb15-34**										
2	**Part/Acid**	**pH**	**$[H_3O^+]$**	**K_{a1}**	**K_{a2}**	**K_{a3}**	**α_0**	**α_1**	**α_2**	**α_3**	**Alpha sum**
3	(a)	2.00	1.00E-02	1.12E-03	3.91E-06		0.899	0.101	3.94E-05		1.0000000
4	phthallic	6.00	1.00E-06				1.82E-04	0.204	7.96E-01		1.0000000
5		10.00	1.00E-10				2.28E-12	2.56E-05	1.00E+00		1.0000000
6	(b)	2.00	1.00E-02	7.11E-03	6.32E-08	4.50E-13	0.584	0.416	2.63E-06	1.18E-16	1.0000000
7	phosphoric	6.00	1.00E-06				1.32E-04	0.940	5.94E-02	2.67E-08	1.0000000
8		10.00	1.00E-10				2.21E-11	1.57E-03	9.94E-01	4.47E-03	1.0000000
9	(c)	2.00	1.00E-02	7.45E-04	1.73E-05	4.02E-07	0.931	6.93E-02	1.20E-04	4.82E-09	1.0000000
10	citric	6.00	1.00E-06				5.31E-05	3.96E-02	6.85E-01	2.75E-01	1.0000000
11		10.00	1.00E-10				1.93E-16	1.44E-09	2.49E-04	1.000	1.0000000
12	(d)	2.00	1.00E-02	5.80E-03	1.10E-07	3.20E-12	0.633	0.367	4.04E-06	1.29E-15	1.0000000
13	aresenic	6.00	1.00E-06				1.55E-04	0.901	9.91E-02	3.17E-07	1.0000000
14		10.00	1.00E-10				1.52E-11	8.80E-04	9.68E-01	3.10E-02	1.0000000
15	(e)	2.00	1.00E-02	3.0E-02	1.62E-07		0.250	0.750	1.21E-05		1.0000000
16	phosphorous	6.00	1.00E-06				2.87E-05	0.861	1.39E-01		1.0000000
17		10.00	1.00E-10				2.06E-12	6.17E-04	0.999		1.0000000
18	(f)	2.00	1.00E-02	5.60E-02	5.42E-05		0.151	0.845	4.58E-03		1.0000000
19	oxalic	6.00	1.00E-06				3.23E-07	0.018	9.82E-01		1.0000000
20		10.00	1.00E-10				3.29E-15	1.85E-06	1.000		1.0000000
21											
22	**Spreadsheet Documentation**										
23	Cell C3=10^(-B3)										
24	Cell G3=$C3^2/($C3^2+$D$3*$C3+$D$3*$E$3)										
25	Cell H3=$C3*$D$3/($C3^2+$D$3*$C3+$D$3*$E$3)										
26	Cell I3=$D$3*$E$3/($C3^2+$D$3*$C3+$D$3*$E$3)										
27	Cell K3=SUM(G3:J3)										
28	Cell G6=$C6^3/($C6^3+$D$6*$C6^2+$D$6*$E$6*$C6+$D$6*$E$6*$F$6)										
29	Cell H6=$D$6*$C6^2/($C6^3+$D$6*$C6^2+$D$6*$E$6*$C6+$D$6*$E$6*$F$6)										
30	Cell I6=$D$6*$E$6*$C6/($C6^3+$D$6*$C6^2+$D$6*$E$6*$C6+$D$6*$E$6*$F$6)										
31	Cell J6=$D$6*$E$6*$F$6/($C6^3+$D$6*$C6^2+$D$6*$E$6*$C6+$D$6*$E$6*$F$6)										

15-35. Let H_3A =H_3AsO_4. We can then write

$$K_{a1} = \frac{[H_3O^+][H_2A^-]}{[H_3A]} \quad (1) \qquad K_{a2} = \frac{[H_3O^+][HA^{2-}]}{[H_2A^-]} \qquad K_{a3} = \frac{[H_3O^+][A^{3-}]}{[HA^-]}$$

$$K_{a1}K_{a2} = \frac{[H_3O^+]^2[HA^{2-}]}{[H_3A]} \quad (2) \qquad K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[A^{3-}]}{[H_3A]} \quad (3)$$

By definition

$$\alpha_0 = \frac{[H_3A]}{c_T} \qquad \alpha_1 = \frac{[H_2A^-]}{c_T} \qquad \alpha_2 = \frac{[HA^{2-}]}{c_T} \qquad \alpha_3 = \frac{[A^{3-}]}{c_T}$$

where $c_T = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}]$ (4)

Substituting Equations (1), (2), and (3) into (4) yields

$$c_T = [H_3A] + \frac{K_{a1}[H_3A]}{[H_3O^+]} + \frac{K_{a1}K_{a2}[H_3A]}{[H_3O^+]^2} + \frac{K_{a1}K_{a2}K_{a3}[H_3A]}{[H_3O^+]^3}$$

$$\frac{c_T}{[H_3A]} = 1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H_3O^+]^3}$$

Multiplying the numerator and denominator of the right side of this equation by $[H_3O^+]^3$ gives

$$\frac{c_T}{[H_3A]} = \frac{[H_3O^+]^3 + K_{a1}[H_3O^+]^2 + K_{a1}K_{a2}[H_3O^+] + K_{a1}K_{a2}K_{a3}}{[H_3O^+]^3}$$

Letting $D = [H_3O^+]^3 + K_{a1}[H_3O^+]^2 + K_{a1}K_{a2}[H_3O^+] + K_{a1}K_{a2}K_{a3}$ (5)

Gives

$$\frac{c_T}{[H_3A]} = \frac{D}{[H_3O^+]^3}$$

$$\frac{[H_3A]}{c_T} = \frac{[H_3O^+]^3}{D} = \alpha_0 \qquad (6)$$

Substitutation Equation (1) into (6) gives

$$\frac{[H_3O^+][H_2A^-]}{K_{a1}c_T} = \frac{[H_3O^+]^3}{D}$$

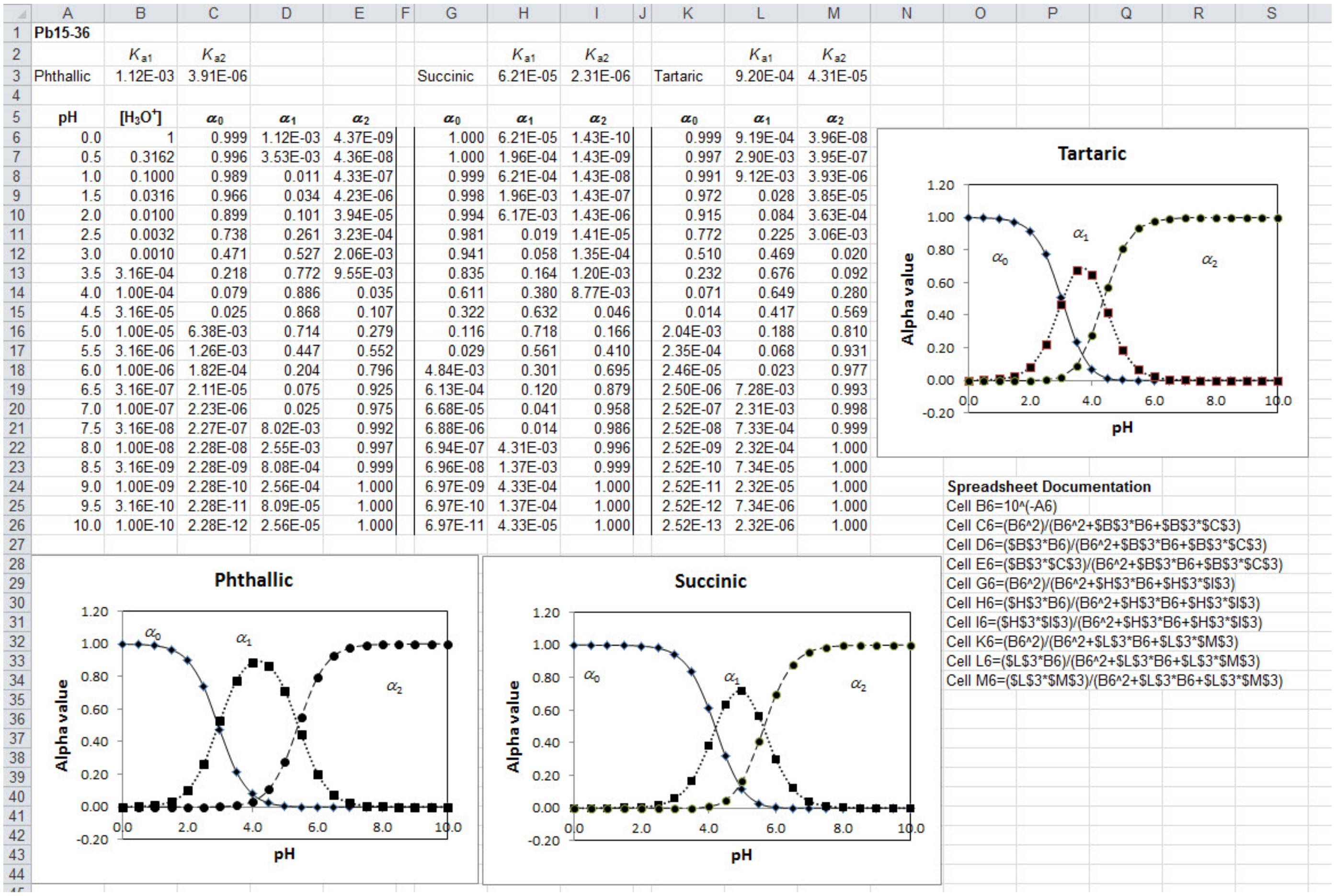
$$\frac{[H_2A^-]}{c_T} = \frac{K_{a2}[H_3O^+]^2}{D} = \alpha_1$$

In the same way, substituting Equation (2) into (6) gives after rearrangement

$$\frac{[HA^{2-}]}{c_T} = \frac{K_{a1}K_{a2}[H_3O^+]}{D} = \alpha_2$$

Likewise, substituting Equation (3) into (6) yields

$$\frac{[A^{3-}]}{c_T} = \frac{K_{a1}K_{a2}K_{a3}}{D} = \alpha_3$$

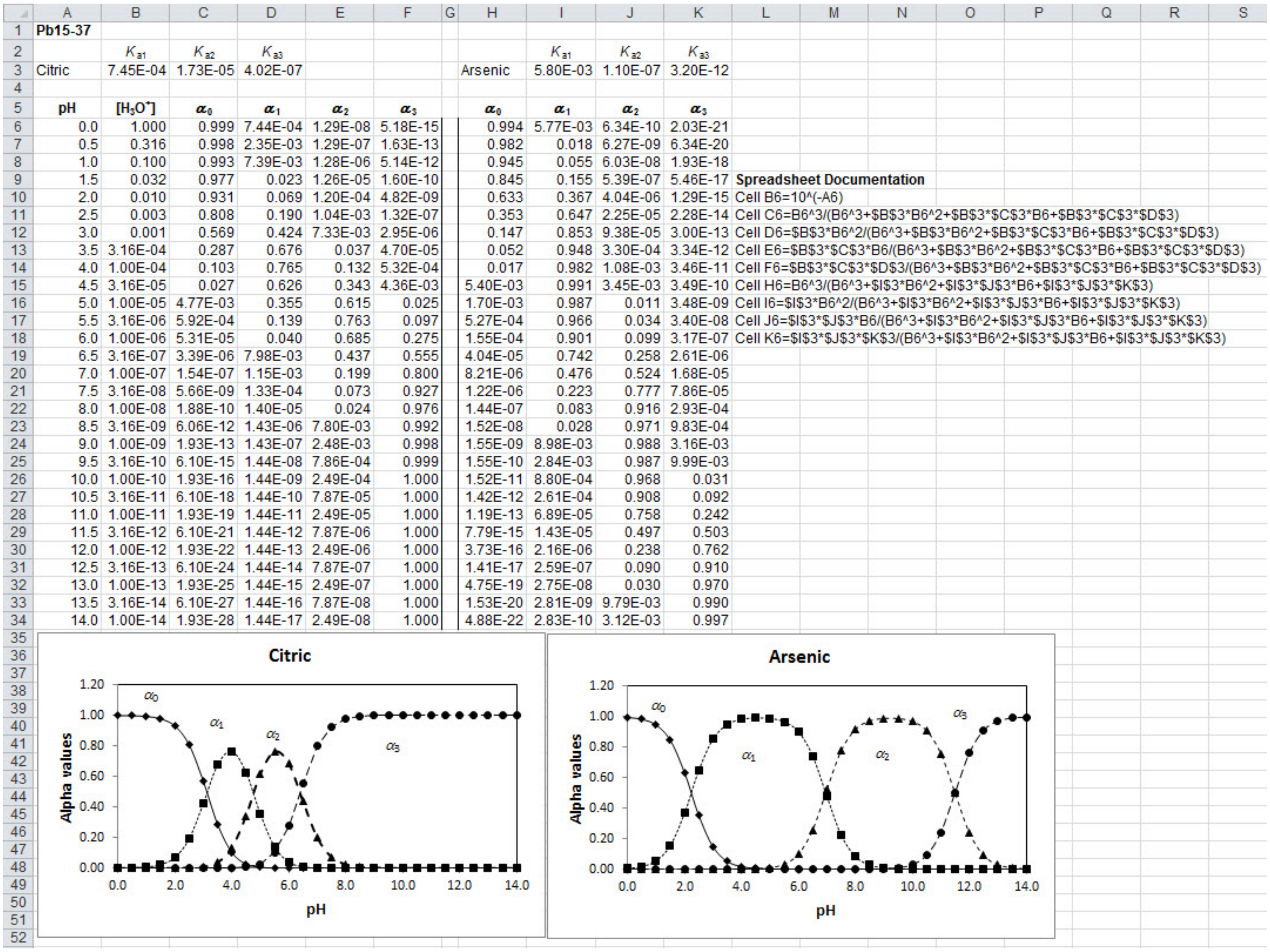


	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Pb15-36**												
2		K_{a1}	K_{a2}					K_{a1}	K_{a2}			K_{a1}	K_{a2}
3	Phthallic	1.12E-03	3.91E-06				Succinic	6.21E-05	2.31E-06		Tartaric	9.20E-04	4.31E-05
4													
5	**pH**	**$[H_3O^+]$**	**α_0**	**α_1**	**α_2**		**α_0**	**α_1**	**α_2**		**α_0**	**α_1**	**α_2**
6	0.0	1	0.999	1.12E-03	4.37E-09		1.000	6.21E-05	1.43E-10		0.999	9.19E-04	3.96E-08
7	0.5	0.3162	0.996	3.53E-03	4.36E-08		1.000	1.96E-04	1.43E-09		0.997	2.90E-03	3.95E-07
8	1.0	0.1000	0.989	0.011	4.33E-07		0.999	6.21E-04	1.43E-08		0.991	9.12E-03	3.93E-06
9	1.5	0.0316	0.966	0.034	4.23E-06		0.998	1.96E-03	1.43E-07		0.972	0.028	3.85E-05
10	2.0	0.0100	0.899	0.101	3.94E-05		0.994	6.17E-03	1.43E-06		0.915	0.084	3.63E-04
11	2.5	0.0032	0.738	0.261	3.23E-04		0.981	0.019	1.41E-05		0.772	0.225	3.06E-03
12	3.0	0.0010	0.471	0.527	2.06E-03		0.941	0.058	1.35E-04		0.510	0.469	0.020
13	3.5	3.16E-04	0.218	0.772	9.55E-03		0.835	0.164	1.20E-03		0.232	0.676	0.092
14	4.0	1.00E-04	0.079	0.886	0.035		0.611	0.380	8.77E-03		0.071	0.649	0.280
15	4.5	3.16E-05	0.025	0.868	0.107		0.322	0.632	0.046		0.014	0.417	0.569
16	5.0	1.00E-05	6.38E-03	0.714	0.279		0.116	0.718	0.166		2.04E-03	0.188	0.810
17	5.5	3.16E-06	1.26E-03	0.447	0.552		0.029	0.561	0.410		2.35E-04	0.068	0.931
18	6.0	1.00E-06	1.82E-04	0.204	0.796		4.84E-03	0.301	0.695		2.46E-05	0.023	0.977
19	6.5	3.16E-07	2.11E-05	0.075	0.925		6.13E-04	0.120	0.879		2.50E-06	7.28E-03	0.993
20	7.0	1.00E-07	2.23E-06	0.025	0.975		6.68E-05	0.041	0.958		2.52E-07	2.31E-03	0.998
21	7.5	3.16E-08	2.27E-07	8.02E-03	0.992		6.88E-06	0.014	0.986		2.52E-08	7.33E-04	0.999
22	8.0	1.00E-08	2.28E-08	2.55E-03	0.997		6.94E-07	4.31E-03	0.996		2.52E-09	2.32E-04	1.000
23	8.5	3.16E-09	2.28E-09	8.08E-04	0.999		6.96E-08	1.37E-03	0.999		2.52E-10	7.34E-05	1.000
24	9.0	1.00E-09	2.28E-10	2.56E-04	1.000		6.97E-09	4.33E-04	1.000		2.52E-11	2.32E-05	1.000
25	9.5	3.16E-10	2.28E-11	8.09E-05	1.000		6.97E-10	1.37E-04	1.000		2.52E-12	7.34E-06	1.000
26	10.0	1.00E-10	2.28E-12	2.56E-05	1.000		6.97E-11	4.33E-05	1.000		2.52E-13	2.32E-06	1.000

Spreadsheet Documentation

Cell B6=10^(-A6)
Cell C6=(B6^2)/(B6^2+$B$3*B6+$B$3*$C$3)
Cell D6=($B$3*B6)/(B6^2+$B$3*B6+$B$3*$C$3)
Cell E6=($B$3*$C$3)/(B6^2+$B$3*B6+$B$3*$C$3)
Cell G6=(B6^2)/(B6^2+$H$3*B6+$H$3*$I$3)
Cell H6=($H$3*B6)/(B6^2+$H$3*B6+$H$3*$I$3)
Cell I6=($H$3*$I$3)/(B6^2+$H$3*B6+$H$3*$I$3)
Cell K6=(B6^2)/(B6^2+$L$3*B6+$L$3*$M$3)
Cell L6=($L$3*B6)/(B6^2+$L$3*B6+$L$3*$M$3)
Cell M6=($L$3*$M$3)/(B6^2+$L$3*B6+$L$3*$M$3)

15-37.



	A	B	C	D	E	F	G	H	I	J	K	L
1	**Pb15-37**											
2		K_{a1}	K_{a2}	K_{a3}					K_{a1}	K_{a2}	K_{a3}	
3	Citric	7.45E-04	1.73E-05	4.02E-07				Arsenic	5.80E-03	1.10E-07	3.20E-12	
4												
5	**pH**	**[H$_3$O$^+$]**	**α_0**	**α_1**	**α_2**	**α_3**		**α_0**	**α_1**	**α_2**	**α_3**	
6	0.0	1.000	0.999	7.44E-04	1.29E-08	5.18E-15		0.994	5.77E-03	6.34E-10	2.03E-21	
7	0.5	0.316	0.998	2.35E-03	1.29E-07	1.63E-13		0.982	0.018	6.27E-09	6.34E-20	
8	1.0	0.100	0.993	7.39E-03	1.28E-06	5.14E-12		0.945	0.055	6.03E-08	1.93E-18	
9	1.5	0.032	0.977	0.023	1.26E-05	1.60E-10		0.845	0.155	5.39E-07	5.46E-17	**Spreadsheet Documentation**
10	2.0	0.010	0.931	0.069	1.20E-04	4.82E-09		0.633	0.367	4.04E-06	1.29E-15	Cell B6=10^(-A6)
11	2.5	0.003	0.808	0.190	1.04E-03	1.32E-07		0.353	0.647	2.25E-05	2.28E-14	Cell C6=B6^3/(B6^3+$B$3*B6^2+$B$3*$C$3*B6+$B$3*$C$3*$D$3)
12	3.0	0.001	0.569	0.424	7.33E-03	2.95E-06		0.147	0.853	9.38E-05	3.00E-13	Cell D6=$B$3*B6^2/(B6^3+$B$3*B6^2+$B$3*$C$3*B6+$B$3*$C$3*$D$3)
13	3.5	3.16E-04	0.287	0.676	0.037	4.70E-05		0.052	0.948	3.30E-04	3.34E-12	Cell E6=$B$3*$C$3*B6/(B6^3+$B$3*B6^2+$B$3*$C$3*B6+$B$3*$C$3*$D$3)
14	4.0	1.00E-04	0.103	0.765	0.132	5.32E-04		0.017	0.982	1.08E-03	3.46E-11	Cell F6=$B$3*$C$3*$D$3/(B6^3+$B$3*B6^2+$B$3*$C$3*B6+$B$3*$C$3*$D$3)
15	4.5	3.16E-05	0.027	0.626	0.343	4.36E-03		5.40E-03	0.991	3.45E-03	3.49E-10	Cell H6=B6^3/(B6^3+$I$3*B6^2+$I$3*$J$3*B6+$I$3*$J$3*$K$3)
16	5.0	1.00E-05	4.77E-03	0.355	0.615	0.025		1.70E-03	0.987	0.011	3.48E-09	Cell I6=$I$3*B6^2/(B6^3+$I$3*B6^2+$I$3*$J$3*B6+$I$3*$J$3*$K$3)
17	5.5	3.16E-06	5.92E-04	0.139	0.763	0.097		5.27E-04	0.966	0.034	3.40E-08	Cell J6=$I$3*$J$3*B6/(B6^3+$I$3*B6^2+$I$3*$J$3*B6+$I$3*$J$3*$K$3)
18	6.0	1.00E-06	5.31E-05	0.040	0.685	0.275		1.55E-04	0.901	0.099	3.17E-07	Cell K6=$I$3*$J$3*$K$3/(B6^3+$I$3*B6^2+$I$3*$J$3*B6+$I$3*$J$3*$K$3)
19	6.5	3.16E-07	3.39E-06	7.98E-03	0.437	0.555		4.04E-05	0.742	0.258	2.61E-06	
20	7.0	1.00E-07	1.54E-07	1.15E-03	0.199	0.800		8.21E-06	0.476	0.524	1.68E-05	
21	7.5	3.16E-08	5.66E-09	1.33E-04	0.073	0.927		1.22E-06	0.223	0.777	7.86E-05	
22	8.0	1.00E-08	1.88E-10	1.40E-05	0.024	0.976		1.44E-07	0.083	0.916	2.93E-04	
23	8.5	3.16E-09	6.06E-12	1.43E-06	7.80E-03	0.992		1.52E-08	0.028	0.971	9.83E-04	
24	9.0	1.00E-09	1.93E-13	1.43E-07	2.48E-03	0.998		1.55E-09	8.98E-03	0.988	3.16E-03	
25	9.5	3.16E-10	6.10E-15	1.44E-08	7.86E-04	0.999		1.55E-10	2.84E-03	0.987	9.99E-03	
26	10.0	1.00E-10	1.93E-16	1.44E-09	2.49E-04	1.000		1.52E-11	8.80E-04	0.968	0.031	
27	10.5	3.16E-11	6.10E-18	1.44E-10	7.87E-05	1.000		1.42E-12	2.61E-04	0.908	0.092	
28	11.0	1.00E-11	1.93E-19	1.44E-11	2.49E-05	1.000		1.19E-13	6.89E-05	0.758	0.242	
29	11.5	3.16E-12	6.10E-21	1.44E-12	7.87E-06	1.000		7.79E-15	1.43E-05	0.497	0.503	
30	12.0	1.00E-12	1.93E-22	1.44E-13	2.49E-06	1.000		3.73E-16	2.16E-06	0.238	0.762	
31	12.5	3.16E-13	6.10E-24	1.44E-14	7.87E-07	1.000		1.41E-17	2.59E-07	0.090	0.910	
32	13.0	1.00E-13	1.93E-25	1.44E-15	2.49E-07	1.000		4.75E-19	2.75E-08	0.030	0.970	
33	13.5	3.16E-14	6.10E-27	1.44E-16	7.87E-08	1.000		1.53E-20	2.81E-09	9.79E-03	0.990	
34	14.0	1.00E-14	1.93E-28	1.44E-17	2.49E-08	1.000		4.88E-22	2.83E-10	3.12E-03	0.997	

Chapter 16

16-1. Nitric acid is seldom used as a standard because it is an oxidizing agent and thus will react with reducible species in titration mixtures.

16-2. Primary standard Na_2CO_3 can be obtained by heating primary standard grade $NaHCO_3$ for about an hour at 270°C to 300°C. The reaction is

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

16-3. Carbon dioxide is not strongly bonded by water molecules, and thus is readily volatilized from aqueous solution by briefly boiling. On the other hand, HCl molecules are fully dissociated into H_3O^+ and Cl^- when dissolved in water. Neither the H_3O^+ nor the Cl^- species is volatile.

16-4. Near the equivalence point in the titration of Na_2CO_3, the solution contains a buffer made up of a high concentration of H_2CO_3 and a small amount of Na_2CO_3. Boiling removes the H_2CO_3 as CO_2, which causes the pH of the solution to rise sharply (see Figure 16-1). Then the change in pH, when titration is resumed, is much greater than it would otherwise be. Thus, a sharper end point results.

16-5. Let us consider the standardization of 40 mL of 0.010 M NaOH using $KH(IO_3)_2$,

$$\frac{0.010\text{ mmol NaOH}}{\text{mL}} \times 40\text{ mL NaOH} \times \frac{1\text{ mmol KH(IO}_3)_2}{1\text{ mmol NaOH}} \times \frac{390\text{ g KH(IO}_3)_2}{1000\text{ mmol}} = 0.16\text{ g KH(IO}_3)_2$$

Now using benzoic acid,

$$\frac{0.010\text{ mmol NaOH}}{\text{mL}} \times 40\text{ mL NaOH} \times \frac{1\text{ mmol C}_6\text{H}_5\text{COOH}}{1\text{ mmol NaOH}} \times$$

$$\frac{122\text{ g C}_6\text{H}_5\text{COOH}}{1000\text{ mmol}} = 0.049\text{ g C}_6\text{H}_5\text{COOH}$$

The primary standard $KH(IO_3)_2$ is preferable because the relative mass measurement error would be less with a 0.16 g sample of $KH(IO_3)_2$ as opposed to 0.049 g sample of benzoic acid. A second reason for preferring $KH(IO_3)_2$ is because it is a strong acid and benzoic acid is not. A smaller titration error occurs when using a strong acid as a primary standard and the choice of indicator is not critical.

16-6. Unless a reducing agent is introduced into the H_2SO_4 prior to digestion, nitro-, azo- and azoxy- groups will be partially converted to N_2 or nitrogen oxides that are then lost by volatilization. Heterocyclic compounds containing nitrogen also yield low results in many instances because these compounds tend to be incompletely decomposed under the usual digestion procedure.

16-7. If the sodium hydroxide solution is to be used for titrations with an acid-range indicator, the carbonate in the base solution will consume two analyte hydronium ions just as would the two hydroxides lost in the formation of Na_2CO_3.

16-8. **(a)**

$$\frac{0.200 \text{ mmol } H_2SO_4}{\text{mL}} \times 500.0 \text{ mL} \times \frac{98.08 \text{ g } H_2SO_4}{1000 \text{ mmol}} \times \frac{\text{mL reagent}}{1.1539 \text{ g reagent}} \times \frac{100 \text{ g reagent}}{21.8 \text{ g } H_2SO_4}$$
$$= 39.0 \text{ mL reagent}$$

Dilute 39.0 mL reagent to 500.0 mL total volume.

(b)

$$\frac{0.250 \text{ mmol NaOH}}{\text{mL}} \times 500.0 \text{ mL} \times \frac{39.997 \text{ g NaOH}}{1000 \text{ mmol}} = 5.0 \text{ g NaOH}$$

Dissolve 5.0 g NaOH in water and dilute to 500.0 mL total volume

(c)

$$\frac{0.07500 \text{ mmol } Na_2CO_3}{\text{mL}} \times 500.0 \text{ mL} \times \frac{105.989 \text{ g } Na_2CO_3}{1000 \text{ mmol}} = 3.97 \text{ g } Na_2CO_3$$

Dissolve 3.97 g Na_2CO_3 in water and dilute to 500.0 mL total volume.

16-9. **(a)**

$$\frac{0.10\text{ mole KOH}}{\text{L}} \times 2.00\text{ L} \times \frac{56.106\text{ g KOH}}{\text{mole}} = 11\text{ g KOH}$$

Dissolve 11 g KOH in water and dilute to 2.00 L total volume.

(b)

$$\frac{0.010\text{ mole Ba(OH)}_2\cdot 8\text{H}_2\text{O}}{\text{L}} \times 2.00\text{ L} \times \frac{315.46\text{ g Ba(OH)}_2\cdot 8\text{H}_2\text{O}}{\text{mole}} = 6.3\text{ g Ba(OH)}_2\cdot 8\text{H}_2\text{O}$$

Dissolve 6.3 g $Ba(OH)_2\cdot 8H_2O$ in water and dilute to 2.00 L total volume.

(c)

$$\frac{0.150\text{ mole HCl}}{\text{L}} \times 2.00\text{ L} \times \frac{36.461\text{ g HCl}}{\text{mole}} \times \frac{\text{mL reagent}}{1.0579\text{ g reagent}} \times \frac{100\text{ g reagent}}{11.50\text{ g HCl}} = 90\ \text{ mL reagent}$$

Dilute 90 mL reagent to 2.00 L total volume.

16-10. For the first data set

$$c_{\text{sample 1}} = \frac{0.7987\text{ g KHP} \times \dfrac{1000\text{ mmol KHP}}{204.224\text{ g}} \times \dfrac{1\text{ mmol NaOH}}{1\text{ mmol KHP}}}{38.29\text{ mL NaOH}} = 0.10214\text{ M NaOH}$$

The results in the following table were calculated in the same way.

Sample	$c_{\text{sample i}}$, M	$c_{\text{sample i}}^2$
1	0.10214	1.0433×10^{-2}
2	0.10250	1.0506×10^{-2}
3	0.10305	1.0619×10^{-2}
4	0.10281	1.0570×10^{-2}
	$\sum c_{\text{sample i}} = 0.4105$	$\sum c_{\text{sample i}}^2 = 4.2128\times10^{-2}$

(a) $$\bar{c}_{\text{sample i}} = \frac{0.4105}{4} = 0.1026\text{ M NaOH}$$

(b)

$$s = \sqrt{\frac{(4.2128 \times 10^{-2}) - (0.4105)^2/4}{3}} = \sqrt{\frac{4.657 \times 10^{-7}}{3}} = 3.9 \times 10^{-4}$$

$$CV = \frac{3.9 \times 10^{-4}}{0.1026} \times 100\% = 0.38\%$$

(c) Spread, $w = 0.10305 - 0.10214 = 0.00091$

16-11. For the first data set,

$$c_{\text{sample 1}} = \frac{0.2068\text{ g Na}_2\text{CO}_3 \times \dfrac{1000\text{ mmol Na}_2\text{CO}_3}{105.99\text{ g}} \times \dfrac{2\text{ mmol HClO}_4}{1\text{ mmol Na}_2\text{CO}_3}}{36.31\text{ mL HClO}_4} = 0.10747\text{ M HClO}_4$$

The results in the accompanying table were calculated in the same way.

Sample	$c_{\text{sample i}}$, M	$c_{\text{sample i}}^2$
1	0.10747	1.15499×10^{-2}
2	0.10733	1.15196×10^{-2}
3	0.10862	1.17987×10^{-2}
4	0.10742	1.15385×10^{-2}
	$\sum c_{\text{sample i}} = 0.43084$	$\sum c_{\text{sample i}}^2 = 4.64069 \times 10^{-2}$

(a) $\bar{c}_{\text{sample i}} = \dfrac{0.43084}{4} = 0.1077\text{ M HClO}_4$

(b)

$$s = \sqrt{\frac{(4.64069 \times 10^{-2}) - (0.43084)^2/4}{3}} = \sqrt{\frac{1.11420 \times 10^{-6}}{3}} = 6.1 \times 10^{-4}$$

$$CV = \frac{6.1 \times 10^{-4}}{0.1077} \times 100\% = 0.57\%$$

(c)

$$Q = \frac{0.10862 - 0.10747}{0.10862 - 0.10733} = 0.89$$

$Q_{crit} = 0.829$ at the 95% confidence level

$Q_{crit} = 0.926$ at the 99% confidence level

Thus, 0.10862 could be rejected at 95% level but must be retained at 99% level.

16-12. **(a)** With phenolphthalein, the CO_3^{2-} consumes 1 mmol H_3O^+ per mmol CO_2. Thus, the effective amount of NaOH is lowered by 11.2 mmol, and

$$c_{\text{base}} = \frac{\left(\dfrac{0.1500\text{ mmol NaOH}}{\text{mL}} \times 1000\text{ mL}\right) - \left(11.2\text{ mmol CO}_2 \times \dfrac{1\text{ mmol NaOH}}{1\text{ mmol CO}_2}\right)}{1000\text{ mL}}$$

$=0.1388$ M NaOH

(b) When bromocresol green is the indicator,

$$CO_3^{2-} + 2H_3O^+ \rightarrow H_2CO_3 + 2H_2O$$

and the effective concentration of the base is unchanged. Thus,

$c_{\text{base}} = 0.1500$ M

16-13. As in part (a) of problem 16-23,

$$c_{\text{base}} = \frac{\left(\dfrac{0.1019\text{ mmol NaOH}}{\text{mL}} \times 500\text{ mL}\right) - \left(0.652\text{ g CO}_2 \times \dfrac{1000\text{ mmol CO}_2}{44.01\text{ g}} \times \dfrac{1\text{ mmol NaOH}}{1\text{ mmol CO}_2}\right)}{500\text{ mL}}$$

$= 0.07227$ M NaOH

$$\text{relative carbonate error} = \frac{0.07227 - 0.1019}{0.1019} \times 100\% = -29\%$$

16-14. (a)

$$\frac{0.5902\text{ g AgCl}\times\dfrac{1000\text{ mmol AgCl}}{143.32\text{ g}}\times\dfrac{1\text{ mmol HCl}}{1\text{ mmol AgCl}}}{50.00\text{ mL HCl}}=0.08236\text{ M HCl}$$

(b)

$$\frac{\dfrac{0.03970\text{ mmol Ba(OH)}_2}{\text{mL}}\times 25.00\text{ mL Ba(OH)}_2\times\dfrac{2\text{ mmol HCl}}{1\text{ mmol Ba(OH)}_2}}{17.93\text{ mL HCl}}=0.1107\text{ M HCl}$$

(c)

$$\frac{0.2459\text{ g Na}_2\text{CO}_3\times\dfrac{1000\text{ mmol Na}_2\text{CO}_3}{105.99\text{ g}}\times\dfrac{2\text{ mmol HCl}}{1\text{ mmol Na}_2\text{CO}_3}}{36.52\text{ mL HCl}}=0.1271\text{ M HCl}$$

16-15. (a)

$$\frac{0.1791\text{ g BaSO}_4\times\dfrac{1000\text{ mmol BaSO}_4}{233.39\text{ g}}\times\dfrac{1\text{ mmol Ba(OH)}_2}{1\text{ mmol BaSO}_4}}{50.00\text{ mL Ba(OH)}_2}=0.01535\text{ M Ba(OH)}_2$$

(b)

$$\frac{0.4512\text{ g KHP}\times\dfrac{1000\text{ mmol KHP}}{204.224\text{ g}}\times\dfrac{1\text{ mmol Ba(OH)}_2}{2\text{ mmol KHP}}}{26.46\text{ mL Ba(OH)}_2}=0.04175\text{ M Ba(OH)}_2$$

(c)

$$\text{amnt C}_6\text{H}_5\text{COOH}=0.3912\text{ g C}_6\text{H}_5\text{COOH}\times\frac{1000\text{ mmol C}_6\text{H}_5\text{COOH}}{122.123\text{ g}}=3.2033\text{ mmol}$$

$$\text{amnt HCl}=\frac{0.05317\text{ mmol HCl}}{\text{mL}}\times 4.67\text{ mL HCl}=0.2483\text{ mmol}$$

total amnt acid = 3.2034 + 0.2483 = 3.4516 mmol

$$\frac{3.4516\text{ mmol acid} \times \dfrac{1\text{ mmol Ba(OH)}_2}{2\text{ mmol acid}}}{50.00\text{ mL Ba(OH)}_2} = 0.03452\text{ M Ba(OH)}_2$$

16-16. (a) For 35 mL,

$$\frac{0.175\text{ mmol HClO}_4}{\text{mL}} \times 35\text{ mL HClO}_4 \times \frac{1\text{ mmol Na}_2\text{CO}_3}{2\text{ mmol HClO}_4} \times \frac{105.989\text{ g Na}_2\text{CO}_3}{1000\text{ mmol}} = 0.32\text{ g Na}_2\text{CO}_3$$

Substituting 45 mL in the equation above gives 0.42 g Na_2CO_3.

Proceeding as in part (a), we obtain

(b) 0.20 to 0.26 g $Na_2C_2O_4$

(c) 0.64 to 0.82 g benzoic acid

(d) 1.36 to 1.75 g $KH(IO_3)_2$

(e) 0.32 to 0.41 g TRIS

(f) 0.67 to 0.86 g $Na_2B_4O_7 \cdot 10H_2O$

16-17. In Example 16-1, we found that 20.00 mL of 0.0200 M HCl requires 0.048 g TRIS, 0.021 g Na_2CO_3 and 0.08 g $Na_2B_4O_7 \cdot 10H_2O$. In each case, the absolute standard deviation in computed molar concentration of 0.0200 M HCl is

TRIS: $s_c = \dfrac{0.0001}{0.048} \times 0.0200\text{ M} = 4 \times 10^{-5}\text{ M}$

Na_2CO_3: $s_c = \dfrac{0.0001}{0.021} \times 0.0200\text{ M} = 1 \times 10^{-4}\text{ M}$

$Na_2B_4O_7 \cdot 10H_2O$: $s_c = \dfrac{0.0001}{0.076} \times 0.0200\text{ M} = 2.5 \times 10^{-5}\text{ M} \approx 3.0 \times 10^{-5}\text{ M}$

Proceeding as above, we calculate the relative standard deviation in the computed molar concentrations of 30.00 mL, 40.00 mL and 50.00 mL of 0.0200 M HCl and the results are shown in the table that follows.

$V_{0.0200\ \mathrm{M\ HCl}}$ (mL)	Calculated masses	s_c (0.0200 M
30.00		
TRIS	0.073	3×10^{-5}
Na_2CO_3	0.032	6×10^{-5}
$Na_2B_4O_7{\cdot}10H_2O$	0.11	2×10^{-5}
40.00		
TRIS	0.097	2×10^{-5}
Na_2CO_3	0.042	5×10^{-5}
$Na_2B_4O_7{\cdot}10H_2O$	0.15	1×10^{-5}
50.00		
TRIS	0.12	2×10^{-5}
Na_2CO_3	0.053	4×10^{-5}
$Na_2B_4O_7{\cdot}10H_2O$	0.19	1×10^{-5}

16-18. (a) In each case

$$\text{amnt NaOH} = \frac{0.0400\ \text{mmol NaOH}}{\text{mL}} \times 30.00\ \text{mL} = 1.20\ \text{mmol}$$

For KHP:

$$1.20\ \text{mmol NaOH} \times \frac{1\ \text{mmol KHP}}{1\ \text{mmol NaOH}} \times \frac{204.224\ \text{g KHP}}{1000\ \text{mmol}} = 0.245\ \text{g}$$

For $KH(IO_3)_2$:

$$1.20\ \text{mmol NaOH} \times \frac{1\ \text{mmol KH(IO}_3)_2}{1\ \text{mmol NaOH}} \times \frac{389.912\ \text{g KH(IO}_3)_2}{1000\ \text{mmol}} = 0.468\ \text{g}$$

For benzoic acid:

$$1.20\ \text{mmol C}_6\text{H}_5\text{COOH} \times \frac{1\ \text{mmol C}_6\text{H}_5\text{COOH}}{1\ \text{mmol NaOH}} \times \frac{122.123\ \text{g C}_6\text{H}_5\text{COOH}}{1000\ \text{mmol}} = 0.147\ \text{g}$$

For KHP:

$$\text{RSD} = \frac{0.002\text{ g}}{0.245\text{ g}} \times 100\% = 0.82\%$$

For $KH(IO_3)_2$:

$$\text{RSD} = \frac{0.002\text{ g}}{0.468\text{ g}} \times 100\% = 0.43\%$$

For benzoic acid:

$$\text{RSD} = \frac{0.002\text{ g}}{0.147\text{ g}} \times 100\% = 1.4\%$$

16-19.

$$\text{amnt NaOH} = \frac{0.03291\text{ mmol NaOH}}{\text{mL}} \times 24.57\text{ mL NaOH} = 0.80860\text{ mol NaOH}$$

$$\frac{\left(0.80860\text{ mol NaOH} \times \dfrac{1\text{ mmol }H_2C_4H_4O_6}{2\text{ mmol NaOH}} \times \dfrac{150.09\text{ g }H_2C_4H_4O_6}{1000\text{ mmol}}\right)}{50.00\text{ mL}} \times 100\text{ mL}$$

$$= 0.1214\text{ g }H_2C_4H_4O_6\text{ per }100\text{ mL}$$

16-20.

$$\frac{\left(\dfrac{0.08960\text{ mmol NaOH}}{\text{mL}} \times 35.23\text{ mL NaOH} \times \dfrac{1\text{ mmol HOAc}}{1\text{ mmol NaOH}} \times \dfrac{60.053\text{ g HOAc}}{1000\text{ mmol}}\right)}{\left(\dfrac{50.0\text{ mL}}{250\text{ mL}} \times 25.00\text{ mL}\right)} \times 100\%$$

$$= 3.79\%\ (w/v)\text{ HOAc}$$

16-21. For each part, we can write

$$\frac{\dfrac{0.1129\text{ mmol HCl}}{\text{mL}} \times 30.79\text{ mL HCl}}{0.7513\text{ g sample}} = 4.6269\ \frac{\text{mmol HCl}}{\text{g sample}}$$

(a)

$$4.6269\ \frac{\text{mmol HCl}}{\text{g sample}} \times \frac{1\ \text{mmol Na}_2\text{B}_4\text{O}_7}{2\ \text{mmol HCl}} \times \frac{201.222\ \text{g Na}_2\text{B}_4\text{O}_7}{1000\ \text{mmol}} \times 100\% = 46.55\%\ \text{Na}_2\text{B}_4\text{O}_7$$

Proceeding in the same way

(b)

$$4.6269\ \frac{\text{mmol HCl}}{\text{g sample}} \times \frac{1\ \text{mmol Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}}{2\ \text{mmol HCl}} \times \frac{381.372\ \text{g Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}}{1000\ \text{mmol}} \times 100\%$$
$$= 88.23\%\ \text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$$

(c)

$$4.6269\ \frac{\text{mmol HCl}}{\text{g sample}} \times \frac{1\ \text{mmol B}_2\text{O}_3}{1\ \text{mmol HCl}} \times \frac{69.620\ \text{g B}_2\text{O}_3}{1000\ \text{mmol}} \times 100\% = 32.21\%\ \text{B}_2\text{O}_3$$

(d)

$$4.6269\ \frac{\text{mmol HCl}}{\text{g sample}} \times \frac{2\ \text{mmol B}}{1\ \text{mmol HCl}} \times \frac{10.811\ \text{g B}}{1000\ \text{mmol}} \times 100\% = 10.00\%\ \text{B}$$

16-22.

$$\frac{\left(\frac{0.1092\ \text{mmol HCl}}{\text{mL}} \times 40.39\ \text{mL HCl} \times \frac{1\ \text{mmol OH}^-}{1\ \text{mmol HCl}} \times \frac{1\ \text{mmol HgO}}{2\ \text{mmol OH}^-} \times \frac{216.589\ \text{g HgO}}{1000\ \text{mmol}}\right)}{0.6915\ \text{g sample}} \times 100\%$$
$$= 69.07\%\ \text{HgO}$$

16-23.

$$\text{amnt NaOH consumed} = \left(\frac{0.0959\text{ mmol NaOH}}{\text{mL}} \times 50.0\text{ mL NaOH}\right) -$$

$$\left(\frac{0.05370\text{ mmol H}_2\text{SO}_4}{\text{mL}} \times 22.71\text{ mL H}_2\text{SO}_4 \times \frac{2\text{ mmol NaOH}}{1\text{ mmol H}_2\text{SO}_4}\right) = 2.356\text{ mmol}$$

$$\frac{2.356\text{ mmol NaOH} \times \dfrac{1\text{ mmol HCHO}}{1\text{ mmol NaOH}} \times \dfrac{30.026\text{ g HCHO}}{1000\text{ mmol}}}{0.2985\text{ g sample}} \times 100\% = 23.7\%\text{ HCHO}$$

16-24.

$$\frac{\left(\dfrac{0.0501\text{ mmol NaOH}}{\text{mL}} \times 12.91\text{ mL NaOH} \times \dfrac{1\text{ mmol NaO}_2\text{CC}_6\text{H}_5}{1\text{ mmol NaOH}} \times \dfrac{144.10\text{ g NaO}_2\text{CC}_6\text{H}_5}{1000\text{ mmol}}\right)}{97.2\text{ g sample}} \times 100\%$$

$$= 0.096\%\text{ NaO}_2\text{CC}_6\text{H}_5$$

16-25. Tetraethylthiuram disulfide, TS_4

$1\text{ mmol TS}_4 \equiv 4\text{ mmol SO}_2 \equiv 4\text{ mmol H}_2\text{SO}_4 \equiv 8\text{ mmol NaOH}$

$$\frac{\left(\dfrac{0.04216\text{ mmol NaOH}}{\text{mL}} \times 19.25\text{ mL NaOH} \times \dfrac{1\text{ mmol TS}_4}{8\text{ mmol NaOH}} \times \dfrac{296.54\text{ g TS}_4}{1000\text{ mmol}}\right)}{0.4169\text{ g sample}} \times 100\%$$

$$= 7.216\%\text{ TS}_4$$

16-26.

$$\frac{\left(\dfrac{0.1943\text{ mmol HCl}}{\text{mL}} \times 41.27\text{ mL HCl} \times \dfrac{1\text{ mmol NH}_3}{1\text{ mmol HCl}} \times \dfrac{17.031\text{ g NH}_3}{1000\text{ mmol}}\right)}{\left(\dfrac{50.00\text{ mL}}{250.0\text{ mL}} \times 25.00\text{ mL}\right)} \times 100\%$$

$$= 2.731\%\text{ (w/v) NH}_3$$

16-27.

$$\text{amnt HCl} = \text{mmol NaOH} - 2\times\text{mmol CO}_3^{2-}$$

$$\text{amnt CO}_3^{2-} = \frac{\left(\dfrac{0.1140\ \text{mmol HCl}}{\text{mL}}\times 50.00\ \text{mL HCl}\right) - \left(\dfrac{0.09802\ \text{mmol NaOH}}{\text{mL}}\times 24.21\ \text{mL NaOH}\right)}{2}$$

$$=1.6635\ \text{mmol CO}_3^{2-}$$

$$\text{molar mass carbonate salt} = \frac{0.1401\ \text{g salt}}{1.6635\ \text{mmol CO}_3^{2-}}\times\frac{1000\ \text{mmol}}{\text{mole}} = 84.22\ \frac{\text{g salt}}{\text{mole CO}_3^{2-}}$$

$$\text{molar mass of carbonate salt cation} = \left(84.22\ \frac{\text{g salt}}{\text{mole CO}_3^{2-}}\times\frac{1\ \text{mole CO}_3^{2-}}{1\ \text{mole salt}}\right) - 60.01\ \frac{\text{g CO}_3^{2-}}{\text{mole}}$$

$$= 24.21\ \frac{\text{g cation}}{\text{mole}}$$

$MgCO_3$ with a molar mass of 84.31 g/mole appears to be a likely candidate

16-28.

$$\text{amnt NaA} = \frac{0.1084\ \text{mmol NaOH}}{\text{mL}}\times 28.62\ \text{mL NaOH}\times\frac{1\ \text{mmol NaA}}{1\ \text{mmol NaOH}} = 3.1024\ \text{mmol}$$

$$\text{molar mass NaA} = \frac{0.2110\ \text{g NaA}}{3.1024\ \text{mmol NaA}}\times\frac{1000\ \text{mmol}}{\text{mole}} = 68.01\ \frac{\text{g NaA}}{\text{mole}}$$

molar mass HA = equivalent mass = molar mass NaA − atomic mass Na + atomic mass H

$$= 68.01 - 22.99 + 1.008 = 46.03\ \frac{\text{g HA}}{\text{mole}}$$

16-29.

$$\text{amnt Ba(OH)}_2 = \text{mmol CO}_2 + \frac{\text{mmol HCl}}{2}$$

$$\text{amnt CO}_2 = \left(\frac{0.0116\text{ mmol Ba(OH)}_2}{\text{mL}} \times 50.0\text{ mL Ba(OH)}_2\right) - \left(\frac{\frac{0.0108\text{ mmol HCl}}{\text{mL}} \times 23.6\text{ mL HCl}}{2}\right)$$

$$= 4.526\times10^{-1}\text{ mmol}$$

$$\frac{0.4526\text{ mmol CO}_2 \times \frac{44.01\text{ g CO}_2}{1000\text{ mmol}}}{3.00\text{ L}} \times \frac{1\text{ L CO}_2}{1.98\text{ g CO}_2} \times 10^6\text{ppm} = 3.35 \times 10^3\text{ppm CO}_2$$

16-30.

$$\frac{0.00197\text{ mmol NaOH}}{\text{mL}} \times 11.70\text{ mL NaOH} \times \frac{1\text{ mmol SO}_2}{2\text{ mmol NaOH}} \times \frac{64.06\text{ g SO}_2}{1000\text{ mmol}} = 7.383\times10^{-4}\text{ g SO}_4$$

$$7.383 \times 10^{-4}\text{ g SO}_4 \times \frac{1\text{ min}}{30.0\text{ L sample}} \times \frac{1}{10.0\text{ min}} \times \frac{1.00\text{ L SO}_2}{2.85\text{ g SO}_2} \times 10^6\text{ppm} = 0.863\text{ ppm SO}_2$$

16-31. $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3(s) + 26\text{OH}^- \rightarrow \text{HPO}_4^{2-} + 12\text{MoO}_4^{2-} + 14\text{H}_2\text{O} + 3\text{NH}_3(g)$

$$\text{amnt NaOH consumed} = \left(\frac{0.2000\text{ mmol NaOH}}{\text{mL}} \times 50.00\text{ mL NaOH}\right) - \left(\frac{0.1741\text{ mmol HCl}}{\text{mL}} \times 14.17\text{ mL HCl}\right) = 7.533\text{ mmol}$$

$$\text{amnt P} = 7.533\text{ mmol NaOH} \times \frac{1\text{ mmol (NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3}{26\text{ mmol NaOH}} \times \frac{1\text{ mmol P}}{1\text{ mmol (NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3} = 2.897\times10^{-1}\text{ mmol}$$

$$\frac{2.897 \times 10^{-1}\text{ mmol P} \times \frac{30.974\text{ g P}}{1000\text{ mmol}}}{0.1417\text{ g sample}} \times 100\% = 6.333\%\text{ P}$$

16-32. $\text{C}_6\text{H}_4(\text{COOCH}_3)_2 + 2\text{OH}^- \rightarrow \text{C}_6\text{H}_4(\text{COO})_2^{2-} + 2\text{CH}_3\text{OH}$

$$C_6H_4(COOCH_3)_2 = \text{DMP}$$

$$\text{amnt NaOH consumed} = \left(\frac{0.1215\ \text{mmol NaOH}}{\text{mL}} \times 50.00\ \text{mL NaOH}\right) -$$

$$\left(\frac{0.1644\ \text{mmol HCl}}{\text{mL}} \times 24.27\ \text{mL HCl}\right) = 2.0850\ \text{mmol}$$

$$\text{mmol DMP} = 2.0850\ \text{mmol NaOH} \times \frac{1\ \text{mmol DMP}}{2\ \text{mmol NaOH}} = 1.0425\ \text{mmol DMP}$$

$$\frac{1.0425\ \text{mmol DMP} \times \dfrac{194.19\ \text{g DMP}}{1000\ \text{mmol}}}{0.9471\ \text{g sample}} \times 100\% = 21.38\%\ \text{DMP}$$

16-33.

$$\text{Neohetramine}, C_{16}H_{21}ON_4 = RN_4$$

$$1\ \text{mmol}\ RN_4 \equiv 3\ \text{mmol}\ NH_3 \equiv 4\ \text{mmol HCl}$$

$$\frac{\dfrac{0.01477\ \text{mmol HCl}}{\text{mL}} \times 26.13\ \text{mL HCl} \times \dfrac{1\ \text{mmol}\ RN_4}{4\ \text{mmol HCl}} \times \dfrac{285.37\ \text{g}\ RN_4}{1000\ \text{mmol}}}{0.1247\ \text{g sample}} \times 100\% = 22.08\%\ RN_4$$

16-34. **(a)**

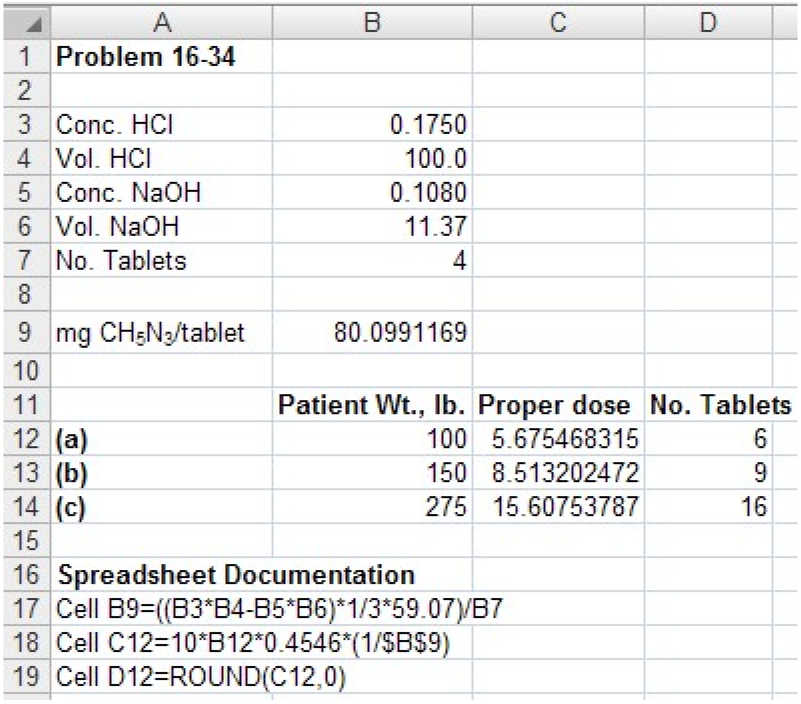
$$\text{amnt HCl consumed} = \left(\frac{0.1750\ \text{mmol HCl}}{\text{mL}} \times 100.0\ \text{mL HCl}\right) -$$

$$\left(\frac{0.1080\ \text{mmol NaOH}}{\text{mL}} \times 11.37\ \text{mL NaOH}\right) = 16.272\ \text{mmol}$$

$$\frac{16.272\ \text{mmol HCl} \times \dfrac{1\ \text{mmol}\ CH_5N_3}{3\ \text{mmol HCl}} \times \dfrac{59.07\ \text{mg}\ CH_5N_3}{\text{mmol}}}{4\ \text{tablets}} = 80.10\ \text{mg/tablet}$$

$$\text{no. tablets} = \frac{10\ \text{mg}\ CH_5N_3}{\text{kg}} \times 100\ \text{lb} \times \frac{4.536\times10^{-1}\text{kg}}{\text{lb}} \times \frac{1\ \text{tablet}}{80.10\ \text{mg}} = 5.68\ \text{or 6 tablets}$$

Proceeding in the same way as part (a), we find the results for parts (b) and (c) in the spreadsheet that follows.



	A	B	C	D
1	**Problem 16-34**			
2				
3	Conc. HCl	0.1750		
4	Vol. HCl	100.0		
5	Conc. NaOH	0.1080		
6	Vol. NaOH	11.37		
7	No. Tablets	4		
8				
9	mg CH_5N_3/tablet	80.0991169		
10				
11		**Patient Wt., lb.**	**Proper dose**	**No. Tablets**
12	**(a)**	100	5.675468315	6
13	**(b)**	150	8.513202472	9
14	**(c)**	275	15.60753787	16
15				
16	**Spreadsheet Documentation**			
17	Cell B9=((B3*B4-B5*B6)*1/3*59.07)/B7			
18	Cell C12=10*B12*0.4546*(1/$B$9)			
19	Cell D12=ROUND(C12,0)			

16-35.

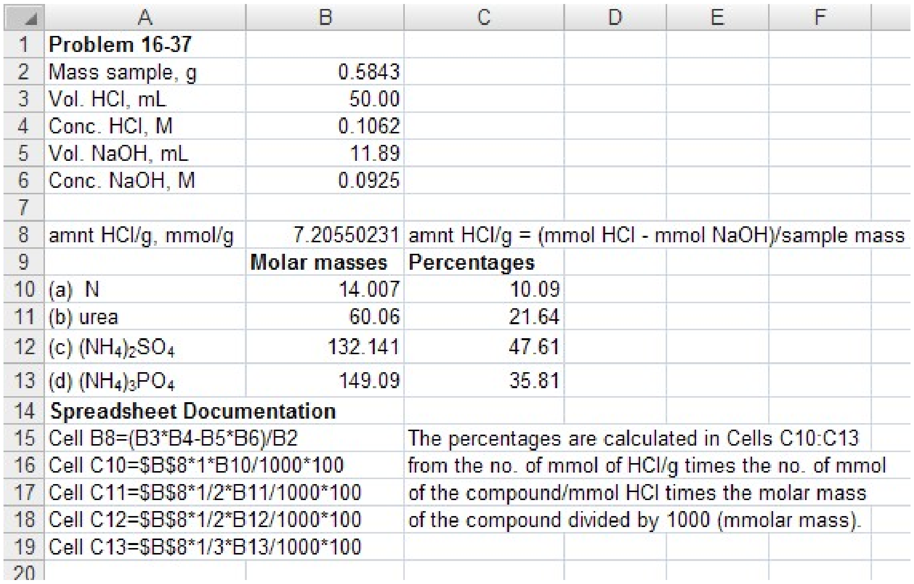
$$\%\text{N} = \frac{\left(\dfrac{0.1249\text{ mmol HCl}}{\text{mL}} \times 20.59\text{ mL HCl}\right) \times \dfrac{1\text{ mmol N}}{\text{mmol HCl}} \times \dfrac{14.007\text{ g N}}{1000\text{ mmol}}}{0.917\text{ g sample}} \times 100\% = 3.93\%\text{ N}$$

16-36. Multiplication factor for meat is 6.25 protein/N (FAC9, p. 388).

$$3.9282\ \%\text{ N} \times \frac{6.25\text{ protein}}{\text{N}} = 24.55\%\text{ protein}$$

$$\frac{6.50\text{ oz tuna}}{\text{can}} \times \frac{28.3\text{ g}}{\text{oz}} \times \frac{24.55\text{ g protein}}{100\text{ g tuna}} = 45.2\text{ g protein/can}$$

16-37.



	A	B	C	D	E	F
1	**Problem 16-37**					
2	Mass sample, g	0.5843				
3	Vol. HCl, mL	50.00				
4	Conc. HCl, M	0.1062				
5	Vol. NaOH, mL	11.89				
6	Conc. NaOH, M	0.0925				
7						
8	amnt HCl/g, mmol/g	7.20550231	amnt HCl/g = (mmol HCl - mmol NaOH)/sample mass			
9		**Molar masses**	**Percentages**			
10	(a) N	14.007	10.09			
11	(b) urea	60.06	21.64			
12	(c) $(NH_4)_2SO_4$	132.141	47.61			
13	(d) $(NH_4)_3PO_4$	149.09	35.81			
14	**Spreadsheet Documentation**					
15	Cell B8=(B3*B4-B5*B6)/B2		The percentages are calculated in Cells C10:C13			
16	Cell C10=$B$8*1*B10/1000*100		from the no. of mmol of HCl/g times the no. of mmol			
17	Cell C11=$B$8*1/2*B11/1000*100		of the compound/mmol HCl times the molar mass			
18	Cell C12=$B$8*1/2*B12/1000*100		of the compound divided by 1000 (mmolar mass).			
19	Cell C13=$B$8*1/3*B13/1000*100					
20						

16-38.

$$\text{amnt HCl consumed} = \left(\frac{0.05063\text{ mmol}}{\text{mL}} \times 50.00\text{ mL}\right) - \left(\frac{0.04829\text{ mmol}}{\text{mL}} \times 7.73\text{ mL}\right) = 2.158\text{ mmol}$$

$$\%\text{N} = \frac{2.158\text{ mmol HCl} \times \frac{1\text{ mmol N}}{1\text{ mmol HCl}} \times \frac{14.007\text{ g}}{1000\text{ mmol}}}{0.9325\text{ g}} \times 100\% = 3.242\%\text{ N}$$

protein percentage = 3.242% × 5.7 = 18.5%

16-39. In the first titration,

$$\text{amnt HCl consumed} = \left(\frac{0.08421\text{ mmol HCl}}{\text{mL}} \times 30.00\text{ mL}\right) -$$

$$\left(\frac{0.08802\text{ mmol NaOH}}{\text{mL}} \times 10.17\text{ mL}\right) = 1.63114\text{ mmol}$$

and

$$1.63114\text{ mmol HCl} = \text{mmol } NH_4NO_3 + \left(2 \times \text{mmol } (NH_4)_2SO_4\right)$$

The amounts of the two species in the original sample are

$$\text{mmol NH}_4\text{NO}_3 + \left(2 \times \text{mmol (NH}_4)_2\text{SO}_4\right) = 1.63114 \text{ mmol} \times \frac{200 \text{ mL}}{50 \text{ mL}} = 6.5246 \text{ mmol} \quad (1)$$

In the second titration,

$$\text{amnt HCl consumed} = \left(\frac{0.08421 \text{ mmol HCl}}{\text{mL}} \times 30.00 \text{ mL}\right) -$$

$$\left(\frac{0.08802 \text{ mmol NaOH}}{\text{mL}} \times 14.16 \text{ mL}\right) = 1.27994 \text{ mmol HCl}$$

and

$$1.27994 \text{ mmol HCl} = (2 \times \text{mmol NH}_4\text{NO}_3) + \left(2 \times \text{mmol (NH}_4)_2\text{SO}_4\right)$$

The amounts of the two species in the original sample are

$$(2 \times \text{mmol NH}_4\text{NO}_3) + \left(2\times\text{mmol (NH}_4)_2\text{SO}_4\right) = 1.27994 \text{ mmol} \times \frac{200 \text{ mL}}{25 \text{ mL}} = 10.2395 \text{ mmol} \quad (2)$$

Subtracting equation (1) from equation (2) gives

$$\text{amnt NH}_4\text{NO}_3 = 10.2395 \text{ mmol} - 6.52455 \text{ mmol} = 3.7149 \text{ mmol}$$

$$\text{amnt (NH}_4)_2\text{SO}_4 = \frac{10.2395 \text{ mmol} - (2 \times 3.7149 \text{ mmol})}{2} = 1.4048 \text{ mmol}$$

$$\text{percentage NH}_4\text{NO}_3 = \frac{3.7149 \text{ mmol NH}_4\text{NO}_3 \times \dfrac{80.04 \text{ g NH}_4\text{NO}_3}{1000 \text{ mmol}}}{1.219 \text{ g sample}} \times 100\% = 24.39\%$$

$$\text{percentage (NH}_4)_2\text{SO}_4 = \frac{1.4048 \text{ mmol (NH}_4)_2\text{SO}_4 \times \dfrac{132.14 \text{ g (NH}_4)_2\text{SO}_4}{1000 \text{ mmol}}}{1.219 \text{ g sample}} \times 100\%$$

$$= 15.23\%$$

16-40. For the first aliquot,

$$\text{amnt HCl consumed} = \text{mmol NaOH} + \text{mmol KOH} + (2 \times \text{mmol K}_2\text{CO}_3)$$

$$\text{mmol KOH} + (2 \times \text{mmol K}_2\text{CO}_3) = \left(\frac{0.05304\ \text{mmol HCL}}{\text{mL}} \times 40.00\ \text{mL HCl}\right) -$$

$$\left(\frac{0.04983\ \text{mmol NaOH}}{\text{mL}} \times 4.74\ \text{mL NaOH}\right) = 1.8854\ \text{mmol}$$

For the second aliquot,

$$\text{amnt HCl} = \text{mmol KOH} = \frac{0.05304\ \text{mmol HCl}}{\text{mL}} \times 28.56\ \text{mL HCl} = 1.5148\ \text{mmol HCl(KOH)}$$

$$\text{amnt K}_2\text{CO}_3 = \frac{1.8854\ \text{mmol} - 1.5148}{2} = 0.1853\ \text{mmol}$$

$$\text{percentage KOH} = \frac{1.5148\ \text{mmol KOH} \times \dfrac{56.11\ \text{g KOH}}{1000\ \text{mmol}}}{\left(1.217\ \text{g} \times \dfrac{50\ \text{mL}}{500\ \text{mL}}\right)} \times 100\% = 69.84\%$$

$$\text{percentage K}_2\text{CO}_3 = \frac{0.18530\ \text{mmol K}_2\text{CO}_3 \times \dfrac{138.21\ \text{g K}_2\text{CO}_3}{1000\ \text{mmol}}}{\left(1.217\ \text{g} \times \dfrac{50\ \text{mL}}{500\ \text{mL}}\right)} \times 100\% = 21.04\%$$

100% – (69.84% + 21.04%) = 9.12% H_2O

16-41. For the first aliquot,

$$\text{amnt HCl} = \text{mmol NaOH} + \text{mmol NaHCO}_3 + (2 \times \text{mmol Na}_2\text{CO}_3)$$

$$\text{mmol NaHCO}_3 + (2 \times \text{mmol Na}_2\text{CO}_3) = \left(\frac{0.01255\ \text{mmol HCl}}{\text{mL}} \times 50.00\ \text{mL HCl}\right) -$$

$$\left(\frac{0.01063\ \text{mmol NaOH}}{\text{mL}} \times 2.34\ \text{mL NaOH}\right) = 0.6026\ \text{mmol}$$

For the second aliquot,

$$\text{amnt NaHCO}_3 = \text{mmol NaOH} - \text{mmol HCl}$$

$$= \left(\frac{0.01063\ \text{mmol NaOH}}{\text{mL}} \times 25.00\ \text{mL NaOH}\right) - \left(\frac{0.01255\ \text{mmol HCl}}{\text{mL}} \times 7.63\ \text{mL HCl}\right)$$

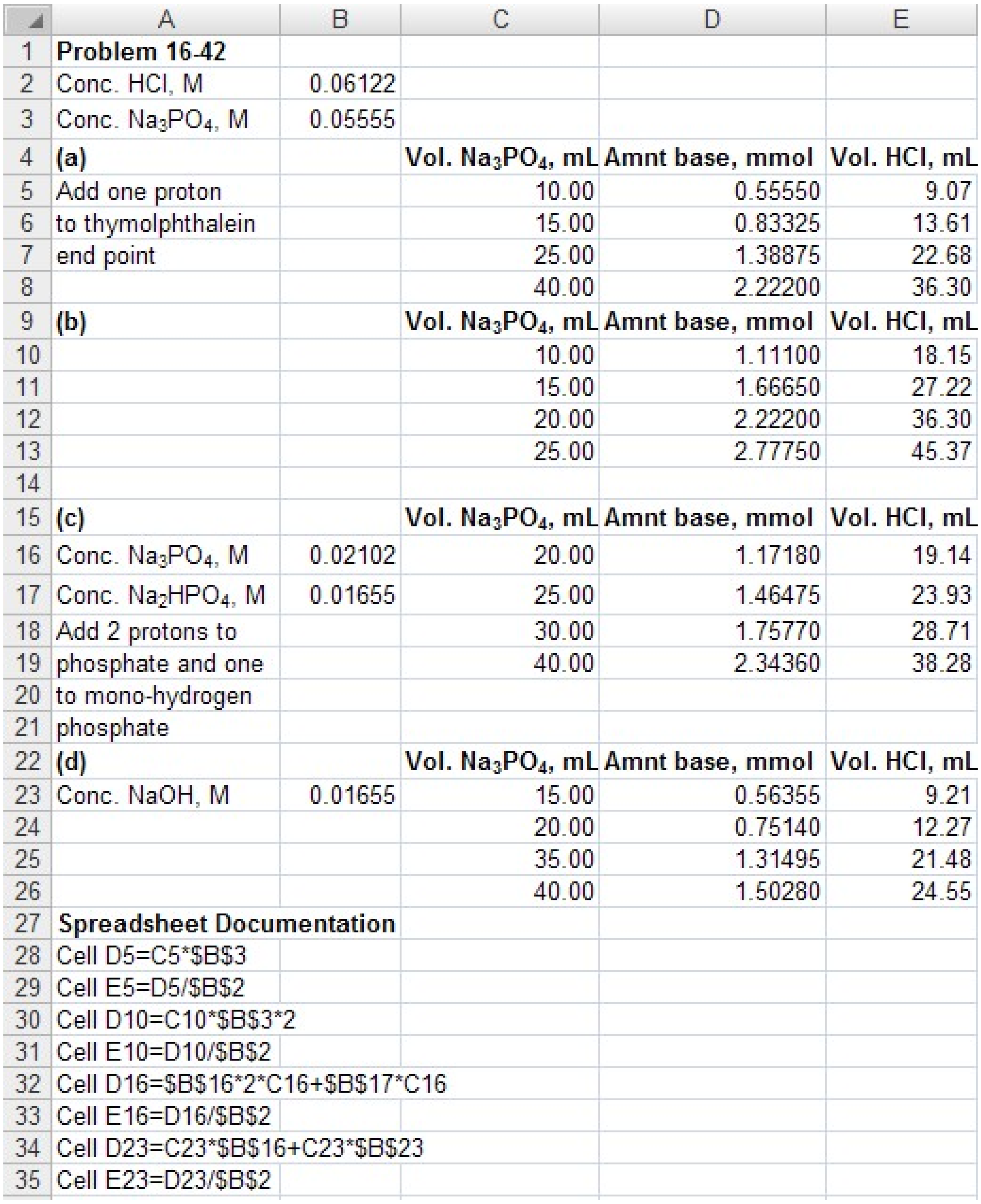
$$= 0.1700\ \text{mmol}$$

$$\text{percentage NaHCO}_3 = \frac{0.1700\ \text{mmol NaHCO}_3 \times \dfrac{84.01\ \text{g NaHCO}_3}{1000\ \text{mmol}}}{\left(0.5000\ \text{g} \times \dfrac{25.00\ \text{g}}{250.0\ \text{g}}\right)} \times 100\% = 28.56\%$$

$$\text{percentage Na}_2\text{CO}_3 = \frac{0.2163\ \text{mmol Na}_2\text{CO}_3 \times \dfrac{105.99\ \text{g Na}_2\text{CO}_3}{1000\ \text{mmol}}}{\left(0.5000\ \text{g} \times \dfrac{25.00\ \text{mL}}{250.0\ \text{mL}}\right)} \times 100\% = 45.85\%$$

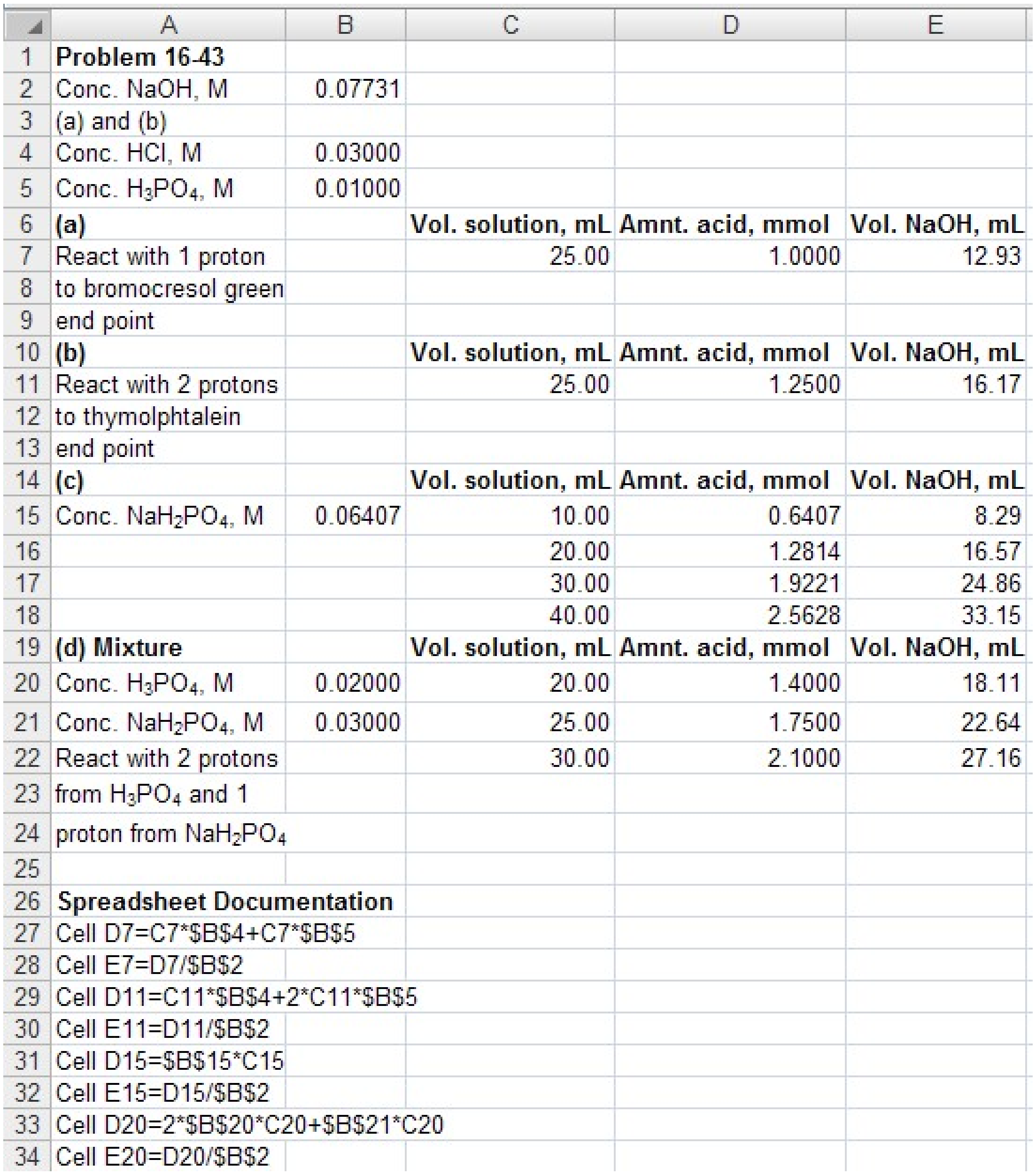
$$100\% - (28.56\% + 45.85\%) = 25.59\%\ \text{H}_2\text{O}$$

16-42.



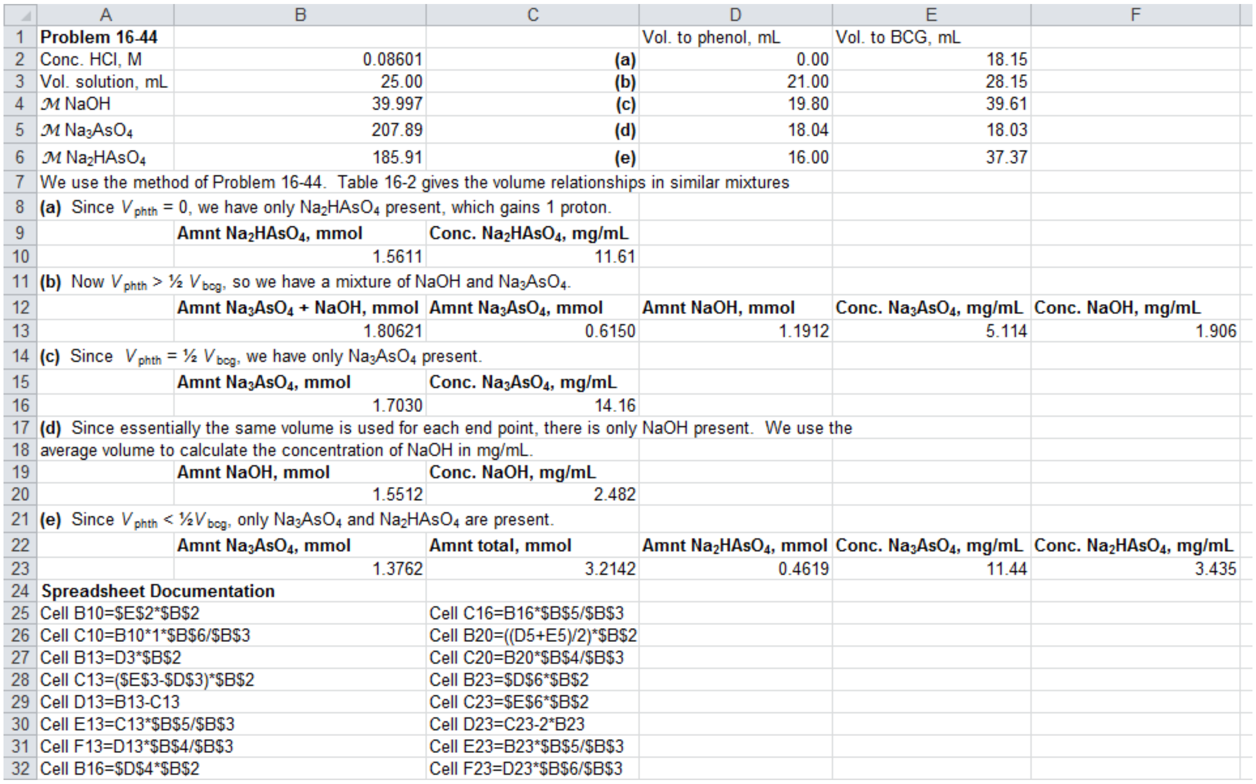
	A	B	C	D	E
1	**Problem 16-42**				
2	Conc. HCl, M	0.06122			
3	Conc. Na_3PO_4, M	0.05555			
4	**(a)**		**Vol. Na_3PO_4, mL**	**Amnt base, mmol**	**Vol. HCl, mL**
5	Add one proton		10.00	0.55550	9.07
6	to thymolphthalein		15.00	0.83325	13.61
7	end point		25.00	1.38875	22.68
8			40.00	2.22200	36.30
9	**(b)**		**Vol. Na_3PO_4, mL**	**Amnt base, mmol**	**Vol. HCl, mL**
10			10.00	1.11100	18.15
11			15.00	1.66650	27.22
12			20.00	2.22200	36.30
13			25.00	2.77750	45.37
14					
15	**(c)**		**Vol. Na_3PO_4, mL**	**Amnt base, mmol**	**Vol. HCl, mL**
16	Conc. Na_3PO_4, M	0.02102	20.00	1.17180	19.14
17	Conc. Na_2HPO_4, M	0.01655	25.00	1.46475	23.93
18	Add 2 protons to		30.00	1.75770	28.71
19	phosphate and one		40.00	2.34360	38.28
20	to mono-hydrogen				
21	phosphate				
22	**(d)**		**Vol. Na_3PO_4, mL**	**Amnt base, mmol**	**Vol. HCl, mL**
23	Conc. NaOH, M	0.01655	15.00	0.56355	9.21
24			20.00	0.75140	12.27
25			35.00	1.31495	21.48
26			40.00	1.50280	24.55
27	**Spreadsheet Documentation**				
28	Cell D5=C5*$B$3				
29	Cell E5=D5/$B$2				
30	Cell D10=C10*$B$3*2				
31	Cell E10=D10/$B$2				
32	Cell D16=$B$16*2*C16+$B$17*C16				
33	Cell E16=D16/$B$2				
34	Cell D23=C23*$B$16+C23*$B$23				
35	Cell E23=D23/$B$2				

16-43.



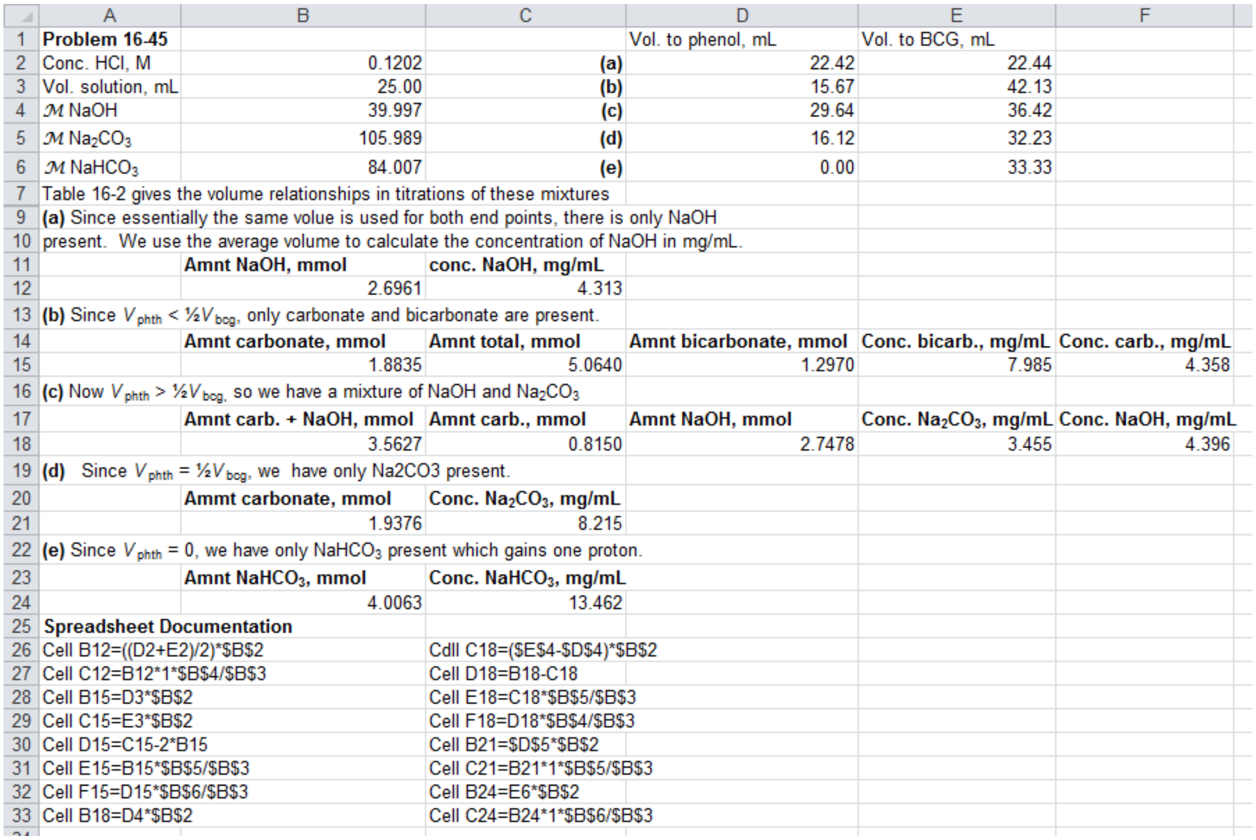
	A	B	C	D	E
1	**Problem 16-43**				
2	Conc. NaOH, M	0.07731			
3	(a) and (b)				
4	Conc. HCl, M	0.03000			
5	Conc. H_3PO_4, M	0.01000			
6	**(a)**		**Vol. solution, mL**	**Amnt. acid, mmol**	**Vol. NaOH, mL**
7	React with 1 proton		25.00	1.0000	12.93
8	to bromocresol green				
9	end point				
10	**(b)**		**Vol. solution, mL**	**Amnt. acid, mmol**	**Vol. NaOH, mL**
11	React with 2 protons		25.00	1.2500	16.17
12	to thymolphtalein				
13	end point				
14	**(c)**		**Vol. solution, mL**	**Amnt. acid, mmol**	**Vol. NaOH, mL**
15	Conc. NaH_2PO_4, M	0.06407	10.00	0.6407	8.29
16			20.00	1.2814	16.57
17			30.00	1.9221	24.86
18			40.00	2.5628	33.15
19	**(d) Mixture**		**Vol. solution, mL**	**Amnt. acid, mmol**	**Vol. NaOH, mL**
20	Conc. H_3PO_4, M	0.02000	20.00	1.4000	18.11
21	Conc. NaH_2PO_4, M	0.03000	25.00	1.7500	22.64
22	React with 2 protons		30.00	2.1000	27.16
23	from H_3PO_4 and 1				
24	proton from NaH_2PO_4				
25					
26	**Spreadsheet Documentation**				
27	Cell D7=C7*$B$4+C7*$B$5				
28	Cell E7=D7/$B$2				
29	Cell D11=C11*$B$4+2*C11*$B$5				
30	Cell E11=D11/$B$2				
31	Cell D15=$B$15*C15				
32	Cell E15=D15/$B$2				
33	Cell D20=2*$B$20*C20+$B$21*C20				
34	Cell E20=D20/$B$2				

16-44.



	A	B	C	D	E	F
1	**Problem 16-44**			Vol. to phenol, mL	Vol. to BCG, mL	
2	Conc. HCl, M	0.08601	**(a)**	0.00	18.15	
3	Vol. solution, mL	25.00	**(b)**	21.00	28.15	
4	$\mathcal{M}$ NaOH	39.997	**(c)**	19.80	39.61	
5	$\mathcal{M}$ Na_3AsO_4	207.89	**(d)**	18.04	18.03	
6	$\mathcal{M}$ Na_2HAsO_4	185.91	**(e)**	16.00	37.37	
7	We use the method of Problem 16-44. Table 16-2 gives the volume relationships in similar mixtures					
8	**(a)** Since V_{phth} = 0, we have only Na_2HAsO_4 present, which gains 1 proton.					
9		**Amnt Na_2HAsO_4, mmol**	**Conc. Na_2HAsO_4, mg/mL**			
10		1.5611	11.61			
11	**(b)** Now $V_{phth} > ½ V_{bcg}$, so we have a mixture of NaOH and Na_3AsO_4.					
12		**Amnt Na_3AsO_4 + NaOH, mmol**	**Amnt Na_3AsO_4, mmol**	**Amnt NaOH, mmol**	**Conc. Na_3AsO_4, mg/mL**	**Conc. NaOH, mg/mL**
13		1.80621	0.6150	1.1912	5.114	1.906
14	**(c)** Since $V_{phth} = ½ V_{bcg}$, we have only Na_3AsO_4 present.					
15		**Amnt Na_3AsO_4, mmol**	**Conc. Na_3AsO_4, mg/mL**			
16		1.7030	14.16			
17	**(d)** Since essentially the same volume is used for each end point, there is only NaOH present. We use the					
18	average volume to calculate the concentration of NaOH in mg/mL.					
19		**Amnt NaOH, mmol**	**Conc. NaOH, mg/mL**			
20		1.5512	2.482			
21	**(e)** Since $V_{phth} < ½V_{bcg}$, only Na_3AsO_4 and Na_2HAsO_4 are present.					
22		**Amnt Na_3AsO_4, mmol**	**Amnt total, mmol**	**Amnt Na_2HAsO_4, mmol**	**Conc. Na_3AsO_4, mg/mL**	**Conc. Na_2HAsO_4, mg/mL**
23		1.3762	3.2142	0.4619	11.44	3.435
24	**Spreadsheet Documentation**					
25	Cell B10=$E$2*$B$2		Cell C16=B16*$B$5/$B$3			
26	Cell C10=B10*1*$B$6/$B$3		Cell B20=((D5+E5)/2)*$B$2			
27	Cell B13=D3*$B$2		Cell C20=B20*$B$4/$B$3			
28	Cell C13=($E$3-$D$3)*$B$2		Cell B23=$D$6*$B$2			
29	Cell D13=B13-C13		Cell C23=$E$6*$B$2			
30	Cell E13=C13*$B$5/$B$3		Cell D23=C23-2*B23			
31	Cell F13=D13*$B$4/$B$3		Cell E23=B23*$B$5/$B$3			
32	Cell B16=$D$4*$B$2		Cell F23=D23*$B$6/$B$3			

16-45.



	A	B	C	D	E	F
1	**Problem 16-45**			Vol. to phenol, mL	Vol. to BCG, mL	
2	Conc. HCl, M	0.1202	**(a)**	22.42	22.44	
3	Vol. solution, mL	25.00	**(b)**	15.67	42.13	
4	$\mathcal{M}$ NaOH	39.997	**(c)**	29.64	36.42	
5	$\mathcal{M}$ Na_2CO_3	105.989	**(d)**	16.12	32.23	
6	$\mathcal{M}$ $NaHCO_3$	84.007	**(e)**	0.00	33.33	
7	Table 16-2 gives the volume relationships in titrations of these mixtures					
9	**(a)** Since essentially the same volue is used for both end points, there is only NaOH					
10	present. We use the average volume to calculate the concentration of NaOH in mg/mL.					
11		**Amnt NaOH, mmol**	**conc. NaOH, mg/mL**			
12		2.6961	4.313			
13	**(b)** Since $V_{phth} < ½V_{bcg}$, only carbonate and bicarbonate are present.					
14		**Amnt carbonate, mmol**	**Amnt total, mmol**	**Amnt bicarbonate, mmol**	**Conc. bicarb., mg/mL**	**Conc. carb., mg/mL**
15		1.8835	5.0640	1.2970	7.985	4.358
16	**(c)** Now $V_{phth} > ½V_{bcg}$, so we have a mixture of NaOH and Na_2CO_3					
17		**Amnt carb. + NaOH, mmol**	**Amnt carb., mmol**	**Amnt NaOH, mmol**	**Conc. Na_2CO_3, mg/mL**	**Conc. NaOH, mg/mL**
18		3.5627	0.8150	2.7478	3.455	4.396
19	**(d)** Since $V_{phth} = ½V_{bcg}$, we have only Na2CO3 present.					
20		**Ammt carbonate, mmol**	**Conc. Na_2CO_3, mg/mL**			
21		1.9376	8.215			
22	**(e)** Since $V_{phth} = 0$, we have only $NaHCO_3$ present which gains one proton.					
23		**Amnt $NaHCO_3$, mmol**	**Conc. $NaHCO_3$, mg/mL**			
24		4.0063	13.462			
25	**Spreadsheet Documentation**					
26	Cell B12=((D2+E2)/2)*$B$2		Cdll C18=($E$4-$D$4)*$B$2			
27	Cell C12=B12*1*$B$4/$B$3		Cell D18=B18-C18			
28	Cell B15=D3*$B$2		Cell E18=C18*$B$5/$B$3			
29	Cell C15=E3*$B$2		Cell F18=D18*$B$4/$B$3			
30	Cell D15=C15-2*B15		Cell B21=$D$5*$B$2			
31	Cell E15=B15*$B$5/$B$3		Cell C21=B21*1*$B$5/$B$3			
32	Cell F15=D15*$B$6/$B$3		Cell B24=E6*$B$2			
33	Cell B18=D4*$B$2		Cell C24=B24*1*$B$6/$B$3			

16-46. **(a)** The equivalent mass of an acid is that mass of the pure material that contains one mole of titratable protons in a specified reaction.

(b) The equivalent mass of a base is that mass of the pure material that consumes one mole of protons in a specified reaction.

16-47. **(a)** With bromocresol green, only one of the two protons in the oxalic acid will react. Therefore, the equivalent mass is the molar mass, or 126.066 g.

(b) When phenolphthalein is the indicator, two of the protons are consumed. Therefore, the equivalent mass of oxalic acid is one-half the molar mass, or 63.03 g.

16-48. (a)

$$\frac{\dfrac{0.1008\text{ mmol NaOH}}{\text{mL}} \times 45.62\text{ mL NaOH} \times \dfrac{1\text{ mmol CH}_3\text{COOH}}{\text{mmol NaOH}}}{10.00\text{ mL}} = 0.4598\text{ M CH}_3\text{COOH}$$

(b)

$$\frac{0.4598\text{ mmol CH}_3\text{COOH}}{\text{mL}} \times \frac{60.053\text{ mg CH}_3\text{COOH}}{\text{mmol}} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mL CH}_3\text{COOH}}{1.004\text{ g}} \times 100\%$$
$$= 2.75\%\text{ CH}_3\text{COOH}$$

Chapter 17

17-1. **(a)** A *ligand* is a species that contains one or more electron pair donor groups that tend to form bonds with metal ions.

(b). A *chelate* is a cyclic complex consisting of metal ion and a reagent that contains two or more electron donor groups located in such a position that they can bond with the metal ion to form a heterocyclic ring structure.

(**c).** A *tetradentate chelating agent* is a molecule that contains four pairs of donor electron located in such positions that they all can bond to a metal ion, thus forming two rings.

(d). An *adsorption indicator* is an organic compound that adsorbs onto the surface of the solid in a precipitation titration. Adsorption or desorption of the indicator occurs near the equivalence point and results in a color change and transfer of color from the solution to the solid or vice versa.

(e). *Argentometric titrations* are titrations based on the formation of precipitates with standard solutions of silver nitrate. An example is the titration of a halide ion with silver nitrate to form the isoluble silver halide.

(f). A *conditional formation constant* is an equilibrium constant for the reaction between a metal ion and a complexing agent that applies only when the pH and/or the concentration of other complexing ions are carefully specified.

(g). In an *EDTA displacement titration*, an unmeasured excess of a solution containing the magnesium or zinc complex of EDTA is introduced into the solution of an analyte that forms a more stable complex that that of magnesium or zinc. The liberated magnesium or zinc ions are then titrated with a standard solution of EDTA. Displacement titrations are used for the determination of cations for which no good indicator exists.

(h). *Water hardness* is the concentration of calcium carbonate that is equivalent to the total concentration of all of the multivalent metal carbonates in the water.

17-2. Multidentate ligands offer the advantage that they usually form more stable complexes than do unidentate ligands. Furthermore, they often form but a single complex with the cation, which simplifies their titration curves and makes end-point detection easier.

17-3. Three general methods for performing EDTA titrations are (1) direct titration, (2) back titration, and (3) displacement titration. Method (1) is simple, rapid, but requires one standard reagent. Method (2) is advantageous for those metals that react so slowly with EDTA as to make direct titration inconvenient. In addition, this procedure is useful for cations for which satisfactory indicators are not available. Finally, it is useful for analyzing samples that contain anions that form sparingly soluble precipitates with the analyte under analytical conditions. Method (3) is particularly useful in situations where no satisfactory indicators are available for direct titration.

17-4. (a)

$$Ag^+ + S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)^- \qquad K_1 = \frac{[Ag(S_2O_3)^-]}{[Ag^+][S_2O_3^{2-}]}$$

$$Ag(S_2O_3)^- + S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} \qquad K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag(S_2O_3)^-][S_2O_3^{2-}]}$$

(b)

$Ni^{2+} + CN^- \rightleftharpoons Ni(CN)^+$ $$K_1 = \frac{[Ni(CN)^+]}{[Ni^{2+}][CN^-]}$$

$Ni(CN)^+ + CN^- \rightleftharpoons Ni(CN)_2$ $$K_2 = \frac{[Ni(CN)_2]}{[Ni(CN)^+][CN^-]}$$

$Ni(CN)_2 + CN^- \rightleftharpoons Ni(CN)_3^-$ $$K_3 = \frac{[Ni(CN)_3^-]}{[Ni(CN)_2][CN^-]}$$

$Ni(CN)_3^- + CN^- \rightleftharpoons Ni(CN)_4^{2-}$ $$K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni(CN)_3^-][CN^-]}$$

(c)

$Cd^{2+} + SCN^- \rightleftharpoons Cd(SCN)^+$ $$K_1 = \frac{[Cd(SCN)^+]}{[Cd^{2+}][SCN^-]}$$

$Cd(SCN)^+ + SCN^- \rightleftharpoons Cd(SCN)_2$ $$K_2 = \frac{[Cd(SCN)_2]}{[Cd(SCN)^+][SCN^-]}$$

$Cd(SCN)_2 + SCN^- \rightleftharpoons Cd(SCN)_3^-$ $$K_3 = \frac{[Cd(SCN)_3^-]}{[Cd(SCN)_2][SCN^-]}$$

17-5. The overall formation constant β_n is equal to the product of the individual stepwise constants. Thus, the overall constant for formation of $Ag(S_2O_3)_2^{3-}$ in Problem 17-4 (a) is

$$\beta_2 = K_1K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag^+][S_2O_3^{2-}]^2}$$

17-6. **(a)** hexaaminezinc(II), $Zn(NH_3)_6^{2}$

(b) dichloroargentate, $Ag(Cl)_2$

(c) disulfatocuprate(II), $Cu(SO_4)_2^{2-}$

(d) trioxalotoferrate(III), $Fe(C_2O_4)_3^{3-}$

(e) hexacyanoferrate(II), $Fe(CN)_6^{4-}$

17-7. The Fajans determination of chloride involves a direct titration, while a Volhard titration requires two standard solutions and a flitration step to remove AgCl before back titration of the excess SCN^-.

17-8. The solubility of the silver salt of the analyte with respect to AgSCN in the acidic environment needed to keep the iron(III) indicator in solution determines whether a filtration step is needed.

(a) The solubility of AgCl is unaffected by the acidity. Filtration is nevertheless required because AgCl is more soluble than AgSCN.

(b) The solubility of AgCN is less than that for AgSCN in a neutral or nearly neutral solution, but is appreciable in an acidic solution because CN^- is the conjugate base of the weak acid HCN. Filtration is required.

(c) Silver carbonate is more soluble than AgSCN and its solubility increases in acidic solution. Filtration is required for both reasons.

17-9. The ions that are preferentially absorbed on the surface of an ionic solid are generally lattice ions. Thus, in the beginning stages of a precipitation titration, one of the lattice ions is in excess and its charge determines the sign of the charge of the particles. After the equivalence point, the ion of the opposite charge is present in excess and determines the sign of the charge on the particle. Thus, in the equivalence-point region, the charge shift from positive to negative, or the reverse.

17-10. Potassium is determined by precipitation with an excess of a standard solution of sodium tetraphenylborate. An excess of standard $AgNO_3$ is then added, which precipites the excess tetraphenylborate ion. The excess $AgNO_3$ is then titrated with a standard solution of SCN^-. The reactions are

$K^+ + B(C_6H_5)_4^- \rightleftharpoons KB(C_6H_5)_4(s)$ [measured excess $B(C_6H_5)_4^-$]

$Ag^+ + B(C_6H_5)_4^- \rightleftharpoons AgB(C_6H_5)_4(s)$ [measured excess $AgNO_3$]

The excess $AgNO_3$ is then determined by a Volhard titration with KSCN.

17-11. **(a)** Acetate (OAc^-)

$HOAc \rightleftharpoons OAc^- + H^+$ $$K_a = \frac{[OAc^-][H^+]}{[HOAc]}$$

$c_T = [HOAc] + [OAc^-]$

$$= \frac{[OAc^-][H^+]}{K_a} + [OAc^-] = [OAc^-]\left\{\frac{[H^+]}{K_a} + 1\right\} = [OAc^-]\left\{\frac{[H^+] + K_a}{K_a}\right\}$$

$$\alpha_1 = \frac{[OAc^-]}{c_T} = \frac{K_a}{[H^+] + K_a}$$

(b) Tartrate (T^{2-})

$H_2T \rightleftharpoons HT^- + H^+$ $$K_{a1} = \frac{[HT^-][H^+]}{[H_2T]}$$

$HT^- \rightleftharpoons T^{2-} + H^+$ $$K_{a2} = \frac{[T^{2-}][H^+]}{[HT^-]}$$

$c_T = [H_2T] + [HT^-] + [T^{2-}]$

$$= \frac{[HT^-][H^+]}{K_{a1}} + \frac{[T^{2-}][H^+]}{K_{a2}} + [T^{2-}] = \frac{[T^{2-}][H^+]^2}{K_{a1}K_{a2}} + \frac{[T^{2-}][H^+]}{K_{a2}} + [T^{2-}]$$

$$= [T^{2-}]\left\{\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}} + 1\right\} = [T^{2-}]\left\{\frac{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}{K_{a1}K_{a2}}\right\}$$

$$\alpha_2 = \frac{[T^{2-}]}{c_T} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

(c) Phosphate

$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ $\qquad K_{a1} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]}$

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ $\qquad K_{a2} = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]}$

$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$ $\qquad K_{a3} = \frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]}$

$c_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

Proceeding as in the preceeding problem, we obtain

$$c_T = [PO_4^{3-}]\left\{\frac{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}{K_{a1}K_{a2}K_{a3}}\right\}$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{c_T} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

17-12. (a)

$Fe^{3+} + OAc^- \rightleftharpoons Fe(OAc)^{2+}$ $\qquad K_1 = \frac{[Fe(OAc)^{2+}]}{[Fe^{3+}][OAc^-]} = \frac{[Fe(OAc)^{2+}]}{[Fe^{3+}]\alpha_1 c_T}$

$$K_1' = \alpha_1 K_1 = \frac{[Fe(OAc)^+]}{[Fe^{3+}]c_T}$$

(b)

$Fe^{3+} + T^{2-} \rightleftharpoons FeT^{+}$ $$K_1 = \frac{[FeT^+]}{[Fe^{3+}][T^{2-}]} = \frac{[FeT^+]}{[Fe^{3+}]\alpha_2 c_T}$$

$$K_1' = \alpha_2 K_1 = \frac{[FeT^+]}{[Fe^{3+}]c_T}$$

(c)

$Fe^{3+} + PO_4^{3-} \rightleftharpoons FePO_4$ $$K_1 = \frac{[FePO_4]}{[Fe^{3+}][PO_4^{3-}]} = \frac{[FePO_4]}{[Fe^{3+}]\alpha_3 c_T}$$

$$K_1' = \alpha_3 K_1 = \frac{[FePO_4]}{[Fe^{3+}]c_T}$$

17-13.

$Fe^{3+} + 3Ox^{2-} \rightleftharpoons Fe(Ox)_3^{3-}$ $$\beta_3 = \frac{[Fe(Ox)_3^{3-}]}{[Fe^{3+}][Ox^{2-}]^3}$$

$\alpha_2 = \frac{[Ox^{2-}]}{c_T}$ so $[Ox^{2-}] = \alpha_2 c_T$

$$\beta_3 = \frac{[Fe(Ox)_3^{3-}]}{[Fe^{3+}][Ox^{2-}]^3} = \frac{[Fe(Ox)_3^{3-}]}{[Fe^{3+}](\alpha_2 c_T)^3}$$

$$\beta_3' = (\alpha_2)^3 \beta_3 = \frac{[Fe(Ox)_3^{3-}]}{[Fe^{3+}](c_T)^3}$$

17-14. Titrate the three ions in an aliquot of the sample that has been buffered to a pH of about 10. Buffer a second aliquot to a pH of about 4 and titrate the zinc and indium ions. Finally, titrate an aliquot that has been brought to a pH of about 1.5. Only the indium is complexed under these conditions.

17-15.

$$\beta_n = \frac{[\mathrm{ML}_n]}{[\mathrm{M}][\mathrm{L}]^n}$$

Taking the logarithm of both sides of the above equation yields

$\log \beta_n = \log[\mathrm{ML}_n] - \log[\mathrm{M}] - n\log[\mathrm{L}]$

Now write the right hand side of the equation as a *p* function (i.e. pM = –log[M]).

$\log \beta_n = \mathrm{pM} + n\mathrm{pL} - \mathrm{pML}_n$

17-16. The MgY^{2-} is added to assure a sufficient analytical concentration of Mg^{2+} to provide a sharp end point with Eriochrome Black T indicator.

17-17.

$$\frac{3.426\ \cancel{\text{g reagent}} \times \dfrac{99.7\ \cancel{\text{g Na}_2\text{H}_2\text{Y}\cdot 2\text{H}_2\text{O}}}{100\ \cancel{\text{g reagent}}} \times \dfrac{1\ \text{mole EDTA}}{372.24\ \cancel{\text{g Na}_2\text{H}_2\text{Y}\cdot 2\text{H}_2\text{O}}}}{1.000\ \text{L}} = 0.00918\ \text{M EDTA}$$

17-18.
$$\frac{50.00\ \cancel{\text{mL}} \times \dfrac{0.004423\ \cancel{\text{mmol Mg}^{2+}}}{\cancel{\text{mL}}} \times \dfrac{1\ \text{mmol EDTA}}{\cancel{\text{mmol Mg}^{2+}}}}{30.27\ \text{mL}} = 0.00731\ \text{M EDTA}$$

17-19. First calculate the $\mathrm{CoSO_4}$ concentration

$$\frac{1.569\ \cancel{\text{mg}}}{\text{mL}} \times \frac{1\ \text{mmol CoSO}_4}{155.0\ \cancel{\text{mg}}} = 0.010123\ \text{M}$$

In each part 25.00 mL of this solution is taken, so

$$\text{amount CoSO}_4 = 25.00\ \text{mL} \times \frac{0.010123\ \text{mmol}}{\text{mL}} = 0.25306\ \text{mmol}$$

(a)

$$\text{Vol. EDTA} = 0.25306\ \cancel{\text{mmol CoSO}_4} \times \frac{1\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mmol CoSO}_4}} \times \frac{1\ \text{mL}}{0.007840\ \cancel{\text{mmol EDTA}}} = 32.28\ \text{mL}$$

(b)

$$\text{amnt excess EDTA} = \left(\frac{0.007840\ \text{mmol}}{\text{mL}} \times 50.00\ \text{mL}\right) - \left(0.25306\ \text{mmol CoSO}_4 \times \frac{1\ \text{mmol}}{\text{mmol CoSO}_4}\right) = 0.1389\ \text{mmol}$$

$$\text{Vol. Zn}^{2+} = 0.1389\ \cancel{\text{mmol EDTA}} \times \frac{1\ \cancel{\text{mmol Zn}^{2+}}}{\cancel{\text{mmol EDTA}}} \times \frac{1\ \text{mL}}{0.009275\ \cancel{\text{mmol Zn}^{2+}}} = 14.98\ \text{mL}$$

(c)

$$\text{Vol. EDTA} = 0.25306\ \cancel{\text{mmol CoSO}_4} \times \frac{1\ \cancel{\text{mmol Zn}^{2+}}}{\cancel{\text{mmol CoSO}_4}} \times \frac{1\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mmol Zn}^{2+}}} \times \frac{1\ \text{mL}}{0.007840\ \cancel{\text{mmol EDTA}}}$$

$$= 32.28\ \text{mL}$$

17-20. (a)

$$\text{Vol. EDTA} = \frac{0.0598\ \cancel{\text{mmol Mg(NO}_3)_2}}{\cancel{\text{mL}}} \times 29.13\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mmol Mg(NO}_3)_2}} \times \frac{\text{mL}}{0.0500\ \cancel{\text{mmol EDTA}}}$$

$$= 34.84\ \text{mL}$$

(b)

$$\text{Vol. EDTA} = 0.1598\ \cancel{\text{g}} \times \frac{1000\ \cancel{\text{mmol CaCO}_3}}{100.09\ \cancel{\text{g}}} \times \frac{1\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mmol CaCO}_3}} \times \frac{1\ \text{mL}}{0.0500\ \cancel{\text{mmol EDTA}}}$$

$$= 31.93\ \text{mL}$$

(c)

$$\text{Amnt. } CaHPO_4\cdot 2H_2O = 0.4861\ \cancel{\text{g}} \times \frac{81.4\text{ g }\cancel{CaHPO_4\cdot 2H_2O}}{100\ \cancel{\text{g}}} \times \frac{1000\text{ mmol}}{172.09\text{ g }\cancel{CaHPO_4\cdot 2H_2O}}$$

$$= 2.2993\text{ mmol}$$

$$\text{Vol. EDTA} = 2.2993\ \cancel{\text{mmol } CaHPO_4\cdot 2H_2O} \times \frac{1\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mmol } CaHPO_4\cdot 2H_2O}} \times \frac{1\text{ mL}}{0.0500\ \cancel{\text{mmol EDTA}}}$$

$$= 45.99\text{ mL}$$

(d)

$$\text{Vol. EDTA} = 0.1795\ \cancel{\text{g}} \times \frac{1000\ \cancel{\text{mmol hydro}}}{365.3\ \cancel{\text{g}}} \times \frac{4\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mmol hydro}}} \times \frac{1\text{ mL}}{0.0500\ \cancel{\text{mmol EDTA}}}$$

$$= 38.32\text{ mL}$$

(e)

$$\text{Vol. EDTA} = 0.1612\text{ g} \times \frac{92.5\text{ g}}{100\text{ g}} \times \frac{1000\text{ mmol dolo}}{184.4\text{ g}} \times \frac{2\text{ mmol EDTA}}{\text{mmol dolo}} \times \frac{1\text{ mL}}{0.0500\text{ mmol EDTA}}$$

$$= 32.34\text{ mL}$$

17-21.

$$\text{Wt. Zn} = \frac{0.01639\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mL}}} \times 22.57\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{mmol } Zn^{2+}}}{\cancel{\text{mmol EDTA}}} \times \frac{65.39\text{ g}}{1000\ \cancel{\text{mmol } Zn^{2+}}} = 0.024189\text{ g}$$

$$\text{Percentage Zn} = \frac{0.024189\text{ g Zn}}{0.7457\text{ g sample}} \times 100\% = 3.244\%$$

17-22.

$$\text{EDTA added} = \left(\frac{0.01768\ \text{mmol}}{\cancel{\text{ml EDTA}}}\times 15.00\ \cancel{\text{mL EDTA}}\right)$$

$$-\left(\frac{0.008120\ \cancel{\text{mmol Cu}^{2+}}}{\cancel{\text{mL}}}\times 4.30\ \cancel{\text{mL}}\times\frac{1\ \text{mmol EDTA}}{\cancel{\text{mmol Cu}^{2+}}}\right) = 0.2303\ \text{mmol EDTA}$$

$$\text{Wt. Cr/cm}^2 = \left(\frac{0.2303\ \cancel{\text{mmol EDTA}}\times\dfrac{1\ \cancel{\text{mmol Cr}}}{\cancel{\text{mmol EDTA}}}\times\dfrac{51.996\ \text{mg}}{\cancel{\text{mmol Cr}}}}{(3.00\ \times 4.00)\ \text{cm}^2}\right) = 0.998\ \frac{\text{mg}}{\text{cm}^2}$$

17-23. $\text{Conc. AgNO}_3 = \dfrac{14.77\ \text{g}}{\text{L}}\times\dfrac{1\ \text{mol AgNO}_3}{169.873\ \text{g}} = 0.08695\ \text{M}$

(a)

$$\text{Vol. AgNO}_3 = 0.2631\ \cancel{\text{g}}\times\frac{\cancel{\text{mmol NaCl}}}{0.05833\ \cancel{\text{g}}}\times\frac{1\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol NaCl}}}\times\frac{1\ \text{mL AgNO}_3}{0.08695\ \cancel{\text{mmol AgNO}_3}} = 51.78\ \text{mL}$$

(b)

$$V_{\text{AgNO}_3} = 0.1788\ \cancel{\text{g}}\times\frac{1\ \cancel{\text{mmol Na}_2\text{CrO}_4}}{0.16973\ \cancel{\text{g}}}\times\frac{2\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol Na}_2\text{CrO}_4}}\times\frac{1\ \text{mL}}{0.08695\ \cancel{\text{mmol AgNO}_3}} = 25.55\ \text{mL}$$

(c)

$$V_{\text{AgNO}_3} = 64.13\ \cancel{\text{mg}}\times\frac{\cancel{\text{mmol Na}_3\text{AsO}_4}}{207.89\ \cancel{\text{mg}}}\times\frac{3\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol Na}_3\text{AsO}_4}}\times\frac{1\ \text{mL}}{0.08695\ \cancel{\text{mmol AgNO}_3}} = 10.64\ \text{mL}$$

(d)

$$V_{\text{AgNO}_3} = 381.1\ \cancel{\text{mg}}\times\frac{\cancel{\text{mmol BaCl}_2\cdot 2\text{H}_2\text{O}}}{244.26\ \cancel{\text{mg}}}\times\frac{2\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol BaCl}_2\cdot 2\text{H}_2\text{O}}}\times\frac{1\ \text{mL}}{0.08695\ \cancel{\text{mmol AgNO}_3}} = 35.89\ \text{mL}$$

(e)

$$V_{\text{AgNO}_3} = 25.00\ \cancel{\text{mL}}\times\frac{0.05361\ \cancel{\text{mmol Na}_3\text{PO}_4}}{\cancel{\text{mL}}}\times\frac{3\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol Na}_3\text{PO}_4}}\times\frac{1\ \text{mL}}{0.08695\ \cancel{\text{mmol AgNO}_3}} = 46.24\ \text{mL}$$

(f)

$$V_{\text{AgNO}_3} = 50.00\ \cancel{\text{mL}} \times \frac{0.01808\ \cancel{\text{mmol H}_2\text{S}}}{\cancel{\text{mL}}} \times \frac{2\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol H}_2\text{S}}} \times \frac{1\ \text{mL}}{0.08695\ \cancel{\text{mmol AgNO}_3}} = 20.79\ \text{mL}$$

17-24.

(a)

$$\text{Amnt NaCl} = 0.2631\ \cancel{\text{g}} \times \frac{\text{mmol NaCl}}{0.05844\ \cancel{\text{g}}} = 4.50205\ \text{mmol}$$

$$\text{Conc. AgNO}_3 = \frac{4.50205\ \cancel{\text{mmol NaCl}} \times \dfrac{1\ \text{mmol AgNO}_3}{\cancel{\text{mmol NaCl}}}}{25.00\ \text{mL}} = 0.1801\ \text{M}$$

(b) As in part (a)

$$\frac{0.1799\ \cancel{\text{g}}}{25.00\ \text{mL}} \times \frac{\text{mmol}\ \cancel{\text{Na}_2\text{CrO}_4}}{0.1617\ \cancel{\text{g}}} \times \frac{2\ \text{mmol AgNO}_3}{\cancel{\text{mmol Na}_2\text{CrO}_4}} = 0.08886\ \text{M}\ \ \text{AgNO}_3$$

(c) As in part (a)

$$\frac{64.13\ \cancel{\text{mg}}}{25.00\ \text{mL}} \times \frac{\cancel{\text{mmol Na}_3\text{AsO}_4}}{207.888\ \cancel{\text{mg}}} \times \frac{3\ \text{mmol AgNO}_3}{\cancel{\text{mmol Na}_3\text{AsO}_4}} = 0.03702\ \text{M}\ \ \text{AgNO}_3$$

(d) As in part (a)

$$\frac{38.11\ \cancel{\text{mg}}}{25.00\ \text{mL}} \times \frac{\cancel{\text{mmol BaCl}_2 \cdot 2\text{H}_2\text{O}}}{244.26\ \cancel{\text{m}}\text{g}} \times \frac{2\ \text{mmol AgNO}_3}{\cancel{\text{mmol BaCl}_2 \cdot 2\text{H}_2\text{O}}} = 0.01248\ \text{M}\ \ \text{AgNO}_3$$

(e) As in part (a)

$$\frac{25.00\ \cancel{\text{mL}}}{25.00\ \text{mL}} \times \frac{0.05361\ \cancel{\text{mmol Na}_3\text{PO}_4}}{\cancel{\text{mL}}} \times \frac{3\ \text{mmol AgNO}_3}{\cancel{\text{mmol Na}_3\text{PO}_4}} = 0.1608\ \text{M}\ \ \text{AgNO}_3$$

(f) As in part (a)

$$\frac{50.00\ \cancel{\text{mL}}}{25.00\ \text{mL}}\times\frac{0.01808\ \cancel{\text{mmol H}_2\text{S}}}{\cancel{\text{mL}}}\times\frac{2\ \text{mmol AgNO}_3}{\cancel{\text{mmol H}_2\text{S}}} = 0.07232\ \text{M}\ \ \text{AgNO}_3$$

17-25. **(a)** An excess is assured if the calculation is based on a pure sample.

$$\text{Vol. AgNO}_3 = \ 0.2513\ \cancel{\text{g}}\times\frac{1\ \cancel{\text{mmol NaCl}}}{0.05844\ \cancel{\text{g}}}\times\frac{1\ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol NaCl}}}\times\frac{1\ \text{mL}}{0.09621\ \cancel{\text{mmol AgNO}_3}} = 44.70\ \text{mL}$$

(b)

$$\text{Vol. AgNO}_3 = 0.3462\ \cancel{\text{g}}\times\frac{0.7452\ \ \cancel{\text{g ZnCl}_2}}{\cancel{\text{g}}}\times\frac{1\ \ \cancel{\text{mmol ZnCl}_2}}{0.1363\ \text{g}\ \ \cancel{\text{ZnCl}_2}}\times\frac{2\ \ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmol ZnCl}_2}}\times$$

$$\frac{1\ \text{mL}}{0.09621\ \ \cancel{\text{mmol AgNO}_3}} = 39.35\ \text{mL}$$

(c)

$$\text{Vol. AgNO}_3 = 25.00\ \cancel{\text{mL}}\times\frac{0.01907\ \ \cancel{\text{mmolAlCl}_3}}{\cancel{\text{mL}}}\times\frac{3\ \ \cancel{\text{mmol AgNO}_3}}{\cancel{\text{mmolAlCl}_3}}\times\frac{1\ \text{mL}}{0.09621\ \ \cancel{\text{mmol AgNO}_3}} = 14.87\ \text{mL}$$

17-26. **(a)**

$$\text{Percent Cl} = \frac{45.32\ \cancel{\text{mL}}\ \times 0.1046\ \dfrac{\cancel{\text{mmol AgNO}_3}}{\cancel{\text{mL}}}\times\dfrac{1\ \ \cancel{\text{mmol Cl}^-}}{\cancel{\text{mmol AgNO}_3}}\times\dfrac{0.035453\ \text{g}}{\cancel{\text{mmol Cl}^-}}}{0.7908\ \text{g sample}}\times 100\% = 21.25\%$$

(b)

$$\frac{(45.32\times 0.1046)\ \ \cancel{\text{mmol AgNO}_3}\times\dfrac{1\ \ \cancel{\text{mmol BaCl}_2\cdot 2\text{H}_2\text{O}}}{2\ \ \cancel{\text{mmol AgNO}_3}}\times\dfrac{0.24426\ \ \cancel{\text{g}}}{\cancel{\text{mmol BaCl}_2\cdot 2\text{H}_2\text{O}}}}{0.7908\ \cancel{\text{g}}\ \ \text{sample}}\times 100\%$$

$$=\ 73.21\%\ \text{BaCl}_2\cdot 2\text{H}_2\text{O}$$

(c)

$$\frac{(45.32\times 0.1046)\ \ \cancel{\text{mmol AgNO}_3}\times\dfrac{1\ \ \cancel{\text{mmol analyte}}}{4\ \text{mmol}\ \ \cancel{\text{AgNO}_3}}\times\dfrac{0.24328\ \ \cancel{\text{g}}}{\cancel{\text{mmol analyte}}}}{0.7908\ \cancel{\text{g}}\ \ \text{sample}}\times 100\% = 36.46\%\ \text{analyte}$$

17-27.

$$\text{Percent Tl}_2\text{SO}_4 = \frac{\left(\dfrac{0.03610\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mL}}}\times 12.77\ \cancel{\text{mL}}\times\dfrac{1\ \cancel{\text{mmol Tl}_2\text{SO}_4}}{2\ \cancel{\text{mmol EDTA}}}\times\dfrac{504.8\ \cancel{\text{g}}}{\cancel{\text{mmol Tl}_2\text{SO}_4}}\right)}{9.57\ \cancel{\text{g}}\ \text{sample}}\times 100\%$$

$= 1.216\%$

17-28. (a)

$$\text{Conc. EDTA} = \frac{\left(\dfrac{0.7682\ \cancel{\text{g}}}{1000\ \cancel{\text{mL MgCO}_3}}\times\dfrac{1000\ \cancel{\text{mmol MgCO}_3}}{84.314\ \cancel{\text{g}}}\times 50.0\ \cancel{\text{mL MgCO}_3}\times\dfrac{1\,\text{mmol EDTA}}{\cancel{\text{mmol MgCO}_3}}\right)}{42.35\ \text{mL}}$$

$= 0.1076\ \text{M}$

(b) $$\text{Total Conc.} = \frac{\left(\dfrac{1.076\times10^{-2}\ \text{mmol}}{\text{mL}}\times 18.81\,\text{mL}\right)}{25.00\,\text{mL}} = 8.094\times10^{-3}\,\text{M}$$

$$\text{Conc. CaCO}_3 = \frac{\text{mmol CaCO}_3}{\text{mL sample}} = \frac{\left(\dfrac{1.076\times10^{-2}\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mL}}}\times 31.54\ \cancel{\text{mL}}\times\dfrac{1\,\text{mmol CaCO}_3}{\cancel{\text{mmol EDTA}}}\right)}{50.00\,\text{mL}}$$

$= 6.786\times10^{-3}\,M$

$$\text{Conc. MgCO}_3 = \frac{\text{mmol MgCO}_3}{\text{mL sample}} = 8.094\times10^{-3}\,\text{M} - 6.786\times10^{-3}\,\text{M} = 1.308\times10^{-3}\,\text{M}$$

$$\text{Conc. CaCO}_3\ \text{(ppm)} = \frac{6.786\times10^{-3}\ \cancel{\text{mmol CaCO}_3}}{\cancel{\text{mL sample}}}\times\frac{100.09\ \cancel{\text{g}}}{1000\ \cancel{\text{mmol CaCO}_3}}\times\frac{1.000\ \cancel{\text{mL sample}}}{\cancel{\text{g}}\ \text{sample}}\times 10^6\,\text{ppm}$$

$= 679.2\ \text{ppm}$

(c)

$$\text{Conc. MgCO}_3\text{(ppm)} = \frac{1.308\times10^{-3}\ \cancel{\text{mmol MgCO}_3}}{\cancel{\text{mL sample}}}\times\frac{84.314\ \cancel{\text{g}}}{1000\ \cancel{\text{mmol MgCO}_3}}\times\frac{1.000\ \cancel{\text{mL sample}}}{\cancel{\text{g}}\ \text{sample}}\times 10^6\,\text{ppm}$$

$= 110.3\ \text{ppm}$

17-29.

$$\text{Amnt Fe}^{3+} = \frac{0.01500\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mL}}} \times 10.98\ \cancel{\text{mL}} \times \frac{1\ \text{mmol Fe}^{3+}}{\cancel{\text{mmol EDTA}}} = 0.1647\ \text{mmol}$$

$$\text{Amnt Fe}^{2+} = \frac{0.01500\ \cancel{\text{mmol EDTA}}}{\cancel{\text{mL}}} \times (23.70 - 10.98)\ \cancel{\text{mL}} \times \frac{1\ \text{mmol Fe}^{2+}}{\cancel{\text{mmol EDTA}}} = 0.1908\ \text{mmol}$$

$$\text{Conc. Fe}^{3+} = \frac{\left(0.1647\ \cancel{\text{mmol Fe}^{3+}} \times \dfrac{55.847\ \text{mg}}{\cancel{\text{mmol Fe}^{3+}}}\right)}{50.00\ \cancel{\text{mL}} \times \dfrac{\text{L}}{1000\ \cancel{\text{mL}}}} = 183.96\ \text{ppm} \approx 184.0\ \text{ppm}$$

$$\text{Conc. Fe}^{2+} = \frac{\left(0.1908\ \cancel{\text{mmol Fe}^{2+}} \times \dfrac{55.847\ \text{mg}}{\cancel{\text{mmol Fe}^{2+}}}\right)}{50.00\ \cancel{\text{mL}} \times \dfrac{\text{L}}{1000\ \cancel{\text{mL}}}} = 213.1\ \text{ppm}$$

17-30.

$$\text{Amount Mg}^{2+} + \text{Ca}^{2+} =$$

$$\frac{0.004590\ \text{mmol EDTA}}{\text{mL}} \times 23.57\ \text{mL EDTA} \times \frac{1\ \text{mmol (Mg}^{2+} + \text{Ca}^{2+})}{\text{mmol EDTA}} = 0.108186\ \text{mmol}$$

$$\text{Amnt Ca}^{2+} = \frac{0.004590\ \text{mmol EDTA}}{\text{mL}} \times 10.53\ \text{mL EDTA} \times \frac{1\ \text{mmol Ca}^{2+}}{\text{mmol EDTA}} = 0.048333\ \text{mmol}$$

$$\text{Amnt Mg}^{2+} = 0.108186 - 0.048333 = 0.059854\ \text{mmol}$$

$$\frac{\left(0.048333\ \text{mmol Ca}^{2+} \times \dfrac{40.08\ \text{mg}}{\text{mmol Ca}^{2+}}\right)}{10.00\ \text{mL} \times \dfrac{\text{L}}{1000\ \text{mL}} \times \dfrac{1}{2.000\ \text{L}}} = 387.4\ \text{ppm Ca}^{2+}$$

$$\frac{\left(0.059835\ \text{mmol Mg}^{2+} \times \dfrac{24.305\ \text{mg Mg}^{2+}}{\text{mmol}}\right)}{10.00\ \text{mL} \times \dfrac{\text{L}}{1000\ \text{mL}} \times \dfrac{1}{2.000\ \text{L}}} = 290.9\ \text{ppm Mg}^{2+}$$

Both fall within the normal ranges.

17-31.

$$\text{Amount Cd}^{2+} + \text{Pb}^{2+} =$$

$$\frac{0.06950\text{ mmol EDTA}}{\text{mL}}\times 28.89\text{ mL EDTA}\times\frac{1\text{ mmol (Cd}^{2+}+\text{Pb}^{2+})}{\text{mmol EDTA}}=2.00786\text{ mmol}$$

$$\text{Amnt Pb}^{2+}=\frac{0.06950\text{ mmol EDTA}}{\text{mL}}\times 11.56\text{ mL EDTA}\times\frac{1\text{ mmol Pb}^{2+}}{\text{mmol EDTA}}=0.80342\text{ mmol}$$

$$\text{Amnt Cd}^{2+}=2.00786\text{ mmol} - 0.80342\text{ mmol} = 1.20444\text{ mmol}$$

$$\frac{\left(0.80342\text{ mmol Pb}^{2+}\times\frac{207.2\text{ g Pb}^{2+}}{1000\text{ mmol}}\right)}{1.509\text{ g sample}\times\frac{50.00\text{ mL}}{250.0\text{ mL}}}\times 100\% = 55.16\%\text{ Pb}^{2+}$$

$$\frac{\left(1.204\text{ mmol Cd}^{2+}\times\frac{112.41\text{ g Cd}^{2+}}{1000\text{ mmol}}\right)}{1.509\text{ g sample}\times\frac{50.00\text{ mL}}{250.0\text{ mL}}}\times 100\% = 44.86\%\text{ Cd}^{2+}$$

17-32.

$$\text{Amount Ni}^{2+} + \text{Cu}^{2+} =$$

$$\frac{0.05285\text{ mmol EDTA}}{\text{mL}}\times 45.81\text{ mL EDTA}\times\frac{1\text{ mmol (Ni}^{2+}+\text{Cu}^{2+})}{\text{mmol EDTA}}=2.42106\text{ mmol}$$

$$\text{Amnt Cu}^{2+} = \frac{0.07238\text{ mmol Mg}^{2+}}{\text{mL}}\times 22.85\text{ mL Mg}^{2+}\times\frac{1\text{ mmol Cu}^{2+}}{\text{mmol Mg}^{2+}}=1.65388\text{ mmol}$$

$$\text{Amnt Ni}^{2+}=2.42106\text{ mmol} - 1.65388\text{ mmol}=0.76718\text{ mmol}$$

$$\frac{\left(0.76718\text{ mmol Ni}^{2+}\times\frac{58.693\text{ g}}{1000\text{ mmol Ni}^{2+}}\right)}{0.6004\text{ g sample}\times\frac{25.00\text{ mL}}{100.0\text{ mL}}}\times 100\% = 30.00\%\text{ Ni}^{2+}$$

$$\frac{\left(1.65388\text{ mmol Cu}^{2+}\times\frac{63.546\text{ g Cu}^{2+}}{1000\text{ mmol}}\right)}{0.6004\text{ g sample}\times\frac{25.00\text{ mL}}{100.0\text{ mL}}}\times 100\% = 70.02\%\text{ Cu}^{2+}$$

17-33.

$$\frac{\left(\frac{0.01133\text{ mmol EDTA}}{\text{mL}}\times 38.37\text{ mL EDTA}\times\frac{1\text{ mmol ZnO}}{\text{mmol EDTA}}\times\frac{81.379\text{ g ZnO}}{1000\text{ mmol}}\right)}{1.056\text{ g sample}\times\frac{10.00\text{ mL}}{250.0\text{ mL}}}\times 100\%$$

= 83.75% ZnO

$$\frac{\left(\frac{0.002647\text{ mmol ZnY}^{2-}}{\text{mL}}\times 2.30\text{ mL ZnY}^{2-}\times\frac{1\text{ mmol Fe}_2\text{O}_3}{2\text{ mmol ZnY}^{2-}}\times\frac{159.69\text{ g Fe}_2\text{O}_3}{1000\text{ mmol}}\right)}{1.056\text{ g sample}\times\frac{50.00\text{ mL}}{250.0\text{ mL}}}\times 100\%$$

= 0.230% Fe_2O_3

17-34.

1 mmol EDTA ≡ 1 mmol Ni^{2+} ≡ 2 mmol NaBr ≡ 2 mmol $NaBrO_3$

For the 10.00 mL aliquot,

$$\frac{\text{Amnt NaBr + amnt NaBrO}_3}{\text{mL sample solution}}=$$

$$\frac{\left(\frac{0.02089\text{ mmol EDTA}}{\text{mL}}\times 21.94\text{ mL EDTA}\times\frac{2(\text{mmol NaBr+mmol NaBrO}_3)}{\text{mmol EDTA}}\right)}{10.00\text{ mL}} = 0.09166\text{ M}$$

For the 25.00 mL aliquot,

$$\frac{\text{Amnt NaBr}}{\text{mL sample solution}}=$$

$$\frac{\left(\frac{0.02089\text{ mmol EDTA}}{\text{mL}}\times 26.73\text{ mL EDTA}\times\frac{2\text{ mmol NaBr}}{\text{mmol EDTA}}\right)}{25.00\text{ mL}} = 0.04467\text{ M NaBr}$$

$$\frac{\text{Amnt NaBrO}_3}{\text{mL sample solution}} = 0.09166 - 0.04467 = 0.04699\text{ M NaBrO}_3$$

$$\frac{\left(\frac{0.04467\text{ mmol NaBr}}{\text{mL}}\times 250.0\text{ mL}\times\frac{102.9\text{ g NaBr}}{1000\text{ mmol}}\right)}{3.650\text{ g sample}}\times 100\% = 31.48\%\text{ NaBr}$$

$$\frac{\left(\frac{0.04699\text{ mmol NaBrO}_3}{\text{mL}}\times 250.0\text{ mL}\times\frac{150.9\text{ g NaBrO}_3}{1000\text{ mmol}}\right)}{3.650\text{ g sample}}\times 100\% = 48.57\%\text{ NaBrO}_3$$

17-35.

$$1\text{ mmol Mg}^{2+}\equiv 1\text{ mmol EDTA}\equiv \tfrac{1}{4}\text{ mmol B(C}_6\text{H}_5)_4^{-}\equiv \tfrac{1}{4}\text{ K}^{+}$$

$$\frac{\left(\frac{0.05581\text{ mmol Mg}^{2+}}{\text{mL}}\times 29.64\text{ mL Mg}^{2+}\times\frac{1\text{ mmol K}^{+}}{4\text{ mmol Mg}^{2+}}\times\frac{39.098\text{ mg K}^{+}}{\text{mmol}}\right)}{250\text{ mL}\times\frac{\text{L}}{1000\text{ mL}}} = 64.68\text{ ppm K}^{+}$$

17-**36**.

$$\text{Amnt EDTA reacted in 50.00 mL} = \left(\frac{0.05173\text{ mmol EDTA}}{\text{mL}}\times 50.00\text{ mL EDTA}\right) -$$

$$\left(\frac{0.06139\text{ mmol Cu}^{2+}}{\text{mL}}\times 5.34\text{ mL Cu}^{2+}\times\frac{1\text{ mmol EDTA}}{\text{mmol Cu}^{2+}}\right) = 2.2587\ \text{ mmol}$$

$$\text{Amnt EDTA reacted in 250.0 mL} = \text{Amnt (Ni+ Fe+ Cr)} = \frac{2.2587\text{ mmol}}{\left(\frac{50.00\text{ mL}}{250.0\text{ mL}}\right)} = 11.2934\text{ mmol}$$

$$\text{Amnt (Ni + Fe)} = \frac{\left(\frac{0.05173\text{ mmol EDTA}}{\text{mL}}\times 36.98\text{ mL EDTA}\right)}{\frac{50.00\text{ mL}}{250.0\text{ mL}}} = 9.5649\text{ mmol}$$

$$\text{Amnt Cr} = 11.2934\text{ mmol} - 9.5649\text{ mmol} = 1.7285\text{ mmol}$$

$$\text{Amnt Ni} = \frac{\left(\frac{0.05173\text{ mmol EDTA}}{\text{mL}}\times 24.53\text{ mL EDTA}\times\frac{1\text{ mmol Ni}}{\text{mmol EDTA}}\right)}{\frac{50.00\text{ mL}}{250.0\text{ mL}}} = 6.3447\text{ mmol}$$

$$\text{Amnt Fe} = 9.5649\text{ mmol} - 6.3447\text{ mmol} = 3.2202\text{ mmol}$$

$$\%\text{Cr} = \frac{1.7285\text{ mmol Cr} \times \dfrac{51.996\text{ g Cr}}{1000\text{ mmol}}}{0.6553\text{ g}} \times 100\% = 13.72\%$$

$$\%\text{Ni} = \frac{6.3447\text{ mmol Ni} \times \dfrac{58.69\text{ g Ni}}{1000\text{ mmol}}}{0.6553\text{ g}} \times 100\% = 56.82\%$$

$$\%\text{Fe} = \frac{3.2202\text{ mmol Fe} \times \dfrac{55.847\text{ g Fe}}{1000\text{ mmol}}}{0.6553\text{ g}} \times 100\% = 27.44\%$$

17-37.

Amnt EDTA (mmol) =Amnt (Pb+Zn+Cu) in mmol

$$\frac{\left(\dfrac{0.002700\text{ mmol EDTA}}{\text{mL}} \times 34.78\text{ mL EDTA}\right)}{\dfrac{10.00\text{ mL}}{500.0\text{ mL}}} = 4.6953\text{ mmol}$$

$$\text{Amnt (Pb+ Zn)} = \frac{\left(\dfrac{0.002700\text{ mmol EDTA}}{\text{mL}} \times 25.62\text{ mL EDTA}\right)}{\dfrac{25.00\text{ mL}}{500.0\text{ mL}}} = 1.3835\text{ mmol}$$

$$\text{Amnt Cu} = 4.6953\text{ mmol} - 1.3835\text{ mmol} = 3.3118\text{ mmol}$$

$$\text{Amnt Pb} = \frac{\left(\dfrac{0.002700\text{ EDTA}}{\text{mL}} \times 10.00\text{ mL EDTA} \times \dfrac{1\text{ mmol Pb}}{\text{mmol EDTA}}\right)}{\dfrac{100.0\text{ mL}}{500.0\text{ mL}}} = 0.1350\text{ mmol Pb}$$

$$\text{Amnt Zn} = 1.3835\text{ mmol} - 0.1350\text{ mmol} = 1.2485\text{ mmol Zn}$$

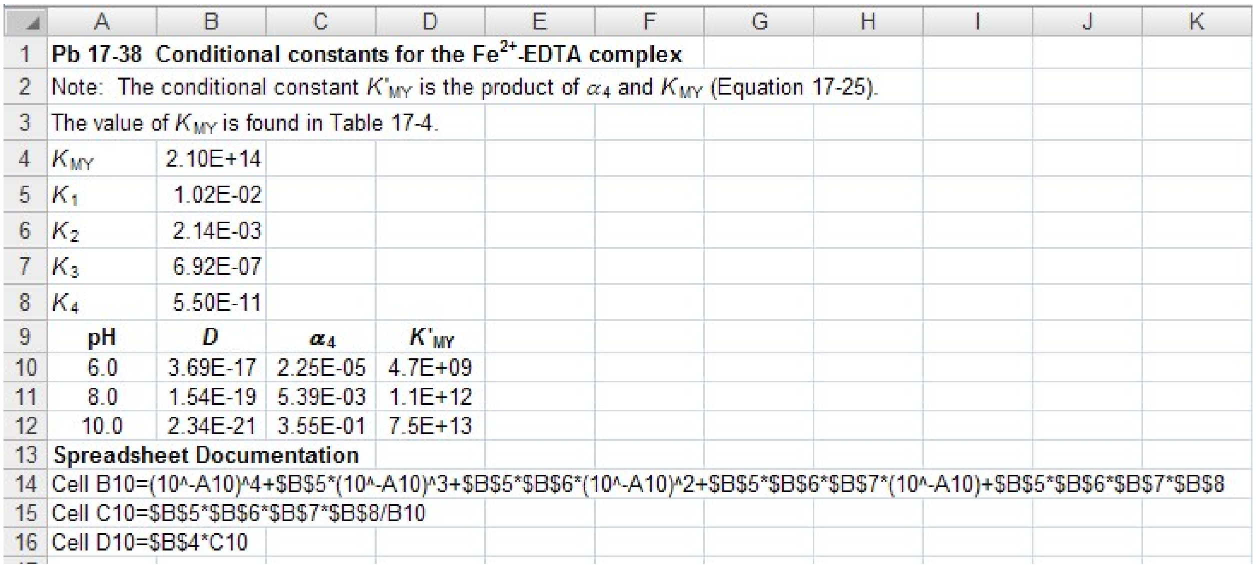
$$\%\text{Cu} = \frac{3.3118\text{ mmol Cu} \times \dfrac{63.55\text{ g Cu}}{1000\text{ mmol}}}{0.3304\text{ g}} \times 100\% = 63.70\%$$

$$\%\text{Pb} = \frac{0.1350 \text{ mmol Pb} \times \dfrac{207.2 \text{ g Pb}}{1000 \text{ mmol}}}{0.3304 \text{ g}} \times 100\% = 8.47\%$$

$$\%\text{Zn} = \frac{1.2485 \text{ mmol Zn} \times \dfrac{65.39 \text{ g Zn}}{1000 \text{ mmol}}}{0.3304 \text{ g}} \times 100\% = 24.71\%$$

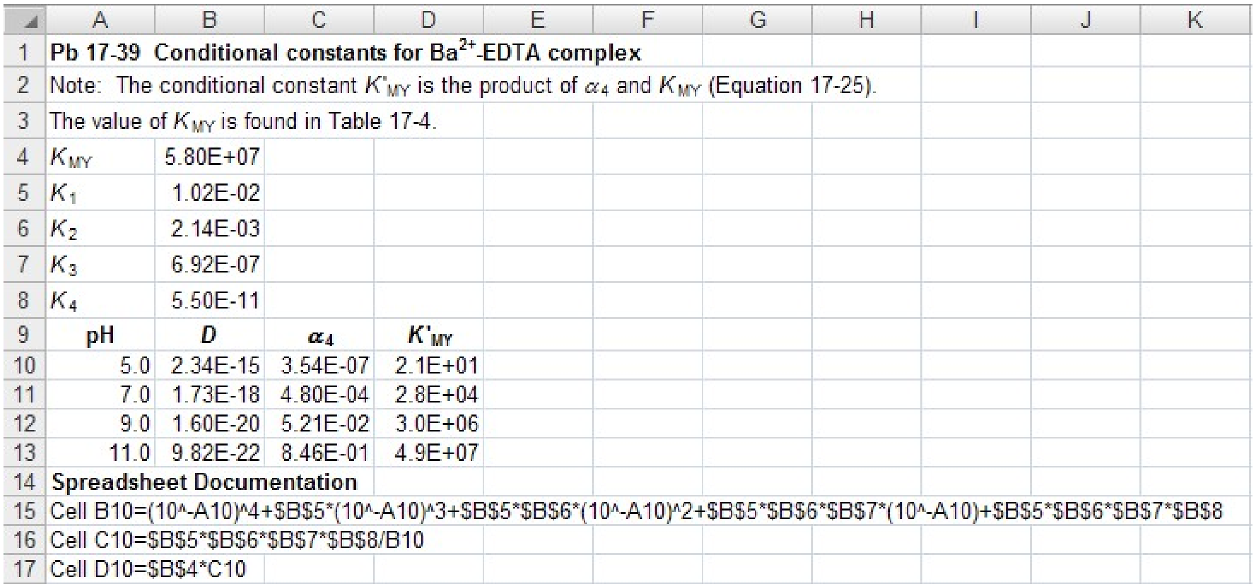
$$\%\text{Sn} = 100\% - (63.70 + 8.47 + 24.71)\% = 3.12\%$$

17-**38**.



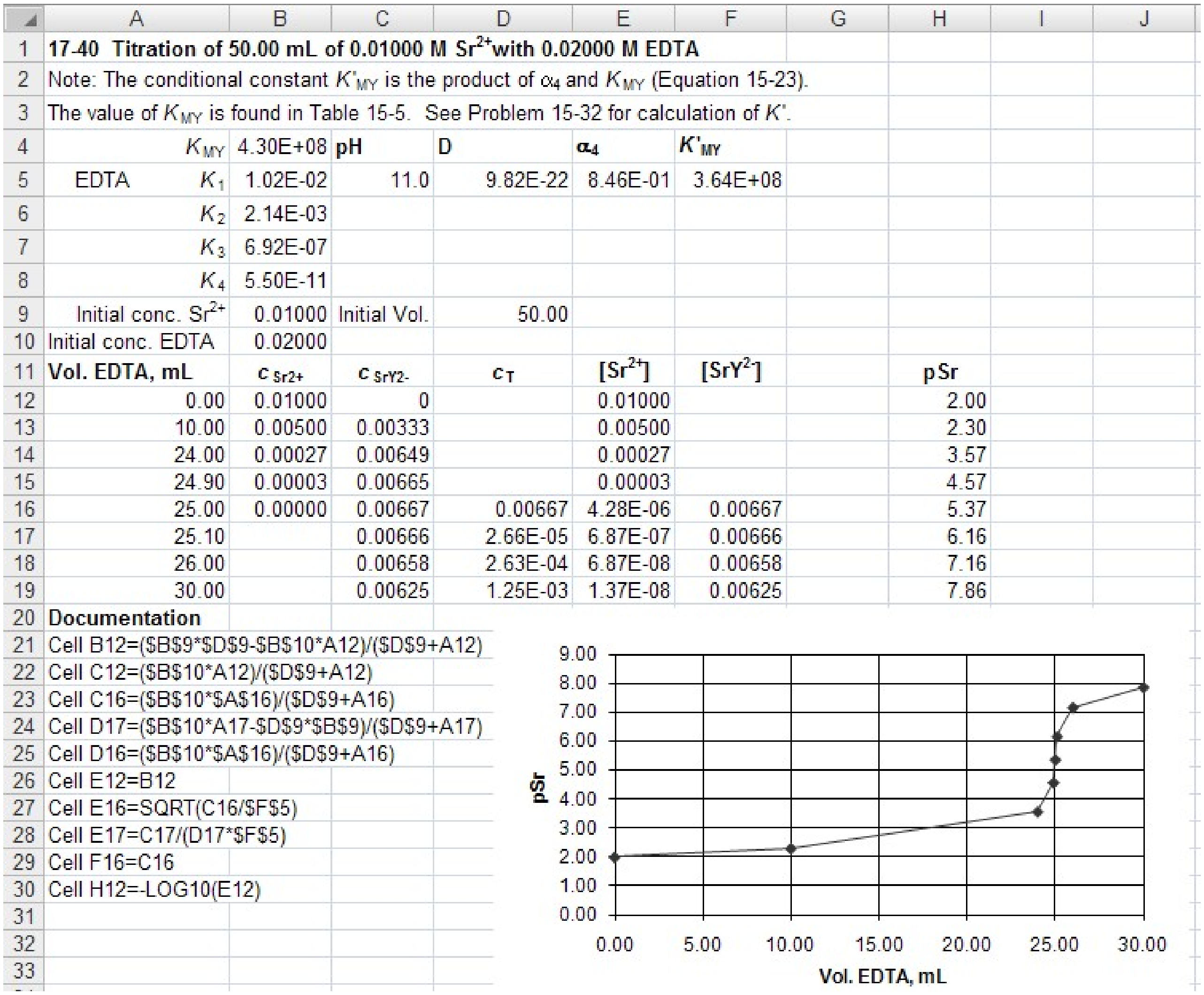
	A	B	C	D
1	**Pb 17-38 Conditional constants for the Fe^{2+}-EDTA complex**			
2	Note: The conditional constant K'_{MY} is the product of α_4 and K_{MY} (Equation 17-25).			
3	The value of K_{MY} is found in Table 17-4.			
4	K_{MY}	2.10E+14		
5	K_1	1.02E-02		
6	K_2	2.14E-03		
7	K_3	6.92E-07		
8	K_4	5.50E-11		
9	**pH**	***D***	$\boldsymbol{\alpha_4}$	$\boldsymbol{K'_{MY}}$
10	6.0	3.69E-17	2.25E-05	4.7E+09
11	8.0	1.54E-19	5.39E-03	1.1E+12
12	10.0	2.34E-21	3.55E-01	7.5E+13
13	**Spreadsheet Documentation**			
14	`Cell B10=(10^-A10)^4+$B$5*(10^-A10)^3+$B$5*$B$6*(10^-A10)^2+$B$5*$B$6*$B$7*(10^-A10)+$B$5*$B$6*$B$7*$B$8`			
15	`Cell C10=$B$5*$B$6*$B$7*$B$8/B10`			
16	`Cell D10=$B$4*C10`			

17-39.



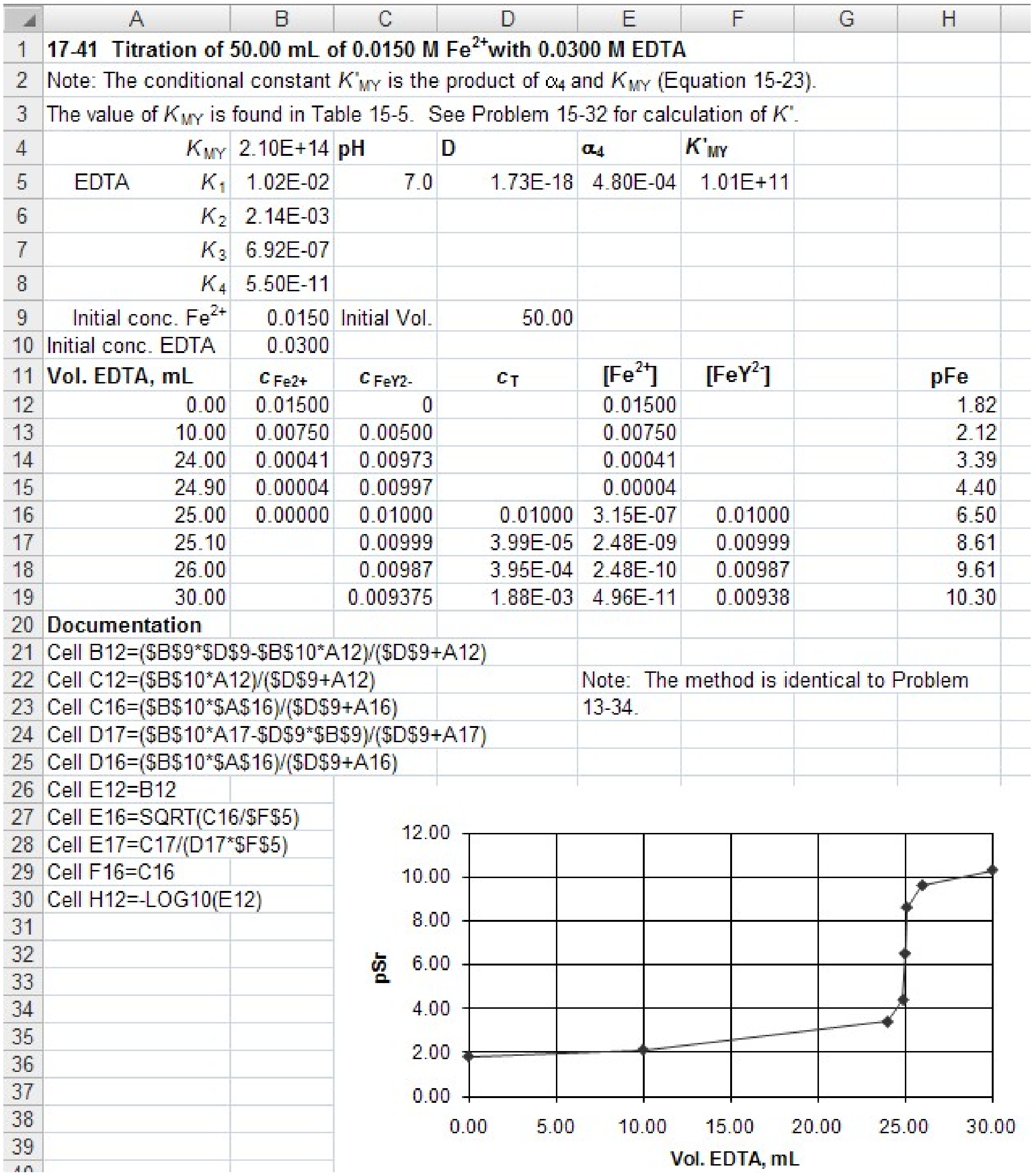
	A	B	C	D
1	**Pb 17-39 Conditional constants for Ba^{2+}-EDTA complex**			
2	Note: The conditional constant K'_{MY} is the product of α_4 and K_{MY} (Equation 17-25).			
3	The value of K_{MY} is found in Table 17-4.			
4	K_{MY}	5.80E+07		
5	K_1	1.02E-02		
6	K_2	2.14E-03		
7	K_3	6.92E-07		
8	K_4	5.50E-11		
9	**pH**	***D***	$\boldsymbol{\alpha_4}$	$\boldsymbol{K'_{MY}}$
10	5.0	2.34E-15	3.54E-07	2.1E+01
11	7.0	1.73E-18	4.80E-04	2.8E+04
12	9.0	1.60E-20	5.21E-02	3.0E+06
13	11.0	9.82E-22	8.46E-01	4.9E+07
14	**Spreadsheet Documentation**			
15	Cell B10=(10^-A10)^4+$B$5*(10^-A10)^3+$B$5*$B$6*(10^-A10)^2+$B$5*$B$6*$B$7*(10^-A10)+$B$5*$B$6*$B$7*$B$8			
16	Cell C10=$B$5*$B$6*$B$7*$B$8/B10			
17	Cell D10=$B$4*C10			

17-40.



	A	B	C	D	E	F	G	H	I	J
1	**17-40 Titration of 50.00 mL of 0.01000 M Sr^{2+} with 0.02000 M EDTA**									
2	Note: The conditional constant K'_{MY} is the product of α_4 and K_{MY} (Equation 15-23).									
3	The value of K_{MY} is found in Table 15-5. See Problem 15-32 for calculation of K'.									
4	K_{MY}	4.30E+08	**pH**	**D**	**α_4**	**K'_{MY}**				
5	EDTA K_1	1.02E-02	11.0	9.82E-22	8.46E-01	3.64E+08				
6	K_2	2.14E-03								
7	K_3	6.92E-07								
8	K_4	5.50E-11								
9	Initial conc. Sr^{2+}	0.01000	Initial Vol.	50.00						
10	Initial conc. EDTA	0.02000								
11	**Vol. EDTA, mL**	**c_{Sr2+}**	**c_{SrY2-}**	**c_T**	**$[Sr^{2+}]$**	**$[SrY^{2-}]$**		**pSr**		
12	0.00	0.01000	0		0.01000			2.00		
13	10.00	0.00500	0.00333		0.00500			2.30		
14	24.00	0.00027	0.00649		0.00027			3.57		
15	24.90	0.00003	0.00665		0.00003			4.57		
16	25.00	0.00000	0.00667	0.00667	4.28E-06	0.00667		5.37		
17	25.10		0.00666	2.66E-05	6.87E-07	0.00666		6.16		
18	26.00		0.00658	2.63E-04	6.87E-08	0.00658		7.16		
19	30.00		0.00625	1.25E-03	1.37E-08	0.00625		7.86		
20	**Documentation**									
21	Cell B12=($B$9*$D$9-$B$10*A12)/($D$9+A12)									
22	Cell C12=($B$10*A12)/($D$9+A12)									
23	Cell C16=($B$10*$A$16)/($D$9+A16)									
24	Cell D17=($B$10*A17-$D$9*$B$9)/($D$9+A17)									
25	Cell D16=($B$10*$A$16)/($D$9+A16)									
26	Cell E12=B12									
27	Cell E16=SQRT(C16/$F$5)									
28	Cell E17=C17/(D17*$F$5)									
29	Cell F16=C16									
30	Cell H12=-LOG10(E12)									
31										
32										
33										

17-41.



	A	B	C	D	E	F	G	H
1	**17-41 Titration of 50.00 mL of 0.0150 M Fe^{2+} with 0.0300 M EDTA**							
2	Note: The conditional constant K'_{MY} is the product of α_4 and K_{MY} (Equation 15-23).							
3	The value of K_{MY} is found in Table 15-5. See Problem 15-32 for calculation of K'.							
4	K_{MY}	2.10E+14	**pH**	**D**	**α_4**	**K'_{MY}**		
5	EDTA K_1	1.02E-02	7.0	1.73E-18	4.80E-04	1.01E+11		
6	K_2	2.14E-03						
7	K_3	6.92E-07						
8	K_4	5.50E-11						
9	Initial conc. Fe^{2+}	0.0150	Initial Vol.	50.00				
10	Initial conc. EDTA	0.0300						
11	**Vol. EDTA, mL**	**c_{Fe2+}**	**c_{FeY2-}**	**c_T**	**$[Fe^{2+}]$**	**$[FeY^{2-}]$**		**pFe**
12	0.00	0.01500	0		0.01500			1.82
13	10.00	0.00750	0.00500		0.00750			2.12
14	24.00	0.00041	0.00973		0.00041			3.39
15	24.90	0.00004	0.00997		0.00004			4.40
16	25.00	0.00000	0.01000	0.01000	3.15E-07	0.01000		6.50
17	25.10		0.00999	3.99E-05	2.48E-09	0.00999		8.61
18	26.00		0.00987	3.95E-04	2.48E-10	0.00987		9.61
19	30.00		0.009375	1.88E-03	4.96E-11	0.00938		10.30
20	**Documentation**							
21	`Cell B12=($B$9*$D$9-$B$10*A12)/($D$9+A12)`							
22	`Cell C12=($B$10*A12)/($D$9+A12)`				Note: The method is identical to Problem			
23	`Cell C16=($B$10*$A$16)/($D$9+A16)`				13-34.			
24	`Cell D17=($B$10*A17-$D$9*$B$9)/($D$9+A17)`							
25	`Cell D16=($B$10*$A$16)/($D$9+A16)`							
26	`Cell E12=B12`							
27	`Cell E16=SQRT(C16/$F$5)`							
28	`Cell E17=C17/(D17*$F$5)`							
29	`Cell F16=C16`							
30	`Cell H12=-LOG10(E12)`							
31								
32								
33								
34								
35								
36								
37								
38								
39								

17-42.

$$\text{Amnt Ca}^{2+} + \text{Amnt Mg}^{2+} = \left(\frac{0.01205\ \text{mmol EDTA}}{\text{mL}} \times 23.65\ \text{mL EDTA}\right) = 0.2850\ \text{mmol}$$

$$\text{Amnt Ca}^{2+} = \left(\frac{0.01205\ \text{mmol EDTA}}{\text{mL}} \times 14.53\ \text{mL EDTA} \times \frac{1\ \text{mmol Ca}^{2+}}{\text{mmol EDTA}}\right) = 0.1751\ \text{mmol}$$

$$\text{Amnt Mg}^{2+} = 0.2850 - 0.1751 = 0.1099\ \text{mmol}$$

(a)

See discussion of water hardness in 17D-9.

$$\text{Water hardness} \cong \text{Conc. CaCO}_3 \text{ in ppm} \approx \text{conc. Ca}^{2+} + \text{Mg}^{2+} \text{ in ppm}$$

$$= \frac{0.2850\ \text{mmol} \times \dfrac{100.087\ \text{mg CaCO}_3}{\text{mmol}}}{50.00\ \text{mL} \times \dfrac{\text{L}}{1000\ \text{mL}}} = 570.5\ \text{ppm CaCO}_3$$

(b)

$$\frac{\left(0.1751\ \text{mmol Ca}^{2+} \times \dfrac{1\ \text{mmol CaCO}_3}{\text{mmol Ca}^{2+}} \times \dfrac{100.08\ \text{mg CaCO}_3}{\text{mmol}}\right)}{50.00\ \text{mL} \times \dfrac{\text{L}}{1000\ \text{mL}}} = 350.5\ \text{ppm CaCO}_3$$

(c)

$$\frac{\left(0.1099\ \text{mmol Mg}^{2+} \times \dfrac{1\ \text{mmol MgCO}_3}{\text{mmol Mg}^{2+}} \times \dfrac{84.30\ \text{mg MgCO}_3}{\text{mmol}}\right)}{50.00\ \text{mL} \times \dfrac{\text{L}}{1000\ \text{mL}}} = 185.3\ \text{ppm MgCO}_3$$

Chapter 18

18-1. **(a)** *Oxidation* is a process in which a species loses one or more electrons.

(b) An *reducing agent* is an electron donor.

(c) A *salt bridge* provides electrical contact but prevents mixing of dissimilar solutions in an electrochemical cell.

(d) A *liquid junction* is the interface between dissimilar liquids. A potential develops across the interface.

(e) The *Nernst equation* relates the potential to the concentrations (strictly, activities) of the participants in an electrochemical reaction.

18-2. **(a)** The *electrode potential* is the potential of an electrochemical cell in which a standard hydrogen electrode acts as the reference electrode on the left and the half-cell of interest is on the right.

(b) The *formal potential* of a half-reaction if the potential of the system (measured against the standard hydrogen electrode) when the concentration of each solute participating in the half-reaction has a concentration of exactly one molar and the concentrations of all other constituents of the solution are carefully specified.

(c) The *standard electrode potential* is the potential of a cell consisting of the half-reaction of interest on the right and a standard hydrogen electrode on the left. The activities of all the participants in the half-reaction are specified as having a value of unity. The standard electrode potential is always a *reduction potential*.

(d) A *liquid-junction potential* is the potential that develops across the interface between two dissimilar solutions.

(e) An *oxidation potential* is the potential of an electrochemical cell in which the cathode is a standard hydrogen electrode and the half-cell of interest acts as anode.

18-3. **(a)** *Oxidation* is the process whereby a substance loses electrons; an *oxidizing agent* causes the loss of electrons.

(b) A *galvanic cell* is one in which a spontaneous electrochemical reaction occurs and is thus a source of energy. The reaction in an *electrolytic cell* is forced in a nonspontaneous direction through application of an external source of electrical energy.

(c) The *cathode* of a cell is the electrode at which reduction occurs. The *right-hand electrode* is the electrode on the right in the cell diagram.

(d) In a *reversible cell,* alteration of the direction of the current simply causes a reversal in the electrochemical process. In an *irreversible cell*, reversal of the current results in a different reaction at one or both of the electrodes.

(e) The *standard electrode potential* is the potential of a cell in which the standard hydrogen electrode acts as the reference electrode on the left and all participants in the right-hand electrode process have unit activity. The *formal potential* differs in that the molar *concentrations* of all the reactants and products are unity and the concentration of other species in the solution are carefully specified.

18-4. The first standard potential is for a solution saturated with I_2, which has an $I_2(aq)$ activity significantly less than one. The second potential is for a *hypothetical* half-cell in which the $I_2(aq)$ activity is unity.

18-5. To keep the solution saturated with $H_2(g)$. Only then is the hydrogen activity constant and the electrode potential constant and reproducible.

18-6. The potential in the presence of base would be more negative because the nickel ion activity in this solution would be far less than 1 M. Consequently the driving force for the reduction if Ni (II) to the metallic state would also be far less, and the electrode potential would be significantly more negative. (In fact the standard electrode potential for the reaction $Ni(OH)_2 + 2e^- \rightleftharpoons Ni(s) + 2OH^-$ has a value of –0.72 V, whereas the standard electrode potential for $Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$ is –0.250 V.)

18-7. **(a)** $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$

(b) $Cr(s) + 3Ag^+ \rightarrow Cr^{3+} + 3Ag(s)$

(c) $2NO_3^- + Cu(s) + 4H^+ \rightarrow 2NO_2(g) + 2H_2O + Cu^{2+}$

(d) $2MnO_4^- + 5H_2SO_3 \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+ + 3H_2O$

(e) $Ti^{3+} + Fe(CN)_6^{3-} + H_2O \rightarrow TiO^{2+} + Fe(CN)_6^{4-} + 2H^+$

(f) $H_2O_2 + 2Ce^{4+} \rightarrow O_2(g) + 2Ce^{3+} + 2H^+$

(g) $2Ag(s) + 2I^- + Sn^{4+} \rightarrow 2AgI(s) + Sn^2$

(h) $UO_2^{2+} + Zn(s) + 4H^+ \rightarrow U^{4+} + Zn^{2+} + 2H_2O$

(i) $5HNO_2 + 2MnO_4^- + H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$

(j) $H_2NNH_2 + IO_3^- + 2H^+ + 2Cl^- \rightarrow N_2(g) + ICl_2^- + 3H_2O$

18-8. **(a)** Oxidizing agent Fe^{3+}; $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

Reducing agent Sn^{2+}; $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$

(b) Oxidizing agent Ag^+; $Ag^+ + e^- \rightleftharpoons Ag(s)$

Reducing agent Cr; $Cr(s) \rightleftharpoons Cr^{3+} + 3e^-$

(c) Oxidizing agent NO_3^-, $NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2(g) + H_2O$

Reducing agent Cu; $Cu(s) \rightleftharpoons Cu^{2+} + 2e^-$

(d) Oxidizing agent MnO_4^-; $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

Reducing agent H_2SO_3; $H_2SO_3 + H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$

(e) Oxidizing agent $Fe(CN)_6^{3-}$; $Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$

Reducing agent Ti^{3+}; $Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$

(f) Oxidizing agent Ce^{4+}; $Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$

Reducing agent H_2O_2; $H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e^-$

(g) Oxidizing agent Sn^{4+}; $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$

Reducing agent Ag; $Ag(s) + I^- \rightleftharpoons AgI(s) + e^-$

(h) Oxidizing agent UO_2^{2+}; $UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$

Reducing agent Zn; $Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$

(i) Oxidizing agent MnO_4^-; $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

Reducing agent HNO_2 $HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$

(j)) Oxidizing agent IO_3^-; $IO_3^- + 6H^+ + 2Cl^- + 4e^- \rightleftharpoons ICl_2^- + 3H_2O$

Reducing agent H_2NNH_2; $H_2NNH_2 \rightleftharpoons N_2(g) + 4H^+ + 4e^-$

18-9. **(a)** $MnO_4^- + 5VO^{2+} + 11H_2O \rightarrow Mn^{2+} + 5V(OH)_4^+ + 2H^+$

(b) $I_2 + H_2S(g) \rightarrow 2I^- + S(s) + 2H^+$

(c) $Cr_2O_7^{2-} + 3U^{4+} + 2H^+ \rightarrow 2Cr^{3+} + 3UO_2^{2+} + H_2O$

(d) $2Cl^- + MnO_2(s) + 4H^+ \rightarrow Cl_2(g) + Mn^{2+} + 2H_2O$

(e) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

(f) $IO_3^- + 2I^- + 6Cl^- + 6H^+ \rightarrow 3ICl_2^- + 3H_2O$

(g) $HPO_3^{2-} + 2MnO_4^- + 3OH^- \rightarrow PO_4^{3-} + 2MnO_4^{2-} + 2H_2O$

(h) $SCN^- + BrO_3^- + H_2O \rightarrow SO_4^{2-} + HCN + Br^- + H^+$

(i) $V^{2+} + 2V(OH)_4^+ + 2H^+ \rightarrow 3VO^{2+} + 5H_2O$

(j) $2MnO_4^- + 3Mn^{2+} + 4OH^- \rightarrow 5MnO_2(s) + 2H_2O$

18-10. **(a)** Oxidizing agent MnO_4^-; $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

Reducing agent VO^{2+}; $VO^{2+} + 3H_2O \rightleftharpoons V(OH)_4^+ + 2H^+ + e^-$

(b) Oxidizing agent I_2; $I_2(aq) + 2e^- \rightleftharpoons 2I^-$

Reducing agent H_2S; $H_2S(g) \rightleftharpoons S(s) + 2H^+ + 2e^-$

(c) Oxidizing agent $Cr_2O_7^{2-}$; $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$

Reducing agent U^{4+}; $U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$

(d) Oxidizing agent MnO_2; $MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$

Reducing agent Cl^-; $2Cl^- \rightleftharpoons Cl_2(g) + 2e^-$

(e) Oxidizing agent IO_3^-; $IO_3^- + 6H^+ + 5e^- \rightleftharpoons 1/2I_2 + 3\,H_2O$

Reducing agent I^-; $I^- \rightleftharpoons 1/2I_2 + e^-$

(f) Oxidizing agent IO_3^-; $IO_3^- + 6H^+ + 2Cl^- + 4e^- \rightleftharpoons ICl_2^- + 3H_2O$

Reducing agent I^-; $I^- + 2Cl^- \rightleftharpoons ICl_2^- + 2e^-$

(g) Oxidizing agent MnO_4^-; $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$

Reducing agent HPO_3^{2-}; $HPO_3^{2-} + 3OH^- \rightleftharpoons PO_4^{3-} + 2H_2O + 2e^-$

(h) Oxidizing agent BrO_3^-; $BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$

Reducing agent SCN^-; $SCN^- + 4H_2O \rightleftharpoons SO_4^{2-} + HCN + 7H^+ + 6e^-$

(i) Oxidizing agent $V(OH)_4^+$; $V(OH)_4^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + 3H_2O$

Reducing agent V^{2+}; $V^{2+} + H_2O \rightleftharpoons VO^{2+} + 2H^+ + 2e^-$

(j) Oxidizing agent MnO_4^-; $MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$

Reducing agent Mn^{2+}; $Mn^{2+} + 2H_2O \rightleftharpoons MnO_2(s) + 4H^+ + 2e^-$

18-11. **(a)** $AgBr(s) + e– \rightleftharpoons Ag(s) + Br–$ $V^{2+} \rightleftharpoons V^{3+} + e^-$

$Ti^{3+} + 2e– \rightleftharpoons Ti^+$ $Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^-$

$V^{3+} + e– \rightleftharpoons V^{2+}$ $Zn \rightleftharpoons Zn^{2+} + 2e^-$

$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$ $Ag(s) + Br– \rightleftharpoons AgBr(s) + e^-$

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $Ti+ \rightleftharpoons Ti^{3+} + 2e^-$

(b), (c)	E^0
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	2.01
$Ti^{3+} + 2e^- \rightleftharpoons Ti^+$	1.25
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.36
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	0.073
$V^{3+} + e^- \rightleftharpoons V^{2+}$	– 0.256
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	– 0.763

18-12. (a)

$Sn(s) \rightleftharpoons Sn^{2+} + 2e^-$	$2H^+ + 2e^- \rightleftharpoons H_2(g)$
$Ag^+ + e^- \rightleftharpoons Ag(s)$	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	$H_2(g) \rightleftharpoons 2H^+ + 2e^-$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	$Co(s) \rightleftharpoons Co^{2+} + 2e^-$

(b), (c)	$E°$
$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.771
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.154
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	–0.136
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	–0.277

18-13. (a)

$$E_{\text{Cu}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{0.0380}\right) = \ 0.295 \text{ V}$$

(b)

$K_{\text{CuCl}} = 1.9 \times 10^{-7} = [\text{Cu}^+][\text{Cl}^-]$

$$E_{\text{Cu}} = 0.521 - \frac{0.0592}{1}\log\left(\frac{1}{[\text{Cu}^+]}\right) = 0.521 - \frac{0.0592}{1}\log\left(\frac{[\text{Cl}^-]}{K_{\text{CuCl}}}\right)$$

$$= 0.521 - \frac{0.0592}{1}\log\left(\frac{0.0650}{1.9 \times 10^{-7}}\right) = 0.521 - \frac{0.0592}{1}\log(3.42 \times 10^{5})$$

$$= 0.521 - 0.328 = 0.193\text{ V}$$

(c) $K_{\text{Cu(OH)}_2} = 4.8 \times 10^{-20} = [\text{Cu}^{2+}][\text{OH}^-]^2$

$$E_{\text{Cu}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{[\text{Cu}^{2+}]}\right) = 0.337 - \frac{0.0592}{2}\log\left(\frac{[\text{OH}^-]^2}{K_{\text{Cu(OH)}_2}}\right)$$

$$= 0.337 - \frac{0.0592}{2}\log\left(\frac{(0.0350)^2}{4.8 \times 10^{-20}}\right) = 0.337 - \frac{0.0592}{2}\log(2.55 \times 10^{16})$$

$$= 0.337 - 0.486 = -0.149\text{ V}$$

(d) $\beta_4 = 5.62 \times 10^{11} = \dfrac{[\text{Cu(NH}_3)_4{}^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$

$$E_{\text{Cu}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{[\text{Cu}^{2+}]}\right) = 0.337 - \frac{0.0592}{2}\log\left(\frac{\beta_4[\text{NH}_3]^4}{[\text{Cu(NH}_3)_4{}^{2+}]}\right)$$

$$= 0.337 - \frac{0.0592}{2}\log\left(\frac{5.62 \times 10^{11}(0.108)^4}{0.0375}\right) = 0.337 - \frac{0.0592}{2}\log(2.04 \times 10^{9})$$

$$= 0.337 - 0.276 = 0.061\text{ V}$$

(e)

$$\frac{[\text{CuY}^{2-}]}{[\text{Cu}^{2+}]c_{\text{T}}} = \alpha_4 K_{\text{CuY}} = (3.6 \times 10^{-9}) \times (6.3 \times 10^{18}) = 2.3 \times 10^{10}$$

$$[\text{CuY}^{2-}] \approx 3.90 \times 10^{-3}$$

$$c_{\text{T}} = (3.90 \times 10^{-2}) - (3.90 \times 10^{-3}) = 0.0351$$

$$E_{\text{Cu}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{[\text{Cu}^{2+}]}\right) = 0.337 - \frac{0.0592}{2}\log\left(\frac{\alpha_4 K_{\text{CuY}^{2-}} c_{\text{T}}}{[\text{CuY}^{2-}]}\right)$$

$$= 0.337 - \frac{0.0592}{2}\log\left(\frac{2.3 \times 10^{10}\left(0.0351\right)}{3.90 \times 10^{-3}}\right) = 0.337 - \frac{0.0592}{2}\log(2.07 \times 10^{11})$$

$$= 0.337 - 0.335 = 0.002 \text{ V}$$

18-14. (a)

$$E_{\text{Zn}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.0500}\right) = -0.802 \text{ V}$$

(b) $K_{\text{Zn(OH)}_2} = 3.0 \times 10^{-16} = [\text{Zn}^{2+}][\text{OH}^-]^2$

$$E_{\text{Zn}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{[\text{Zn}^{2+}]}\right) = -0.763 - \frac{0.0592}{2}\log\left(\frac{[\text{OH}^-]^2}{K_{\text{Zn(OH)}_2}}\right)$$

$$= -0.763 - \frac{0.0592}{2}\log\left(\frac{\left(0.0200\right)^2}{3.0 \times 10^{-16}}\right) = -0.763 - \frac{0.0592}{2}\log(1.33 \times 10^{12})$$

$$= -0.763 - 0.359 = -1.12 \text{ V}$$

(c) $\beta_4 = 7.76 \times 10^8 = \dfrac{[\text{Zn(NH}_3)_4{}^{2+}]}{[\text{Zn}^{2+}][\text{NH}_3]^4}$

$$E_{\text{Zn}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{[\text{Zn}^{2+}]}\right) = -0.763 - \frac{0.0592}{2}\log\left(\frac{\beta_4[\text{NH}_3]^4}{[\text{Zn(NH}_3)_4{}^{2+}]}\right)$$

$$= -0.763 - \frac{0.0592}{2}\log\left(\frac{7.76 \times 10^8\left(0.350\right)^4}{0.0150}\right) = -0.763 - \frac{0.0592}{2}\log(7.76 \times 10^8)$$

$$= -0.763 - 0.263 = -1.03 \text{ V}$$

(d)

$$\frac{[\text{ZnY}^{2-}]}{[\text{Zn}^{2+}]c_{\text{T}}} = \alpha_4 K_{\text{ZnY}} = \left(5.2 \times 10^{-2}\right) \times \left(3.2 \times 10^{16}\right) = 1.7 \times 10^{15}$$

$$[\text{ZnY}^{2-}] \approx 4.00 \times 10^{-3}$$

$$c_{\text{T}} = \left(5.50 \times 10^{-2}\right) - \left(4.00 \times 10^{-3}\right) = 0.051$$

$$E_{\mathrm{Zn}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{[\mathrm{Zn}^{2+}]}\right) = -0.763 - \frac{0.0592}{2}\log\left(\frac{\alpha_4 K_{\mathrm{ZnY}^{2-}} c_{\mathrm{T}}}{[\mathrm{ZnY}^{2-}]}\right)$$

$$= -0.763 - \frac{0.0592}{2}\log\left(\frac{1.7\times10^{15}\,(0.051)}{5.00\times10^{-3}}\right) = -0.763 - \frac{0.0592}{2}\log(1.73\times10^{16})$$

$$= -0.763 - 0.481 = -1.24\ \mathrm{V}$$

18-15. $2H^+ + 2e^- \rightleftharpoons H_2(g)$

$$E = E^o - \frac{0.0592}{2}\log\left(\frac{p_{\mathrm{H_2}}}{\left(a_{\mathrm{H^+}}\right)^2}\right) = 0.00 - \frac{0.0592}{2}\log\left(\frac{1.00}{[\mathrm{H^+}]^2\ \times\ \left(\gamma_{\mathrm{H^+}}\right)^2}\right)$$

The ionic strength of the solution is 0.0100 M.

From Table 10-2,

$$\gamma_{\mathrm{H^+}} = 0.913$$

$$E = 0.00 - \frac{0.0592}{2}\log\left(\frac{1.00}{(0.0100)^2\ \times\ (0.913)^2}\right) = 0.00 - 0.121 = -0.121\ \mathrm{V}$$

18-16. **(a)** $PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4\,Cl^-$ $E^0 = 0.73$ V

$$E_{\mathrm{Pt}} = 0.73 - \frac{0.0592}{2}\log\left(\frac{(0.2450)^4}{0.0160}\right) = 0.73 - (-0.019)\ =\ 0.75\ \mathrm{V}$$

(b) $E^0 = 0.154$

$$E_{\mathrm{Pt}} = 0.154 - \frac{0.0592}{2}\log\left(\frac{3.50\times10^{-3}}{6.50\times10^{-2}}\right) = 0.154 - (-0.038) = 0.192\ \mathrm{V}$$

(c) pH = 6.50, $[H^+] = 3.16\times10^{-7}$

$$E_{\mathrm{Pt}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{1.00}{\left(3.16\times10^{-7}\right)^2}\right) = -0.385\ \mathrm{V}$$

(d) $E^0 = 0.359$ V

$$E_{\text{Pt}} = 0.359 - \frac{0.0592}{1}\log\left(\frac{(0.0686)\times 2}{(0.0255)\times(0.100)^2}\right) = 0.359 - 0.162 = 0.197\text{ V}$$

(e) $2\text{Fe}^{3+} + \text{Sn}^{2+} \rightleftharpoons 2\text{Fe}^{2+} + \text{Sn}^{4+}$

$$\text{amount Sn}^{2+}\text{consumed} = \frac{0.0918\text{ mmol SnCl}_2}{\text{mL}} \times \frac{1\text{ mmol Sn}^{2+}}{\text{mmol SnCl}_2} \times 25.00\text{ mL} = 2.295\text{ mmol}$$

$$\text{amount Fe}^{3+}\text{consumed} = \frac{0.1568\text{ mmol FeCl}_3}{\text{mL}} \times \frac{1\text{ mmol Fe}^{3+}}{\text{mmol FeCl}_3} \times 25.00\text{ mL} = 3.920\text{ mmol}$$

$$\text{amount Sn}^{4+}\text{formed} = 3.920\text{ mmol Fe}^{3+} \times \frac{1\text{ mmol Sn}^{4+}}{2\text{ mmol Fe}^{3+}} = 1.960\text{ mmol}$$

$$\text{amount Sn}^{2+}\text{remaining} = 2.295 - 1.960 = 0.335\text{ mmol}$$

$$E_{\text{Pt}} = 0.154 - \frac{0.0592}{2}\log\left(\frac{(0.335)/50.0}{(1.960)/50.0}\right) = 0.154 - (-0.023) = 0.177\text{ V}$$

(f) $\text{V(OH)}_4^{+} + \text{V}^{3+} + \rightleftharpoons 2\text{VO}^{2+} + 2\text{H}_2\text{O}$

$\text{V(OH)}_4^{+} + 2\text{H}^{+} + 2e^{-} \rightleftharpoons \text{VO}^{2+} + 3\text{H}_2\text{O}$ $E^0 = 1.00$ V

$$\text{amount V(OH)}_4^{+}\text{consumed} = \frac{0.0832\text{ mmol V(OH)}_4^{+}}{\text{mL}} \times 25.00\text{ mL} = 2.08\text{ mmol}$$

$$\text{amount V}^{3+}\text{consumed} = \frac{0.01087\text{ mmol V}_2(\text{SO}_4)_3}{\text{mL}} \times \frac{2\text{ mmol V}^{3+}}{\text{mmol V}_2(\text{SO}_4)_3} \times 50.00\text{ mL} = 1.087\text{ mmol}$$

$$\text{amount VO}^{2+}\text{formed} = 1.087\text{ mmol V}^{3+} \times \frac{2\text{ mmol VO}^{2+}}{\text{mmol V}^{3+}} = 2.174\text{ mmol}$$

$$\text{amount V(OH)}_4^{+}\text{remaining} = 2.08 - 1.087 = 0.993\text{ mmol}$$

$$E_{\text{Pt}} = 1.00 - 0.0592\log\left(\frac{(2.174)/75.00}{(0.993/75.00)(0.1000)^2}\right) = 1.00 - 0.139 = 0.86\text{ V}$$

18-17. (a)

$$E_{\mathrm{Pt}}=0.36-0.0592\log\left(\frac{0.0613}{0.00669}\right)=0.36-0.057=0.30\ \mathrm{V}$$

(b) $E_{Pt}=0.771-0.0592\log\left(\dfrac{0.0400}{\left(0.00915\right)\times 2}\right)=0.771-0.020=0.751\ \mathrm{V}$

(c) pH = 5.55 $[\mathrm{H_3O^+}] = 2.82\times10^{-6}$

$$E_{\mathrm{Pt}}=0.000-\frac{0.0592}{2}\log\left(\frac{1.00}{\left(2.82\times10^{-6}\right)^2}\right)=0.000-0.329=-0.329\ \mathrm{V}$$

(d) $E_{\mathrm{Pt}}=1.00-0.0592\log\left(\dfrac{0.0799}{\left(0.1015\right)\left(0.0800\right)^2}\right)=1.00-0.124=0.876\ \mathrm{V}$

(e)

$$\text{amount Ce}^{4+}\text{consumed} = \frac{0.0607\ \text{mmol Ce(SO}_4)_2}{\text{mL}}\times\frac{1\ \text{mmol Ce}^{4+}}{\text{mmol Ce(SO}_4)_2}\times 50.00\ \text{mL}$$
$$=3.04\ \text{mmol Ce}^{4+}$$

$$\text{amount Fe}^{2+}\text{consumed} = \frac{0.100\ \text{mmol FeCl}_2}{\text{mL}}\times\frac{1\ \text{mmol Fe}^{2+}}{\text{mmol FeCl}_2}\times 50.00\ \text{mL} = 5.00\ \text{mmol}$$

amount $\mathrm{Fe^{3+}}$formed = mmol $\mathrm{Ce^{4+}}$consumed = 3.04 mmol $\mathrm{Fe^{3+}}$

amount $\mathrm{Fe^{2+}}$remaining = 5.00 – 3.04 = 0.196 mmol

$$E_{\mathrm{Pt}}=0.68-0.0592\log\left(\frac{1.965/100.0}{3.04/100.0}\right)=0.68-(-0.011)=0.69\ \mathrm{V}$$

(f) $\mathrm{V(OH)_4^+ + V^{3+} + \rightleftharpoons 2VO^{2+} + 2H_2O}$

$$\text{amount V(OH)}_4^{+}\text{consumed} = \frac{0.0628\ \text{mmol V(OH)}_4^{+}}{\text{mL}}\times 50.00\ \text{mL} = 0.314\ \text{mmol}$$

$$\text{amount } V^{3+}\text{consumed} = \frac{0.0832 \text{ mmol } V_2(SO_4)_3}{\text{mL}} \times \frac{2 \text{ mmol } V^{3+}}{\text{mmol } V_2(SO_4)_3} \times 25.00 \text{ mL}$$

$=4.16$ mmol

$$\text{amount } VO^{2+}\text{formed} = 0.314 \text{ mmol } V^{3+} \times \frac{2 \text{ mmol } VO^{2+}}{\text{mmol } V^{3+}} = 0.628 \text{ mmol}$$

$$\text{amount } V(OH)_4{}^{+}\text{remaining} = 4.16 - 0.314 = 3.85 \text{ mmol}$$

$$E_{\text{Pt}} = 0.337 - 0.0592\log\left(\frac{3.85/75.00}{(0.628/75.00)(0.100)^2}\right) = 0.337 - 0.172 = 0.194 \text{ V}$$

18-18. **(a)**

$$E_{\text{Ni}} = -0.250 - \frac{0.0592}{2}\log\left(\frac{1.00}{0.0883}\right) = -0.250 - 0.031 = -0.281 \text{ V anode}$$

(b) $E_{\text{Ag}} = -0.151 - 0.0592\log(0.0898) = -0.151 - (-0.062) = -0.089 \text{ V anode}$

(c)

$$E_{O_2} = 1.229 - \frac{0.0592}{4}\log\left(\frac{1.00}{(780/760)(2.50\times10^{-4})^4}\right) = 1.229 - 0.213 = 1.016 \text{ V cathode}$$

(d) $E_{\text{Pt}} = 0.154 - \frac{0.0592}{2}\log\left(\frac{0.0893}{0.215}\right) = 0.154 - (-0.011) = 0.165 \text{ V cathode}$

(e) $E_{\text{Ag}} = 0.017 - 0.0592\log\left(\frac{(0.1035)^2}{0.00891}\right) = 0.017 - 0.005 = 0.012 \text{ V cathode}$

18-19. **(a)** $E_{\text{Cu}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1.00}{0.0805}\right) = 0.337 - 0.032 = 0.305 \text{ V cathode}$

(b) $E_{\text{Pt}} = -0.185 - 0.0592\log(0.0993) = -0.185 - (-0.059) = -0.126 \text{ V anode}$

(c) $E_{\text{Pt}} = 0.00 - \frac{0.0592}{2}\log\left(\frac{0.914}{(1.00\times10^{-4})^2}\right) = 0.00 - 0.236 = -0.236 \text{ V anode}$

(d) $E_{\text{Pt}} = 0.771 - 0.0592\log\left(\dfrac{0.1420}{0.0886}\right) = 0.771 - 0.012 = 0.759\text{ V cathode}$

(e) $E_{\text{Ag}} = -0.31 - 0.0592\log\left(\dfrac{(0.0651)^2}{0.0778}\right) = -0.31 - (-0.075) = -0.24\text{ V anode}$

18-20. $2Ag^+ + 2e^- \rightleftharpoons 2Ag(s) \qquad E^o = 0.779$

$[Ag^+]^2[SO_3{}^{2-}] = 1.5 \times 10^{-14} = K_{sp}$

$$E = 0.799 - \frac{0.0592}{2}\log\left(\frac{1}{[Ag^+]^2}\right) = 0.799 - \frac{0.0592}{2}\log\left(\frac{[SO_3{}^{2-}]}{K_{sp}}\right)$$

When $[SO_3{}^{2-}] = 1.00$, $E = E^o$ for $Ag_2SO_3(s) + 2e^- \rightleftharpoons 2Ag(s) + SO_3{}^{2-}$.

Thus,

$$E = 0.799 - \frac{0.0592}{2}\log\left(\frac{1.00}{K_{sp}}\right) = 0.799 - \frac{0.0592}{2}\log\left(\frac{1.00}{1.5\times10^{-14}}\right) = 0.799 - 0.409 = 0.390\text{ V}$$

18-21. $2Ni^{2+} + 4e^- \rightleftharpoons 2Ni(s) \qquad E^o = -0.250$

$[Ni^{2+}]^2[P_2O_7{}^{4-}] = 1.7 \times 10^{-13} = K_{sp}$

$$E = -0.250 - \frac{0.0592}{4}\log\left(\frac{1}{[Ni^{2+}]^2}\right) = -0.250 - \frac{0.0592}{4}\log\left(\frac{[P_2O_7{}^{4-}]}{K_{sp}}\right)$$

When $[P_2O_7{}^{4-}] = 1.00$, $E = E^o$ for $Ni_2P_2O_7(s) + 4e^- \rightleftharpoons 2Ni(s) + P_2O_7{}^{4-}$.

Thus,

$$E = -0.250 - \frac{0.0592}{4}\log\left(\frac{1.00}{K_{sp}}\right) = -0.250 - \frac{0.0592}{4}\log\left(\frac{1.00}{1.7\times10^{-13}}\right)$$
$$= -0.250 - 0.189 = 0.439\text{ V}$$

18-22. $2Tl^+ + 2e^- \rightleftharpoons 2Tl(s) \qquad E^o = -0.336$

$[Tl^+]^2[S^{2-}] = 6 \times 10^{-22} = K_{sp}$

$$E = -0.336 - \frac{0.0592}{2}\log\left(\frac{1}{[Tl^+]^2}\right) = -0.336 - \frac{0.0592}{2}\log\left(\frac{[S^{2-}]}{K_{sp}}\right)$$

When $[S^{2-}] = 1.00$, $E = E^o$ for $Tl_2S(s) + 2e^- \rightleftharpoons 2Tl(s) + S^{2-}$.

Thus,

$$E = -0.336 - \frac{0.0592}{2}\log\left(\frac{1.00}{K_{sp}}\right) = -0.336 - \frac{0.0592}{2}\log\left(\frac{1.00}{6\times10^{-22}}\right)$$
$$= -0.336 - 0.628 = -0.96 \text{ V}$$

18-23. $3Pb^{3+} + 6e^- \rightleftharpoons 3Pb(s) \qquad E^o = -0.126$

$[Pb^{2+}]^3[AsO_4{}^{2-}]^2 = 4.1 \times 10^{-36} = K_{sp}$

$$E = -0.126 - \frac{0.0592}{6}\log\left(\frac{1}{[Pb^{2+}]^3}\right) = -0.126 - \frac{0.0592}{6}\log\left(\frac{[AsO_4{}^{2-}]^2}{K_{sp}}\right)$$

When $[AsO_4{}^{2-}] = 1.00$, $E = E^o$ for $Pb_3\left(AsO_4\right)_2(s) + 4e^- \rightleftharpoons 3Pb(s) + 2AsO_4{}^{2-}$.

Thus,

$$E = -0.126 - \frac{0.0592}{6}\log\left(\frac{1.00}{K_{sp}}\right) = -0.126 - \frac{0.0592}{6}\log\left(\frac{1.00}{4.1\times10^{-36}}\right)$$
$$= -0.126 - 0.349 = -0.475 \text{ V}$$

18-24. $E = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{[Zn^{2+}]}\right)$

$$\frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]} = 3.2 \times 10^{16}$$

$$E = -0.763 - \frac{0.0592}{2}\log\left(\frac{[Y^{4-}]\left(3.2\times10^{16}\right)}{[ZnY^{2-}]}\right)$$

When $[\mathrm{Y}^{4-}] = [\mathrm{ZnY}^{2-}] = 1.00$, $E = E^{\mathrm{o}}_{\mathrm{ZnY}^{2-}}$

$$E = -0.763 - \frac{0.0592}{2}\log\left(\frac{1.00\left(3.2\times10^{16}\right)}{1.00}\right) = -0.763 - 0.489 = -1.25\text{ V}$$

18-25. $[\mathrm{Fe}^{3+}] = \dfrac{[\mathrm{FeY}^{-}]}{[\mathrm{Y}^{4-}]\left(1.3\times10^{25}\right)}$ and $[\mathrm{Fe}^{2+}] = \dfrac{[\mathrm{FeY}^{2-}]}{[\mathrm{Y}^{4-}]\left(2.1\times10^{14}\right)}$

$$E = 0.771 - 0.0592\log\left(\frac{[\mathrm{Fe}^{2+}]}{[\mathrm{Fe}^{3+}]}\right)$$
$$= 0.771 - 0.0592\log\left(\frac{[\mathrm{FeY}^{2-}]\left(1.3\times10^{25}\right)}{[\mathrm{FeY}^{-}]\left(2.1\times10^{14}\right)}\right)$$

When $[\mathrm{FeY}^{2-}] = [\mathrm{FeY}^{-}] = 1.00$, $E = E^{\mathrm{o}}_{\mathrm{FeY}^{-}}$

$$E = 0.771 - 0.0592\log\left(\frac{1.00\left(1.3\times10^{25}\right)}{1.00\left(2.1\times10^{14}\right)}\right) = 0.771 - 0.64 = 0.13\text{ V}$$

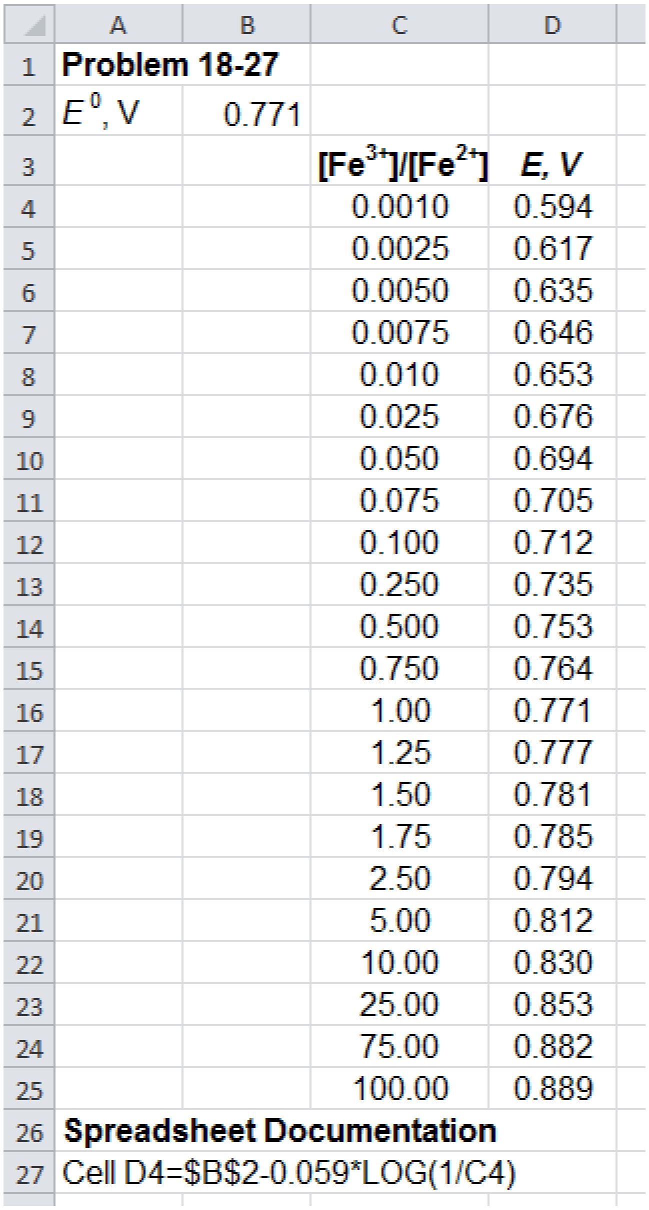
18-26. $[\mathrm{Cu}^{+}] = \dfrac{[\mathrm{Cu(NH_3)_2}^{+}]}{[\mathrm{NH_3}]^2\left(7.2\times10^{10}\right)}$ and $[\mathrm{Cu}^{2+}] = \dfrac{[\mathrm{Cu(NH_3)_2}^{2+}]}{[\mathrm{NH_3}]^2\left(5.62\times10^{11}\right)}$

$$E = 0.153 - 0.0592\log\left(\frac{[\mathrm{Cu}^{+}]}{[\mathrm{Cu}^{2+}]}\right)$$
$$= 0.153 - 0.0592\log\left(\frac{[\mathrm{Cu(NH_3)_2}^{+}]\left(5.62\times10^{11}\right)}{[\mathrm{Cu(NH_3)_2}^{2+}]\left(7.2\times10^{10}\right)}\right)$$

When $[\mathrm{Cu(NH_3)_2}^{+}] = [\mathrm{Cu(NH_3)_2}^{2+}] = 1.00$, $E = E^{\mathrm{o}}_{\mathrm{Cu(NH_3)_2}^{2+}}$

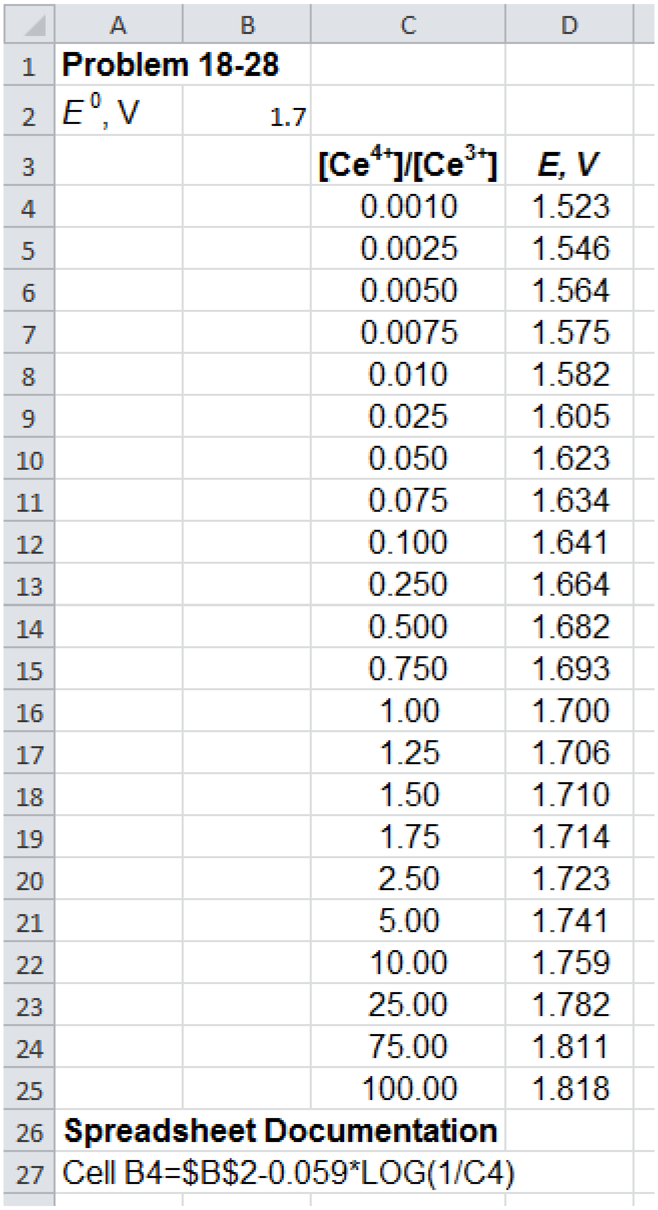
$$E = 0.153 - 0.0592\log\left(\frac{1.00\left(5.62\times10^{11}\right)}{1.00\left(7.2\times10^{10}\right)}\right) = 0.153 - 0.053 = 0.100\text{ V}$$

18-27.



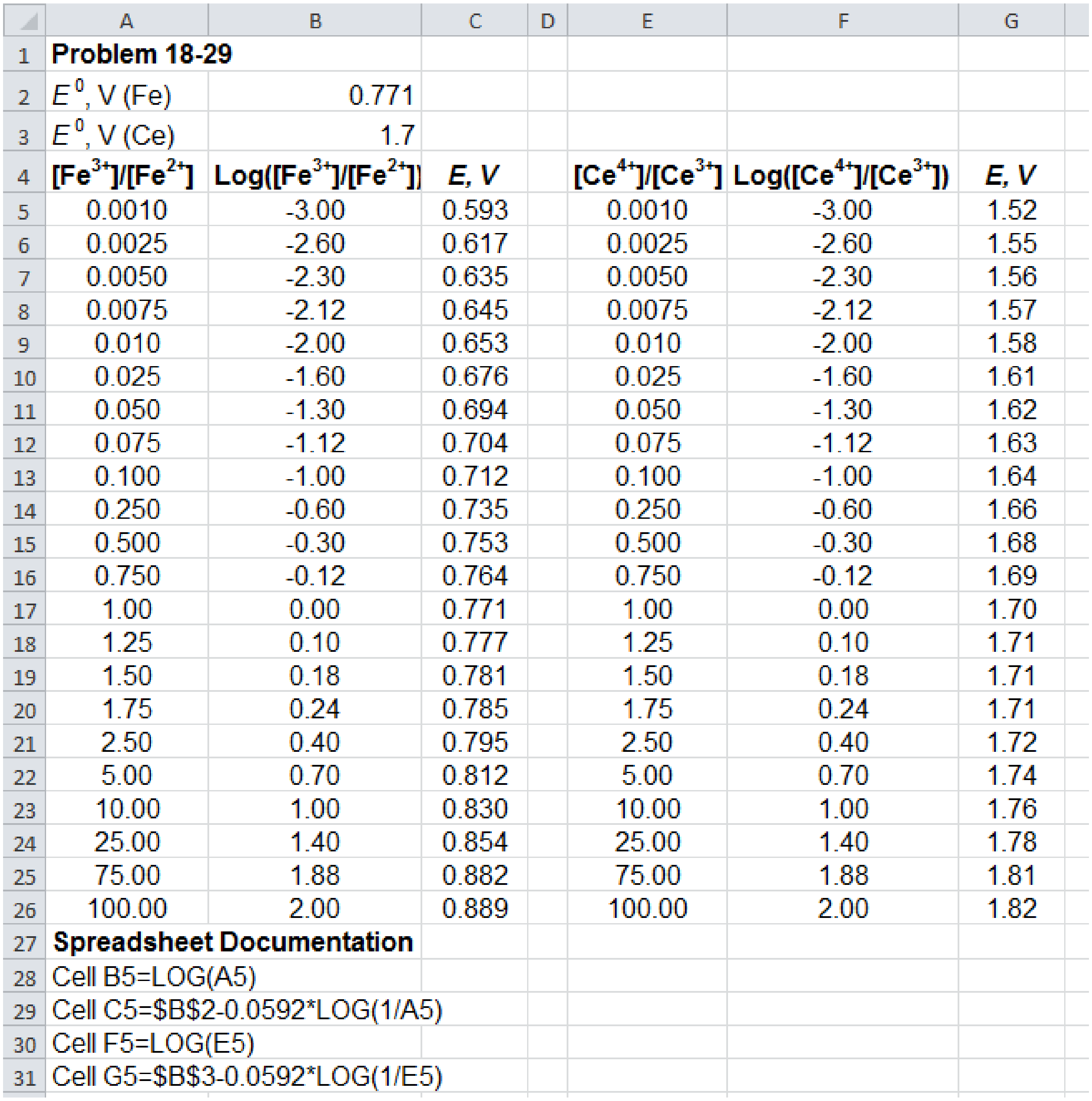
	A	B	C	D
1	**Problem 18-27**			
2	*E*^{0}, V	0.771		
3			**[Fe^{3+}]/[Fe^{2+}]**	***E*, *V***
4			0.0010	0.594
5			0.0025	0.617
6			0.0050	0.635
7			0.0075	0.646
8			0.010	0.653
9			0.025	0.676
10			0.050	0.694
11			0.075	0.705
12			0.100	0.712
13			0.250	0.735
14			0.500	0.753
15			0.750	0.764
16			1.00	0.771
17			1.25	0.777
18			1.50	0.781
19			1.75	0.785
20			2.50	0.794
21			5.00	0.812
22			10.00	0.830
23			25.00	0.853
24			75.00	0.882
25			100.00	0.889
26	**Spreadsheet Documentation**			
27	Cell D4=$B$2-0.059*LOG(1/C4)			

18-28.



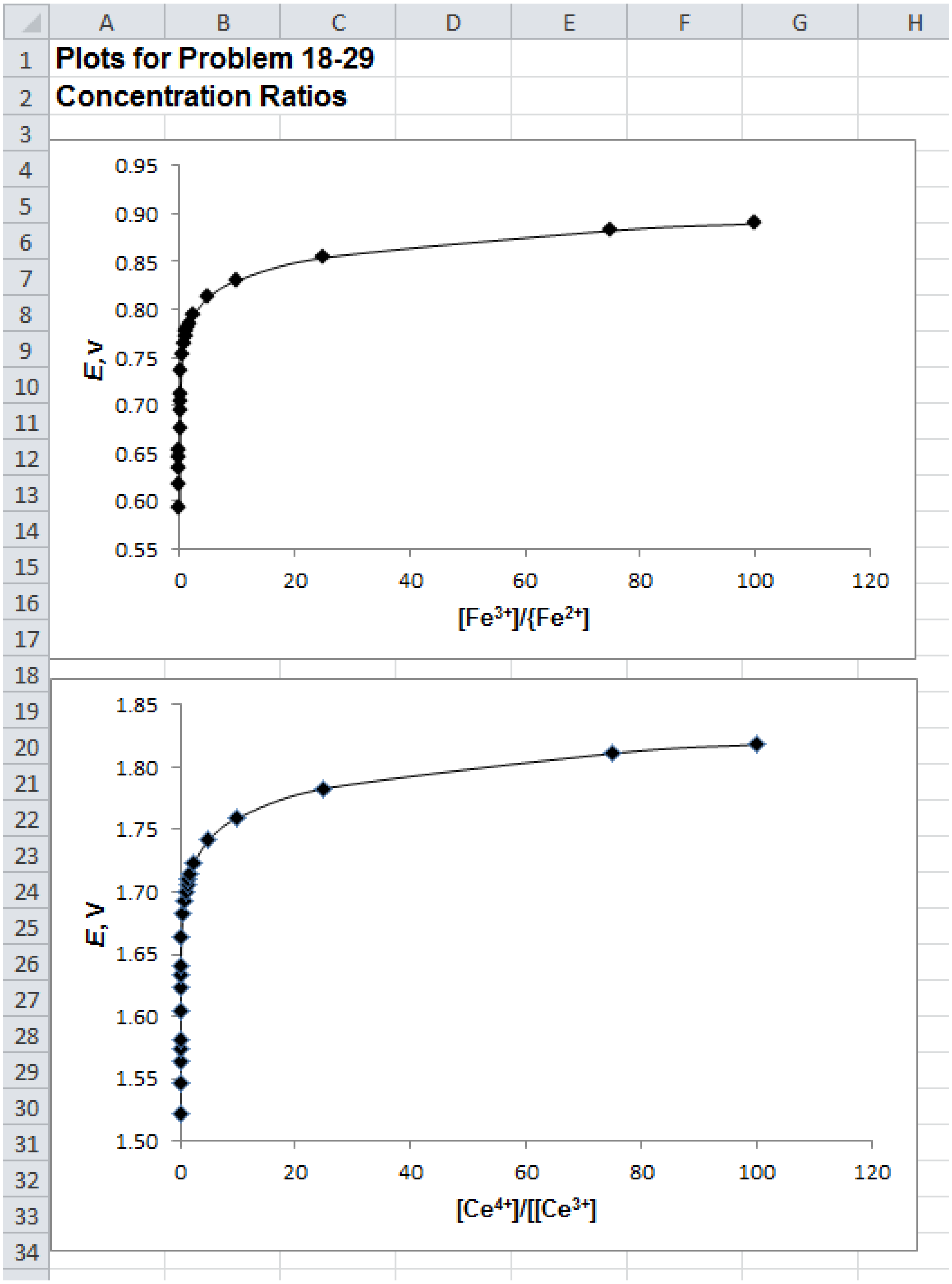
	A	B	C	D
1	**Problem 18-28**			
2	E^0, V	1.7		
3			**$[Ce^{4+}]/[Ce^{3+}]$**	***E*, *V***
4			0.0010	1.523
5			0.0025	1.546
6			0.0050	1.564
7			0.0075	1.575
8			0.010	1.582
9			0.025	1.605
10			0.050	1.623
11			0.075	1.634
12			0.100	1.641
13			0.250	1.664
14			0.500	1.682
15			0.750	1.693
16			1.00	1.700
17			1.25	1.706
18			1.50	1.710
19			1.75	1.714
20			2.50	1.723
21			5.00	1.741
22			10.00	1.759
23			25.00	1.782
24			75.00	1.811
25			100.00	1.818
26	**Spreadsheet Documentation**			
27	Cell B4=$B$2-0.059*LOG(1/C4)			

18-29.



	A	B	C	D	E	F	G
1	**Problem 18-29**						
2	E^0, V (Fe)	0.771					
3	E^0, V (Ce)	1.7					
4	**$[Fe^{3+}]/[Fe^{2+}]$**	**Log($[Fe^{3+}]/[Fe^{2+}]$)**	***E*, *V***		**$[Ce^{4+}]/[Ce^{3+}]$**	**Log($[Ce^{4+}]/[Ce^{3+}]$)**	***E*, *V***
5	0.0010	-3.00	0.593		0.0010	-3.00	1.52
6	0.0025	-2.60	0.617		0.0025	-2.60	1.55
7	0.0050	-2.30	0.635		0.0050	-2.30	1.56
8	0.0075	-2.12	0.645		0.0075	-2.12	1.57
9	0.010	-2.00	0.653		0.010	-2.00	1.58
10	0.025	-1.60	0.676		0.025	-1.60	1.61
11	0.050	-1.30	0.694		0.050	-1.30	1.62
12	0.075	-1.12	0.704		0.075	-1.12	1.63
13	0.100	-1.00	0.712		0.100	-1.00	1.64
14	0.250	-0.60	0.735		0.250	-0.60	1.66
15	0.500	-0.30	0.753		0.500	-0.30	1.68
16	0.750	-0.12	0.764		0.750	-0.12	1.69
17	1.00	0.00	0.771		1.00	0.00	1.70
18	1.25	0.10	0.777		1.25	0.10	1.71
19	1.50	0.18	0.781		1.50	0.18	1.71
20	1.75	0.24	0.785		1.75	0.24	1.71
21	2.50	0.40	0.795		2.50	0.40	1.72
22	5.00	0.70	0.812		5.00	0.70	1.74
23	10.00	1.00	0.830		10.00	1.00	1.76
24	25.00	1.40	0.854		25.00	1.40	1.78
25	75.00	1.88	0.882		75.00	1.88	1.81
26	100.00	2.00	0.889		100.00	2.00	1.82
27	**Spreadsheet Documentation**						
28	Cell B5=LOG(A5)						
29	Cell C5=$B$2-0.0592*LOG(1/A5)						
30	Cell F5=LOG(E5)						
31	Cell G5=$B$3-0.0592*LOG(1/E5)						

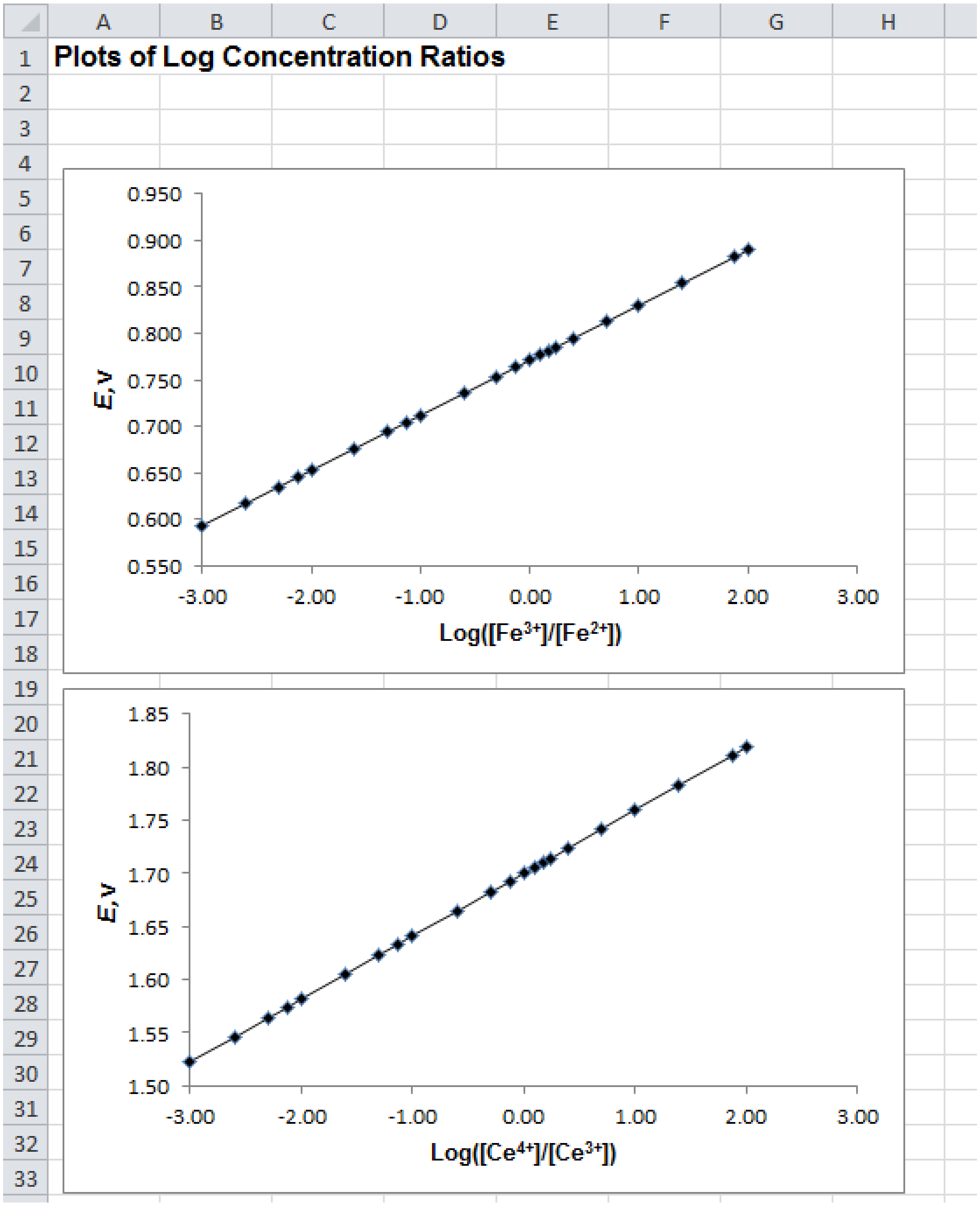
Plots of Concentration Ratios



Plots for Problem 18-29

Concentration Ratios

Plot of Log Concentration Ratios



Plots of Log Concentration Ratios

Chapter 19

19-1. The electrode potential of a system that contains two or more redox couples is the electrode potential of all half-cell processes at equilibrium in the system.

19-2. **(a)** *Equilibrium* is the state that a system assumes after each addition of reagent. *Equivalence* refers to a particular equilibrium state when a stoichiometric amount of titrant has been added.

(b) A *true oxidation/reduction indicator* owes its color change to changes in the electrode potential of the system. A *specific indicator* exhibits its color change as a result of reactions with a particular solute species.

19-3. The electrode potentials for all half-cell processes in an oxidation/reduction system have the same numerical value when the system is at equilibrium.

19-4. For points before the equivalence point, potential data are computed from the analyte standard potential and the analytical concentrations of the analyte and its reaction product. Post-equivalence point data are based upon the standard potential for the titrant and its analytical concentrations. The equivalence point potential is computed from the two standard potentials and the stoichiometric relation between the analyte and titrant.

19-5. In contrast to all other points on the titration curve, the concentrations of all of the participants in one of the half-reactions or the other cannot be derived from stoichiometric calculations. Instead, the equivalence point potential is computed from the two standard potentials and the stoichiometric relation between the analyte and titrant.

19-6. An asymmetric titration curve will be encountered whenever the titrant and the analyte react in a ratio that is not 1:1.

19-7. **(a)**

$$E_{\text{right}} = -0.403 - \frac{0.0592}{2}\log\left(\frac{1}{0.0500}\right) = -0.442\ \text{V}$$

$$E_{\text{left}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{1}{0.1200}\right) = -0.153\ \text{V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.442 - (-0.153) = -\ 0.289\ \text{V}$$

Because E_{cell} is negative, the spontaneous reaction is not oxidation on the left and reduction on the right. An external source would be needed to force this reaction to occur.

(b)

$$E_{\text{right}} = 1.25 - \frac{0.0592}{2}\log\left(\frac{0.0400}{9.06 \times 10^{-2}}\right)$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.0420}\right) = -0.804\ \text{V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 1.26 - (-0.804) = 2.06\ \text{V}$$

Because E_{cell} is positive the reaction would proceed spontaneously in the direction considered (oxidation on the left, reduction on the right).

(c)

$$E_{\text{right}} = -0.250 - \frac{0.0592}{2}\log\left(\frac{1}{0.0400}\right) = -0.291\ \text{V}$$

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{757/760}{\left(2.00 \times 10^{-4}\right)^2}\right) = -0.219\ \text{V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.291 - (-0.219) = -\ 0.072\ \text{V}$$

Because E_{cell} is negative, the spontaneous reaction is not oxidation on the left and reduction on the right. An external source would be needed to force this reaction to occur.

(d) $$E_{\text{right}} = 0.854 - \frac{0.0592}{2}\log\left(\frac{1}{2.60 \times 10^{-3}}\right) = 0.777\ \text{V}$$

$$[\text{Pb}^{2+}][\text{I}^-]^2 = 7.9\times10^{-9} \text{ and } [\text{Pb}^{2+}] = \frac{7.9\times10^{-9}}{[\text{I}^-]^2}$$

$$E_{\text{left}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{(0.0220)^2}{7.9 \times 10^{-9}}\right) = -0.268\ \text{V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.777 - (-0.268) = 1.045\ \text{V}$$

Because E_{cell} is positive the reaction would proceed spontaneously in the direction considered (oxidation on the left, reduction on the right).

(e)

$$\frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^{\ +}]} = 5.70 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+]0.400}{0.200}$$

$$[\text{H}_3\text{O}^+] = \frac{(5.70 \times 10^{-10})(0.200)}{0.400} = 2.85 \times 10^{-10}$$

$$E_{\text{right}} = 0.000\,V$$

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{1.00}{(2.85 \times 10^{-10})^2}\right) = -0.565\,V$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.000 - (-0.565) = 0.565\ \text{V}$$

Because E_{cell} is positive, the reaction would proceed spontaneously in the direction considered.

(f)

$$E_{\text{right}} = 0.359 - 0.0592\log\left(\frac{0.0800}{0.1600(0.0100)^2}\right) = 0.140\text{ V}$$

$$E_{\text{left}} = 0.099 - 0.0592\log\left(\frac{0.00320}{0.0450(3.00\times10^{-2})^2}\right) = -0.013\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.140 - (-0.013) = 0.153\text{ V}$$

Because E_{cell} is positive, the reaction would proceed spontaneously in the direction considered.

19-8. **(a)**

$$E_{\text{right}} = -0.277 - \frac{0.0592}{2}\log\left(\frac{1}{5.87\times10^{-4}}\right) = -0.373\text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.100}\right) = -0.793\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.373 - (-0.793) = 0.420\text{ V}$$

Because E_{cell} is positive, the reaction would proceed spontaneously in the direction considered (oxidation on the left, reduction on the right).

(b) $$E_{\text{right}} = 0.854 - \frac{0.0592}{2}\log\left(\frac{1}{0.0350}\right) = 0.811\text{ V}$$

$$E_{\text{left}} = 0.771 - \frac{0.0592}{1}\log\left(\frac{0.0700}{0.1600}\right) = 0.792\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.811 - 0.792 = 0.019\text{ V}$$

Because E_{cell} is positive, the spontaneous reaction would be oxidation on the left and reduction on the right.

(c)

$$E_{\text{right}} = 1.229 - \frac{0.0592}{4}\log\left(\frac{1}{1.12\left(0.0333\right)^4}\right) = 1.142\text{ V}$$

$$E_{\text{left}} = 0.799 - 0.0592\log\left(\frac{1}{0.0575}\right) = 0.726\,V$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 1.142 - 0.726 = 0.416\text{ V}$$

The spontaneous reaction would be oxidation on the left, reduction on the right.

(d)

$$E_{\text{right}} = -0.151 - 0.0592\log\left(0.1220\right) = -0.097\text{ V}$$

$$E_{\text{left}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{0.0420}\right) = 0.296\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.097 - 0.296 = -0.393\text{ V}$$

The spontaneous reaction would be reduction on the left, oxidation on the right, not the reaction in the direction considered.

(e)

$$\frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.80 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]0.0700}{0.1400}$$

$$[\text{H}_3\text{O}^+] = \frac{\left(1.80 \times 10^{-4}\right)\left(0.1400\right)}{0.0700} = 3.60 \times 10^{-4}$$

$$E_{\text{right}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{1.00}{\left(3.60 \times 10^{-4}\right)^2}\right) = -0.204\text{ V}$$

$$E_{\text{left}} = 0.000\,V$$

$$E_{\text{cell}} = -0.204 - 0.000 = -0.204\text{ V}$$

Because E_{cell} is negative, the reaction woulds not proceed spontaneously in the direction considered (reduction on the left, oxidation on the right).

(f)

$$E_{\text{right}} = 0.771 - 0.0592 \log\left(\frac{0.1134}{0.003876}\right) = 0.684 \text{ V}$$

$$E_{\text{left}} = 0.334 - \frac{0.0592}{2} \log\left(\frac{4.00 \times 10^{-2}}{\left(8.00 \times 10^{-3}\right)\left(1.00 \times 10^{-3}\right)^4}\right) = -0.042\,V$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.684 - (-0.042) = 0.726 \text{ V}$$

The direction considered (oxidation on the left, reduction on the right) is the spontaneous direction.

19-9. (a)

$$E_{\text{Pb}^{2+}} = -0.126 - \frac{0.0592}{2} \log\left(\frac{1}{0.0220}\right) = -0.175 \text{ V}$$

$$E_{\text{Zn}^{2+}} = -0.763 - \frac{0.0592}{2} \log\left(\frac{1}{0.1200}\right) = -0.790 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.175 - (-0.790) = 0.615 \text{ V}$$

(b)

$$E_{\text{left}} = 0.771 - 0.0592 \log\left(\frac{0.0890}{0.0445}\right) = 0.753 \text{ V}$$

$$E_{\text{right}} = 0.36 - 0.0592 \log\left(\frac{0.00300}{0.1564}\right) = 0.462 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.462 - 0.753 = -0.291 \text{ V}$$

(c)

$$E_{\text{SHE}} = 0.000\,V$$

$$E_{\text{TiO}^{2+}} = 0.099 - 0.0592\log\left(\frac{0.07000}{\left(3.50\times10^{-3}\right)\left(10^{-3}\right)^{2}}\right) = -0.333\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.333 - 0.000 = -0.333\text{ V}$$

19-10. **(a)** Zn| Zn^{2+}(0.1200 M)| | Pb^{2+}(0.0848 M)| Pb

(b) Pt| Fe^{3+}(0.0445 M), Fe^{2+}(0.0890 M)| | $Fe(CN)_6^{4-}$(0.00300 M), $Fe(CN)_6^{3-}$(0.1564 M)| Pt

(c) SHE| | TiO^{+}(3.50×10^{-3}M), Ti^{3+}(0.07000 M), H^{+}(1.00×10^{-3}M)| Pt

19-11. Note that in these calculations, it is necessary to round the answers to either one or two significant figures because the final step involves taking the antilogarithm of a large number.

(a) $Fe^{3+} + V^{2+} \rightleftharpoons Fe^{2+} + V^{3+} \quad E^{o}_{Fe^{3+}} = 0.771 \quad E^{o}_{V^{3+}} = -0.256$

$$0.771 - 0.0592\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) = -0.256 - 0.0592\log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$\frac{0.771-(-0.256)}{0.0592} = \log\left(\frac{[Fe^{2+}][V^{3+}]}{[Fe^{3+}][V^{2+}]}\right) = \log K_{\text{eq}} = 17.348$$

$K_{\text{eq}} = 2.23\times10^{17}$ (2.2×10^{17})

(b) $Fe(CN)_6^{3-} + Cr^{2+} \rightleftharpoons Fe(CN)_6^{4-} + Cr^{3+} \quad E^{o}_{Fe(CN)_6^{3-}} = 0.36 \quad E^{o}_{Cr^{3+}} = -0.408$

$$0.36 - 0.0592\log\left(\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}\right) = -0.408 - 0.0592\log\left(\frac{[Cr^{2+}]}{[Cr^{3+}]}\right)$$

$$\frac{0.36-(-0.408)}{0.0592} = \log\left(\frac{[Fe(CN)_6^{4-}][Cr^{3+}]}{[Fe(CN)_6^{3-}][Cr^{2+}]}\right) = \log K_{\text{eq}} = 12.973$$

$K_{\text{eq}} = 9.4 \times 10^{12}$ (9×10^{12})

(c) $2V(OH)_4{}^+ + U^{4+} \rightleftharpoons 2VO^{2+} + UO_2{}^{2+} + 4H_2O \quad E^o_{V(OH)_4{}^+} = 1.00 \quad E^o_{UO_2{}^{2+}} = 0.334$

$$1.00 - \frac{0.0592}{2}\log\left(\frac{[VO^{2+}]^2}{[V(OH)_4{}^+]^2[H^+]^4}\right) = 0.334 - \frac{0.0592}{2}\log\left(\frac{[U^{4+}]}{[UO_2{}^{2+}][H^+]^4}\right)$$

$$\frac{(1.00-0.334)\,2}{0.0592} = \log\left(\frac{[VO^{2+}]^2[UO_2{}^{2+}]}{[V(OH)_4{}^+]^2[U^{4+}]}\right) = \log K_{eq} = 22.50$$

$$K_{eq} = 3.2 \times 10^{22} \ \ (3 \times 10^{22})$$

(d) $Tl^{3+} + 2Fe^{2+} \rightleftharpoons Tl^+ + 2Fe^{3+} \quad E^o_{Fe^{3+}} = 0.771 \quad E^o_{Tl^+} = 1.25$

$$1.25 - \frac{0.0592}{2}\log\left(\frac{[Tl^+]}{[Tl^{3+}]}\right) = 0.771 - \frac{0.0592}{2}\log\left(\frac{[Fe^{2+}]^2}{[Fe^{3+}]^2}\right)$$

$$\frac{(1.25-0.771)\,2}{0.0592} = \log\left(\frac{[Tl^+][Fe^{3+}]^2}{[Tl^{3+}][Fe^{2+}]^2}\right) = \log K_{eq} = 16.18$$

$$K_{eq} = 1.5\times10^{16} \ \ (2 \times 10^{16})$$

(e)

$$2Ce^{4+} + H_3AsO_3 + H_2O \rightleftharpoons 2Ce^{3+} + H_3AsO_4 + 2H^+$$
$$E^o_{Ce^{4+}}(\text{in } 1\,M\ HClO_4) = 1.70 \quad E^o_{H_3AsO_4} = 0.577$$

$$1.70 - \frac{0.0592}{2}\log\left(\frac{[Ce^{3+}]^2}{[Ce^{4+}]^2}\right) = 0.577 - \frac{0.0592}{2}\log\left(\frac{[H_3AsO_4]}{[H_3AsO_3][H^+]^2}\right)$$

$$\frac{(1.70-0.577)\,2}{0.0592} = \log\left(\frac{[Ce^{3+}]^2[H_3AsO_3][H^+]^2}{[Ce^{4+}]^2[H_3AsO_4]}\right) = \log K_{eq} = 37.94$$

$$K_{eq} = 8.9\times10^{37} \ \ (9 \times 10^{37})$$

(f) $2V(OH)_4{}^+ + H_2SO_3 \rightleftharpoons 2VO^{2+} + SO_4{}^{2-} + 5H_2O \quad E^o_{V(OH)_4{}^+} = 1.00 \quad E^o_{SO_4{}^{2-}} = 0.172$

$$1.00-\frac{0.0592}{2}\log\left(\frac{[\mathrm{VO}^{2+}]^2}{[\mathrm{V(OH)_4}^+]^2[\mathrm{H}^+]^4}\right)=0.172-\frac{0.0592}{2}\log\left(\frac{[\mathrm{H_2SO_3}]}{[\mathrm{SO_4}^{2-}][\mathrm{H}^+]^4}\right)$$

$$\frac{(1.00-0.172)\,2}{0.0592}=\log\left(\frac{[\mathrm{VO}^{2+}]^2[\mathrm{SO_4}^{2-}]}{[\mathrm{V(OH)_4}^+]^2[\mathrm{H_2SO_3}]}\right)=\log K_{\mathrm{eq}}=27.97$$

$K_{\mathrm{eq}}=9.4\times10^{27}$ (9×10^{27})

(g) $\mathrm{VO}^{2+}+\mathrm{V}^{2+}+2\mathrm{H}^+ \rightleftharpoons 2\mathrm{V}^{3+}+\mathrm{H_2O}$ $E^{\mathrm{o}}_{\mathrm{VO}^{2+}}=0.359$ $E^{\mathrm{o}}_{\mathrm{V}^{3+}}=-0.256$

$$0.359-0.0592\log\left(\frac{[\mathrm{V}^{3+}]}{[\mathrm{VO}^{2+}][\mathrm{H}^+]^2}\right)=-0.256-0.0592\log\left(\frac{[\mathrm{V}^{2+}]}{[\mathrm{V}^{3+}]}\right)$$

$$\frac{0.359-(-0.256)}{0.0592}=\log\left(\frac{[\mathrm{V}^{3+}]^2}{[\mathrm{VO}^{2+}][\mathrm{H}^+]^2[\mathrm{V}^{2+}]}\right)=\log K_{\mathrm{eq}}=10.389$$

$K_{\mathrm{eq}} = 2.4 \times 10^{10}$

(h) $\mathrm{TiO}^{2+}+\mathrm{Ti}^{2+}+2\mathrm{H}^+ \rightleftharpoons 2\mathrm{Ti}^{3+}+\mathrm{H_2O}$ $E^{\mathrm{o}}_{\mathrm{TiO}^{2+}}=0.099$ $E^{\mathrm{o}}_{\mathrm{Ti}^{3+}}=-0.369$

$$0.099-0.0592\log\left(\frac{[\mathrm{Ti}^{3+}]}{[\mathrm{TiO}^{2+}][\mathrm{H}^+]^2}\right)=-0.369-0.0592\log\left(\frac{[\mathrm{Ti}^{2+}]}{[\mathrm{Ti}^{3+}]}\right)$$

$$\frac{0.099-(-0.369)}{0.0592}=\log\left(\frac{[\mathrm{Ti}^{3+}]^2}{[\mathrm{TiO}^{2+}][\mathrm{H}^+]^2[\mathrm{Ti}^{2+}]}\right)=\log K_{\mathrm{eq}}=7.9054$$

$K_{\mathrm{eq}} = 8.0 \times 10^7$

19-12. **(a)** At the equivalence point, $[\mathrm{Fe}^{2+}] = [\mathrm{V}^{3+}]$ and $[\mathrm{Fe}^{3+}] = [\mathrm{V}^{2+}]$

$$2E_{\mathrm{eq}}=0.771+(-0.256)-0.0592\log\left(\frac{[\mathrm{Fe}^{2+}][\mathrm{V}^{2+}]}{[\mathrm{Fe}^{3+}][\mathrm{V}^{3+}]}\right)$$

$$E_{\mathrm{eq}}=\frac{0.771-0.256}{2}=0.258\ \mathrm{V}$$

(b) At the equivalence point, $[\mathrm{Fe(CN)_6}^{3-}] = [\mathrm{Cr}^{2+}]$ and $[\mathrm{Fe(CN)_6}^{4-}] = [\mathrm{Cr}^{3+}]$

$$2E_{\mathrm{eq}}=0.36+(-0.408)-0.0592\log\left(\frac{[\mathrm{Fe(CN)_6}^{4-}][\mathrm{Cr}^{2+}]}{[\mathrm{Fe(CN)_6}^{3-}][\mathrm{Cr}^{3+}]}\right)$$

$$E_{\text{eq}} = \frac{0.36 - 0.408}{2} = –0.024\text{ V}$$

(c) At equivalence, $[VO^{2+}] = 2[UO_2^{2+}]$ and $[V(OH)_4^+] = 2[U^{4+}]$

$$3E_{\text{eq}} = 1.00 + 2(0.344) - 0.0592\log\left(\frac{[VO^{2+}][U^{4+}]}{[V(OH)_4^{\,+}][UO_2^{\,2+}][H^+]^6}\right)$$

$$3E_{\text{eq}} = 1.00 + 2(0.344) - 0.0592\log\left(\frac{1}{(0.100)^6}\right) = 1.688 - 0.355 = 1.333\text{ V}$$

$$E_{\text{eq}} = \frac{1.333}{3} = 0.444\text{ V}$$

(d) At equivalence, $[Fe^{2+}] = 2[Tl^{3+}]$ and $[Fe^{3+}] = 2[Tl^+]$

$$3E_{\text{eq}} = 0.771 + 2(1.25) - 0.0592\log\left(\frac{[Fe^{2+}][Tl^+]}{[Fe^{3+}][Tl^{3+}]}\right) = 3.27 - 0.0592\log\left(\frac{2[Tl^{3+}][Tl^+]}{2[Tl^+][Tl^{3+}]}\right)$$

$$E_{\text{eq}} = \frac{3.27}{3} = 1.09\text{ V}$$

(e) At equivalence, $[Ce^{3+}] = 2[H_3AsO_4]$, $[Ce^{4+}] = 2[H_3AsO_3]$ and $[H^+] = 1.00$

$$3E_{\text{eq}} = 1.70 + 2(0.577) - 0.0592\log\left(\frac{[Ce^{3+}][H_3AsO_3]}{[Ce^{4+}][H_3AsO_4][H^+]^2}\right)$$

$$= 2.854 - 0.0592\log\left(\frac{2[H_3AsO_4][H_3AsO_3]}{2[H_3AsO_3][H_3AsO_4][H^+]^2}\right) = 2.854 - 0.0592\log\left(\frac{1}{(1.00)^2}\right)$$

$$E_{\text{eq}} = \frac{2.854}{3} = 0.951\text{ V}$$

(f) At equivalence, $[V(OH)_4^+] = 2[H_2SO_3]$ and $[VO^{2+}] = 2[SO_4^{2-}]$

$$3E_{\text{eq}} = 1.00 + 2(0.172) - 0.0592\log\left(\frac{[VO^{2+}][H_2SO_3]}{[V(OH)_4^{\,+}][SO_4^{\,2-}][H^+]^6}\right)$$

$$3E_{\text{eq}} = 1.00 + 2(0.172) - 0.0592\log\left(\frac{1}{(0.100)^6}\right) = 1.344 - 0.355 = 0.989\text{ V}$$

$$E_{\text{eq}} = \frac{0.989}{3} = 0.330 \text{ V}$$

(g) At equivalence, $[\text{VO}^+] = [\text{V}^{2+}]$

$$2E_{\text{eq}} = 0.359 + (-0.256) - 0.0592\log\left(\frac{[\text{V}^{2+}]}{[\text{VO}^+][\text{H}^+]^2}\right) = 0.103 - 0.0592\log\left(\frac{[\text{V}^{2+}]}{[\text{V}^{2+}][\text{H}^+]^2}\right)$$

$$2E_{\text{eq}} = 0.103 - 0.0592\log\left(\frac{1}{(0.100)^2}\right) = 0.103 - 0.118 = -0.154\,V$$

$$E_{\text{eq}} = \frac{-0.154}{2} = -0.008 \text{ V}$$

(h) At equivalence, $[\text{Ti}^{2+}] = [\text{TiO}^{2+}]$

$$2E_{\text{eq}} = 0.099 + (-0.369) - 0.0592\log\left(\frac{[\text{Ti}^{2+}]}{[\text{TiO}^+][\text{H}^+]^2}\right) = 0.103 - 0.0592\log\left(\frac{[\text{Ti}^{2+}]}{[\text{Ti}^{2+}][\text{H}^+]^2}\right)$$

$$2E_{\text{eq}} = -0.270 - 0.0592\log\left(\frac{1}{(0.100)^2}\right) = -0.270 - 0.118 = -0.388\,V$$

$$E_{\text{eq}} = \frac{-0.388}{2} = -0.194 \text{ V}$$

19-13. (a) In the solution to Problem 19-11(a) we find

$$K_{\text{eq}} = \frac{[\text{V}^{3+}][\text{Fe}^{2+}]}{[\text{V}^{2+}][\text{Fe}^{3+}]} = 2.23\times10^{17}$$

At the equivalence point,

$[\text{V}^{2+}] = [\text{Fe}^{3+}] = x$

$[\text{V}^{3+}] = [\text{Fe}^{2+}] = \dfrac{0.1000}{2} = 0.0500$

Substituting into the first equation we find

$$2.23\times10^{17} = \frac{\left(0.0500\right)^2}{x^2}$$

$$x = \sqrt{\frac{0.00250}{2.23\times10^{17}}} = 1.06\times10^{-10}$$

Thus,

$[V^{2+}] = [Fe^{3+}] = 1.06 \times 10^{-10}$ M

$[V^{3+}] = [Fe^{2+}] = 0.0500$ M

(c) At equivalence

$$[V(OH)_4{}^+] = 2[U^{4+}] = x$$

$$[VO_2{}^{2+}] = 2[UO_2{}^{2+}] = \frac{2\left(0.1000\right)}{3} - 2x = \frac{0.2000}{3} = 0.0667\text{ M}$$

$$[UO_2{}^{2+}] = \frac{0.1000}{3} = 0.0333\text{ M}$$

From the solution for Problem 19-11(c)

$$\frac{[VO_2{}^{2+}]^2[UO_2{}^{2+}]}{[V(OH)_4{}^+]^2[U^{4+}]} = 3.2\times10^{22} = \frac{\left(0.0667\right)^2\left(0.0333\right)}{x^2\left(x/2\right)}$$

$$\frac{x^3}{2} = \frac{\left(0.0667\right)^2\left(0.0333\right)}{3.2\times10^{22}}$$

$$x = \sqrt[3]{2\times\left(4.62\times10^{-27}\right)} = 2.10 \times 10^{-9}\text{ M}$$

$$[V(OH)_4{}^+] = 2.1 \times 10^{-9}\text{ M and } [U^{4+}] = \frac{2.1 \times 10^{-9}}{2} = 1.0 \times 10^{-9}\text{ M}$$

(f) Proceeding as in part (c)

$[VO^+] = 0.067$ M

$[SO_4{}^{2-}] = 0.033$ M

$[V(OH)_4{}^+] = 3.2 \times 10^{-11}$ M

$[H_2SO_3] = 1.6 \times 10^{-11}$M

(g)

$$x = [\mathrm{V}^{2+}] = [\mathrm{VO}^{2+}]$$

$$[\mathrm{V}^{3+}] = \frac{0.200}{2} = 0.100$$

Assume $[\mathrm{H}^+] = 0.1000$. From the solution to Problem 19-11(g)

$$\frac{[\mathrm{V}^{3+}]^2}{[\mathrm{VO}^{2+}][\mathrm{V}^{2+}][\mathrm{H}^+]^2} = 2.4 \times 10^{10} = \frac{(0.100)^2}{[\mathrm{VO}^{2+}][\mathrm{V}^{2+}](0.100)^2}$$

$$2.4 \times 10^{10} = \frac{1.00}{x^2}$$

$$x = [\mathrm{VO}^{2+}] = [\mathrm{V}^{2+}] = 6.5 \times 10^{-6}\ \mathrm{M}$$

$$[\mathrm{V}^{3+}] = 0.100\ \mathrm{M}$$

19-14.

	E_{eq}, V	**Indicator**
(a)	0.258	Phenosafranine
(b)	–0.024	None
(c)	0.444	Indigo tetrasulfonate or Methylene blue
(d)	1.09	1,10-Phenanthroline
(e)	0.951	Erioglaucin A
(f)	0.330	Indigo tetrasulfonate
(g)	–0.008	None
(h)	–0.194	None

19-15. (a) $2\mathrm{V}^{2+} + \mathrm{Sn}^{4+} \rightleftharpoons 2\mathrm{V}^{3+} + \mathrm{Sn}^{2+}$

Pre-equivalence point. For example, at 10.00 mL

$$[\text{V}^{3+}] = \frac{\left(\dfrac{0.0500\text{ mmol Sn}^{4+}}{\text{mL}} \times 10.00\text{ mL} \times \dfrac{2\text{ mmol V}^{3+}}{\text{mmol Sn}^{4+}}\right)}{60.00\text{ mL}} = 0.0167\text{ M}$$

$$[\text{V}^{2+}] = \frac{\left(\dfrac{0.1000\text{ mmol V}^{2+}}{\text{mL}} \times 50.00\text{ mL}\right)}{60.00\text{ mL}} - 1.67 \times 10^{-2}\,M = 0.0667\text{ M}$$

$$E = -0.256 - 0.0592\log\left(\frac{[\text{V}^{2+}]}{[\text{V}^{3+}]}\right) = -0.256 - 0.0592\log\left(\frac{0.0667}{0.0167}\right) = -0.292\,V$$

The remaining pre-equivalence point data are treated in the same way. The results appear in the spreadsheet that follows.

Equivalence Point, 50.00 mL

Proceeding as in Problem 19-12, we write

$$E = -0.256 - 0.0592\log\left(\frac{[\text{V}^{2+}]}{[\text{V}^{3+}]}\right)$$

$$2E = 2\times 0.154 - 0.0592\log\left(\frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}\right)$$

$$3E = -0.256 + (2\times 0.154) - 0.0592\log\left(\frac{[\text{V}^{2+}][\text{Sn}^{2+}]}{[\text{V}^{3+}][\text{Sn}^{4+}]}\right)$$

At equivalence, $[\text{V}^{2+}] = 2[\text{Sn}^{4+}]$ and $[\text{V}^{3+}] = 2[\text{Sn}^{2+}]$. Thus

$$E_{\text{eq}} = \frac{-0.256 + (2\times 0.154)}{3} - \frac{0.0592\log(1.00)}{3} = 0.017\text{ V}$$

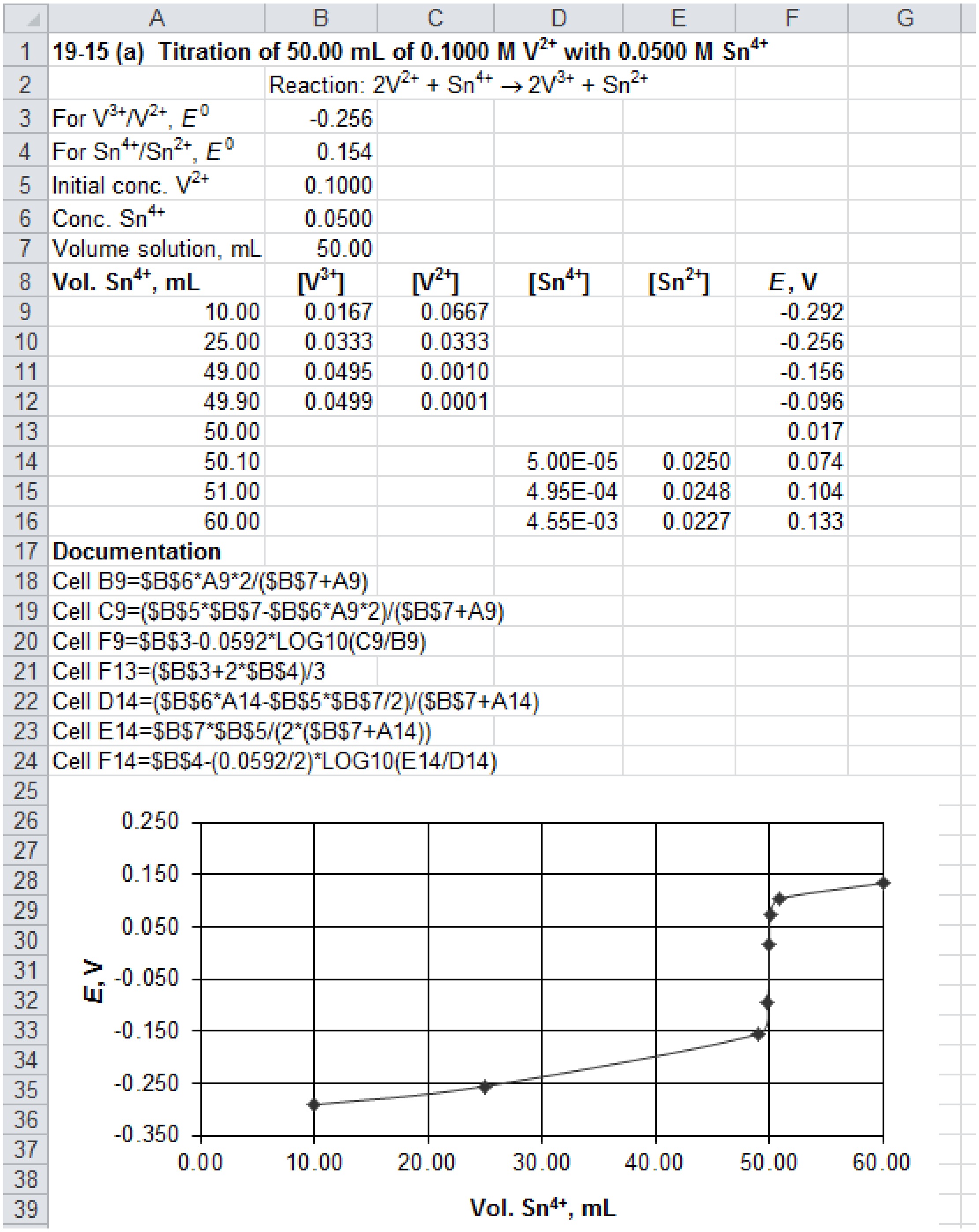
Post-equivalence Point. For example, 50.10 mL

$$c_{\mathrm{Sn^{2+}}} = \frac{\left(\dfrac{0.1000\ \mathrm{mmol\ V^{2+}}}{\mathrm{mL}} \times 50.00\ \mathrm{mL} \times \dfrac{1\ \mathrm{mmol\ Sn^{2+}}}{2\ \mathrm{mmol\ V^{2+}}}\right)}{100.10\ \mathrm{mL}} = 0.025\ \mathrm{M} \approx [\mathrm{Sn^{2+}}]$$

$$c_{\mathrm{Sn^{4+}}} = \frac{\left(\dfrac{0.0500\ \mathrm{mmol\ Sn^{4+}}}{\mathrm{mL}} \times 50.10\ \mathrm{mL}\right)}{100.10\ \mathrm{mL}} - 0.025\ \mathrm{M} = 5.0 \times 10^{-5}\ \mathrm{M} \approx [\mathrm{Sn^{4+}}]$$

$$E = 0.154 - \frac{0.0592}{2}\log\left(\frac{[\mathrm{Sn^{2+}}]}{[\mathrm{Sn^{4+}}]}\right) = 0.154 - \frac{0.0592}{2}\log\left(\frac{2.5\times10^{-2}}{5.0\times10^{-5}}\right) = 0.074\,V$$

The remaining post-equivalence points are obtained in the same way and are found in the spreadsheet that follows.



	A	B	C	D	E	F	G
1	**19-15 (a) Titration of 50.00 mL of 0.1000 M V^{2+} with 0.0500 M Sn^{4+}**						
2		Reaction: $2V^{2+} + Sn^{4+} \rightarrow 2V^{3+} + Sn^{2+}$					
3	For V^{3+}/V^{2+}, E^0	-0.256					
4	For Sn^{4+}/Sn^{2+}, E^0	0.154					
5	Initial conc. V^{2+}	0.1000					
6	Conc. Sn^{4+}	0.0500					
7	Volume solution, mL	50.00					
8	**Vol. Sn^{4+}, mL**	**[V^{3+}]**	**[V^{2+}]**	**[Sn^{4+}]**	**[Sn^{2+}]**	**E, V**	
9	10.00	0.0167	0.0667			-0.292	
10	25.00	0.0333	0.0333			-0.256	
11	49.00	0.0495	0.0010			-0.156	
12	49.90	0.0499	0.0001			-0.096	
13	50.00					0.017	
14	50.10			5.00E-05	0.0250	0.074	
15	51.00			4.95E-04	0.0248	0.104	
16	60.00			4.55E-03	0.0227	0.133	
17	**Documentation**						
18	Cell B9=$B$6*A9*2/($B$7+A9)						
19	Cell C9=($B$5*$B$7-$B$6*A9*2)/($B$7+A9)						
20	Cell F9=$B$3-0.0592*LOG10(C9/B9)						
21	Cell F13=($B$3+2*$B$4)/3						
22	Cell D14=($B$6*A14-$B$5*$B$7/2)/($B$7+A14)						
23	Cell E14=$B$7*$B$5/(2*($B$7+A14))						
24	Cell F14=$B$4-(0.0592/2)*LOG10(E14/D14)						

(b)

$$\text{Fe(CN)}_6{}^{3-} + \text{Cr}^{2+} \rightleftharpoons \text{Fe(CN)}_6{}^{4-} + \text{Cr}^{3+}$$

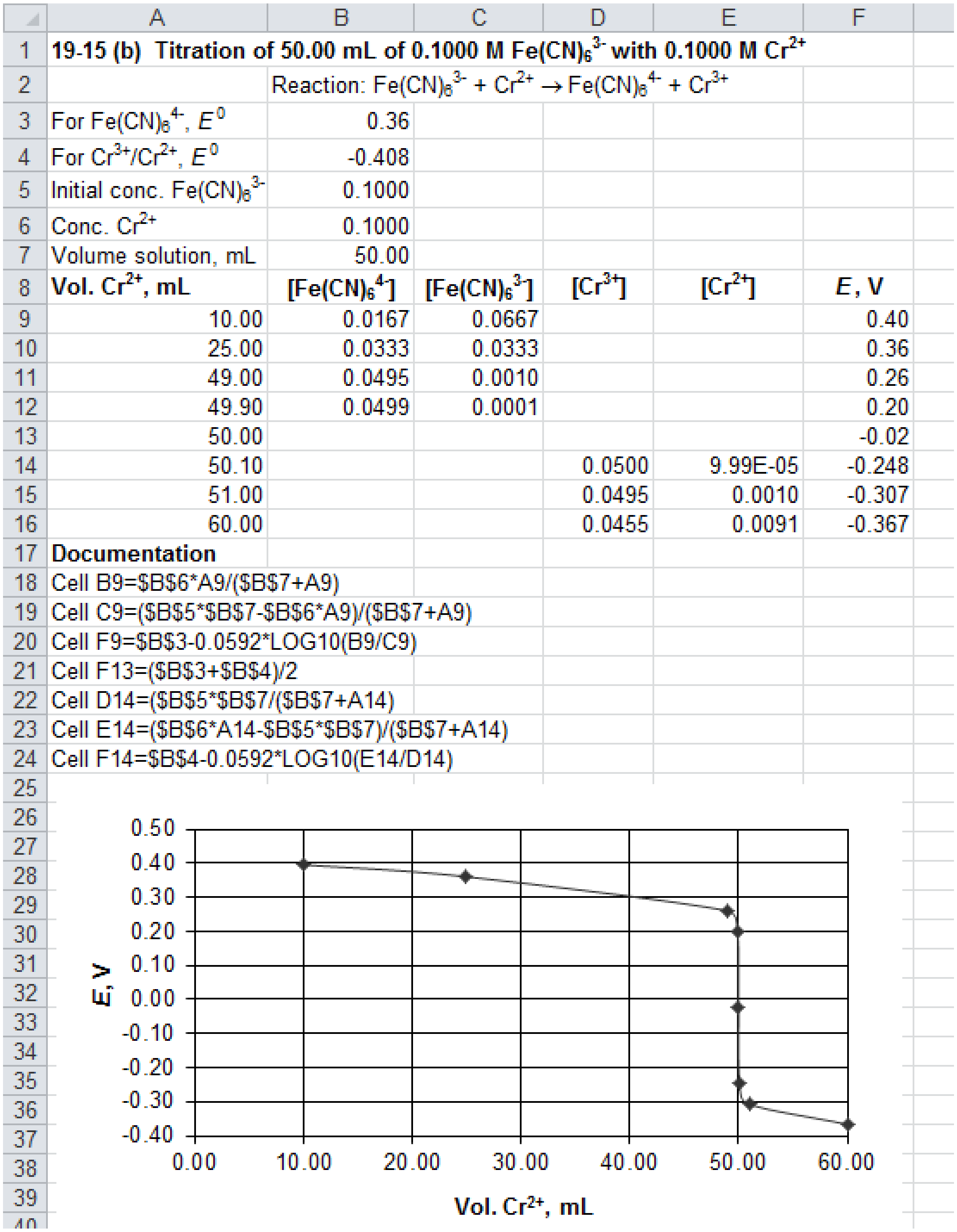
The pre-equivalence point data are obtained by substituting concentrations into the equation

$$E = 0.36 - 0.0592\log\left(\frac{[\text{Fe(CN)}_6{}^{4-}]}{[\text{Fe(CN)}_6{}^{3-}]}\right)$$

The post-equivalence point data are obtained with the Nernst expression for the Cr^{2+}/ Cr^{3+} system. That is,

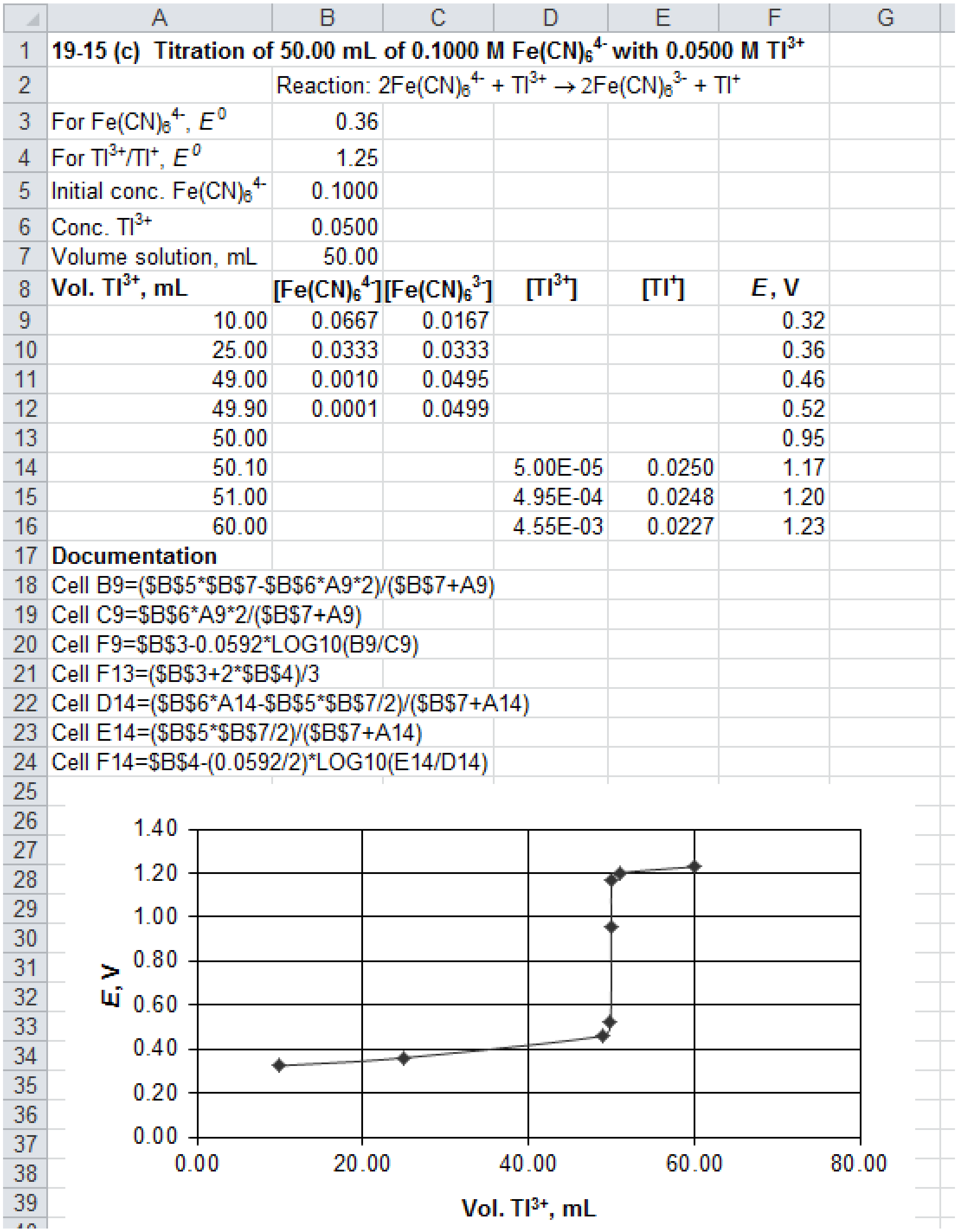
$$E = -0.0408 - 0.0592\log\left(\frac{[\text{Cr}^{2+}]}{[\text{Cr}^{3+}]}\right)$$

The equivalence point potential is found following the procedure in Problem 19-12. The results for all data points are found in the spreadsheet that follows



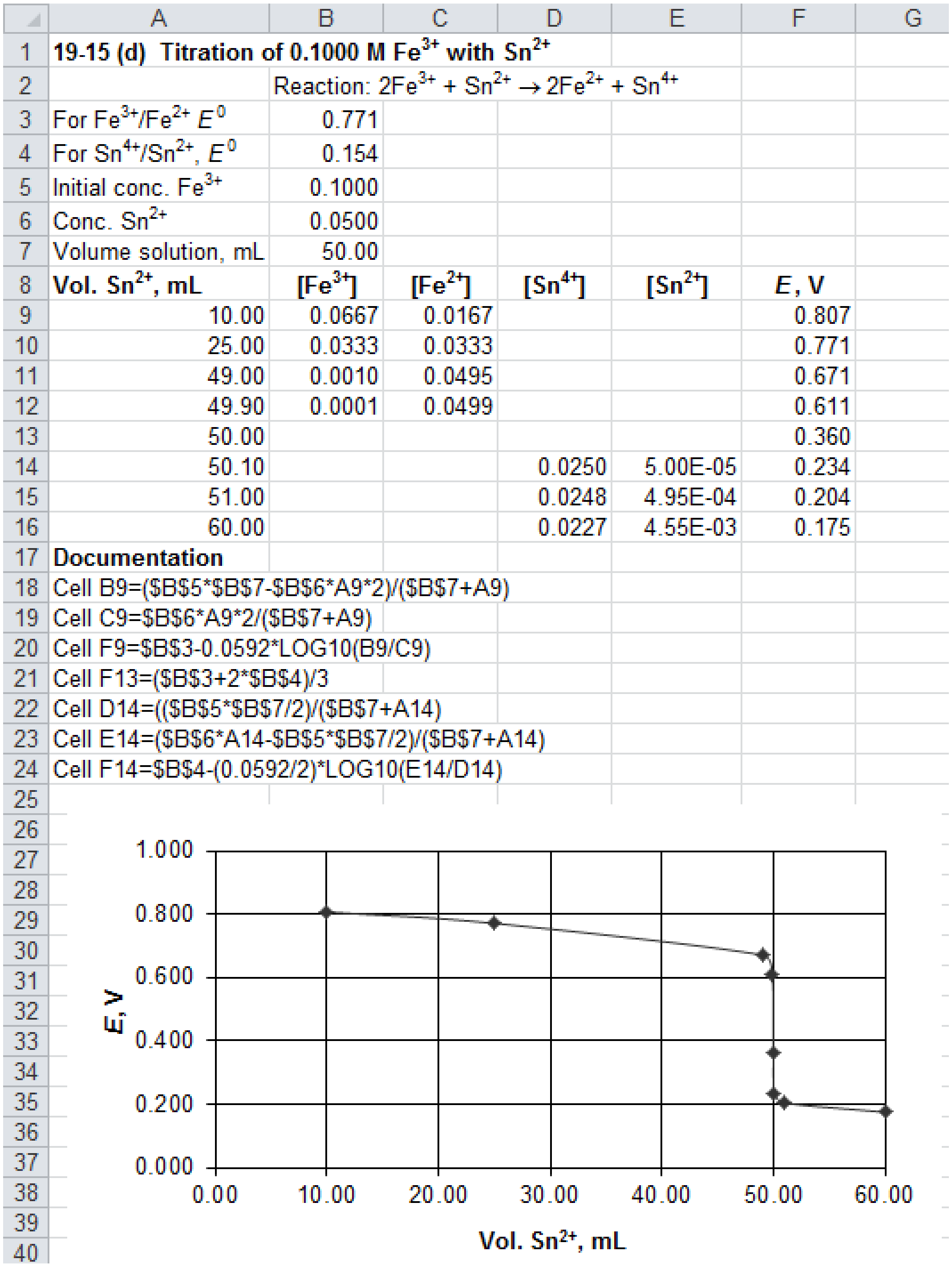
	A	B	C	D	E	F
1	**19-15 (b) Titration of 50.00 mL of 0.1000 M $Fe(CN)_6^{3-}$ with 0.1000 M Cr^{2+}**					
2		Reaction: $Fe(CN)_6^{3-} + Cr^{2+} \rightarrow Fe(CN)_6^{4-} + Cr^{3+}$				
3	For $Fe(CN)_6^{4-}$, E^0	0.36				
4	For Cr^{3+}/Cr^{2+}, E^0	-0.408				
5	Initial conc. $Fe(CN)_6^{3-}$	0.1000				
6	Conc. Cr^{2+}	0.1000				
7	Volume solution, mL	50.00				
8	**Vol. Cr^{2+}, mL**	**$[Fe(CN)_6^{4-}]$**	**$[Fe(CN)_6^{3-}]$**	**$[Cr^{3+}]$**	**$[Cr^{2+}]$**	***E*, V**
9	10.00	0.0167	0.0667			0.40
10	25.00	0.0333	0.0333			0.36
11	49.00	0.0495	0.0010			0.26
12	49.90	0.0499	0.0001			0.20
13	50.00					-0.02
14	50.10			0.0500	9.99E-05	-0.248
15	51.00			0.0495	0.0010	-0.307
16	60.00			0.0455	0.0091	-0.367
17	**Documentation**					
18	Cell B9=$B$6*A9/($B$7+A9)					
19	Cell C9=($B$5*$B$7-$B$6*A9)/($B$7+A9)					
20	Cell F9=$B$3-0.0592*LOG10(B9/C9)					
21	Cell F13=($B$3+$B$4)/2					
22	Cell D14=($B$5*$B$7/($B$7+A14)					
23	Cell E14=($B$6*A14-$B$5*$B$7)/($B$7+A14)					
24	Cell F14=$B$4-0.0592*LOG10(E14/D14)					

(c) The data points for this titration, which are found in the spreadsheet that follows, are obtained in the same way as those for parts **(a)** and **(b)**.



	A	B	C	D	E	F	G
1	**19-15 (c) Titration of 50.00 mL of 0.1000 M $Fe(CN)_6^{4-}$ with 0.0500 M Tl^{3+}**						
2		Reaction: $2Fe(CN)_6^{4-} + Tl^{3+} \rightarrow 2Fe(CN)_6^{3-} + Tl^+$					
3	For $Fe(CN)_6^{4-}$, E^0	0.36					
4	For Tl^{3+}/Tl^+, E^0	1.25					
5	Initial conc. $Fe(CN)_6^{4-}$	0.1000					
6	Conc. Tl^{3+}	0.0500					
7	Volume solution, mL	50.00					
8	**Vol. Tl^{3+}, mL**	**$[Fe(CN)_6^{4-}]$**	**$[Fe(CN)_6^{3-}]$**	**$[Tl^{3+}]$**	**$[Tl^+]$**	***E*, V**	
9	10.00	0.0667	0.0167			0.32	
10	25.00	0.0333	0.0333			0.36	
11	49.00	0.0010	0.0495			0.46	
12	49.90	0.0001	0.0499			0.52	
13	50.00					0.95	
14	50.10			5.00E-05	0.0250	1.17	
15	51.00			4.95E-04	0.0248	1.20	
16	60.00			4.55E-03	0.0227	1.23	
17	**Documentation**						
18	Cell B9=($B$5*$B$7-$B$6*A9*2)/($B$7+A9)						
19	Cell C9=$B$6*A9*2/($B$7+A9)						
20	Cell F9=$B$3-0.0592*LOG10(B9/C9)						
21	Cell F13=($B$3+2*$B$4)/3						
22	Cell D14=($B$6*A14-$B$5*$B$7/2)/($B$7+A14)						
23	Cell E14=($B$5*$B$7/2)/($B$7+A14)						
24	Cell F14=$B$4-(0.0592/2)*LOG10(E14/D14)						

(d) The results for this titration are obtained as in parts **(a)** and **(b)**.



	A	B	C	D	E	F	G
1	**19-15 (d) Titration of 0.1000 M Fe^{3+} with Sn^{2+}**						
2		Reaction: $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$					
3	For Fe^{3+}/Fe^{2+} E^0	0.771					
4	For Sn^{4+}/Sn^{2+}, E^0	0.154					
5	Initial conc. Fe^{3+}	0.1000					
6	Conc. Sn^{2+}	0.0500					
7	Volume solution, mL	50.00					
8	**Vol. Sn^{2+}, mL**	**[Fe^{3+}]**	**[Fe^{2+}]**	**[Sn^{4+}]**	**[Sn^{2+}]**	***E*, V**	
9	10.00	0.0667	0.0167			0.807	
10	25.00	0.0333	0.0333			0.771	
11	49.00	0.0010	0.0495			0.671	
12	49.90	0.0001	0.0499			0.611	
13	50.00					0.360	
14	50.10			0.0250	5.00E-05	0.234	
15	51.00			0.0248	4.95E-04	0.204	
16	60.00			0.0227	4.55E-03	0.175	
17	**Documentation**						
18	Cell B9=($B$5*$B$7-$B$6*A9*2)/($B$7+A9)						
19	Cell C9=$B$6*A9*2/($B$7+A9)						
20	Cell F9=$B$3-0.0592*LOG10(B9/C9)						
21	Cell F13=($B$3+2*$B$4)/3						
22	Cell D14=(($B$5*$B$7/2)/($B$7+A14)						
23	Cell E14=($B$6*A14-$B$5*$B$7/2)/($B$7+A14)						
24	Cell F14=$B$4-(0.0592/2)*LOG10(E14/D14)						

(e) $2MnO_4^- + 5U^{4+} + 2H_2O \rightleftharpoons 2Mn^{2+} + 5UO_2^{2+} + 4H^+$

Pre-equivalence Point. For example, 10.00 mL

$$\frac{0.02000\text{ mmol MnO}_4^-}{\text{mL}} \times 10.00\text{ mL MnO}_4^- = 0.2000\text{ mmol MnO}_4^-$$

$$\frac{0.05000\text{ mmol U}^{4+}}{\text{mL}} \times 50.00\text{ mL U}^{4+} = 2.500\text{ mmol U}^{4+}$$

$$c_{UO_2^{2+}} = [UO_2^{2+}] = \frac{\left(0.2000\text{ mmol MnO}_4^- \times \frac{5\text{ mmol UO}_2^{2+}}{2\text{ mmol MnO}_4^-}\right)}{60.00\text{ mL solution}} = 8.33 \times 10^{-3}\text{ M UO}_2^{2+}$$

$$c_{U^{4+}} = [U^{4+}] = \frac{\left(2.5000\text{ mmol U}^{4+}\right)}{60.00\text{ mL}} - 8.33 \times 10^{-3} = 0.0333\text{ M U}^{4+}$$

$$E = 0.334 - \frac{0.0592}{2}\log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right) = 0.334 - \frac{0.0592}{2}\log\left(\frac{3.33 \times 10^{-2}}{\left([8.33 \times 10^{-3}\right)\left(1.00\right)^4}\right) = 0.316\,V$$

The remaining pre-equivalence point data are in the spreadsheet that follows.

Equivalence Point, 50.00 mL

$$5E_{eq} = 5\times1.51 - 0.0592\log\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right)$$

$$2E_{eq} = 2\times0.334 - 0.0592\log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right)$$

Adding the two equations gives

$$7E_{eq} = \left(5\times1.51\right) + \left(2\times0.334\right) - 0.0592\log\left(\frac{[Mn^{2+}][U^{4+}]}{[MnO_4^-][UO_2^{2+}][H^+]^{12}}\right)$$

At equivalence, $[MnO_4^-] = 2/5[U^{4+}]$ and $[Mn^{2+}] = 2/5[UO_2^{2+}]$

Substituting these equalities and $[H^+] = 1.00$ into the equation above gives

$$E_{eq} = \frac{8.218}{7} - \frac{0.0592\log\left(1.00\right)}{7} = \frac{8.218}{7} = 1.17\text{ V}$$

Post-equivalence Point. For example, 50.10 mL

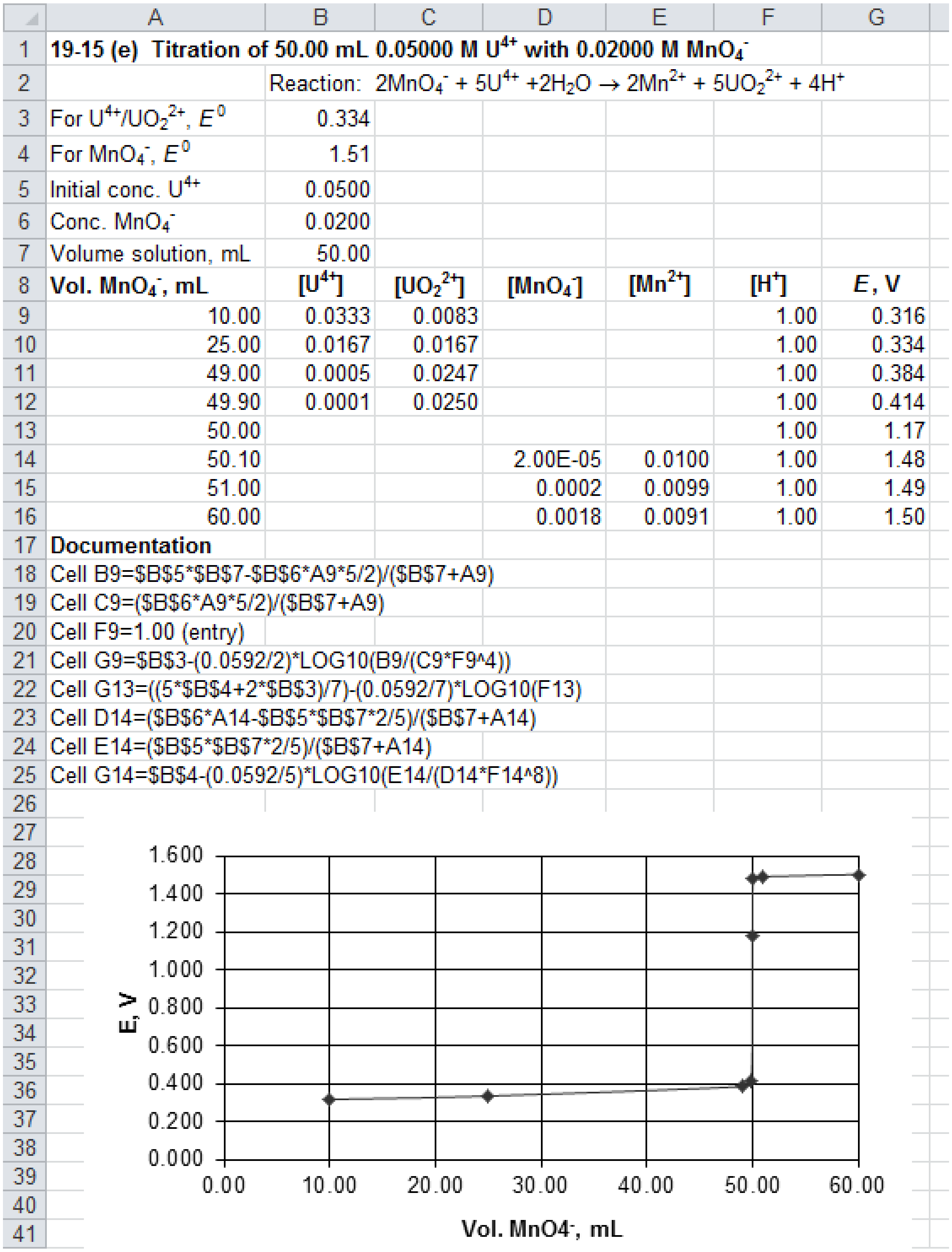
$$\text{amount MnO}_4{}^- \text{ added} = \frac{0.02000 \text{ mmol MnO}_4{}^-}{\text{mL}} \times 50.10 \text{ mL} = 1.0020 \text{ mmol}$$

$$\text{amount Mn}^{2+} \text{ formed} = \frac{0.05000 \text{ mmol U}^{4+}}{\text{mL}} \times 50.00 \text{ mL} \times \frac{2 \text{ mmol Mn}^{2+}}{5 \text{ mmol U}^{4+}} = 1.000 \text{ mmol}$$

$$\text{amount MnO}_4{}^- \text{ remaining} = 1.0020 - 1.000 = 2.0 \times 10^{-3} \text{ mmol}$$

$$E = 1.51 - \frac{0.0592}{5}\log\left(\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4{}^-][\text{H}^+]^8}\right) = 1.51 - \frac{0.0592}{5}\log\left(\frac{(1.000/100.10)}{(1.0020/100.10)(1.00)^8}\right) = 1.48 \text{ V}$$

The other post equivalence point results are derived in the same way and are given in the spreadsheet that follows.



	A	B	C	D	E	F	G
1	**19-15 (e) Titration of 50.00 mL 0.05000 M U^{4+} with 0.02000 M MnO_4^-**						
2		Reaction: $2MnO_4^- + 5U^{4+} + 2H_2O \rightarrow 2Mn^{2+} + 5UO_2^{2+} + 4H^+$					
3	For U^{4+}/UO_2^{2+}, E^0	0.334					
4	For MnO_4^-, E^0	1.51					
5	Initial conc. U^{4+}	0.0500					
6	Conc. MnO_4^-	0.0200					
7	Volume solution, mL	50.00					
8	**Vol. MnO_4^-, mL**	**$[U^{4+}]$**	**$[UO_2^{2+}]$**	**$[MnO_4^-]$**	**$[Mn^{2+}]$**	**$[H^+]$**	**E, V**
9	10.00	0.0333	0.0083			1.00	0.316
10	25.00	0.0167	0.0167			1.00	0.334
11	49.00	0.0005	0.0247			1.00	0.384
12	49.90	0.0001	0.0250			1.00	0.414
13	50.00					1.00	1.17
14	50.10			2.00E-05	0.0100	1.00	1.48
15	51.00			0.0002	0.0099	1.00	1.49
16	60.00			0.0018	0.0091	1.00	1.50
17	**Documentation**						
18	Cell B9=\$B\$5*\$B\$7-\$B\$6*A9*5/2)/(\$B\$7+A9)						
19	Cell C9=(\$B\$6*A9*5/2)/(\$B\$7+A9)						
20	Cell F9=1.00 (entry)						
21	Cell G9=\$B\$3-(0.0592/2)*LOG10(B9/(C9*F9^4))						
22	Cell G13=((5*\$B\$4+2*\$B\$3)/7)-(0.0592/7)*LOG10(F13)						
23	Cell D14=(\$B\$6*A14-\$B\$5*\$B\$7*2/5)/(\$B\$7+A14)						
24	Cell E14=(\$B\$5*\$B\$7*2/5)/(\$B\$7+A14)						
25	Cell G14=\$B\$4-(0.0592/5)*LOG10(E14/(D14*F14^8))						

Chapter 20

20-1. **(a)** $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 10SO_4^{2-} + 2MnO_4^{-} + 16H^{+}$

(b) $NaBiO_3(s) + 2Ce^{3+} + 4H^{+} \rightarrow BiO^{+} + 2Ce^{4+} + 2H_2O + Na^{+}$

(c) $H_2O_2 + U^{4+} \rightarrow UO_2^{2+} + 2H^{+}$

(d) $V(OH)_4^{+} + Ag(s) + Cl^{-} + 2H^{+} \rightarrow VO^{2+} + AgCl(s) + 3H_2O$

(e) $2MnO_4^{-} + 5H_2O_2 + 6H^{+} \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$

(f) $ClO_3^{-} + 6I^{-} + 6H^{+} \rightarrow 3I_2 + Cl^{-} + 3H_2O$

20-2. Only in the presence of Cl^{-} ion is Ag a sufficiently good reducing agent to be very useful for prereductions. In the presence of Cl^{-}, the half-reaction occurring in the Walden reductor is

$$Ag(s) + Cl^{-} \rightarrow AgCl(s) + e^{-}$$

The excess HCl increases the tendency of this reaction to occur by the common ion effect.

20-3. $UO_2^{2+} + 2Ag(s) + 4H^{+} + 2Cl^{-} \rightleftharpoons U^{4+} + 2AgCl(s) + H_2O$

20-4. Standard solutions of reductants find somewhat limited use because of their susceptibility to air oxidation.

20-5. Cerium (IV) precipitates as a basic oxide in alkaline solution.

20-6. Freshly prepared solutions of permanganate are inevitably contaminated with small amounts of solid manganese dioxide, which catalyzes the further decompositions of permanganate ion. By removing the dioxide at the outset, a much more stable standard reagent is produced.

20-7. Standard permanganate and thiosulfate solutions are generally stored in the dark because their decomposition reactions are catalyzed by light.

20-8. Solutions of $K_2Cr_2O_7$ are used extensively for back-titrating solutions of Fe^{2+} when the latter is being used as a standard reductant for the determination of oxidizing agents.

20-9. The solution concentration of I_3^- becomes stronger because of air oxidation of the excess I^-. The reaction is

$$6I^- + O_2(g) + 4H^+ \rightarrow 2I_3^- + 2H_2O$$

20-10. When a measured volume of a standard solution of KIO_3 is introduced into an acidic solution containing an excess of iodide ion, a known amount of iodine is produced as a result of:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

20-11.

$$Cr_2O_7^{2-} + \underset{excess}{6I^-} + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

20-12. Starch decomposes in the presence of high concentrations of iodine to give products that do not behave satisfactorily as indicators. This reaction is prevented by delaying the addition of the starch until the iodine concentration is very small.

20-13. $0.2541 \text{ g sample} \times \dfrac{1000 \text{ mmol Fe}^{2+}}{55.847 \text{ g}} = 4.5499 \text{ mmol Fe}^{2+}$

(a) $\dfrac{4.5499 \text{ mmol Fe}^{2+}}{36.76 \text{ mL}} \times \dfrac{1 \text{ mmol Ce}^{4+}}{\text{mmol Fe}^{2+}} = 0.1238 \text{ M Ce}^{4+}$

(b) $$\frac{4.5499\text{ mmol Fe}^{2+}}{36.76\text{ mL}} \times \frac{1\text{ mmol Cr}_2\text{O}_7^{2-}}{6\text{ mmol Fe}^{2+}} = 0.02062\text{ M Cr}_2\text{O}_7^{2-}$$

(c) $$\frac{4.5499\text{ mmol Fe}^{2+}}{36.76\text{ mL}} \times \frac{1\text{ mmol MnO}_4^{-}}{5\text{ mmol Fe}^{2+}} = 0.02475\text{ M MnO}_4^{-}$$

(d) $$\frac{4.5499\text{ mmol Fe}^{2+}}{36.76\text{ mL}} \times \frac{1\text{ mmol V(OH)}_4^{+}}{\text{mmol Fe}^{2+}} = 0.1238\text{ M V(OH)}_4^{+}$$

(e) $$\frac{4.5499\text{ mmol Fe}^{2+}}{36.76\text{ mL}} \times \frac{1\text{ mmol IO}_3^{-}}{4\text{ mmol Fe}^{2+}} = 0.03094\text{ M IO}_3^{-}$$

20-14. $$\frac{0.05000\text{ mol KBrO}_3}{\text{L}} \times 1.000\text{ L} \times \frac{167.001\text{ g KBrO}_3}{\text{mol}} = 8.350\text{ g KBrO}_3$$

Dissolve 8.350 g $KBrO_3$ in water and dilute to 1.000 L.

20-15.

$$\frac{0.0600\text{ mol I}_3^{-}}{\text{L}} \times \frac{1\text{ mol I}_2}{\text{mol I}_3^{-}} \times 2.5\text{ L} \times \frac{253.809\text{ g I}_2}{\text{mol}} = 38.07\text{ g I}_2$$

Dissolve about 38 g I_2 in a concentrated solution of KI and dilute to 2.5 L.

20-16. $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

$$\frac{0.2219\text{ g}}{34.65\text{ mL Ce}^{4+}} \times \frac{1000\text{ mL}}{\text{L}} \times \frac{1\text{ mol Fe}}{55.847\text{ g}} \times \frac{1\text{ mol Fe}^{2+}}{\text{mol Fe}} \times \frac{1\text{ mol Ce}^{4+}}{\text{mol Fe}^{2+}} = 0.1147\text{ M Ce}^{4+}$$

20-17.

$$\text{BrO}_3^{-} + 6\text{I}^{-} + 6\text{H}^{+} \rightarrow \text{Br}^{-} + 3\text{I}_2 + 3\text{H}_2\text{O}$$
$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^{-} + \text{S}_4\text{O}_6^{2-}$$

1 mmol BrO_3^{-} = 3 mmol I_2 = 6 mmol $S_2O_3^{2-}$

$$\frac{0.1298\text{ g KBrO}_3}{41.32\text{ mL Na}_2\text{S}_2\text{O}_3} \times \frac{1000\text{ mmol KBrO}_3}{167.001\text{ g}} \times \frac{6\text{ mmol S}_2\text{O}_3^{2-}}{\text{mmol KBrO}_3} = 0.1129\text{ M Na}_2\text{S}_2\text{O}_3$$

20-18.

$$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

1 mmol MnO_2 = 1 mmol I_2 = 2 mmol $S_2O_3^{2-}$

$$\frac{\left(\frac{0.08041\text{ mmol}}{\text{mL}} \times 29.62\text{ mL Na}_2\text{S}_2\text{O}_3 \times \frac{1\text{ mmol MnO}_2}{2\text{ mmol Na}_2\text{S}_2\text{O}_3} \times \frac{86.937\text{ g MnO}_2}{1000\text{ mmol}}\right)}{0.1267\text{ g sample}} \times 100\%$$

=81.71% MnO_2

20-19. $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

1 mmol MnO_4^- = 5 mmol Fe^{2+} = 5/2 mmol Fe_2O_3

$$\text{amount KMnO}_4 = \frac{0.01926\text{ mol KMnO}_4}{\text{mL}} \times 41.63\text{ mL KMnO}_4 = 0.80179\text{ mmol KMnO}_4$$

(a)

$$\frac{\left(0.80179\text{ mmoL KMnO}_4 \times \frac{5\text{ mmol Fe}^{2+}}{\text{mmol KMnO}_4} \times \frac{1\text{ mmol Fe}}{\text{mmol Fe}^{2+}} \times \frac{55.847\text{ g Fe}}{1000\text{ mmol}}\right)}{0.7120\text{ g sample}} \times 100\%$$

=31.45% Fe

(b)

$$\frac{\left(0.80179\text{ mmoL KMnO}_4 \times \frac{5\text{ mmol Fe}_2\text{O}_3}{2\text{ mmol KMnO}_4} \times \frac{159.692\text{ g Fe}_2\text{O}_3}{1000\text{ mmol}}\right)}{0.7120\text{ g sample}} \times 100\%$$

=44.96% Fe_2O_3

20-20.

$$2H_2NOH + 4Fe^{3+} \rightleftharpoons N_2O(g) + 4Fe^{2+} + 4H^+ + H_2O$$
$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

1 mmol $Cr_2O_7^{2-}$= 6 mmol Fe^{3+} = 3 mmol H_2NOH

$$\frac{\left(\frac{0.01528\text{ mmol }K_2Cr_2O_7}{\text{mL}} \times 14.48\text{ mL }K_2Cr_2O_7 \times \frac{3\text{ mmol }H_2NOH}{\text{mmol }K_2Cr_2O_7}\right)}{25.00\text{ mL sample}}$$

$= 0.0266\text{ M }H_2NOH$

20-21. $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 3H_2O + 6Fe^{3+}$

$$\text{amount }Fe^{2+} = \frac{0.07654\text{ mmol }Fe^{2+}}{\text{mL}} \times 50.00\text{ mL }Fe^{2+} = 3.827\text{ mmol}$$

$$\text{amnt }Fe^{2+}\text{titrated} = \frac{0.07654\text{ mmol }Ce^{4+}}{\text{mL}} \times 13.26\text{ mL }Ce^{4+} \times \frac{1\text{ mmol }Fe^{2+}}{\text{mmol }Ce^{4+}} = 1.0149\text{ mmol}$$

$$\text{amnt }Fe^{2+}\text{reacted with }KClO_3 = 3.827 - 1.0149 = 2.8121\text{ mmol}$$

$$\frac{\left(2.8121\text{ mmoL }Fe^{2+} \times \frac{1\text{ mmol }KClO_3}{6\text{ mmol }Fe^{2+}} \times \frac{122.549\text{ g }KClO_3}{1000\text{ mmol}}\right)}{0.1862\text{ g sample}} \times 100\%$$

$=30.85\%\ KClO_3$

20-22. $H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2I^- + 2H^+$

$1\text{ mmol }I_2 = 1\text{ mmol }H_3AsO_3 = ½\text{ mmol }As_2O_3$

$$\frac{\left(\frac{0.03142\text{ mmol }I_2}{\text{mL}} \times 31.36\text{ mL }I_2 \times \frac{1\text{ mmol }As_2O_3}{2\text{ mmol }I_2} \times \frac{197.841\text{ g }As_2O_3}{1000\text{ mmol}}\right)}{8.13\text{ g sample}} \times 100\%$$

$= 1.199\%\ As_2O_3$

20-23. $2C_2H_5SH + I_2 \rightarrow C_2H_5SSC_2H_5 + 2I^- + 2H^+$

$$\text{amount }I_2 = \frac{0.01204\text{ mmol }I_2}{\text{mL}} \times 50.0\text{ mL} = 0.6020\text{ mmol}$$

amnt I_2 titrated by $S_2O_3^{2-}$

$$= \frac{0.01437\text{ mmol }Na_2S_2O_3}{\text{mL}} \times 18.23\text{ mL }Na_2S_2O_3 \times \frac{1\text{ mmol }I_2}{2\text{ mmol }Na_2S_2O_3} = 0.2620\text{ mmol}$$

$$\text{amnt }I_2\text{ reacted with }C_2H_5SH = 0.6020 - 0.2620 = 0.3400\text{ mmol}$$

$$\frac{\left(0.3400\ \text{mmoL I}_2 \times \frac{2\ \text{mmol C}_2\text{H}_5\text{SH}}{\text{mmol I}_2} \times \frac{62.14\ \text{g C}_2\text{H}_5\text{SH}}{1000\ \text{mmol}}\right)}{2.043\ \text{g sample}} \times 100\%$$

$= 2.07\%\ C_2H_5SH$

20-24.

$$2I^- + Br_2 \rightarrow I_2 + 2Br^-$$
$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

1 mmol KI = 1 mmol IO_3^- = 3 mmol I_2 = 6 mmol $S_2O_3^{2-}$

$$\frac{\left(\frac{0.04926\ \text{mmol Na}_2\text{S}_2\text{O}_3}{\text{mL}} \times 19.72\ \text{mL Na}_2\text{S}_2\text{O}_3 \times \frac{1\ \text{mmol KI}}{6\ \text{mmol Na}_2\text{S}_2\text{O}_3} \times \frac{166.00\ \text{g KI}}{1000\ \text{mmol}}\right)}{1.307\ \text{g sample}} \times 100\%$$

= 2.056% KI

20-25. In the Walden reductor, $V(OH)_4^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + 3H_2O$

In the Jones reductor, $V(OH)_4^+ + 4H^+ + 3e^- \rightleftharpoons V^{2+} + 4H_2O$

In the first titration,

$$Ce^{4+} + Fe^{2+} \rightarrow Fe^{3+} + Ce^{3+}$$
$$Ce^{4+} + VO^{2+} + 3H_2O \rightarrow V(OH)_4^+ + Ce^{3+} + 2H^+$$

amount Fe and V = amount Ce^{4+} $= \frac{0.1000\ \text{mmol Ce}^{4+}}{\text{mL}} \times 18.31\ \text{mL Ce}^{4+} = 1.831\ \text{mmol Fe and V}$

In the second titration,

$$Ce^{4+} + Fe^{2+} \rightarrow Fe^{3+} + Ce^{3+}$$
$$3Ce^{4+} + V^{2+} + 4H_2O \rightarrow V(OH)_4^+ + 3Ce^{3+} + 4H^+$$

amount Fe and 3 × V = amount Ce^{4+}

$$= \frac{0.1000\text{ mmol Ce}^{4+}}{\text{mL}} \times 42.41\text{ mL Ce}^{4+} = 4.241\text{ mmol Fe and } 3\times\text{V}$$

Subtracting the first equation from the second equation gives

$$4.241 - 1.831 = 2.410 = 2\times\text{ amount V}$$

$$\text{amount V} = \frac{2.410}{2} = 1.205\text{ mmol}$$

$$\text{amount V}_2\text{O}_5 = \frac{1.205\text{ mmol V}}{2} = 0.6025\text{ mmol}$$

$$\text{amount Fe} = 1.831 - 1.205 = 0.626\text{ mmol}$$

$$\text{amount Fe}_2\text{O}_3 = \frac{0.626\text{ mmol Fe}}{2} = 0.3130\text{ mmol}$$

$$\frac{(0.6025\text{ mmol V}_2\text{O}_5)\times\dfrac{181.88\text{ g V}_2\text{O}_5}{1000\text{ mmol}}}{2.667\text{ g sample}\times\dfrac{50.00\text{ mL}}{500.0\text{ mL}}}\times 100\%$$

$= 41.09\%\ V_2O_5$

$$\frac{(0.3130\text{ mmol Fe}_2\text{O}_3)\times\dfrac{159.69\text{ g Fe}_2\text{O}_3}{1000\text{ mmol}}}{2.667\text{ g sample}\times\dfrac{50.00\text{ mL}}{500.0\text{ mL}}}\times 100\%$$

$= 18.74\%\ Fe_2O_3$

20-26.

$$S\text{O}_2(g) + 2\text{OH}^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$$

$$\text{IO}_3^- + 2\text{H}_2\text{SO}_3 + 2\text{Cl}^- \rightarrow \text{ICl}_2^- + 2\text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O}$$

1 mmol IO_3^- = 2 mmol H_2SO_3 =2 mmol SO_2

In $\frac{2.50\text{ L}}{\text{min}} \times 59.00\text{ min} = 147.5\text{ L of sample, there are}$

$$\frac{0.002997\text{ mmol KIO}_3}{\text{mL}} \times 5.15\text{ mL KIO}_3 \times \frac{2\text{ mmol SO}_2}{\text{mmol KIO}_3} \times \frac{64.065\text{ g SO}_2}{1000\text{ mmol}} = 1.9776 \times 10^{-3}\text{ g SO}_2$$

$$\left(\frac{1.9776 \times 10^{-3}\text{ g SO}_2}{147.5\text{ L} \times \frac{1.20\text{ g}}{\text{L}}}\right) \times 10^6\text{ ppm}$$

$= 11.2\text{ ppm SO}_2$

20-27.

$$S^{2-} + I_2 \rightarrow S(s) + 2I^-$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

$1\text{ mmol I}_2 = 1\text{ mmol H}_2\text{S} = 2\text{ mmol S}_2\text{O}_3^{2-}$

$$\text{amount I}_2\text{ added} = \frac{0.00432\text{ mmol I}_2}{\text{mL}} \times 25.00\text{ mL I}_2 = 0.1080\text{ mmol I}_2$$

$$\text{amount I}_2\text{ in excess} = \frac{0.01143\text{ mmol S}_2\text{O}_3^{2-}}{\text{mL}} \times 15.62\text{ mL S}_2\text{O}_3^{2-} \times \frac{1\text{ mmol I}_2}{2\text{ mmol S}_2\text{O}_3^{2-}}$$

$= 0.08927\text{ mmol}$

$\text{amount I}_2\text{ reacted} = \text{amount H}_2\text{S} = 0.1080 - 0.08927 = 0.01873\text{ mmol}$

$$\left(\frac{0.01873\text{ mmol H}_2\text{S} \times \frac{34.082\text{ g H}_2\text{S}}{1000\text{ mmol}}}{25.00\text{ L} \times \frac{1.2\text{ g}}{\text{L}}}\right) \times 10^6\text{ ppm}$$

$=21.3\text{ ppm H}_2\text{S}$

20-28.

$$O_2 + 4Mn(OH)_2(s) + 2H_2O \rightleftharpoons 4Mn(OH)_3(s)$$

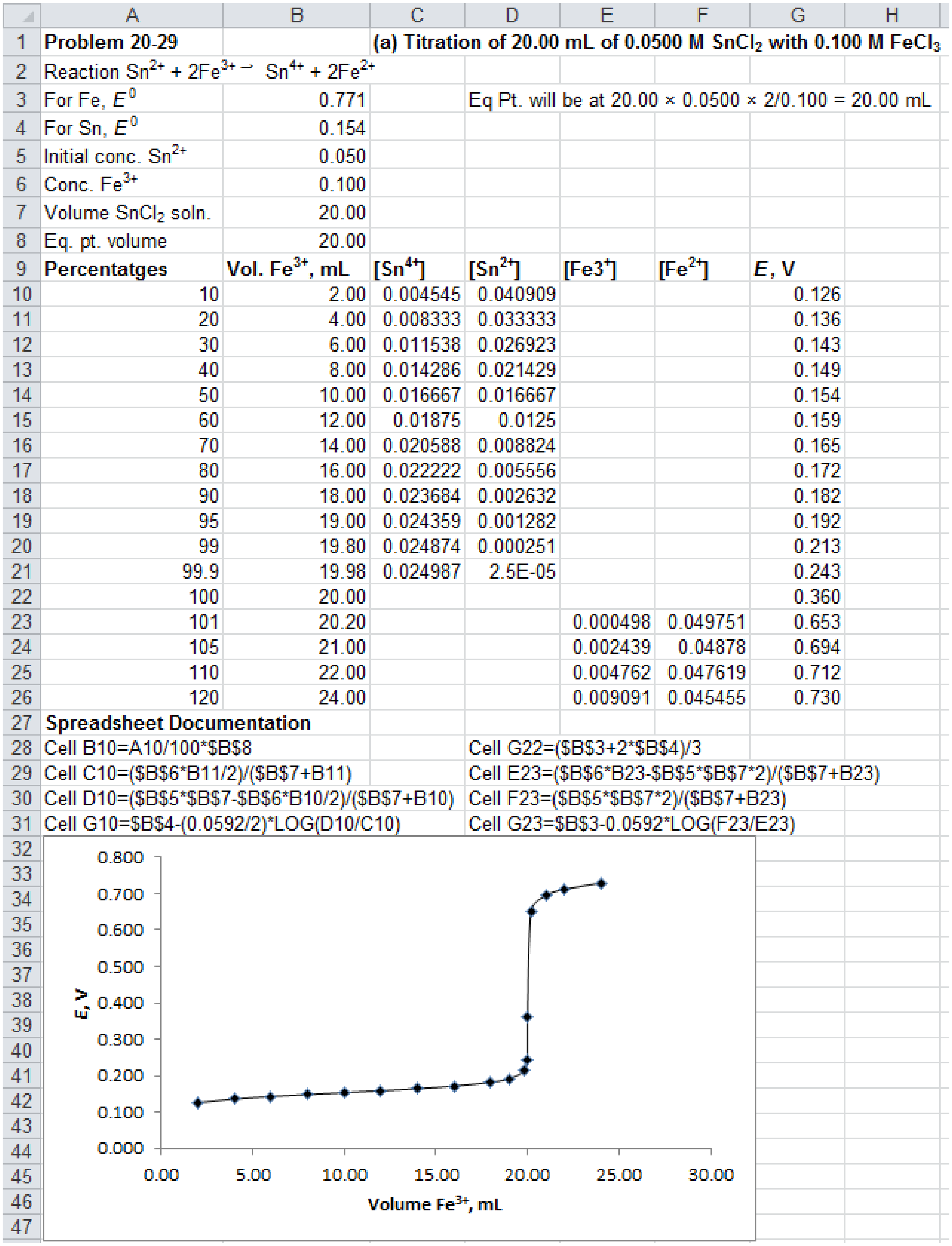
$$4Mn(OH)_3(s) + 12H^+ + 4I^- \rightleftharpoons 4Mn^{2+} + 2I_2 + 6H_2O$$

$$\frac{0.00897\text{ mmol S}_2\text{O}_3{}^{2-}}{\text{mL}}\times 14.60\text{ mL S}_2\text{O}_3{}^{2-}\times\frac{1\text{ mmol O}_2}{4\text{ mmol S}_2\text{O}_3{}^{2-}}\times\frac{32.0\text{ mg O}_2}{\text{mmol}}=1.0477\text{ mg O}_2$$

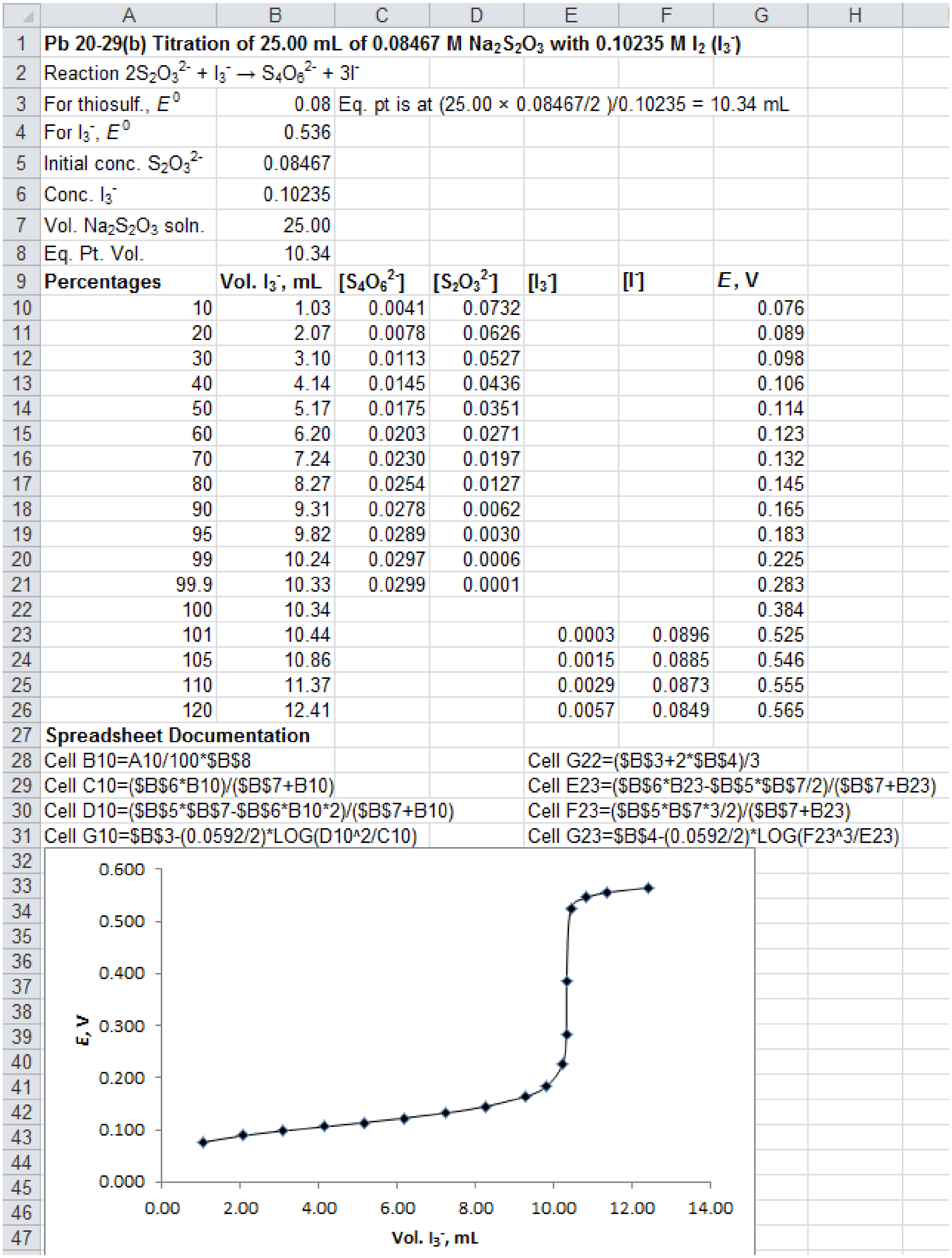
$$\frac{1.0477\text{ mg O}_2}{\left(25\text{ mL sample}\times\frac{250\text{ mL}}{254\text{ mL}}\right)}$$

$$= 0.0426\text{ mg O}_2\text{/mL sample}$$

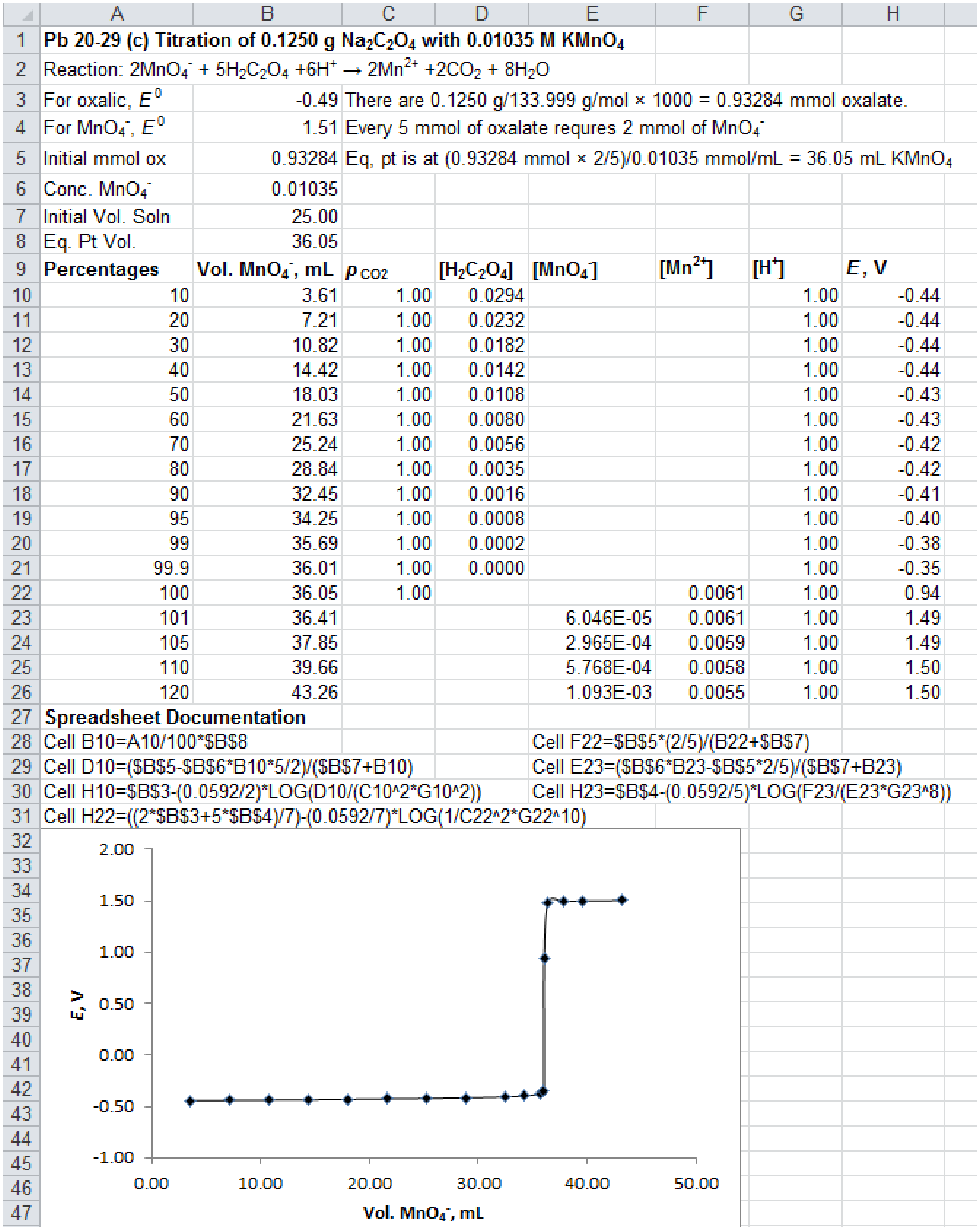
20-29. See spreadsheets on the following pages.



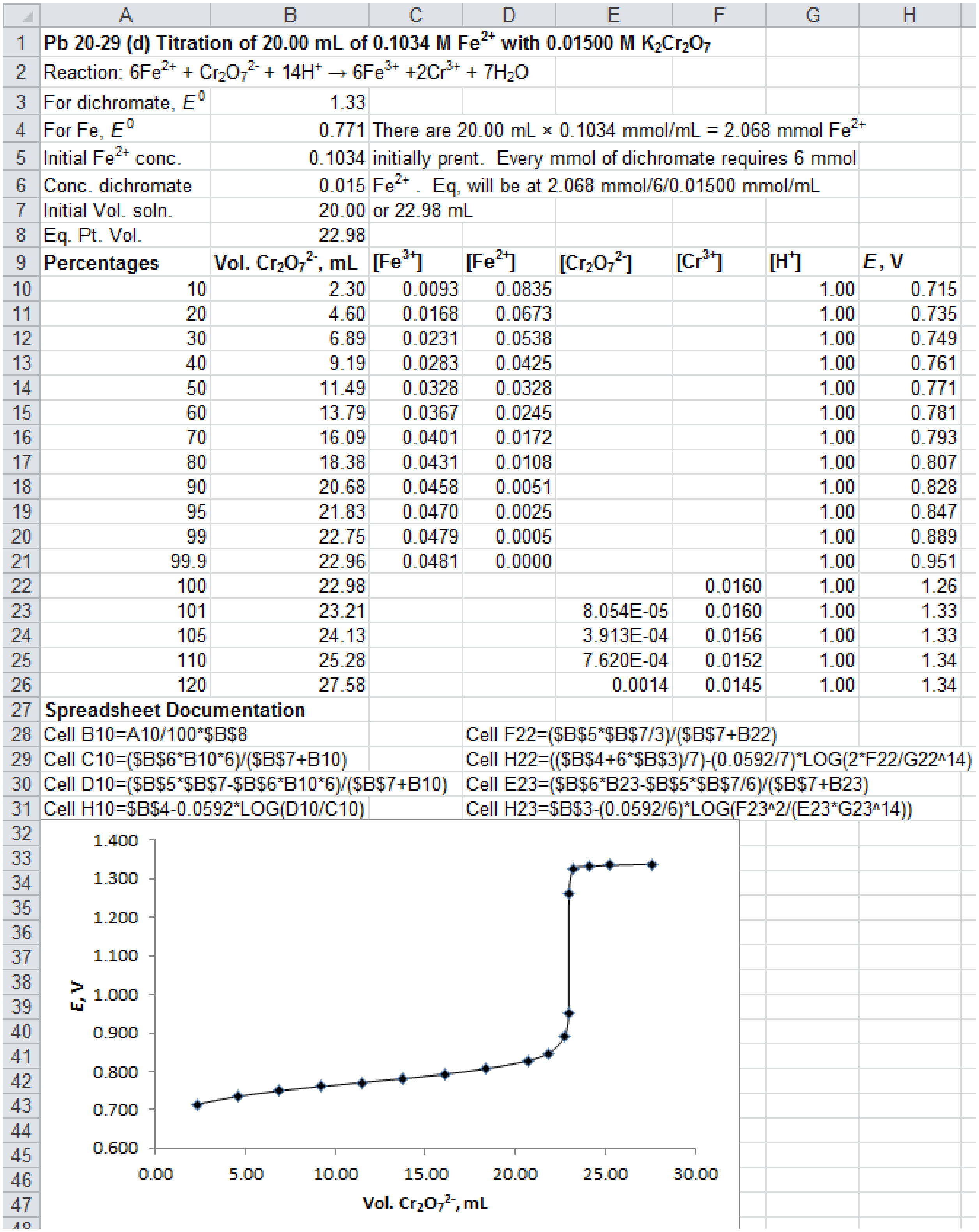
	A	B	C	D	E	F	G	H
1	**Problem 20-29**		**(a) Titration of 20.00 mL of 0.0500 M $SnCl_2$ with 0.100 M $FeCl_3$**					
2	Reaction $Sn^{2+} + 2Fe^{3+} \rightleftharpoons Sn^{4+} + 2Fe^{2+}$							
3	For Fe, E^0	0.771		Eq Pt. will be at 20.00 × 0.0500 × 2/0.100 = 20.00 mL				
4	For Sn, E^0	0.154						
5	Initial conc. Sn^{2+}	0.050						
6	Conc. Fe^{3+}	0.100						
7	Volume $SnCl_2$ soln.	20.00						
8	Eq. pt. volume	20.00						
9	**Percentatges**	**Vol. Fe^{3+}, mL**	**[Sn^{4+}]**	**[Sn^{2+}]**	**[Fe3^{+}]**	**[Fe^{2+}]**	***E*, V**	
10	10	2.00	0.004545	0.040909			0.126	
11	20	4.00	0.008333	0.033333			0.136	
12	30	6.00	0.011538	0.026923			0.143	
13	40	8.00	0.014286	0.021429			0.149	
14	50	10.00	0.016667	0.016667			0.154	
15	60	12.00	0.01875	0.0125			0.159	
16	70	14.00	0.020588	0.008824			0.165	
17	80	16.00	0.022222	0.005556			0.172	
18	90	18.00	0.023684	0.002632			0.182	
19	95	19.00	0.024359	0.001282			0.192	
20	99	19.80	0.024874	0.000251			0.213	
21	99.9	19.98	0.024987	2.5E-05			0.243	
22	100	20.00					0.360	
23	101	20.20			0.000498	0.049751	0.653	
24	105	21.00			0.002439	0.04878	0.694	
25	110	22.00			0.004762	0.047619	0.712	
26	120	24.00			0.009091	0.045455	0.730	
27	**Spreadsheet Documentation**							
28	Cell B10=A10/100*$B$8			Cell G22=($B$3+2*$B$4)/3				
29	Cell C10=($B$6*B11/2)/($B$7+B11)			Cell E23=($B$6*B23-$B$5*$B$7*2)/($B$7+B23)				
30	Cell D10=($B$5*$B$7-$B$6*B10/2)/($B$7+B10)			Cell F23=($B$5*$B$7*2)/($B$7+B23)				
31	Cell G10=$B$4-(0.0592/2)*LOG(D10/C10)			Cell G23=$B$3-0.0592*LOG(F23/E23)				



	A	B	C	D	E	F	G	H
1	**Pb 20-29(b) Titration of 25.00 mL of 0.08467 M $Na_2S_2O_3$ with 0.10235 M I_2 (I_3^-)**							
2	Reaction $2S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3I^-$							
3	For thiosulf., E^0	0.08	Eq. pt is at (25.00 × 0.08467/2)/0.10235 = 10.34 mL					
4	For I_3^-, E^0	0.536						
5	Initial conc. $S_2O_3^{2-}$	0.08467						
6	Conc. I_3^-	0.10235						
7	Vol. $Na_2S_2O_3$ soln.	25.00						
8	Eq. Pt. Vol.	10.34						
9	**Percentages**	**Vol. I_3^-, mL**	**[$S_4O_6^{2-}$]**	**[$S_2O_3^{2-}$]**	**[I_3^-]**	**[I^-]**	***E*, V**	
10	10	1.03	0.0041	0.0732			0.076	
11	20	2.07	0.0078	0.0626			0.089	
12	30	3.10	0.0113	0.0527			0.098	
13	40	4.14	0.0145	0.0436			0.106	
14	50	5.17	0.0175	0.0351			0.114	
15	60	6.20	0.0203	0.0271			0.123	
16	70	7.24	0.0230	0.0197			0.132	
17	80	8.27	0.0254	0.0127			0.145	
18	90	9.31	0.0278	0.0062			0.165	
19	95	9.82	0.0289	0.0030			0.183	
20	99	10.24	0.0297	0.0006			0.225	
21	99.9	10.33	0.0299	0.0001			0.283	
22	100	10.34					0.384	
23	101	10.44			0.0003	0.0896	0.525	
24	105	10.86			0.0015	0.0885	0.546	
25	110	11.37			0.0029	0.0873	0.555	
26	120	12.41			0.0057	0.0849	0.565	
27	**Spreadsheet Documentation**							
28	Cell B10=A10/100*$B$8				Cell G22=($B$3+2*$B$4)/3			
29	Cell C10=($B$6*B10)/($B$7+B10)				Cell E23=($B$6*B23-$B$5*$B$7/2)/($B$7+B23)			
30	Cell D10=($B$5*$B$7-$B$6*B10*2)/($B$7+B10)				Cell F23=($B$5*B$7*3/2)/($B$7+B23)			
31	Cell G10=$B$3-(0.0592/2)*LOG(D10^2/C10)				Cell G23=$B$4-(0.0592/2)*LOG(F23^3/E23)			



	A	B	C	D	E	F	G	H
1	**Pb 20-29 (c) Titration of 0.1250 g $Na_2C_2O_4$ with 0.01035 M $KMnO_4$**							
2	Reaction: $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 2CO_2 + 8H_2O$							
3	For oxalic, E^0	-0.49	There are 0.1250 g/133.999 g/mol × 1000 = 0.93284 mmol oxalate.					
4	For MnO_4^-, E^0	1.51	Every 5 mmol of oxalate requres 2 mmol of MnO_4^-					
5	Initial mmol ox	0.93284	Eq. pt is at (0.93284 mmol × 2/5)/0.01035 mmol/mL = 36.05 mL $KMnO_4$					
6	Conc. MnO_4^-	0.01035						
7	Initial Vol. Soln	25.00						
8	Eq. Pt Vol.	36.05						
9	**Percentages**	**Vol. MnO_4^-, mL**	**p_{CO2}**	**$[H_2C_2O_4]$**	**$[MnO_4^-]$**	**$[Mn^{2+}]$**	**$[H^+]$**	***E*, V**
10	10	3.61	1.00	0.0294			1.00	-0.44
11	20	7.21	1.00	0.0232			1.00	-0.44
12	30	10.82	1.00	0.0182			1.00	-0.44
13	40	14.42	1.00	0.0142			1.00	-0.44
14	50	18.03	1.00	0.0108			1.00	-0.43
15	60	21.63	1.00	0.0080			1.00	-0.43
16	70	25.24	1.00	0.0056			1.00	-0.42
17	80	28.84	1.00	0.0035			1.00	-0.42
18	90	32.45	1.00	0.0016			1.00	-0.41
19	95	34.25	1.00	0.0008			1.00	-0.40
20	99	35.69	1.00	0.0002			1.00	-0.38
21	99.9	36.01	1.00	0.0000			1.00	-0.35
22	100	36.05	1.00			0.0061	1.00	0.94
23	101	36.41			6.046E-05	0.0061	1.00	1.49
24	105	37.85			2.965E-04	0.0059	1.00	1.49
25	110	39.66			5.768E-04	0.0058	1.00	1.50
26	120	43.26			1.093E-03	0.0055	1.00	1.50
27	**Spreadsheet Documentation**							
28	Cell B10=A10/100*$B$8				Cell F22=$B$5*(2/5)/(B22+$B$7)			
29	Cell D10=($B$5-$B$6*B10*5/2)/($B$7+B10)				Cell E23=($B$6*B23-$B$5*2/5)/($B$7+B23)			
30	Cell H10=$B$3-(0.0592/2)*LOG(D10/(C10^2*G10^2))				Cell H23=$B$4-(0.0592/5)*LOG(F23/(E23*G23^8))			
31	Cell H22=((2*$B$3+5*$B$4)/7)-(0.0592/7)*LOG(1/C22^2*G22^10)							



	A	B	C	D	E	F	G	H
1	**Pb 20-29 (d) Titration of 20.00 mL of 0.1034 M Fe^{2+} with 0.01500 M $K_2Cr_2O_7$**							
2	Reaction: $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$							
3	For dichromate, E^0	1.33						
4	For Fe, E^0	0.771	There are 20.00 mL × 0.1034 mmol/mL = 2.068 mmol Fe^{2+}					
5	Initial Fe^{2+} conc.	0.1034	initially prent. Every mmol of dichromate requires 6 mmol					
6	Conc. dichromate	0.015	Fe^{2+} . Eq, will be at 2.068 mmol/6/0.01500 mmol/mL					
7	Initial Vol. soln.	20.00	or 22.98 mL					
8	Eq. Pt. Vol.	22.98						
9	**Percentages**	**Vol. $Cr_2O_7^{2-}$, mL**	**$[Fe^{3+}]$**	**$[Fe^{2+}]$**	**$[Cr_2O_7^{2-}]$**	**$[Cr^{3+}]$**	**$[H^+]$**	***E*, V**
10	10	2.30	0.0093	0.0835			1.00	0.715
11	20	4.60	0.0168	0.0673			1.00	0.735
12	30	6.89	0.0231	0.0538			1.00	0.749
13	40	9.19	0.0283	0.0425			1.00	0.761
14	50	11.49	0.0328	0.0328			1.00	0.771
15	60	13.79	0.0367	0.0245			1.00	0.781
16	70	16.09	0.0401	0.0172			1.00	0.793
17	80	18.38	0.0431	0.0108			1.00	0.807
18	90	20.68	0.0458	0.0051			1.00	0.828
19	95	21.83	0.0470	0.0025			1.00	0.847
20	99	22.75	0.0479	0.0005			1.00	0.889
21	99.9	22.96	0.0481	0.0000			1.00	0.951
22	100	22.98				0.0160	1.00	1.26
23	101	23.21			8.054E-05	0.0160	1.00	1.33
24	105	24.13			3.913E-04	0.0156	1.00	1.33
25	110	25.28			7.620E-04	0.0152	1.00	1.34
26	120	27.58			0.0014	0.0145	1.00	1.34
27	**Spreadsheet Documentation**							
28	Cell B10=A10/100*$B$8			Cell F22=($B$5*$B$7/3)/($B$7+B22)				
29	Cell C10=($B$6*B10*6)/($B$7+B10)			Cell H22=(($B$4+6*$B$3)/7)-(0.0592/7)*LOG(2*F22/G22^14)				
30	Cell D10=($B$5*$B$7-$B$6*B10*6)/($B$7+B10)			Cell E23=($B$6*B23-$B$5*$B$7/6)/($B$7+B23)				
31	Cell H10=$B$4-0.0592*LOG(D10/C10)			Cell H23=$B$3-(0.0592/6)*LOG(F23^2/(E23*G23^14))				

Chapter 21

21-1. **(a)** An *indicator electrode* is an electrode used in potentiometry that responds to variations in the activity of an analyte ion or molecule.

(b) A *reference electrode* is an electrode whose potential is known, constant and independent of the type of solution in which it is immersed.

(c) An *electrode of the first kind* is a metal electrode that responds to the activity of its cation in solution.

(d) An *electrode of the second kind* is a metal electrode that is used to determine the concentration of an anion that forms a precipitate or a stable complex with the cation of the electrode metal.

21-2. **(a)** A *liquid junction potential* is the potential that develops across the interface between two solutions having different electrolyte compositions.

(b) A *boundary potential* is the potential that develops across an ion-sensitive membrane when the two side of the membrane are immersed in solutions having different concentrations of the ion to which the membrane is sensitive.

(c) The *asymmetry potential* is a potential that develops across an ion-sensitive membrane when the concentrations of the ion are the same on either side of the membrane. This potential arises from dissimilarities between the inner and outer surface of the membrane.

21-3. **(a)** A titration is generally more accurate than measurements of electrode potential. Therefore, if ppt accuracy is needed, a titration should be picked.

(b) Electrode potentials are related to the activity of the analyte. Thus, pick potential measurements if activity is the desired quantity.

21-4. For the process $M^{n+} + ne^- \rightleftharpoons M(s)$, the Nernst equation predicts

$$E = E^o - \frac{0.0592}{n}\log\left(\frac{1}{[M^{n+}]}\right) = E^o + \frac{0.0592}{n}[M^{n+}] = E^o - \frac{0.0592}{n}\text{pM}$$

The response is Nernstian if a plot of E vs. pM is linear with a slope of –0.0592/n.

21-5. The potential arises from the difference in positions of dissociation equilibria on each of the two surfaces. These equilibria are described by

$$\underset{\text{membrane}}{H^+Gl^-} \rightleftharpoons \underset{\text{solution}}{H^+} + \underset{\text{membrane}}{Gl^-}$$

The surface exposed to the solution having the higher H^+ concentration becomes positive with respect to the other surface. This charge difference, or potential, serves as the analytical parameter when the pH of the solution on one side of the membrane is held constant.

21-6. In order for a glass membrane to be pH sensitive, it is necessary for the two surfaces to be hydrated so that the equilibria shown in the previous problem can be established.

21-7. Uncertainties include (1) the acid error in highly acidic solutions, (2) the alkaline error in strongly basic solutions, (3) the error that arises when the ionic strength of the calibration standards differs from that of the analyte solution, (4) uncertainties in the pH of the standard buffers, (5) nonreproducible junction potentials with solutions of low ionic strength and (6) dehydration of the working surface.

21-8. Because of variables that cannot be controlled, it is necessary to calibrate the response of the electrode against one or more standards. It must then be assumed that the junction potential associated with the external reference electrode does not change when the standard is replaced by the test solution. The uncertainty associated with this assumption translates into uncertainties in the second decimal place of the measured p-value.

21-9. The *alkaline error* arises when a glass electrode is employed to measure the pH of solutions having pH values in the 10 to 12 range or greater. In the presence of alkali ions, the glass surface becomes responsive to not only hydrogen ions but also alkali metal ions. Measured pH values are low as a result.

21-10. A *gas-sensing probe* functions by permitting the gas to penetrate a hydrophobic membrane and altering the composition of liquid on the inner side of the membrane. The changes are registered by an indicator/reference electrode pair in contact with the inner solution. Thus, there is no direct contact between the electrodes and the test solution as there is with membrane electrodes.

21-11. **(a)** The *asymmetry potential* in a membrane arises from differences in the composition or structure of the inner and outer surfaces. These differences may arise from contamination of one of the surfaces, wear and abrasion and/or strains set up during manufacturing.

(b) The *boundary potential* for a membrane electrode is a potential that develops when the membrane separates two solutions that have different concentrations of a cation or an anion that the membrane binds selectively. For an aqueous solution, the following equilibria develop when the membrane is positioned between two solutions of A^+:

$$\underset{\text{membrane}_1}{A^+M^-} \rightleftarrows \underset{\text{solution}_1}{A^+} + \underset{\text{membrane}_1}{M^-}$$

$$\underset{\text{membrane}_2}{A^+M^-} \rightleftarrows \underset{\text{solution}_2}{A^+} + \underset{\text{membrane}_2}{M^-}$$

where the subscripts refer to the two sides of the membrane. A potential develops across this membrane if one of these equilibria proceeds further to the right than the other, and this potential is the boundary potential. For example, if the concentration of A^+ is greater in solution 1 than in solution 2, the negative charge on side 1 of the membrane will be less than that of side 2 because the equilibrium on side 1 will lie further to the left. Thus, a greater fraction of the negative charge on side 1 will be neutralized by A^+.

(c) The *junction potential* in a glass/calomel electrode system develops at the interface between the saturated KCl solution in the salt bridge and the sample solution. It is caused by charge separation created by the differences in the rates at which ions migrate across the interface.

(d) The membrane in a solid-state electrode for F^- is crystalline LaF_3, which when immersed in aqueous solution, dissociates according to the equation

$$LaF_3(s) \rightleftharpoons La^{3+} + 3F^-$$

Thus, the boundary potential develops across this membrane when it separates two solutions of F^- ion concentration. The source of this potential is the same as described in part (b).

21-12. The direct potentiometric measurement of pH provides a measure of the equilibrium activity of hydronium ions in the sample. A potentiometric titration provides information on the amount of reactive protons, both ionized and nonionized, in the sample.

21-13. *Potentiometric titrations* offer many advantages over *direct potentiometry* including (1) yielding equivalence point data that are independent of E_{cell} and free of uncertainties involving the junction potential, (2) electrode fouling and non-Nernstian behavior are not as serious, (3) the reference electrode potential does not need to be known and (4) the result is analyte concentration even though the electrode responds to activity, thus ionic strengths are not important.

21-14. The "operational definition of pH" is based on the direct calibration of the meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions. The relationship is:

$$\text{pH}_\text{U} = \text{pH}_\text{S} = \frac{E_\text{U} - E_\text{S}}{0.0592}$$

Where pH_U is the pH of the unknown solution, pH_S is the pH of the standard buffer, and E_U and E_S are the potentials of the unknown and standard solution respectively. This relationship has been adopted throughout the world as the *operational definition of pH.*

21-15. $\text{AgIO}_3(s) + \text{e}^- \rightleftharpoons \text{Ag}(s) + \text{IO}_3^-$

(a)

$$E_\text{Ag} = 0.799 - 0.0592\log\left(\frac{1}{[\text{Ag}^+]}\right) \quad K_\text{sp} = [\text{Ag}^+][\text{IO}_3^-] = 3.1\times10^{-8}$$

$$E_\text{Ag} = 0.799 - 0.0592\log\left(\frac{[\text{IO}_3^-]}{K_\text{sp}}\right)$$

When $[\text{IO}_3^-] = 1.00$, E_Ag is equal to $E^\text{o}_{\text{AgIO}_3}$ for the reduction of AgIO_3, that is,

$$E^\text{o}_{\text{AgIO}_3} = 0.799 - 0.0592\log\left(\frac{1.00}{3.1\times10^{-8}}\right) = 0.354\text{ V}$$

(b) SCE||IO_3^- (x M), AgIO_3(sat'd)$\,|\,$Ag

(c)

$$\begin{aligned}E_{\text{cell}} &= E_{\text{AgIO}_3} - E_{\text{SCE}}\\ &= \left(0.354 - 0.0592\log\left([\text{IO}_3^-]\right) - 0.244\right)\\ &= 0.110 + 0.0592\text{pIO}_3\end{aligned}$$

$$\text{pIO}_3 = \frac{E_{\text{cell}} - 0.110}{0.0592}$$

(d) $\text{pIO}_3 = \dfrac{0.306 - 0.110}{0.0592}$ = 3.31

21-16. **(a)** Proceeding as in the previous solution, we write

$$E_{\text{Pb}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{1}{[\text{Pb}^{2+}]}\right) \quad K_{\text{sp}} = [P\text{b}^{2+}][\text{I}^-]^2 = 7.9\times10^{-9}$$

$$E_{\text{Pb}} = -0.126 - \frac{0.0592}{2}\log\left(\frac{[\text{I}^-]^2}{K_{\text{sp}}}\right)$$

When [I$^-$] = 1.00, *E* becomes $E^{\text{o}}_{\text{PbI}_2}$ and

$$E^{\text{o}}_{\text{PbI}_2} = -0.126 - \frac{0.0592}{2}\log\left(\frac{1.00}{7.9\times10^{-9}}\right) = -0.366\text{ V}$$

(b) SCE||I$^-$ (*x* M), PbI$_2$(*s*) | Pb

(c)

$$\begin{aligned}E_{\text{cell}} &= E_{\text{PbI}_2} - E_{\text{SCE}}\\ &= \left(-0.366 - \frac{0.0592}{2}\log\left([\text{I}^-]^2\right) - 0.244\right)\\ &= -0.610 + 0.0592\text{pI}\end{aligned}$$

$$\text{pI} = \frac{E_{\text{cell}} + 0.610}{0.0592}$$

(d) $\text{pI} = \dfrac{-0.402 + 0.610}{0.0592}$ = 3.51

21-17. **(a)** SCE||I$^-$ (*x* M), AgI (sat'd) | Ag

(b) SCE||SCN^- (x M), AgSCN (sat'd)|Ag

(c) SCE||PO_4^{3-} (x M), Ag_3PO_4 (sat'd)|Ag

(d) SCE||SO_3^- (x M), Ag_2SO_3 (sat'd)|Ag

21-18. **(a)** $AgI(s) \rightleftharpoons Ag(s) + I^- \quad E^o_{AgI} = -0.151\text{ V}$ (Appendix 5)

$$E_{cell} = -0.151 - 0.0592\log\left([I^-]\right) - 0.244 = -0.395 + 0.0592pI$$

$$pI = \frac{E_{cell} + 0.395}{0.0592}$$

(b) $AgSCN(s) \rightleftharpoons Ag^+ + SCN^- \quad K_{sp} = [Ag^+][SCN^-] = 1.1\times10^{-12}$

To obtain E^o_{AgSCN} we proceed as in Problem 21-16(a). Thus,

$$E^o_{AgSCN} = 0.799 - 0.0592\log\left(\frac{1}{1.1\times10^{-12}}\right) = 0.091\text{ V}$$

$$E_{cell} = 0.091 - 0.0592\log\left([SCN^-]\right) - 0.244 = -0.153 + 0.0592pSCN$$

$$pSCN = \frac{E_{cell} + 0.153}{0.0592}$$

(c) $Ag_3PO_4(s) \rightleftharpoons 3Ag^+ + PO_4^{3-} \quad K_{sp} = [Ag^+]^3[PO_4^{3-}] = 1.3\times10^{-20}$

$$E^o_{Ag_3PO_4} = 0.799 - \frac{0.0592}{3}\log\left(\frac{1}{1.3\times10^{-20}}\right) = 0.407\text{ V}$$

$$E_{cell} = 0.407 - \frac{0.0592}{3}\log\left([PO_4^{3-}]\right) - 0.244 = 0.163 + \frac{0.0592}{3}pPO_4$$

$$pPO_4 = \frac{3\left(E_{cell} - 0.163\right)}{0.0592}$$

(d) $Ag_2SO_3(s) \rightleftharpoons 2Ag^+ + SO_3^{2-} \quad K_{sp} = [Ag^+]^2[SO_3^{2-}] = 1.5\times10^{-14}$

$$E^{\text{o}}_{\text{Ag}_2\text{SO}_3} = 0.799 - \frac{0.0592}{2}\log\left(\frac{1}{1.5\times10^{-14}}\right) = 0.390\,V$$

$$E_{cell} = 0.390 - \frac{0.0592}{2}\log\left([\text{SO}_3{}^{2-}]\right) - 0.244 = 0.146 + \frac{0.0592}{2}\text{pSO}_3$$
$$\text{pSO}_3 = \frac{2\left(E_{\text{cell}} - 0.146\right)}{0.0592}$$

21-19. **(a)** $\text{pI} = \frac{-0.196 + 0.395}{0.0592}$ = 3.36

(b) $\text{pSCN} = \frac{0.137 + 0.153}{0.0592}$ = 4.90

(c) $\text{pPO}_4 = \frac{3\left(0.211 - 0.163\right)}{0.0592}$ = 2.43

(d) $\text{pSO}_3 = \frac{2\left(0.285 - 0.146\right)}{0.0592}$ = 4.70

21-20. SCE||Ag_2CrO_4 (sat'd), CrO_4^{2-} (x M) | Ag

$Ag_2CrO_4(s) + 2e^- \rightleftharpoons 2Ag(s) + CrO_4^{2-}$ $E^o = 0.446$ V

$$0.336 = 0.446 - \frac{0.0592}{2}\log\left([\text{CrO}_4{}^{2-}]\right) - 0.244 = 0.202 + \frac{0.0592}{2}\text{pCrO}_4$$
$$\text{pCrO}_4 = \frac{2\left(0.389 - 0.202\right)}{0.0592}$$

$\text{pCrO}_4 = 6.32$

21-21. Substituting into Equation 21-22 gives

$$\text{pH} = -\frac{1\left(E_{\text{cell}} - K\right)}{0.0592} \quad \text{and} \quad 4.006 = -\frac{\left(0.2106 - K\right)}{0.0592}$$
$$K = \left(4.006\times0.0592\right) + 0.2106 = 0.447755$$

(a) $\text{pH} = -\frac{\left(-0.2902 - 0.447755\right)}{0.0592}$ = 12.47

$$a_{\mathrm{H^+}} = \text{antilog}\left(-12.4655\right) = 3.42 \times 10^{-13}\text{ M}$$

(b) $\text{pH} = -\dfrac{\left(0.1241 - 0.447755\right)}{0.0592} = 5.47$

$$a_{\mathrm{H^+}} = \text{antilog}\left(-5.4671\right) = 3.41 \times 10^{-6}\text{ M}$$

(c) For part (a)

If $E = -0.2902 + 0.002 = -0.2882\ \text{ V}$

$$\text{pH} = -\frac{\left(-0.2882 - 0.447755\right)}{0.0592} = 12.43$$

$$a_{\mathrm{H^+}} = \text{antilog}\left(-12.4317\right) = 3.70 \times 10^{-13}$$

If $E = -0.2902 - 0.002 = -0.2922\text{ V}$

$$\text{pH} = -\frac{\left(-0.2922 - 0.447755\right)}{0.0592} = 12.50$$

$$a_{\mathrm{H^+}} = \text{antilog}\left(-12.4992\right) = 3.17 \times 10^{-13}\ \text{ M}$$

Thus pH should be 12.43 to 12.50 and $a_{\mathrm{H^+}}$ in the range of 3.17 to 3.70 × 10^{-13} M

Proceeding in the same way for (b), we obtain

pH in the range 5.43 to 5.50

$a_{\mathrm{H^+}}$ in the range 3.16×10^{-6} to 3.69×10^{-6} M

21-22.

$$\text{amount HA} = \frac{0.1243\text{ mmol NaOH}}{\text{mL}} \times 18.62\text{ mL NaOH} \times \frac{1\text{ mmol HA}}{\text{mmol NaOH}} = 2.3145\text{ mmol}$$

$$\frac{0.4021\text{ g HA}}{2.3145\text{ mmol HA}} \times \frac{1000\text{ mmol}}{\text{mol}} = \frac{173.7\text{ g HA}}{\text{mol}}$$

$\mathcal{M}_{\text{HA}}$ = 173.7 g/mol

21.23. For all additions, we calculate

$$E_{\text{Ag}} = E^{\text{o}}_{\text{Ag}^+/\text{Ag}} - 0.0592\log\left(\frac{1}{[\text{Ag}^+]}\right) \quad \text{and} \quad E_{\text{cell}} = E_{\text{Ag}} - E_{\text{SCE}}$$

Pre-equivalence point region

$$[\text{SeCN}^-] \approx c_{\text{SeCN}^-} = \frac{\text{mmol KSeCN initially present} - \text{mmol AgNO}_3\text{ added}}{\text{total solution volume in mL}}$$

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{SeCN}^-]}$$

The results are shown in the spreadsheet.

Equivalence point

Here $[\text{Ag}^+] = [\text{SeCN}^-] = \sqrt{K_{\text{sp}}}$ we use the Nernst equation to calculate E_{Ag} and then obtain E_{cell} as before. The result is shown in cell D22 of the spreadsheet.

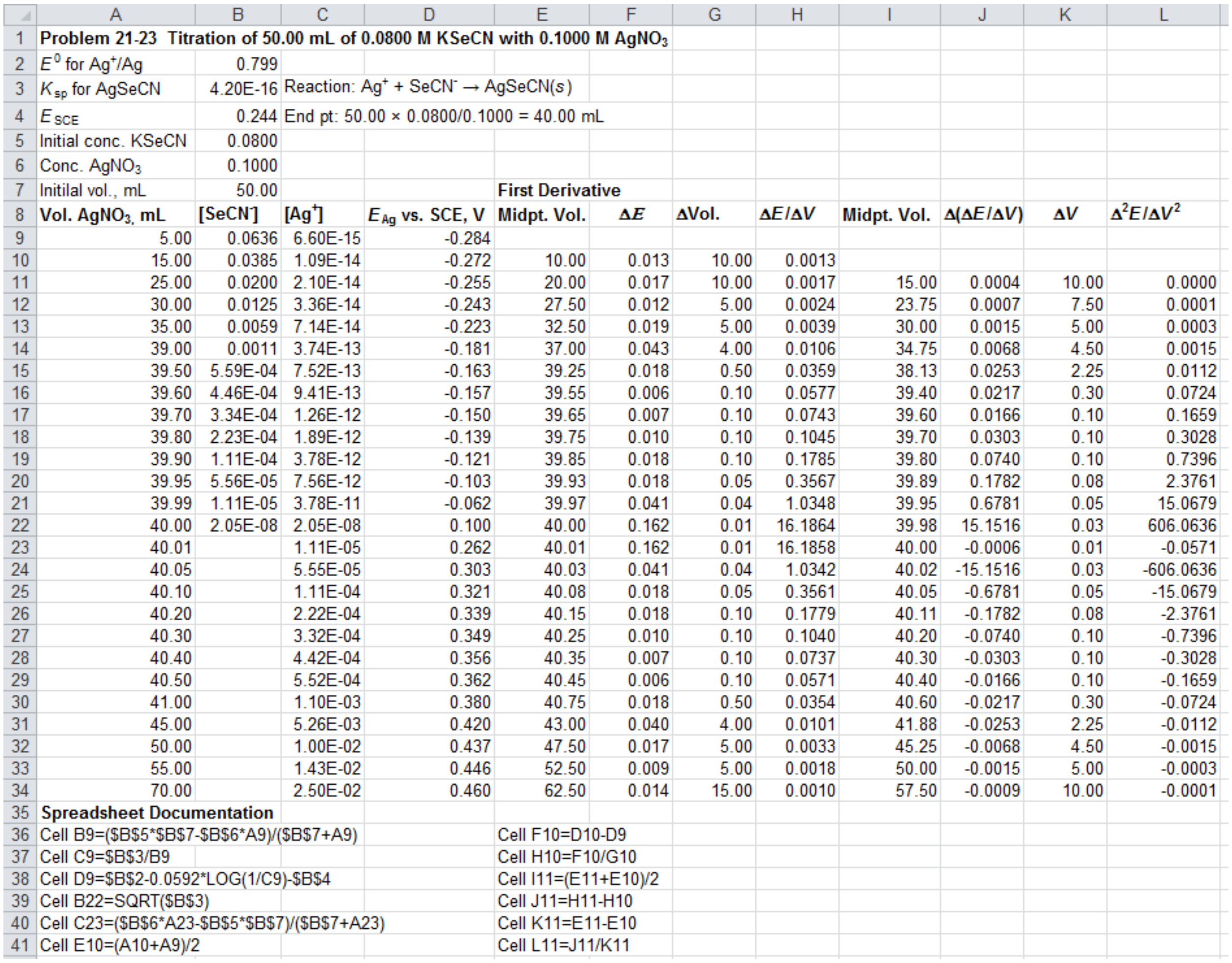
Post equivalence point region

$$[\text{Ag}^+] \approx c_{\text{Ag}^+} = \frac{\text{mmol AgNO}_3\text{ added} - \text{mmol KSeCN initially present}}{\text{total solution volume in mL}}$$

The E_{cell} values are shown in column D of the spreadsheet.

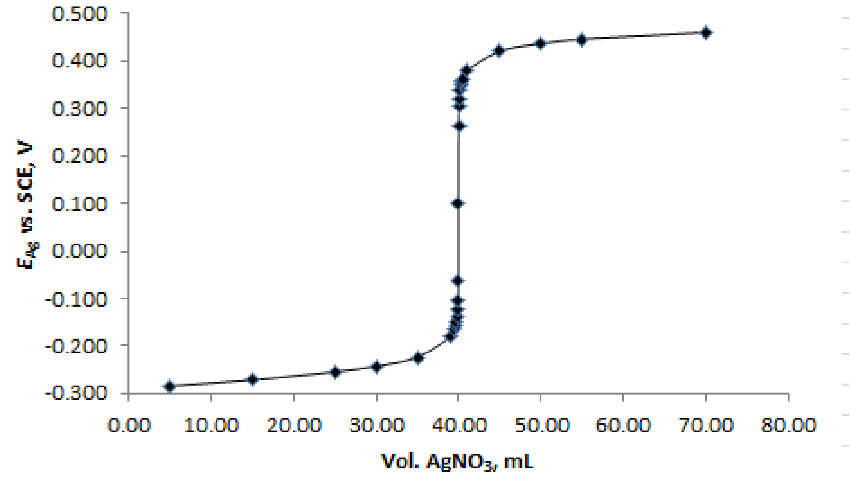
First- and second-derivative plots

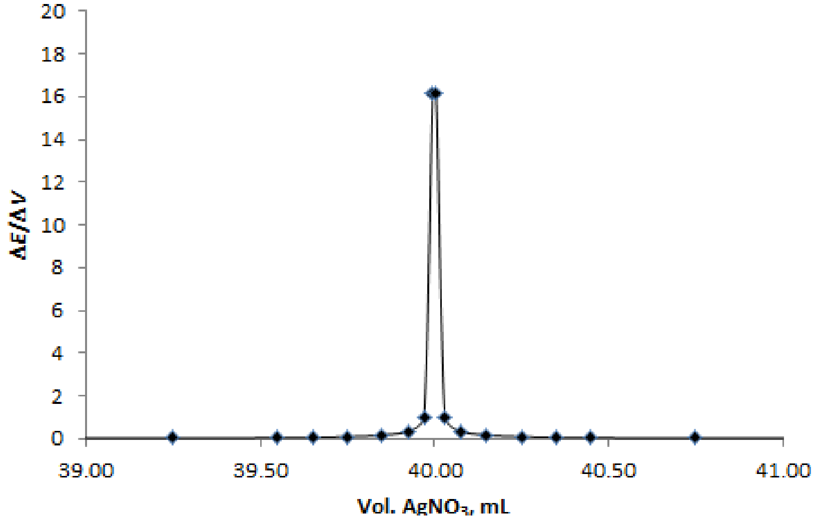
The calculations for the first- and second-derivative plots follow the method shown in *Applications of Microsoft® Excel in Analytical Chemistry 2nd ed., ,* Chapter 7 and in Table 21-4.

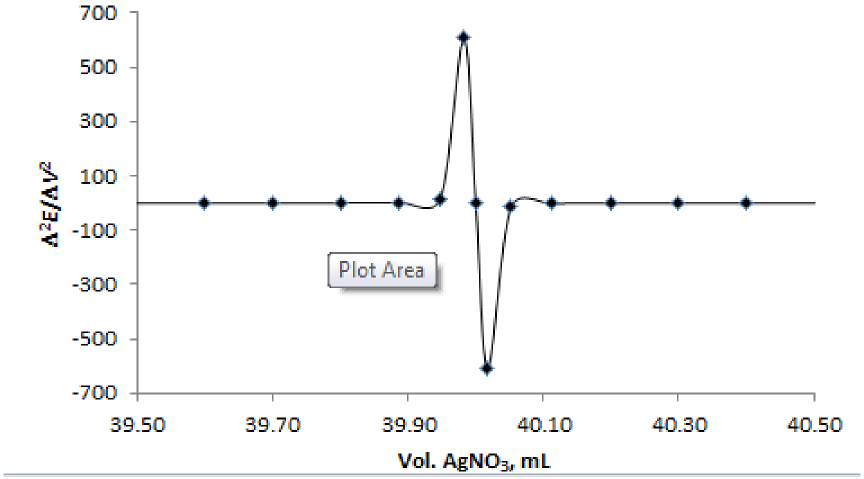


	A	B	C	D	E	F	G	H	I	J	K	L
1	**Problem 21-23 Titration of 50.00 mL of 0.0800 M KSeCN with 0.1000 M $AgNO_3$**											
2	E^0 for Ag^+/Ag	0.799										
3	K_{sp} for AgSeCN	4.20E-16	Reaction: $Ag^+ + SeCN^- \rightarrow AgSeCN(s)$									
4	E_{SCE}	0.244	End pt: 50.00 × 0.0800/0.1000 = 40.00 mL									
5	Initial conc. KSeCN	0.0800										
6	Conc. $AgNO_3$	0.1000										
7	Initilal vol., mL	50.00			**First Derivative**							
8	**Vol. $AgNO_3$, mL**	**[$SeCN^-$]**	**[Ag^+]**	**E_{Ag} vs. SCE, V**	**Midpt. Vol.**	**ΔE**	**ΔVol.**	**$\Delta E/\Delta V$**	**Midpt. Vol.**	**$\Delta(\Delta E/\Delta V)$**	**ΔV**	**$\Delta^2 E/\Delta V^2$**
9	5.00	0.0636	6.60E-15	-0.284								
10	15.00	0.0385	1.09E-14	-0.272	10.00	0.013	10.00	0.0013				
11	25.00	0.0200	2.10E-14	-0.255	20.00	0.017	10.00	0.0017	15.00	0.0004	10.00	0.0000
12	30.00	0.0125	3.36E-14	-0.243	27.50	0.012	5.00	0.0024	23.75	0.0007	7.50	0.0001
13	35.00	0.0059	7.14E-14	-0.223	32.50	0.019	5.00	0.0039	30.00	0.0015	5.00	0.0003
14	39.00	0.0011	3.74E-13	-0.181	37.00	0.043	4.00	0.0106	34.75	0.0068	4.50	0.0015
15	39.50	5.59E-04	7.52E-13	-0.163	39.25	0.018	0.50	0.0359	38.13	0.0253	2.25	0.0112
16	39.60	4.46E-04	9.41E-13	-0.157	39.55	0.006	0.10	0.0577	39.40	0.0217	0.30	0.0724
17	39.70	3.34E-04	1.26E-12	-0.150	39.65	0.007	0.10	0.0743	39.60	0.0166	0.10	0.1659
18	39.80	2.23E-04	1.89E-12	-0.139	39.75	0.010	0.10	0.1045	39.70	0.0303	0.10	0.3028
19	39.90	1.11E-04	3.78E-12	-0.121	39.85	0.018	0.10	0.1785	39.80	0.0740	0.10	0.7396
20	39.95	5.56E-05	7.56E-12	-0.103	39.93	0.018	0.05	0.3567	39.89	0.1782	0.08	2.3761
21	39.99	1.11E-05	3.78E-11	-0.062	39.97	0.041	0.04	1.0348	39.95	0.6781	0.05	15.0679
22	40.00	2.05E-08	2.05E-08	0.100	40.00	0.162	0.01	16.1864	39.98	15.1516	0.03	606.0636
23	40.01		1.11E-05	0.262	40.01	0.162	0.01	16.1858	40.00	-0.0006	0.01	-0.0571
24	40.05		5.55E-05	0.303	40.03	0.041	0.04	1.0342	40.02	-15.1516	0.03	-606.0636
25	40.10		1.11E-04	0.321	40.08	0.018	0.05	0.3561	40.05	-0.6781	0.05	-15.0679
26	40.20		2.22E-04	0.339	40.15	0.018	0.10	0.1779	40.11	-0.1782	0.08	-2.3761
27	40.30		3.32E-04	0.349	40.25	0.010	0.10	0.1040	40.20	-0.0740	0.10	-0.7396
28	40.40		4.42E-04	0.356	40.35	0.007	0.10	0.0737	40.30	-0.0303	0.10	-0.3028
29	40.50		5.52E-04	0.362	40.45	0.006	0.10	0.0571	40.40	-0.0166	0.10	-0.1659
30	41.00		1.10E-03	0.380	40.75	0.018	0.50	0.0354	40.60	-0.0217	0.30	-0.0724
31	45.00		5.26E-03	0.420	43.00	0.040	4.00	0.0101	41.88	-0.0253	2.25	-0.0112
32	50.00		1.00E-02	0.437	47.50	0.017	5.00	0.0033	45.25	-0.0068	4.50	-0.0015
33	55.00		1.43E-02	0.446	52.50	0.009	5.00	0.0018	50.00	-0.0015	5.00	-0.0003
34	70.00		2.50E-02	0.460	62.50	0.014	15.00	0.0010	57.50	-0.0009	10.00	-0.0001
35	**Spreadsheet Documentation**											
36	Cell B9=($B$5*$B$7-$B$6*A9)/($B$7+A9)				Cell F10=D10-D9							
37	Cell C9=$B$3/B9				Cell H10=F10/G10							
38	Cell D9=$B$2-0.0592*LOG(1/C9)-$B$4				Cell I11=(E11+E10)/2							
39	Cell B22=SQRT($B$3)				Cell J11=H11-H10							
40	Cell C23=($B$6*A23-$B$5*$B$7)/($B$7+A23)				Cell K11=E11-E10							
41	Cell E10=(A10+A9)/2				Cell L11=J11/K11							

For the titration curve, plot the potential in column D vs. the volume in column A on an X Y scatter plot. For the first derivative, plot the derivative in column H vs. the midpoint volume in column E. For the second derivative, plot the derivative in column L vs. the midpoint volume in column I. The plots follow.


0.500
0.400
0.300
0.200
0.100
0.000
-0.100
-0.200
-0.300
E_{Ag} vs. SCE, V
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
Vol. $AgNO_3$, mL


20
18
16
14
12
10
8
6
4
2
0
$\Delta E/\Delta V$
39.00
39.50
40.00
40.50
41.00
Vol. $AgNO_3$, mL


700
500
300
100
-100
-300
-500
-700
$\Delta^2E/\Delta V^2$
Plot Area
39.50
39.70
39.90
40.10
40.30
40.50
Vol. $AgNO_3$, mL

21-24. For all, $E_{\text{cell}} = E_{\text{ind}} - E_{\text{SCE.}}$ Note there are 2 mmol of Ce(IV) that react per mmol of HNO_2

Pre-equivalence point region

$$[\text{NO}_3^-] \approx c_{\text{NO}_3^-} = \frac{\text{mmol Ce(IV) added} \times \dfrac{1\text{ mmol HNO}_2}{2\text{ mmol Ce(IV)}}}{\text{total solution volume in mL}}$$

$$[\text{HNO}_2] \approx c_{\text{HNO}_2} = \frac{\text{mmol HNO}_2\text{ initially present} - \left(\text{mmol Ce(IV) added} \times \dfrac{1\text{ mmol HNO}_2}{2\text{ mmol Ce(IV)}}\right)}{\text{total solution volume in mL}}$$

$$E_{\text{ind}} = E^{\text{o}}_{\text{NO}_3^-/\text{HNO}_2} - \frac{0.0592}{2}\log\left(\frac{[\text{HNO}_2]}{[\text{NO}_3^-][\text{H}^+]^3}\right)$$

Equivalence point

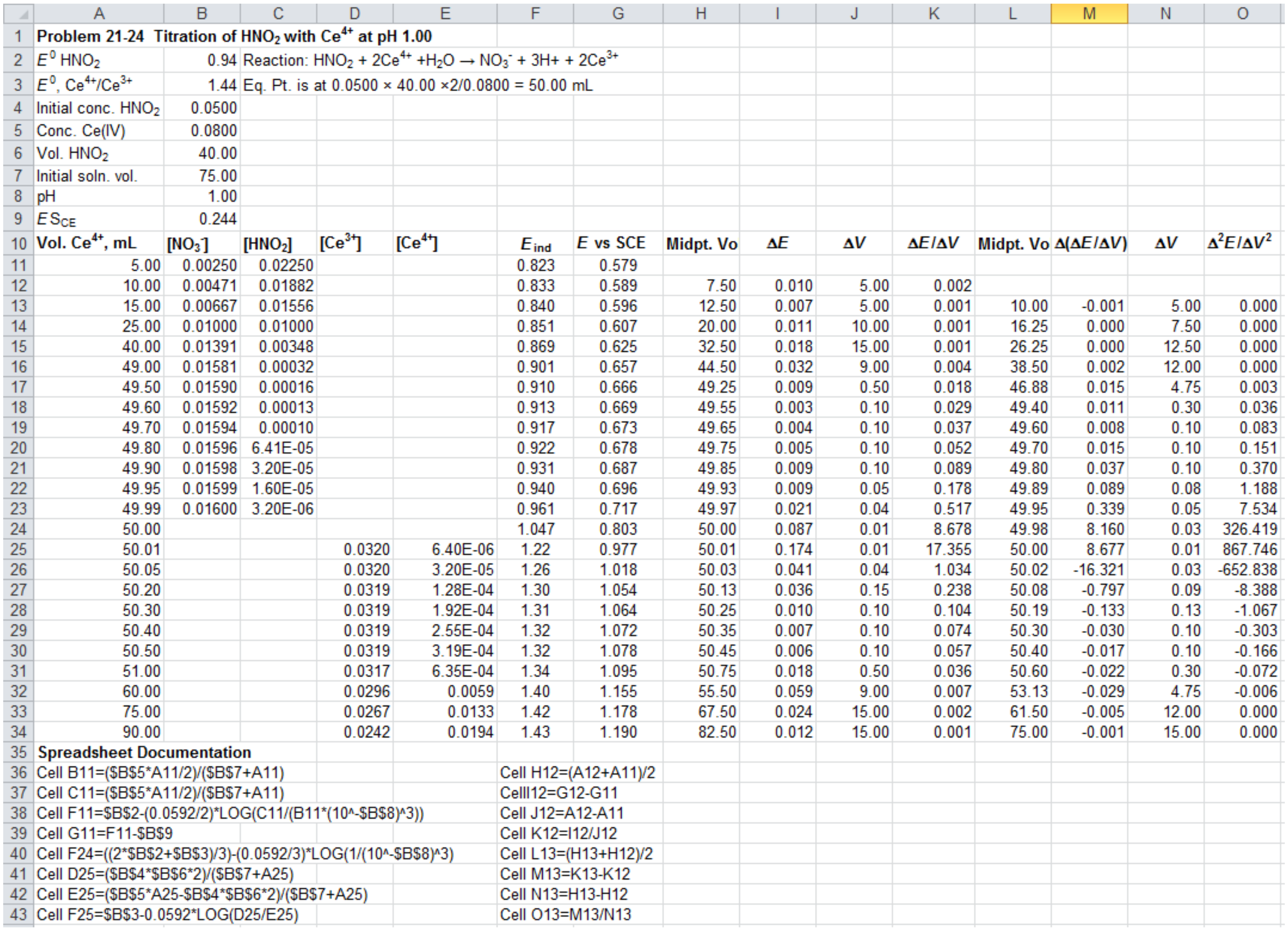
$$E_{\text{eq}} = \left(\frac{2E^{\text{o}}_{\text{NO}_3^-/\text{HNO}_2} + E^{\text{o}}_{\text{Ce}^{4+}/\text{Ce}^{3+}}}{3}\right) - \frac{0.0592}{3}\log\left(\frac{1}{[\text{H}^+]^3}\right)$$

Post equivalence point region

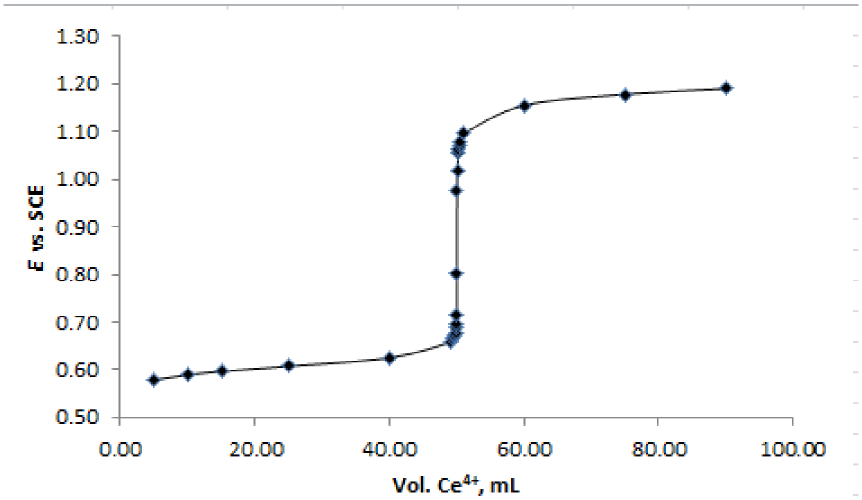
$$[\text{Ce}^{3+}] \approx c_{\text{Ce}^{3+}} = \frac{\text{mmol HNO}_2\text{ initially present} \times \dfrac{2\text{ mmol Ce(III)}}{\text{mmol HNO}_2}}{\text{total solution volume in mL}}$$

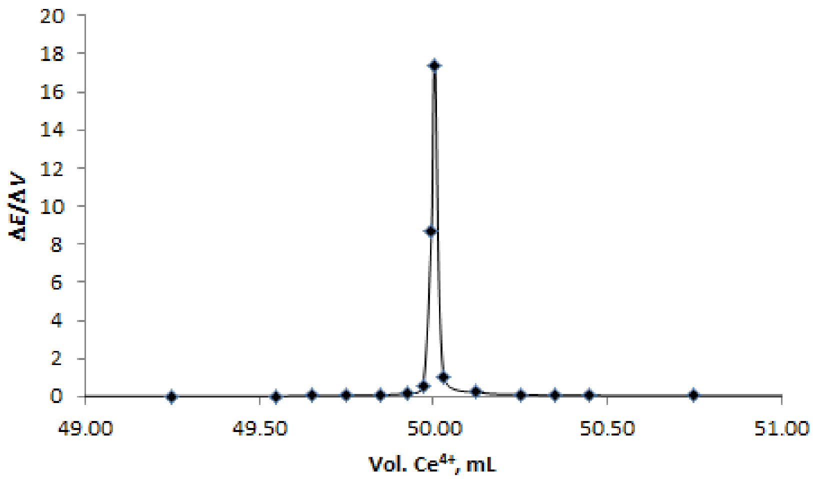
$$[\text{Ce}^{4+}] \approx c_{\text{Ce}^{4+}} = \frac{\text{mmol Ce(IV) added} - \left(\text{mmol HNO}_2\text{ initially present} \times \dfrac{2\text{ mmol Ce(IV)}}{\text{mmol HNO}_2}\right)}{\text{total solution volume in mL}}$$

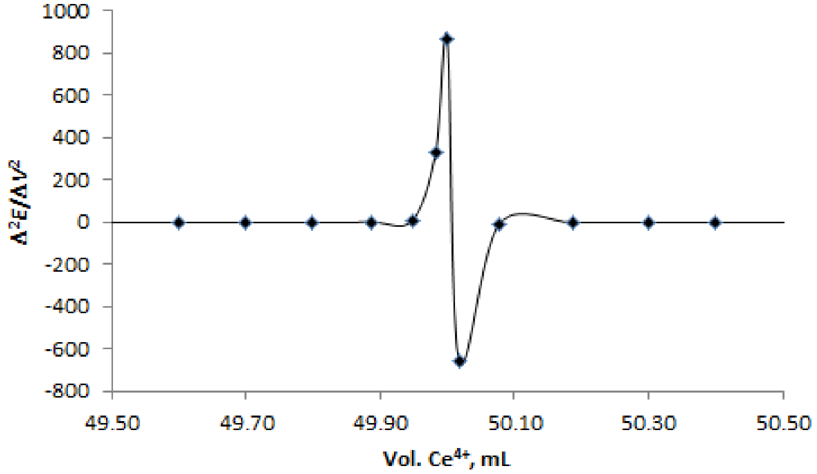
$$E_{\text{ind}} = E^{\text{o}}_{\text{Ce}^{4+}/\text{Ce}^{3+}} - 0.0592\log\left(\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}\right)$$



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	**Problem 21-24 Titration of HNO_2 with Ce^{4+} at pH 1.00**														
2	E^0 HNO_2	0.94	Reaction: $HNO_2 + 2Ce^{4+} + H_2O \rightarrow NO_3^- + 3H+ + 2Ce^{3+}$												
3	E^0, Ce^{4+}/Ce^{3+}	1.44	Eq. Pt. is at 0.0500 × 40.00 ×2/0.0800 = 50.00 mL												
4	Initial conc. HNO_2	0.0500													
5	Conc. Ce(IV)	0.0800													
6	Vol. HNO_2	40.00													
7	Initial soln. vol.	75.00													
8	pH	1.00													
9	E_{SCE}	0.244													
10	**Vol. Ce^{4+}, mL**	**$[NO_3^-]$**	**$[HNO_2]$**	**$[Ce^{3+}]$**	**$[Ce^{4+}]$**	**E_{ind}**	**E vs SCE**	**Midpt. Vo**	**ΔE**	**ΔV**	**$\Delta E/\Delta V$**	**Midpt. Vo**	**$\Delta(\Delta E/\Delta V)$**	**ΔV**	**$\Delta^2E/\Delta V^2$**
11	5.00	0.00250	0.02250			0.823	0.579								
12	10.00	0.00471	0.01882			0.833	0.589	7.50	0.010	5.00	0.002				
13	15.00	0.00667	0.01556			0.840	0.596	12.50	0.007	5.00	0.001	10.00	-0.001	5.00	0.000
14	25.00	0.01000	0.01000			0.851	0.607	20.00	0.011	10.00	0.001	16.25	0.000	7.50	0.000
15	40.00	0.01391	0.00348			0.869	0.625	32.50	0.018	15.00	0.001	26.25	0.000	12.50	0.000
16	49.00	0.01581	0.00032			0.901	0.657	44.50	0.032	9.00	0.004	38.50	0.002	12.00	0.000
17	49.50	0.01590	0.00016			0.910	0.666	49.25	0.009	0.50	0.018	46.88	0.015	4.75	0.003
18	49.60	0.01592	0.00013			0.913	0.669	49.55	0.003	0.10	0.029	49.40	0.011	0.30	0.036
19	49.70	0.01594	0.00010			0.917	0.673	49.65	0.004	0.10	0.037	49.60	0.008	0.10	0.083
20	49.80	0.01596	6.41E-05			0.922	0.678	49.75	0.005	0.10	0.052	49.70	0.015	0.10	0.151
21	49.90	0.01598	3.20E-05			0.931	0.687	49.85	0.009	0.10	0.089	49.80	0.037	0.10	0.370
22	49.95	0.01599	1.60E-05			0.940	0.696	49.93	0.009	0.05	0.178	49.89	0.089	0.08	1.188
23	49.99	0.01600	3.20E-06			0.961	0.717	49.97	0.021	0.04	0.517	49.95	0.339	0.05	7.534
24	50.00					1.047	0.803	50.00	0.087	0.01	8.678	49.98	8.160	0.03	326.419
25	50.01			0.0320	6.40E-06	1.22	0.977	50.01	0.174	0.01	17.355	50.00	8.677	0.01	867.746
26	50.05			0.0320	3.20E-05	1.26	1.018	50.03	0.041	0.04	1.034	50.02	-16.321	0.03	-652.838
27	50.20			0.0319	1.28E-04	1.30	1.054	50.13	0.036	0.15	0.238	50.08	-0.797	0.09	-8.388
28	50.30			0.0319	1.92E-04	1.31	1.064	50.25	0.010	0.10	0.104	50.19	-0.133	0.13	-1.067
29	50.40			0.0319	2.55E-04	1.32	1.072	50.35	0.007	0.10	0.074	50.30	-0.030	0.10	-0.303
30	50.50			0.0319	3.19E-04	1.32	1.078	50.45	0.006	0.10	0.057	50.40	-0.017	0.10	-0.166
31	51.00			0.0317	6.35E-04	1.34	1.095	50.75	0.018	0.50	0.036	50.60	-0.022	0.30	-0.072
32	60.00			0.0296	0.0059	1.40	1.155	55.50	0.059	9.00	0.007	53.13	-0.029	4.75	-0.006
33	75.00			0.0267	0.0133	1.42	1.178	67.50	0.024	15.00	0.002	61.50	-0.005	12.00	0.000
34	90.00			0.0242	0.0194	1.43	1.190	82.50	0.012	15.00	0.001	75.00	-0.001	15.00	0.000
35	**Spreadsheet Documentation**														
36	Cell B11=($B$5*A11/2)/($B$7+A11)					Cell H12=(A12+A11)/2									
37	Cell C11=($B$5*A11/2)/($B$7+A11)					CellI12=G12-G11									
38	Cell F11=$B$2-(0.0592/2)*LOG(C11/(B11*(10^-$B$8)^3))					Cell J12=A12-A11									
39	Cell G11=F11-$B$9					Cell K12=I12/J12									
40	Cell F24=((2*$B$2+$B$3)/3)-(0.0592/3)*LOG(1/(10^-$B$8)^3)					Cell L13=(H13+H12)/2									
41	Cell D25=($B$4*$B$6*2)/($B$7+A25)					Cell M13=K13-K12									
42	Cell E25=($B$5*A25-$B$4*$B$6*2)/($B$7+A25)					Cell N13=H13-H12									
43	Cell F25=$B$3-0.0592*LOG(D25/E25)					Cell O13=M13/N13									


1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
E vs. SCE
0.00
20.00
40.00
60.00
80.00
100.00
Vol. Ce4+, mL


20
18
16
14
12
10
8
6
4
2
0
ΔE/ΔV
49.00
49.50
50.00
50.50
51.00
Vol. Ce4+, mL


1000
800
600
400
200
0
-200
-400
-600
-800
Δ2E/ΔV2
49.50
49.70
49.90
50.10
50.30
50.50
Vol. Ce4+, mL

21-25. Pre-equivalence point region

$$[\mathrm{Fe^{3+}}] \approx c_{\mathrm{Fe^{3+}}} = \frac{\text{mmol MnO}_4^{-}\text{ added} \times \dfrac{5\text{ mmol Fe}^{3+}}{\text{mmol MnO}_4^{-}}}{\text{total solution volume in mL}}$$

$$[\mathrm{Fe^{2+}}] \approx c_{\mathrm{Fe^{2+}}} = \frac{\text{mmol Fe}^{2+}\text{initially present} - \left(\text{mmol MnO}_4^{-}\text{ added} \times \dfrac{5\text{ mmol Fe}^{2+}}{\text{mmol MnO}_4^{-}}\right)}{\text{total solution volume in mL}}$$

$$E_{\mathrm{ind}} = E^{\mathrm{o}}_{\mathrm{Fe^{3+}/Fe^{2+}}} - 0.0592\log\left(\frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]}\right)$$

Equivalence point

$$E_{\mathrm{eq}} = \left(\frac{5E^{\mathrm{o}}_{\mathrm{MnO_4^-/Mn^{2+}}} + E^{\mathrm{o}}_{\mathrm{Fe^{3+}/Fe^{2+}}}}{6}\right) - \frac{0.0592}{6}\log\left(\frac{1}{[\mathrm{H^+}]^8}\right)$$

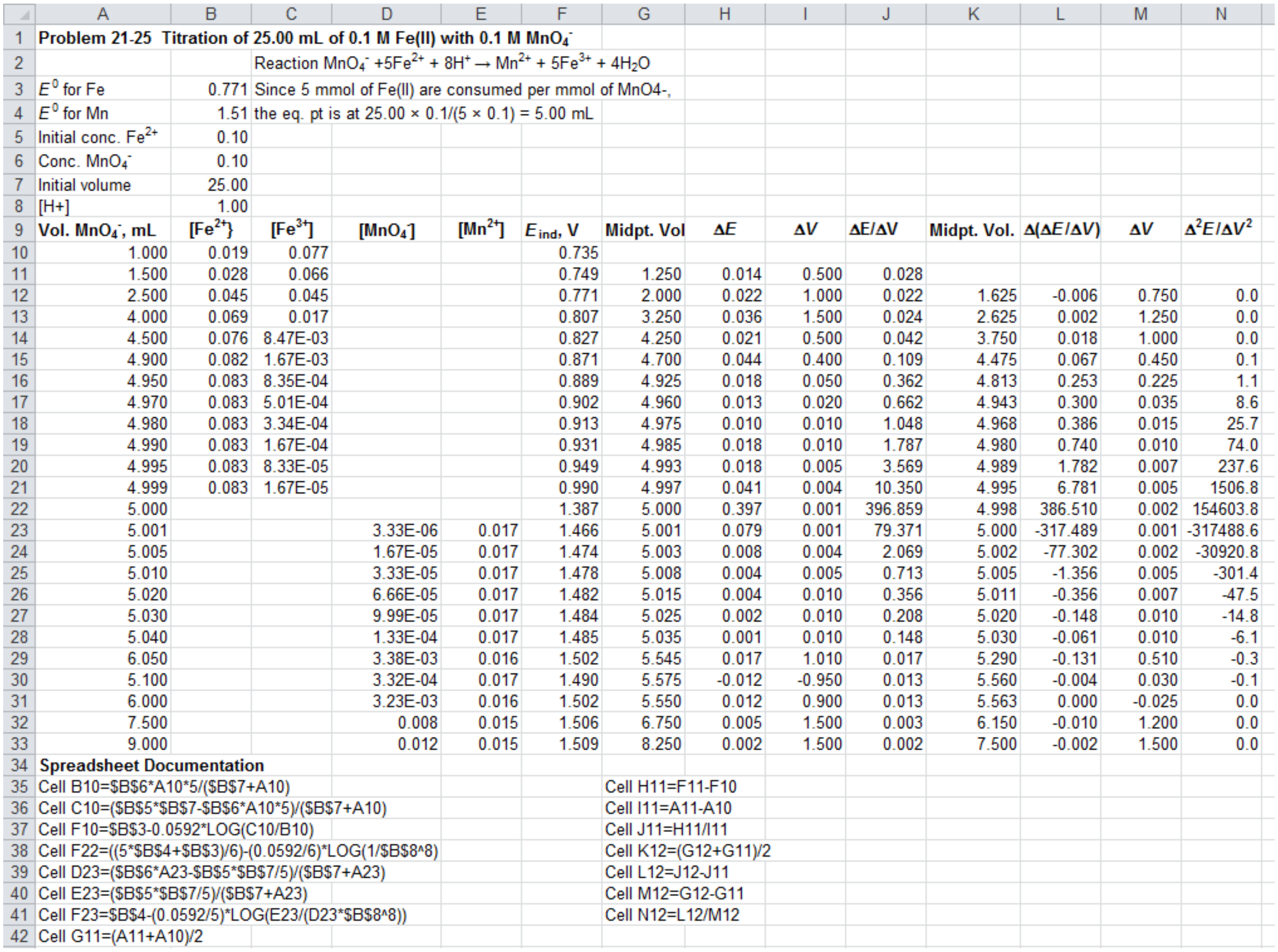
Post equivalence point region

$$[\mathrm{Mn^{2+}}] \approx c_{\mathrm{Mn^{2+}}} = \frac{\text{mmol Fe}^{2+}\text{initially present} \times \dfrac{\text{mmol MnO}_4^{-}}{5\text{ mmol Fe}^{2+}}}{\text{total solution volume in mL}}$$

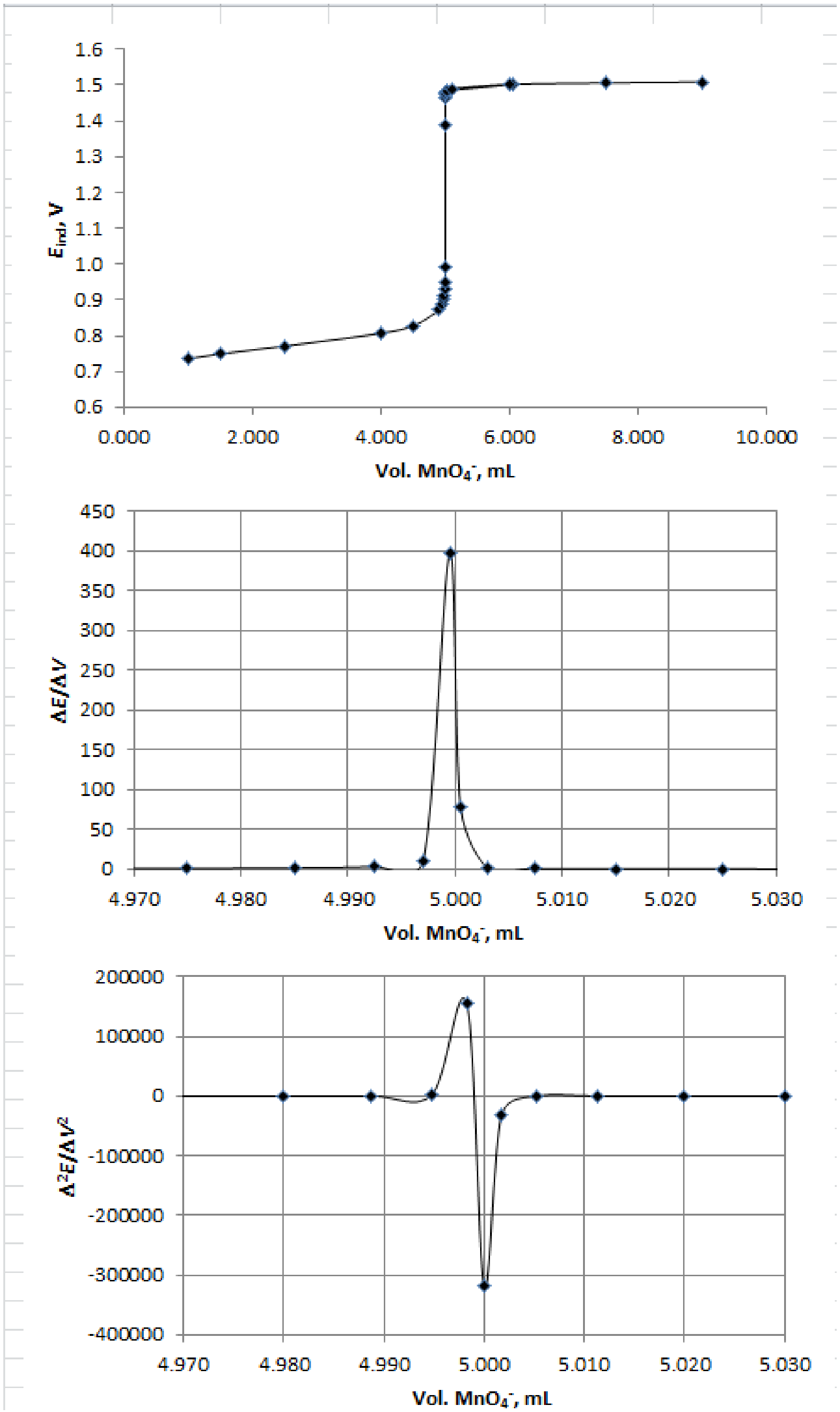
$$[\mathrm{MnO_4^-}] \approx c_{\mathrm{MnO_4^-}} = \frac{\text{mmol MnO}_4^{-}\text{ added} - \left(\text{mmol Fe}^{2+}\text{initially present} \times \dfrac{\text{mmol MnO}_4^{-}}{5\text{ mmol Fe}^{2+}}\right)}{\text{total solution volume in mL}}$$

$$E_{\mathrm{ind}} = E^{\mathrm{o}}_{\mathrm{MnO_4^-/Mn^{2+}}} - \frac{0.0592}{5}\log\left(\frac{[\mathrm{Mn^{2+}}]}{[\mathrm{MnO_4^-}][\mathrm{H^+}]^8}\right)$$

The titration curve is quite asymmetrical because of the different number of electrons involved in the two half reactions. As can be seen in the plots, the maximum of the first derivative does not coincide with the equivalence point, nor does the zero crossing of the second derivative.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	**Problem 21-25 Titration of 25.00 mL of 0.1 M Fe(II) with 0.1 M MnO_4^-**													
2			Reaction $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$											
3	E^0 for Fe	0.771	Since 5 mmol of Fe(II) are consumed per mmol of MnO4-,											
4	E^0 for Mn	1.51	the eq. pt is at 25.00 × 0.1/(5 × 0.1) = 5.00 mL											
5	Initial conc. Fe^{2+}	0.10												
6	Conc. MnO_4^-	0.10												
7	Initial volume	25.00												
8	[H+]	1.00												
9	**Vol. MnO_4^-, mL**	**$[Fe^{2+}\}$**	**$[Fe^{3+}]$**	**$[MnO_4^-]$**	**$[Mn^{2+}]$**	**E_{ind}, V**	**Midpt. Vol**	**ΔE**	**ΔV**	**$\Delta E/\Delta V$**	**Midpt. Vol.**	**$\Delta(\Delta E/\Delta V)$**	**ΔV**	**$\Delta^2E/\Delta V^2$**
10	1.000	0.019	0.077			0.735								
11	1.500	0.028	0.066			0.749	1.250	0.014	0.500	0.028				
12	2.500	0.045	0.045			0.771	2.000	0.022	1.000	0.022	1.625	-0.006	0.750	0.0
13	4.000	0.069	0.017			0.807	3.250	0.036	1.500	0.024	2.625	0.002	1.250	0.0
14	4.500	0.076	8.47E-03			0.827	4.250	0.021	0.500	0.042	3.750	0.018	1.000	0.0
15	4.900	0.082	1.67E-03			0.871	4.700	0.044	0.400	0.109	4.475	0.067	0.450	0.1
16	4.950	0.083	8.35E-04			0.889	4.925	0.018	0.050	0.362	4.813	0.253	0.225	1.1
17	4.970	0.083	5.01E-04			0.902	4.960	0.013	0.020	0.662	4.943	0.300	0.035	8.6
18	4.980	0.083	3.34E-04			0.913	4.975	0.010	0.010	1.048	4.968	0.386	0.015	25.7
19	4.990	0.083	1.67E-04			0.931	4.985	0.018	0.010	1.787	4.980	0.740	0.010	74.0
20	4.995	0.083	8.33E-05			0.949	4.993	0.018	0.005	3.569	4.989	1.782	0.007	237.6
21	4.999	0.083	1.67E-05			0.990	4.997	0.041	0.004	10.350	4.995	6.781	0.005	1506.8
22	5.000					1.387	5.000	0.397	0.001	396.859	4.998	386.510	0.002	154603.8
23	5.001			3.33E-06	0.017	1.466	5.001	0.079	0.001	79.371	5.000	-317.489	0.001	-317488.6
24	5.005			1.67E-05	0.017	1.474	5.003	0.008	0.004	2.069	5.002	-77.302	0.002	-30920.8
25	5.010			3.33E-05	0.017	1.478	5.008	0.004	0.005	0.713	5.005	-1.356	0.005	-301.4
26	5.020			6.66E-05	0.017	1.482	5.015	0.004	0.010	0.356	5.011	-0.356	0.007	-47.5
27	5.030			9.99E-05	0.017	1.484	5.025	0.002	0.010	0.208	5.020	-0.148	0.010	-14.8
28	5.040			1.33E-04	0.017	1.485	5.035	0.001	0.010	0.148	5.030	-0.061	0.010	-6.1
29	6.050			3.38E-03	0.016	1.502	5.545	0.017	1.010	0.017	5.290	-0.131	0.510	-0.3
30	5.100			3.32E-04	0.017	1.490	5.575	-0.012	-0.950	0.013	5.560	-0.004	0.030	-0.1
31	6.000			3.23E-03	0.016	1.502	5.550	0.012	0.900	0.013	5.563	0.000	-0.025	0.0
32	7.500			0.008	0.015	1.506	6.750	0.005	1.500	0.003	6.150	-0.010	1.200	0.0
33	9.000			0.012	0.015	1.509	8.250	0.002	1.500	0.002	7.500	-0.002	1.500	0.0
34	**Spreadsheet Documentation**													
35	`Cell B10=$B$6*A10*5/($B$7+A10)`						`Cell H11=F11-F10`							
36	`Cell C10=($B$5*$B$7-$B$6*A10*5)/($B$7+A10)`						`Cell I11=A11-A10`							
37	`Cell F10=$B$3-0.0592*LOG(C10/B10)`						`Cell J11=H11/I11`							
38	`Cell F22=((5*$B$4+$B$3)/6)-(0.0592/6)*LOG(1/$B$8^8)`						`Cell K12=(G12+G11)/2`							
39	`Cell D23=($B$6*A23-$B$5*$B$7/5)/($B$7+A23)`						`Cell L12=J12-J11`							
40	`Cell E23=($B$5*$B$7/5)/($B$7+A23)`						`Cell M12=G12-G11`							
41	`Cell F23=$B$4-(0.0592/5)*LOG(E23/(D23*$B$8^8))`						`Cell N12=L12/M12`							
42	`Cell G11=(A11+A10)/2`													


1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
E_{ind}, V
0.000
2.000
4.000
6.000
8.000
10.000
Vol. MnO_4^-, mL
450
400
350
300
250
200
150
100
50
0
ΔE/ΔV
4.970
4.980
4.990
5.000
5.010
5.020
5.030
Vol. MnO_4^-, mL
200000
100000
0
-100000
-200000
-300000
-400000
$\Delta^2E/\Delta V^2$
4.970
4.980
4.990
5.000
5.010
5.020
5.030
Vol. MnO_4^-, mL

21-26.

$$\text{pNa} = -\log\left([\text{Na}^+]\right) = -\left(\frac{E'_{\text{cell}} - K}{0.0592}\right) \text{ where } E'_{\text{cell}} = -0.2462\text{ V}$$

After addition $E''_{\text{cell}} = -0.1994$ V

$$-\log\left(\frac{10.00\times[\text{Na}^+]+1.00\times\left(2.00\times10^{-2}\right)}{10.00+1.00}\right) = -\left(\frac{E''_{\text{cell}} - K}{0.0592}\right)$$

$$-\log\left(0.9091[\text{Na}^+]+\left(1.818\times10^{-3}\right)\right) = -\left(\frac{E''_{\text{cell}} - K}{0.0592}\right)$$

Subtracting this latter equation from that for the initial potential gives

$$-\log\left([\text{Na}^+]\right)+\log\left(0.9091[\text{Na}^+]+\left(1.818\times10^{-3}\right)\right) = -\left(\frac{E'_{\text{cell}} - K}{0.0592}\right)+\left(\frac{E''_{\text{cell}} - K}{0.0592}\right)$$

$$= \left(\frac{E''_{\text{cell}} - E'_{\text{cell}}}{0.0592}\right)$$

$$-\log\left(\frac{[\text{Na}^+]}{0.9091[\text{Na}^+]+\left(1.818\times10^{-3}\right)}\right) = \frac{-0.1994+0.2462}{0.0592} = 0.7905$$

$$\text{or,}\quad \log\left(\frac{[\text{Na}^+]}{0.9091[\text{Na}^+]+\left(1.818\times10^{-3}\right)}\right) = -0.7905$$

$$\frac{[\text{Na}^+]}{0.9091[\text{Na}^+]+\left(1.818\times10^{-3}\right)} = \text{antilog}\left(-0.7905\right) = 0.16198$$

$$[\text{Na}^+] = 0.1473[\text{Na}^+]+2.945\times10^{-4}$$

$[\text{Na}^+]$ = 3.453 × 10^{-4} M or rounding 3.5 × 10^{-4} M

21-27.

$$\text{pF} = -\log\left([\text{F}^-]\right) = \frac{E'_{\text{cell}} - K}{0.0592} \quad \text{where} \quad E'_{\text{cell}} = 0.5021\text{ V}$$

$$-\log\left(\frac{25.00\,[\text{F}^-]+\left(2.00\times5.45\times10^{-2}\right)}{25.00+2.00}\right) = \frac{E''_{\text{cell}} - K}{0.0592} \quad \text{where } E''_{\text{cell}} = 0.4213\text{ V}$$

$$-\log\left(0.9259\,[\mathrm{F}^-]+4.04\times10^{-3}\right)+\log\left([\mathrm{F}^-]\right)=\frac{E''_{\mathrm{cell}}-K}{0.0592}-\frac{E'_{\mathrm{cell}}-K}{0.0592}$$

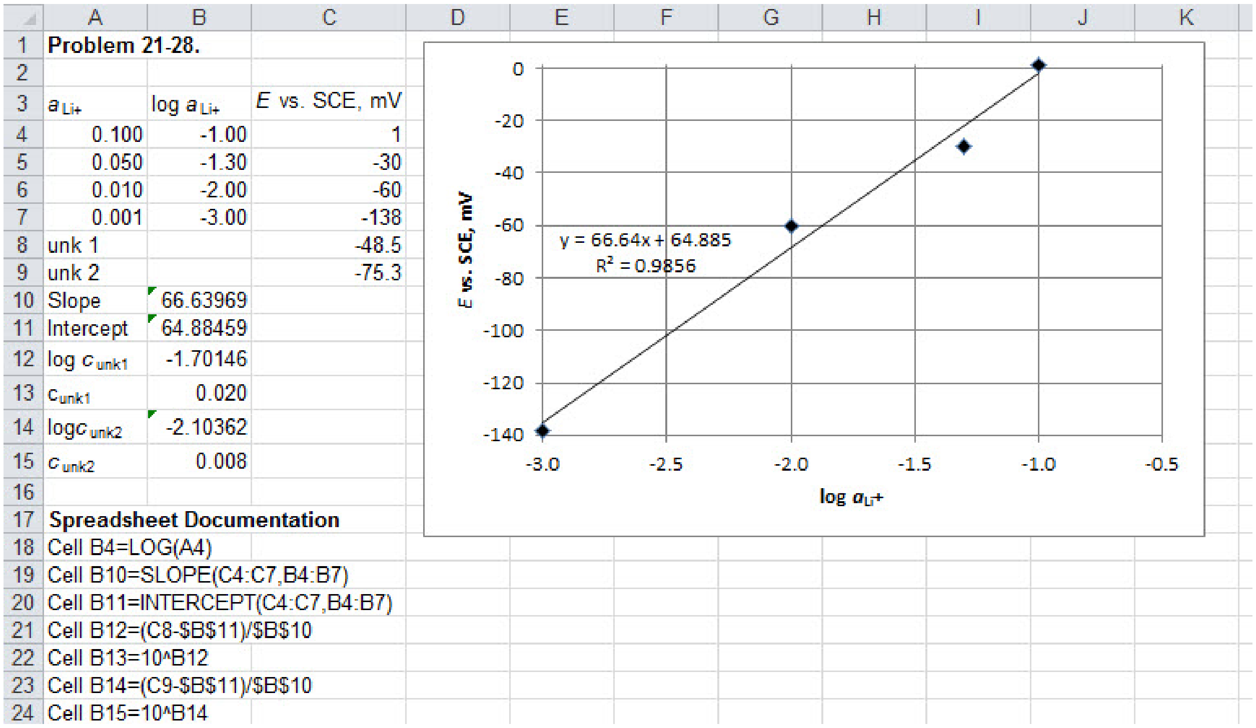
$$=\frac{0.4213-0.5021}{0.0592}=-1.3649$$

$$\frac{[\mathrm{F}^-]}{0.9259\,[\mathrm{F}^-]+4.04\times10^{-3}}=\mathrm{antilog}(-1.3649)=0.04317$$

$$[\mathrm{F}^-]=0.03997\,[\mathrm{F}^-]+1.744\times10^{-4}$$

$[\mathrm{F}^-] = 1.82 \times 10^{-4}$ M

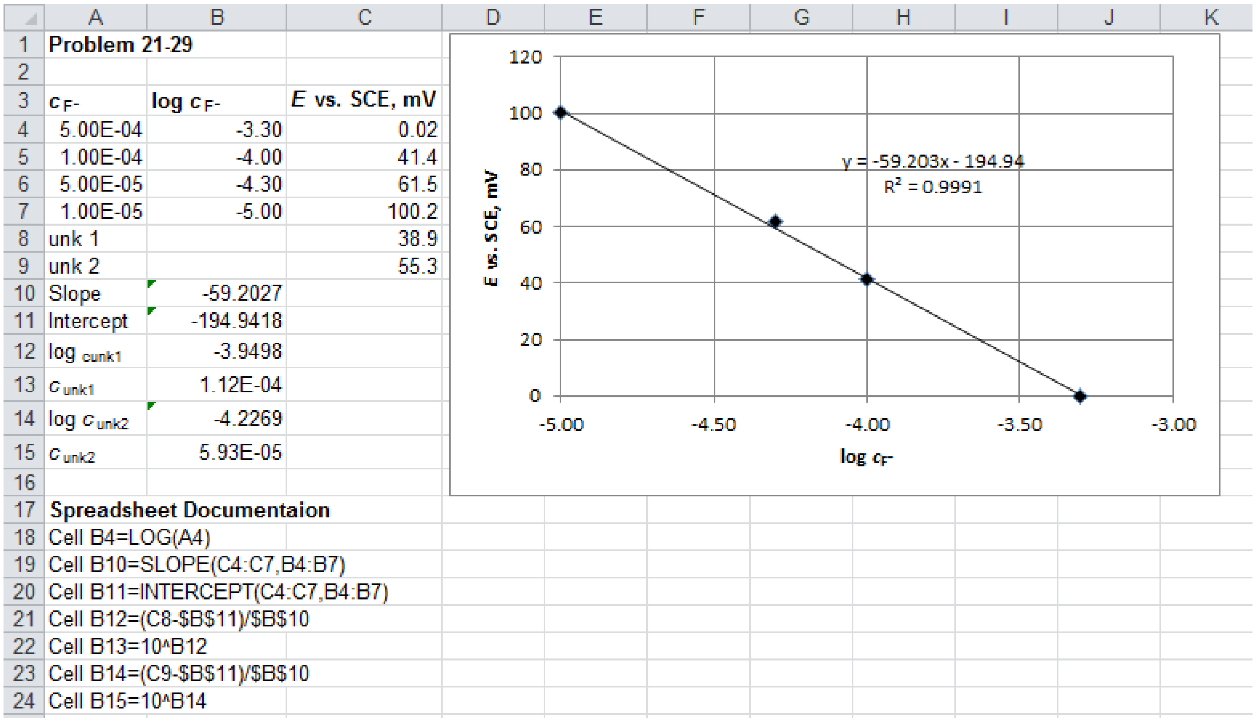
21-28.



	A	B	C
1	**Problem 21-28.**		
2			
3	$a_{\mathrm{Li+}}$	log $a_{\mathrm{Li+}}$	E vs. SCE, mV
4	0.100	-1.00	1
5	0.050	-1.30	-30
6	0.010	-2.00	-60
7	0.001	-3.00	-138
8	unk 1		-48.5
9	unk 2		-75.3
10	Slope	66.63969	
11	Intercept	64.88459	
12	log c_{unk1}	-1.70146	
13	c_{unk1}	0.020	
14	logc_{unk2}	-2.10362	
15	c_{unk2}	0.008	
16			
17	**Spreadsheet Documentation**		
18	Cell B4=LOG(A4)		
19	Cell B10=SLOPE(C4:C7,B4:B7)		
20	Cell B11=INTERCEPT(C4:C7,B4:B7)		
21	Cell B12=(C8-$B$11)/$B$10		
22	Cell B13=10^B12		
23	Cell B14=(C9-$B$11)/$B$10		
24	Cell B15=10^B14		

Theoretically for a cation with n = 1, the slope should be +0.0592 V, or 59.2 mV. Our slope is slightly higher than this as shown in the spreadsheet above, but the plot is linear. Hence, we conclude that the Nernst equation is obeyed with a slightly larger than theoretical slope.

21-29.



	A	B	C
1	**Problem 21-29**		
2			
3	c_{F^-}	log c_{F^-}	*E* vs. SCE, mV
4	5.00E-04	-3.30	0.02
5	1.00E-04	-4.00	41.4
6	5.00E-05	-4.30	61.5
7	1.00E-05	-5.00	100.2
8	unk 1		38.9
9	unk 2		55.3
10	Slope	-59.2027	
11	Intercept	-194.9418	
12	log c_{unk1}	-3.9498	
13	c_{unk1}	1.12E-04	
14	log c_{unk2}	-4.2269	
15	c_{unk2}	5.93E-05	
16			
17	**Spreadsheet Documentaion**		
18	Cell B4=LOG(A4)		
19	Cell B10=SLOPE(C4:C7,B4:B7)		
20	Cell B11=INTERCEPT(C4:C7,B4:B7)		
21	Cell B12=(C8-$B$11)/$B$10		
22	Cell B13=10^B12		
23	Cell B14=(C9-$B$11)/$B$10		
24	Cell B15=10^B14		

Theoretically the slope should be –0.0592 V, or –59.2 mV. Our slope is almost exactly this as shown in the spreadsheet above. The plot is linear so we can conclude that the Nernst equation is obeyed with a nearly theoretical slope.

Chapter 22

22-1. **(a)** In *Concentration polarization*, the current in an electrochemical cell is limited by the rate at which reactants are brought to or removed from the surface of one or both electrodes. In *Kinetic polarization*, the current is limited by the rate at which electrons are transferred between the electrode surfaces and the reactant in solution. For either type, the current is no longer linearly related to cell potential.

(b) The *coulomb* is a unit of electrical charge, whereas the *ampere* is a unit of current measuring the rate of flow of charge. One ampere is one coulomb/second.

(c) *Diffusion* is the movement of species under the influence of a concentration gradient. *Migration* is the movement of an ion under the influence of an electrostatic attractive or repulsive force.

(d) The electrode at which an electrochemical oxidation or reduction occurs is the *working electrode*. The *reference electrode* is an electrode of constant potential against which the potential of the working electrode is measured.

(e) The *electrolysis circuit* consists of a working electrode and a counter electrode. The *control circuit* regulates the applied potential such that the potential between the working electrode and a reference electrode in the control circuit is constant and at a desired level.

22-2. **(a)** *Ohmic potential*, or *IR* drop, of a cell is the product of the current in the cell in amperes and the electrical resistance of the cell in ohms.

(b) *Overvoltage* is the amount of extra voltage that must be applied to a cell to overcome the effects of concentration or kinetic polarization. It is the difference between the theoretical cell potential and the actual cell potential at a given current.

(c) In *controlled-potential electrolysis*, the potential applied to a cell is continuously adjusted to maintain a constant potential between the working electrode and a reference electrode.

(d) A *coulometric titration* is an electroanalytical method in which a constant current of known magnitude generates a reagent that reacts with the analyte. The time required to generate enough reagent to complete the reaction is measured.

(e) *Current efficiency* is a measure of agreement between the number of faradays of charge and the number of moles of reactant oxidized or reduced at a working electrode.

(f) A *galvanostat* is an instrument that provides a constant current.

22-3. *Diffusion* arises from concentration differences between the electrode surface and the bulk of solution. *Migration* results from electrostatic attraction or repulsion. *Convection* results from stirring, vibration or temperature differences.

22-4. A current in an electrochemical cell always causes the cell potential to become less positive or more negative.

22-5. Variables that influence concentration polarization include temperature, stirring, reactant concentrations, presence or absence of other electrolytes and electrode surface areas.

22-6. Both kinetic and concentration polarization cause the potential of an electrode to be more negative than the thermodynamic value. Concentration polarization results from the slow rate at which reactants or products are transported to or away from the electrode surfaces. Kinetic polarization arises from the slow rate of the electrochemical reaction at the electrode surfaces.

22-7. Kinetic polarization is often encountered when the product of a reaction is a gas, particularly when the electrode is a soft metal such as mercury, zinc or copper. It is likely to occur at low temperatures and high current densities.

22-8. High concentration of an inert electrolyte, called the *supporting electrolyte*, are used to minimize the contribution of migration to concentration polarization. The supporting electrolyte also reduces the cell resistance, which decreases the *IR* drop.

22-9. Potentiometric methods are carried out under zero current conditions and the effect of the measurement on analyte concentration is typically undetectable. In contrast, electrogravimetric and coulometric methods depend on the presence of a net current and a net cell reaction (i.e., the analyte is quantitatively converted to a new oxidation state). Unlike potentiometric methods where the cell potential is simply the difference between two electrode potentials, two additional phenomena, *IR* drop and polarization, must be considered in electrogravimetric and coulometric methods where current is present. Finally, the final measurement in electrogravimetric and coulometric methods is the mass of the product produced electrolytically, while in potentiometric methods it is the cell potential.

22-10. A *depolarizer* is a substance that is reduced or oxidized more readily than a potentially interfering species. For example, the codeposition of hydrogen is prevented through the introduction of nitrate ion as a cathodic depolarizer.

22-11. The species produced at the counter electrode are potential interferences by reacting with the products at the working electrode. Isolation of one from the other is ordinarily required.

22-12. An *auxiliary reagent* is generally required in a coulometric titration to permit the analyte to be oxidized or reduced with 100% current efficiency. As a titration proceeds, the potential of the working electrode will inevitably rise as concentration polarization of the analyte begins. Unless an auxiliary reagent is present to terminate this rise by producing a species that reacts with the analyte, some other species will be oxidized or reduced thus lowering the current efficiency and producing erroneous results.

22-13. (a)

$$\frac{0.0175\text{ C}}{\text{s}}\times\frac{1\text{ F}}{96{,}485\text{ C}}\times\frac{1\text{ mol e}^-}{\text{F}}\times\frac{1\text{ mol}}{\text{mol e}^-}\times\frac{6.02\times10^{23}\text{ ions}}{\text{mol}}=\frac{1.1\times10^{17}\text{ ions}}{\text{s}}$$

(b)

$$\frac{0.0175\text{ C}}{\text{s}}\times\frac{1\text{ F}}{96{,}485\text{ C}}\times\frac{1\text{ mol e}^-}{\text{F}}\times\frac{1\text{ mol}}{2\text{ mol e}^-}\times\frac{6.02\times10^{23}\text{ ions}}{\text{mol}}=\frac{5.5\times10^{16}\text{ ions}}{\text{s}}$$

(c)

$$\frac{0.0175\text{ C}}{\text{s}}\times\frac{1\text{ F}}{96{,}485\text{ C}}\times\frac{1\text{ mol e}^-}{\text{F}}\times\frac{1\text{ mol}}{3\text{ mol e}^-}\times\frac{6.02\times10^{23}\text{ ions}}{\text{mol}}=\frac{3.6\times10^{16}\text{ ions}}{\text{s}}$$

22-14. (a)

$$E_{\text{right}}=0.337-\frac{0.0592}{2}\log\left(\frac{1}{0.250}\right)=0.319\text{ V}$$

$$E_{\text{left}}=1.229-\frac{0.0592}{4}\log\left(\frac{1}{1.00\times\ 1.00\times10^{-3}\ ^{4}}\right)=1.051\text{ V}$$

$$E_{\text{applied}}=E_{\text{right}}-E_{\text{left}}=0.319-1.051$$

$$=-0.732\text{ V}$$

(b)

$$E_{\text{right}} = -0.136 - \frac{0.0592}{2}\log\left(\frac{1}{0.220}\right) = -0.155\,V$$

$$E_{\text{left}} = 1.229 - \frac{0.0592}{4}\log\left(\frac{1}{\left(\frac{770}{760}\right)\times\;1.00\times10^{-4}\;{}^{4}}\right) = 0.992\,V$$

$$E_{\text{applied}} = E_{\text{right}} - E_{\text{left}} = -0.155 - 0.992$$

$$= -1.147\text{ V}$$

(c)

$$[\text{H}^+] = \text{antilog}\;\;-3.70\;\; = 1.995\times10^{-4}$$

$$E_{\text{right}} = 0.000 - \frac{0.0592}{2}\log\left(\frac{\frac{765}{760}}{1.995\times10^{-4}\;{}^{2}}\right) = -0.219\text{ V}$$

$$E_{\text{left}} = 0.073 - 0.0592\log\;\;0.0964\;\; = 0.133\text{ V}$$

$$E_{\text{applied}} = E_{\text{right}} - E_{\text{left}} = -0.219 - 0.133$$

$$= -0.352\text{ V}$$

(d)

right electrode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(s)$

left electrode: $2\text{Tl}^+ + 6\text{OH}^- \rightarrow \text{Tl}_2\text{O}_3(s) + 3\text{H}_2\text{O} + 4\text{e}^-$

$$E_{\text{right}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{0.010}\right) = 0.278\text{ V}$$

$$E_{\text{left}} = 0.020 - \frac{0.0592}{4}\log\;\;[\text{Tl}^+]^2[\text{OH}^-]^6$$

pH = 7.50; pOH = 6.5; $[\text{OH}^-] = 3.16 \times 10^{-7}$

$$= 0.020 - \frac{0.0592}{4}\log\left(\left(5\times10^{-3}\right)^2\left(3.16\times10^{-7}\right)^6\right) = 0.665\text{ V}$$

$$E_{\text{applied}} = E_{\text{right}} - E_{\text{left}} = 0.278 - 0.665$$

$$= -0.387\text{ V}$$

22-15.

$$E_{\text{right}} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{2.95\times10^{-3}}\right) = -0.838\text{ V}$$

$$E_{\text{left}} = -0.277 - \frac{0.0592}{2}\log\left(\frac{1}{5.90\times10^{-3}}\right) = -0.343\text{ V}$$

$$E_{\text{cell}} = -0.838 - \;\; -0.343 \;\; - 0.065\times4.50$$

$$= -0.788\text{ V}$$

22-16.

$$E_{\text{right}} = -0.403 - \frac{0.0592}{2}\log\left(\frac{1}{6.59\times10^{-2}}\right) = -0.438\text{ V}$$

$$E_{\text{left}} = -0.136 - \frac{0.0592}{2}\log\left(\frac{1}{7.83\times10^{-4}}\right) = -0.228\text{ V}$$

$$E_{\text{cell}} = -0.438 - \;\; -0.228 \;\; - 0.062\times4.95$$

$$= -0.517\text{ V}$$

22-17. (a)

$$E_{\text{right}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{0.250}\right) = 0.319\text{ V}$$

$$E_{\text{left}} = 1.229 - \frac{0.0592}{4}\log\left(\frac{1}{1.00\times10^{-4}\;\;{}^{4}\times\dfrac{730}{760}}\right) = 0.992\text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.319 - 0.992$$

$$= \qquad -0.673\text{ V}$$

(b) $IR = -0.15 \times 3.60 = -0.54$ V

(c) Recall that the overpotential in an electrolytic cell requires the application of a larger or more negative potential. That is, 0.50 V must be subtracted from the cell potential.

$$E_{\text{applied}} = -0.673 - 0.54 - 0.50 \;\; = -1.71\text{ V}$$

(d)

$$E_{\text{right}} = 0.337 - \frac{0.0592}{2}\log\left(\frac{1}{7.00\times10^{-6}}\right) = 0.184\ \text{V}$$

$$E_{\text{applied}} = 0.184 - 0.992 - 0.54 - 0.50$$

$$= -1.85\ \text{V}$$

22.18. **(a)**

$$E_{\text{right}} = -0.250 - \frac{0.0592}{2}\log\left(\frac{1}{0.150}\right) = -0.274\,V$$

$$E_{\text{left}} = 1.229 - \frac{0.0592}{4}\log\left(\frac{1}{1.00\ \times\ 1.00\times10^{-2}\ {}^{4}}\right) = 1.111\,V$$

$E_{\text{cell}} = -0.274 - 1.111 = -1.39$ V

(b) $IR = -0.10 \times 3.55 = -0.355$ V

(c)

$$\text{current density at cathode} = \frac{1.00\ \text{A}}{120\ \text{cm}^2} = 0.0083\ \text{A/cm}^2$$

$$\text{current density at anode} = \frac{1.00\ \text{A}}{80\ \text{cm}^2} = 0.0125\ \text{A/cm}^2$$

(d) As in 22-17 (c), the overpotential is subtracted from the cell potential or

$$E_{\text{applied}} = -1.39 - 0.355 - 0.52 = -2.26\ \text{V}$$

(e)

$$E_{\text{right}} = -0.250 - \frac{0.0592}{2}\log\left(\frac{1}{1.00\times10^{-4}}\right) = -0.368\ \text{V}$$

$E_{\text{applied}} = -0.368 - 1.11 - 0.355 - 0.52 = -2.35$ V

22-19. Cd begins to form when

$$E = -0.403 - \frac{0.0592}{2}\log\left(\frac{1}{0.0650}\right) = -0.438\text{ V}$$

(a) The Co^{2+} concentration when Cd first begins to deposit is:

$$-0.438 = -0.277 - \frac{0.0592}{2}\log\left(\frac{1}{[Co^{2+}]}\right)$$

$$\log\ [Co^{2+}]\ = \frac{2\ \ -0.438+0.277}{0.0592} = -5.439$$

$$[Co^{2+}] = \text{antilog}\ \ -5.439\ \ = 3.6 \times 10^{-6}\text{ M}$$

$$\textbf{(b)}\ E_{\text{cathode}} = -0.277 - \frac{0.0592}{2}\log\left(\frac{1}{1.00\times10^{-5}}\right) = -0.425\text{ V}$$

(c) Referring to Example 22-2, quantitative separation is assumed to occur when the $[Co^{2+}]$ falls to 10^{-4} of its original concentration or 2.0×10^{-5} M. Thus, if the cathode is maintained between –0.425 V and –0.438 V, the quantitative separation of Co^{2+} from Cd^{2+} is possible in theory.

22-20. pH = 2.50 $[H^+] = 3.16 \times 10^{-3}$

BiO^+ is more readily reduced than Co^{2+}

(a) Deposition of Co begins when

$$E_{\text{cathode}} = -0.277 - \frac{0.0592}{2}\log\left(\frac{1}{0.040}\right) = -0.318\text{ V}$$

$$-0.318 = 0.320 - \frac{0.0592}{3}\log\left(\frac{1}{[BiO^+]\ \ 3.16\times10^{-3}\ \ ^{2}}\right)$$

$$\left(\frac{0.0592}{3}\right)\log\ [BiO^+]\ = -0.318 - 0.320 - \frac{0.0592}{3}\log\ \ \ 3.16\times10^{-3}\ \ ^{2}\ \ = -0.5393$$

$$\log\ [BiO^+]\ = -0.5393\times\frac{3}{0.0592} = -27.33$$

$[BiO^+]$ = antilog(–27.33) = 5×10^{-28} M

(c) Referring to Example 22-2, quantitative separation is assumed to occur when the $[\mathrm{BiO^+}]$ falls to 10^{-4} of its original concentration or 5.0×10^{-6} M. Thus, if the right electrode is maintained between –0.318 V and 0.103 V, the quantitative separation of $\mathrm{BiO^+}$ from $\mathrm{Co^{2+}}$ is possible in theory.

22-21. **(a)** Bi deposits at a lower potential, that is

$$[\mathrm{H^+}] = \text{antilog}\,(-1.95) = 1.12\times10^{-2}\,\mathrm{M}$$

$$E_{\text{cathode}} = 0.320 - \frac{0.0592}{3}\log\left(\frac{1}{(0.250)(1.12\times10^{-2})^2}\right)$$

$$= 0.231\ \mathrm{V}$$

(b) Sn deposits when

$$E_{\text{cathode}} = -0.136 - \frac{0.0592}{2}\log\left(\frac{1}{0.250}\right) = -0.154\ \mathrm{V}$$

$$-0.154 = 0.320 - \frac{0.0592}{3}\log\left(\frac{1}{[\mathrm{BiO^+}](1.12\times10^{-2})^2}\right)$$

$$= 0.320 + \frac{0.0592}{3}\log(1.12\times10^{-2})^2 + \frac{0.0592}{3}\log([\mathrm{BiO^+}])$$

$$\log([\mathrm{BiO^+}]) = \frac{3(-0.154 - 0.320 + 0.077)}{0.0592} = -20.12$$

$[\mathrm{BiO^+}]$ = antilog(–20.12) = 7.6×10^{-21} M

(c) When $[\mathrm{BiO^+}] = 10^{-6}$

$$E_{\text{cathode}} = 0.320 - \frac{0.0592}{3}\log\left(\frac{1}{(1.00\times10^{-6})(1.12\times10^{-2})^2}\right) = 0.124\ \mathrm{V}$$

Sn begins to form when E_{cathode} = –0.154 V (see part (b))

range vs. SCE = 0.124 – 0.244 to –0.154 – 0.244 or –0.12 to –0.398 V

= –0.120 to –0.398 V

22-22. Deposition of A is complete when

$$E_{\mathrm{A}} = E^{\mathrm{o}}_{\mathrm{A}} - \frac{0.0592}{n_{\mathrm{A}}}\log\left(\frac{1}{2.00\times10^{-5}}\right) = E^{\mathrm{o}}_{\mathrm{A}} - \frac{0.278}{n_{\mathrm{A}}}$$

Deposition of B begins when

$$E_{\mathrm{B}} = E^{\mathrm{o}}_{\mathrm{B}} - \frac{0.0592}{n_{\mathrm{B}}}\log\left(\frac{1}{2.00\times10^{-1}}\right) = E^{\mathrm{o}}_{\mathrm{B}} - \frac{0.0414}{n_{\mathrm{B}}}$$

Boundary condition is that $E_{\mathrm{A}} = E_{\mathrm{B}}$. Thus,

$$E^{\mathrm{o}}_{\mathrm{A}} - \frac{0.278}{n_{\mathrm{A}}} = E^{\mathrm{o}}_{\mathrm{B}} - \frac{0.0414}{n_{\mathrm{B}}} \quad \text{or}$$

$$E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{n_{\mathrm{A}}} - \frac{0.0414}{n_{\mathrm{B}}}$$

(a) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{1} - \frac{0.0414}{1}$ = 0.237 V

(b) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{2} - \frac{0.0414}{1}$ = 0.0976 V

(c) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{3} - \frac{0.0414}{1}$ = 0.0513 V

(d) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{1} - \frac{0.0414}{2}$ = 0.257 V

(e) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{2} - \frac{0.0414}{2}$ = 0.118 V

(f) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{3} - \frac{0.0414}{2}$ = 0.0720 V

(g) $E^{\mathrm{o}}_{\mathrm{A}} - E^{\mathrm{o}}_{\mathrm{B}} = \frac{0.278}{1} - \frac{0.0414}{3}$ = 0.264 V

(h) $E^{\text{o}}_{\text{A}} - E^{\text{o}}_{\text{B}} = \dfrac{0.278}{2} - \dfrac{0.0414}{3} = 0.125\text{ V}$

(i) $E^{\text{o}}_{\text{A}} - E^{\text{o}}_{\text{B}} = \dfrac{0.278}{3} - \dfrac{0.0414}{3} = 0.0789\text{ V}$

22-23. **(a)**

$$0.250\text{ g Co} \times \frac{1\text{ mol Co}}{58.93\text{ g}} \times \frac{2\text{ mol e}^-}{\text{mol Co}} \times \frac{1\text{ F}}{\text{mol e}^-} \times \frac{96{,}485\text{ C}}{\text{F}} = 8.186 \times 10^2\text{C}$$

$$8.186 \times 10^2\text{ C} \times \frac{1\text{ A} \times \text{s}}{\text{C}} \times \frac{1}{0.851\text{ A}} \times \frac{1\text{ min}}{60\text{ s}} = 16.0\text{ min}$$

(b) $3\text{Co}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Co}_3\text{O}_4(s) + 8\text{H}^+ + 2\text{e}^-$ $\quad {}^3\!/_2 \text{ mol Co}^{2+} = 1\text{ mol e}^-$

$$0.250\text{ g Co} \times \frac{1\text{ mol Co}}{58.93\text{ g}} \times \frac{2\text{ mol e}^-}{3\text{ mol Co}} \times \frac{1\text{ F}}{\text{mol e}^-} \times \frac{96{,}485\text{ C}}{\text{F}} = 2.727 \times 10^2\text{ C}$$

$$2.727 \times 10^2\text{ C} \times \frac{1\text{ A} \times \text{s}}{\text{C}} \times \frac{1}{0.851\text{ A}} \times \frac{1\text{ min}}{60\text{ s}} = 5.34\text{ min}$$

22-24. **(a)**

$$0.450\ g\text{ Tl} \times \frac{1\text{ mol Tl}}{204.38\text{ g}} \times \frac{3\text{ mol e}^-}{\text{mol Tl}} \times \frac{1\text{ F}}{\text{mol e}^-} \times \frac{96{,}485\text{ C}}{\text{F}} = 6.373 \times 10^2\text{ C}$$

$$6.373 \times 10^2\text{ C} \times \frac{1\text{ A} \times \text{s}}{\text{C}} \times \frac{1}{1.00\text{ A}} \times \frac{1\text{ min}}{60\text{ s}} = 10.6\text{ min}$$

(b) $2\text{Tl}^+ + 3\text{H}_2\text{O} \rightleftharpoons \text{Tl}_2\text{O}_3 + 6\text{H}^+ + 4\text{e}^-$ $\quad 2\text{ mol Tl}^+ = 4\text{ mol e}^-$

$$0.450\text{ g Tl} \times \frac{1\text{ mol Tl}}{204.38\text{ g}} \times \frac{4\text{ mol e}^-}{2\text{ mol Tl}} \times \frac{1\text{ F}}{\text{mol e}^-} \times \frac{96{,}485\text{ C}}{\text{F}} = 4.249 \times 10^2\text{ C}$$

$$4.249 \times 10^2\text{ C} \times \frac{1\text{ A} \times \text{s}}{\text{C}} \times \frac{1}{1.00\text{ A}} \times \frac{1\text{ min}}{60\text{ s}} = 7.08\text{ min}$$

(c) As in part (a)

$$0.450\ g\ \text{Tl} \times \frac{1\,\text{mol Tl}}{204.38\,\text{g}} \times \frac{1\,\text{mol e}^-}{\text{mol Tl}} \times \frac{1\,\text{F}}{\text{mol e}^-} \times \frac{96{,}485\,\text{C}}{\text{F}} = 2.124 \times 10^2\ \text{C}$$

$$2.124 \times 10^2\ \text{C} \times \frac{1\,\text{A} \times \text{s}}{\text{C}} \times \frac{1}{1.00\ \text{A}} \times \frac{1\,\text{min}}{60\,\text{s}} = 3.54\,\text{min}$$

22-25.

$$\left(5\,\text{min} \times \frac{60\,\text{s}}{\text{min}} + 24\,\text{s}\right) \times 0.300\ \text{A} \times \frac{1\ \text{C}}{\text{A} \times \text{s}} \times \frac{1\,\text{F}}{96{,}485\,\text{C}} \times \frac{1\,\text{eq HA}}{\text{F}} = 1.007 \times 10^{-3}\ \text{eq HA}$$

$$\frac{0.1330\ \text{g HA}}{1.007 \times 10^{-3}\ \text{eq HA}} = 132.0\ \text{g/eq}$$

22-26. 1 mol NaCN = 1 mol H^+ = 1 mol e^- 4 min 11 s = 251 s

$$\frac{55.6 \times 10^{-3}\,\text{A} \times 251\,\text{s} \times \dfrac{1\,\text{C}}{\text{A} \times \text{s}} \times \dfrac{1\,\text{F}}{96{,}485\,\text{C}} \times \dfrac{1\,\text{mol NaCN}}{\text{F}} \times \dfrac{49.01\,\text{g NaCN}}{\text{mol}}}{10\ \text{mL sample} \times \dfrac{\text{L}}{1000\ \text{mL}}} = \frac{0.709\ \text{g NaCN}}{\text{L}}$$

$$\frac{\left(55.6 \times 10^{-3}\text{A} \times 251\,\text{s} \times \dfrac{1\,\text{C}}{\text{A} \times \text{s}} \times \dfrac{1\,\text{F}}{96{,}485\,\text{C}} \times \dfrac{1\,\text{mol NaCN}}{\text{F}} \times \dfrac{49.01\,\text{g NaCN}}{\text{mol}}\right)}{10\ \text{mL sample} \times \dfrac{1.00\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}}} \times 10^6\ \text{ppm}$$

= 709 ppm NaCN

22-27. 1 mol $CaCO_3$ = 1 mol $HgNH_3Y^{2-}$ = 2 mol e^-

$$\frac{\left(39.4 \times 10^{-3}\ \text{A} \times 3.52\ \text{min} \times \dfrac{60\ \text{s}}{\text{min}} \times \dfrac{1\,\text{C}}{\text{A} \times \text{s}} \times \dfrac{1\,\text{mol e}^-}{96{,}485\,C} \times \dfrac{1\,\text{mol CaCO}_3}{2\ \text{mol e}^-} \times \dfrac{100.09\ \text{g CaCO}_3}{\text{mol}}\right)}{25.00\ \text{mL sample} \times \dfrac{1.00\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}}} \times 10^6\text{ppm}$$

=173 ppm $CaCO_3$

22-28. Proceeding as in Problem 22-27,

1 mol H_2S = 1 mol I_2 = 2 mol e^-

$$\frac{\left(46.3\times10^{-3}\ \text{A}\times11.05\ \text{min}\times\frac{60\ \text{s}}{\text{min}}\times\frac{1\ \text{C}}{\text{A}\times\text{s}}\times\frac{1\ \text{mol e}^-}{96,485\ \ \text{C}}\times\frac{1\ \text{mol H}_2\text{S}}{2\ \text{mol e}^-}\times\frac{34.08\ \text{g H}_2\text{S}}{\text{mol}}\right)}{100.00\ \text{mL sample}\times\frac{1.00\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}}}\times10^6\ \text{ppm}$$

=54.2 ppm H_2S

22-29. 1 mol $C_6H_5NO_2$ = 4 mol e^-

$$\frac{\left(33.47\ \text{C}\times\frac{1\ \text{F}}{96{,}485\ \text{C}}\times\frac{1\ \text{mol e}^-}{\text{F}}\times\frac{1\ \text{mol C}_6\text{H}_5\text{NO}_2}{4\ \text{mol e}^-}\times\frac{123.11\ \text{g C}_6\text{H}_5\text{NO}_2}{\text{mol}}\right)}{300\ \text{mg sample}\times\frac{\text{g}}{1000\ \text{mg}}}\times100\%$$

=3.56% $C_6H_5NO_2$

22-30. 1 mol C_6H_5OH = 3 mol Br_2 = 6 mol e^- 6 min 22 s = 382 s

$$\frac{\left(0.0503\ \text{A}\times382\ \text{s}\times\frac{1\ \text{C}}{\text{A}\times\text{s}}\times\frac{1\ \text{F}}{96{,}485\ \text{C}}\times\frac{1\ \text{mol e}^-}{\text{F}}\times\frac{1\ \text{mol C}_6\text{H}_5\text{OH}}{6\ \text{mol e}^-}\times\frac{94.11\ \text{g C}_6\text{H}_5\text{OH}}{\text{mol}}\right)}{100.00\ \text{mL sample}\times\frac{1.00\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}}}\times10^6\ \text{ppm}$$

= 31.2 ppm C_6H_5OH

22-31. 1 mol CCl_4 = 1 mol e^- 1 mol $CHCl_3$ = 3 mol e^-. For sample 1,

$$11.63\ \text{C}\times\frac{1\ \text{F}}{96{,}485\ \text{C}}\times\frac{1\ \text{mol e}^-}{\text{F}}\times\frac{1\ \text{mol CCl}_4}{\text{mol e}^-}=1.2054\times10^{-4}\ \text{mol CCl}_4$$

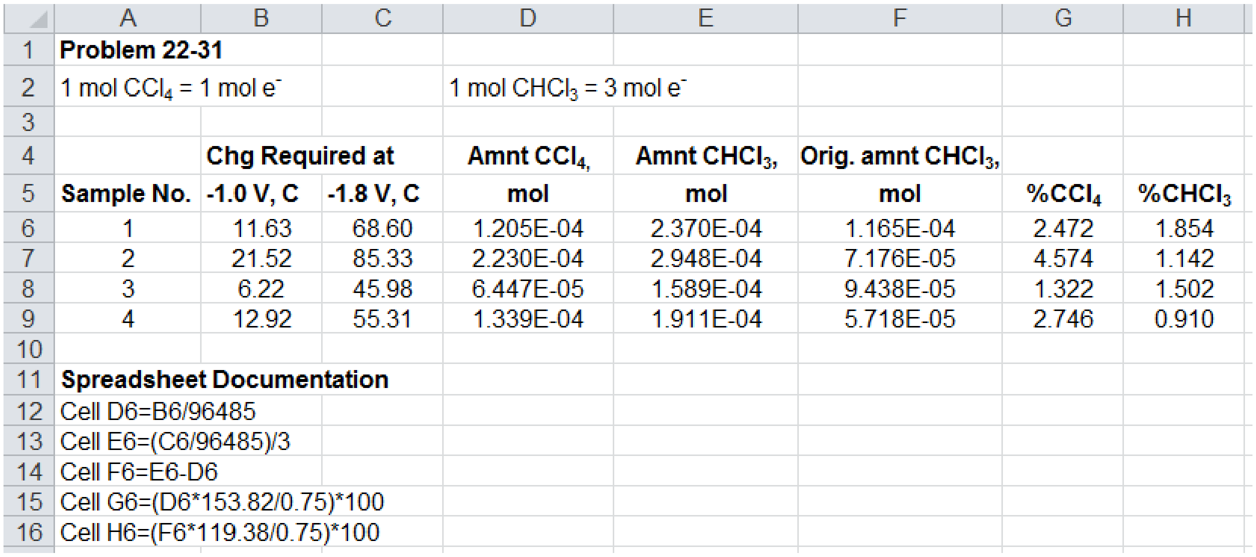
$$68.60\ \text{C}\times\frac{1\ \text{F}}{96{,}485\ \text{C}}\times\frac{1\ \text{mol e}^-}{\text{F}}\times\frac{1\ \text{mol CHCl}_3}{3\ \text{mol e}^-}=2.3700\times10^{-4}\ \text{mol CHCl}_3$$

$$\text{original amount CHCl}_3=\ 2.3700\times10^{-4}\ -\ 1.2054\times10^{-4}\ =1.1646\times10^{-4}\ \text{mol CHCl}_3$$

$$\frac{1.2054\times10^{-4}\ \text{mol CCl}_4\times\frac{153.82\ \text{g CCl}_4}{\text{mol}}}{0.750\ \text{g sample}}\times100\%=2.472\ \%\ \text{CCl}_4$$

$$\frac{1.165\times10^{-4}\ \text{mol CHCl}_3\times\frac{119.38\ \text{g CHCl}_3}{\text{mol}}}{0.750\ \text{g sample}}\times100\%=1.854\ \%\ \text{CHCl}_3$$

The remaining samples are treated similary and the results are in the spreadsheet.



	A	B	C	D	E	F	G	H
1	**Problem 22-31**							
2	1 mol CCl_4 = 1 mol e^-			1 mol $CHCl_3$ = 3 mol e^-				
3								
4		**Chg Required at**		**Amnt CCl_4,**	**Amnt $CHCl_3$,**	**Orig. amnt $CHCl_3$,**		
5	**Sample No.**	**-1.0 V, C**	**-1.8 V, C**	**mol**	**mol**	**mol**	**%CCl_4**	**%$CHCl_3$**
6	1	11.63	68.60	1.205E-04	2.370E-04	1.165E-04	2.472	1.854
7	2	21.52	85.33	2.230E-04	2.948E-04	7.176E-05	4.574	1.142
8	3	6.22	45.98	6.447E-05	1.589E-04	9.438E-05	1.322	1.502
9	4	12.92	55.31	1.339E-04	1.911E-04	5.718E-05	2.746	0.910
10								
11	**Spreadsheet Documentation**							
12	Cell D6=B6/96485							
13	Cell E6=(C6/96485)/3							
14	Cell F6=E6-D6							
15	Cell G6=(D6*153.82/0.75)*100							
16	Cell H6=(F6*119.38/0.75)*100							

22-32.

$$2CHCl_3 + 6H^+ + 6e^- + 6Hg(l) \rightarrow 2CH_4(g) + 3Hg_2Cl_2(s)$$
$$CH_2Cl_2 + 2H^+ + 2e^- + 2Hg(l) \rightarrow CH_4(g) + Hg_2Cl_2(s)$$

1 mol $CHCl_3$ = 3 mol e^- 1 mol CH_2Cl_2 = 2 mol e^-

Let x = mass $CHCl_3$. For sample 1, 0.1309 g – x = mass CH_2Cl_2

$$\left(x\text{ g CHCl}_3 \times \frac{1\text{ mol CHCl}_3}{119.38\text{ g}} \times \frac{3\text{ mol e}^-}{\text{mol CHCl}_3}\right) + \left(0.1309\text{ g} - x \times \frac{1\text{ mol CH}_2\text{Cl}_2}{84.93\text{ g}} \times \frac{2\text{ mol e}^-}{\text{mol CH}_2\text{Cl}_2}\right)$$

$$= \text{total mol e}^- = 306.72\text{ C} \times \frac{\text{F}}{96{,}485\text{ C}} \times \frac{1\text{ mol e}^-}{\text{F}} = 3.1789\times10^{-3}$$

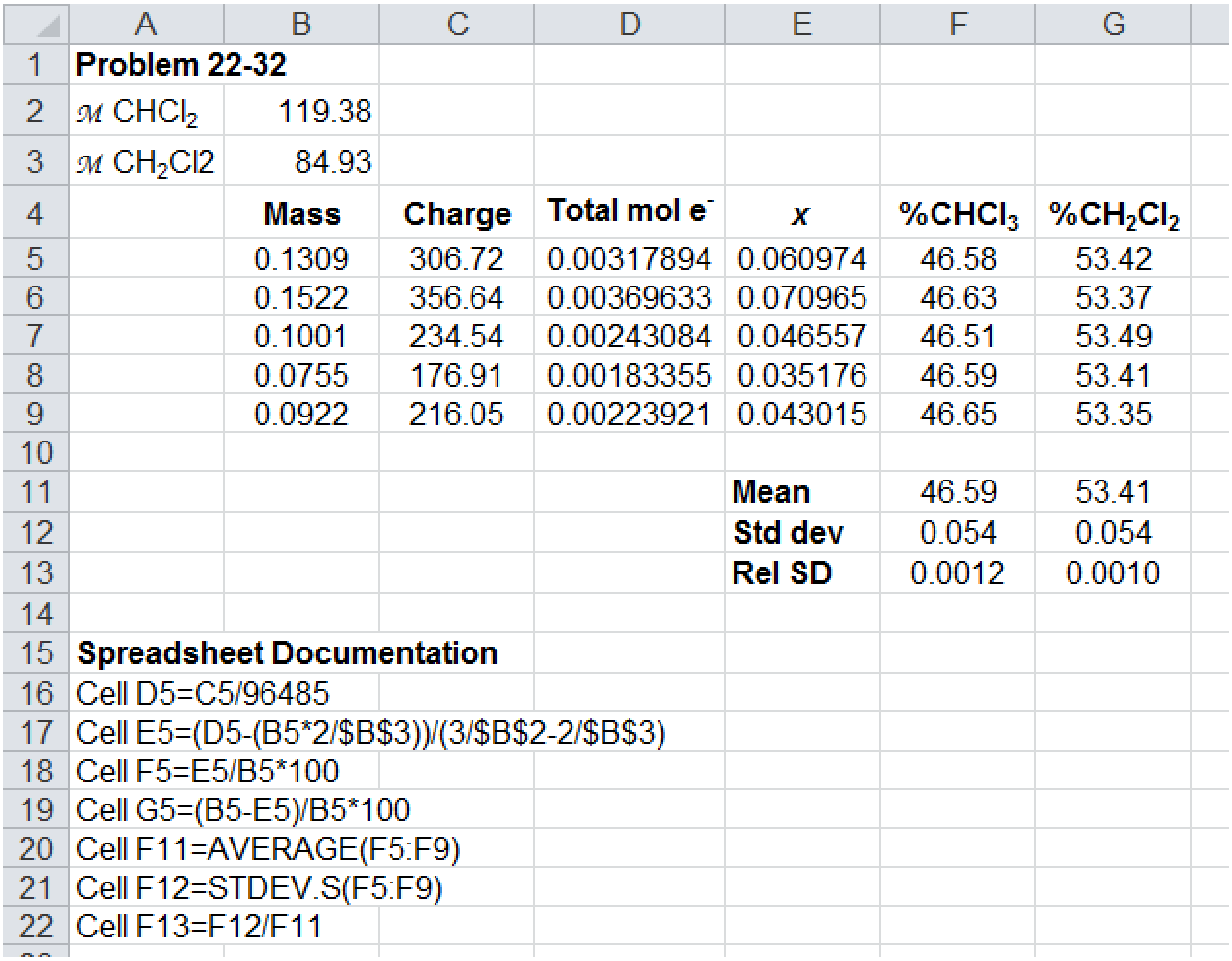
$$2.5130 \times 10^{-2}x + 2.3549\times10^{-2}\ \ 0.1309 - x\ \ = 3.1789\times10^{-3}$$

$$\text{mass CHCl}_3 = x = 6.093 \times 10^{-2}\text{ g}$$

$$\%\text{CHCl}_3 = \left(\frac{6.093 \times 10^{-2}\text{g}}{0.1309\text{ g}}\right) \times 100\% = 46.55\%$$

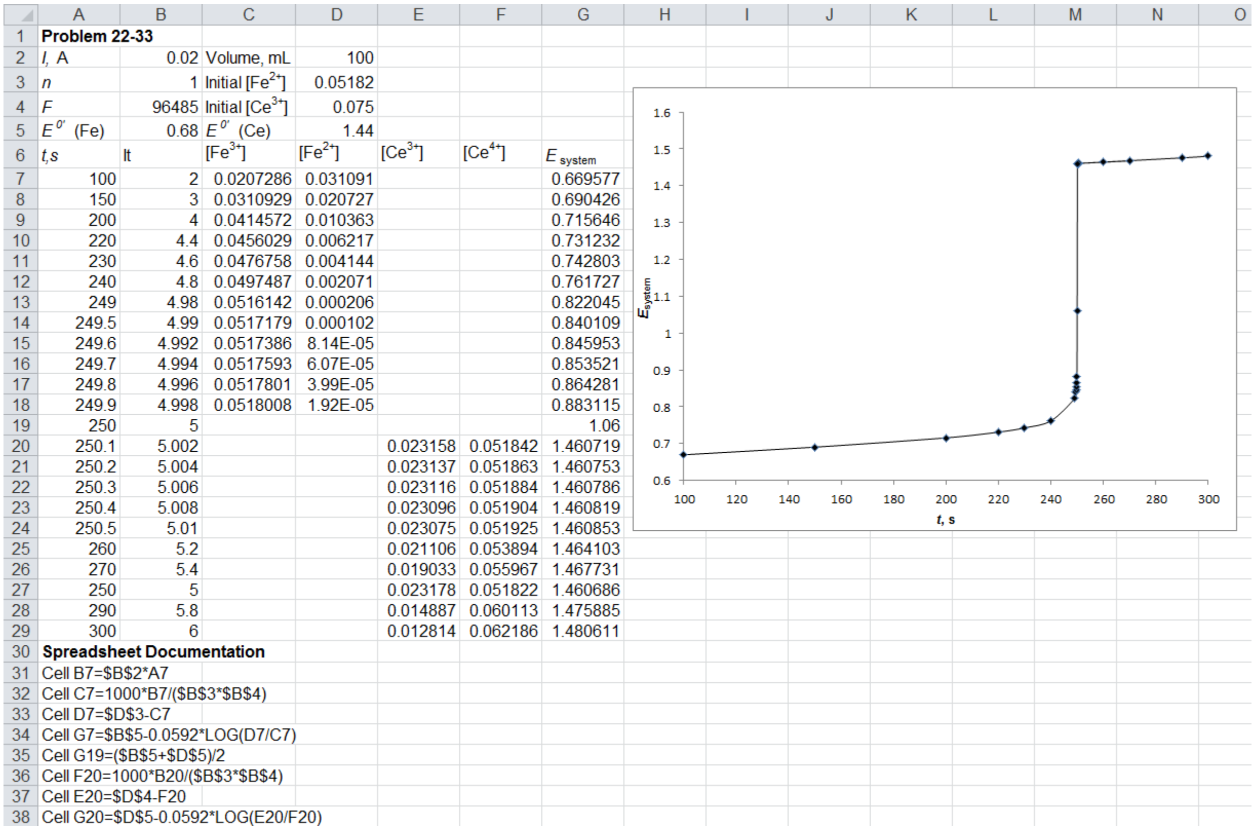
$$\%\text{CH}_2\text{Cl}_2 = 100.00\% - 46.55\% = 53.45\%$$

The remainder of the samples are treated in the same way and the results are in the spreadsheet that follows.



	A	B	C	D	E	F	G
1	**Problem 22-32**						
2	$\mathcal{M}$ CHCl$_2$	119.38					
3	$\mathcal{M}$ CH$_2$Cl2	84.93					
4		**Mass**	**Charge**	**Total mol e$^-$**	***x***	**%CHCl$_3$**	**%CH$_2$Cl$_2$**
5		0.1309	306.72	0.00317894	0.060974	46.58	53.42
6		0.1522	356.64	0.00369633	0.070965	46.63	53.37
7		0.1001	234.54	0.00243084	0.046557	46.51	53.49
8		0.0755	176.91	0.00183355	0.035176	46.59	53.41
9		0.0922	216.05	0.00223921	0.043015	46.65	53.35
10							
11					**Mean**	46.59	53.41
12					**Std dev**	0.054	0.054
13					**Rel SD**	0.0012	0.0010
14							
15	**Spreadsheet Documentation**						
16	Cell D5=C5/96485						
17	Cell E5=(D5-(B5*2/$B$3))/(3/$B$2-2/$B$3)						
18	Cell F5=E5/B5*100						
19	Cell G5=(B5-E5)/B5*100						
20	Cell F11=AVERAGE(F5:F9)						
21	Cell F12=STDEV.S(F5:F9)						
22	Cell F13=F12/F11						

22-33. See spreadsheet, following page.



	A	B	C	D	E	F	G
1	**Problem 22-33**						
2	*I*, A	0.02	Volume, mL	100			
3	*n*	1	Initial [Fe^{2+}]	0.05182			
4	*F*	96485	Initial [Ce^{3+}]	0.075			
5	$E^{0'}$ (Fe)	0.68	$E^{0'}$ (Ce)	1.44			
6	*t*,s	It	[Fe^{3+}]	[Fe^{2+}]	[Ce^{3+}]	[Ce^{4+}]	E_{system}
7	100	2	0.0207286	0.031091			0.669577
8	150	3	0.0310929	0.020727			0.690426
9	200	4	0.0414572	0.010363			0.715646
10	220	4.4	0.0456029	0.006217			0.731232
11	230	4.6	0.0476758	0.004144			0.742803
12	240	4.8	0.0497487	0.002071			0.761727
13	249	4.98	0.0516142	0.000206			0.822045
14	249.5	4.99	0.0517179	0.000102			0.840109
15	249.6	4.992	0.0517386	8.14E-05			0.845953
16	249.7	4.994	0.0517593	6.07E-05			0.853521
17	249.8	4.996	0.0517801	3.99E-05			0.864281
18	249.9	4.998	0.0518008	1.92E-05			0.883115
19	250	5					1.06
20	250.1	5.002			0.023158	0.051842	1.460719
21	250.2	5.004			0.023137	0.051863	1.460753
22	250.3	5.006			0.023116	0.051884	1.460786
23	250.4	5.008			0.023096	0.051904	1.460819
24	250.5	5.01			0.023075	0.051925	1.460853
25	260	5.2			0.021106	0.053894	1.464103
26	270	5.4			0.019033	0.055967	1.467731
27	250	5			0.023178	0.051822	1.460686
28	290	5.8			0.014887	0.060113	1.475885
29	300	6			0.012814	0.062186	1.480611
30	**Spreadsheet Documentation**						
31	Cell B7=$B$2*A7						
32	Cell C7=1000*B7/($B$3*$B$4)						
33	Cell D7=$D$3-C7						
34	Cell G7=$B$5-0.0592*LOG(D7/C7)						
35	Cell G19=($B$5+$D$5)/2						
36	Cell F20=1000*B20/($B$3*$B$4)						
37	Cell E20=$D$4-F20						
38	Cell G20=$D$5-0.0592*LOG(E20/F20)						

23-34. 1 mol $C_6H_5NH_2$ = 3 mol Br_2 = 6 mol e^-

$$\left(3.76-0.27\ \text{min}\times\frac{60\ \text{s}}{\text{min}}\times\frac{1.51\times10^{-3}\ \text{C}}{\text{s}}\times\frac{1\ F}{96,485\ \text{C}}\times\frac{1\ \text{mol e}^-}{F}\times\frac{1\ \text{mol C}_6\text{H}_5\text{NH}_2}{6\ \text{mol e}^-}\right)=5.462\times10^{-7}\ \text{mol C}_6\text{H}_5\text{NH}_2$$

$$5.462\times10^{-7}\ \text{mol C}_6\text{H}_5\text{NH}_2\times\frac{93.128\ \text{g C}_6\text{H}_5\text{NH}_2}{\text{mol}}\times\frac{10^6\ \mu\text{g}}{\text{g}}$$

$$= 50.9\ \mu\text{g C}_6\text{H}_5\text{NH}_2$$

23-35. 1 mol Sn^{4+} = 2 mol e^- $\rightarrow$ 1 mol Sn^{2+} = 2 mol $C_6H_4O_2$

$$\left(\begin{array}{l} 8.34-0.691\ \text{min} \times \frac{60\ \text{s}}{\text{min}} \times \frac{1.062\times10^{-3}\ \text{C}}{\text{s}} \times \frac{1\ F}{96,485\ \text{C}} \\ \times \frac{1\ \text{mol e}^-}{F} \times \frac{1\ \text{mol C}_6\text{H}_5\text{NH}_2}{2\ \text{mol e}^-} \end{array} \right) = 2.526\times10^{-6}\ \text{mol C}_6\text{H}_4\text{O}_2$$

$$2.526\times10^{-6}\ \text{mol C}_6\text{H}_4\text{O}_2 \times \frac{108.10\ \text{g C}_6\text{H}_4\text{O}_2}{\text{mol}}$$

$$= 2.73\times10^{-4}\ \text{g C}_6\text{H}_4\text{O}_2$$

Chapter 23

23-1. **(a)** *Voltammetry* is an analytical technique that is based on measuring the current that develops at a small electrode as the applied potential is varied. *Amperometry* is a technique in which the limiting current is measured at a constant potential.

(b) In *linear scan voltammetry*, the current in a cell is monitored continuously as the applied potential is changed at a constant rate. In *pulse voltammetry*, an excitation signal is used that consists of a series of voltage pulses that increase in size linearly as a function of time.

(c) *Differential pulse* and *square wave voltammetry* differ in the type of pulse sequence used as shown in Figure 23-1b and 23-1c.

(d) A *rotating disk electrode* is a disk electrode rotated rapidly by a motor. The *ring-disk-electrode* is a modified rotating disk with a second ring-shaped electrode isolated electrically from the center disk. These electrodes are shown in Figure 23-19.

(e) In voltammetry, a *limiting current* is a current that is independent of applied potential. Its magnitude is limited by the rate at which a reactant is brought to the surface of the electrode by migration, convection, and/or diffusion. A *diffusion current* is a limiting current when analyte transport is solely by diffusion.

(f) *Laminar flow* is a type of liquid flow in which layers of liquid slide by one another in a direction that is parallel to a solid surface. It is characterized by a parabolic flow profile. *Turbulent flow* is a type of liquid flow that has no regular pattern.

(g) The *half-wave potential* is closely related to the *standard potential* for a reversible reaction. That is,

$$E_{1/2} = E_{\mathrm{A}}^{\mathrm{o}} - \frac{0.0592}{n}\log\left(\frac{k_{\mathrm{A}}}{k_{\mathrm{B}}}\right)$$

where k_A and k_B are constants that are proportional to the diffusion coefficients of the analyte and product. When these are approximately the same, the half-wave potential and the standard potential are essentially equal.

(h) In *stripping methods*, the analyte is first deposited on a working electrode. The deposited analyte is later stripped from the working electrode and determined by an electroanalytical method, often voltammetry. In standard *voltammetry*, the electrode current is measured as a function of applied potential.

23-2. **(a)** A *voltammogram* is a plot of current versus applied potential.

(b) In *hydrodynamic voltammetry*, current-potential curves are obtained in stirred solution.

(c) The *Nernst diffusion layer* is a static layer of solution immediately adjacent to the electrode surface in which mass transport occurs by diffusion alone.

(d) A *mercury film electrode* is formed by electrodepositing a thin layer of mercury onto a disk electrode.

(e) The half-wave potential is the potential on a voltammetric wave when the current is one-half of the limiting current.

(f) The *diffusion current* is a limiting current in voltammetry when the analyte is transported to the electrode surface solely by diffusion.

23-3. A high supporting electrolyte concentration is used in most electroanalytical procedures to minimize the contribution of migration to concentration polarization. The supporting electrolyte also reduces the cell resistance, which decreases the *IR* drop.

23-4. The reference electrode is placed near the working electrode to minimize the *IR* drop that can distort voltammograms.

23-5. Most organic electrode processes consume or produce hydrogen ions. Unless buffered solutions are used, marked pH changes can occur at the electrode surface as the reaction proceeds.

23-6. In stripping methods**,** the electrodeposition step preconcentrates the analyte on the surface of the working electrode. Because of this preconcentration step, stripping methods are more sensitive than ordinary voltammetric methods.

23-7. The purpose of the electrodeposition step in stripping analysis is to preconcentrate the analyte on the surface of the working electrode and to separate it from many interfering species.

23-8. The advantages of a hanging mercury drop electrode compared with platinum or carbon electrodes include (1) the high overvoltage of hydrogen on mercury, (2) the ability to form fresh electrode surfaces of reprodcuble area and (3) the reproducible currents that are achieved on a mercury electrode. The disadvantages include (1) its poor anodic potential range, (2) its relatively large residual current, (3) its inconvenience.

23-9. A plot of E_{appl} versus $\log\frac{i}{i_l - i}$ should yield a straight line having a slope of $\frac{-0.0592}{n}$.

Thus, n is readily obtained from the slope.

23-10. For the reduction of quinone (Q) to hydroquinone (H_2Q), Equation 23-3 takes the form

$$E_{\text{appl}} = E_{\text{Q}}^{\text{o}} - \frac{0.0592}{n}\log\left(\frac{c_{\text{H}_2\text{Q}}^{\text{o}}}{c_{\text{Q}}^{\text{o}}\left(c_{\text{H}^+}^{\text{o}}\right)^2}\right) - E_{\text{ref}}$$

where $c^{\mathrm{o}}_{\mathrm{H}^+}$ is the concentration of H$^+$ at the electrode surface. Substituting Equations 23-7 and 23-10 in to this equation gives

$$E_{\mathrm{appl}} = E^{\mathrm{o}}_{\mathrm{Q}} - \frac{0.0592}{n}\log\left(\frac{k_{\mathrm{Q}}}{k_{\mathrm{H_2Q}}\left(c^{\mathrm{o}}_{\mathrm{H}^+}\right)^2}\right) - \frac{0.0592}{n}\log\left(\frac{i}{i_l - i}\right) - E_{\mathrm{ref}}$$

when $i = i_l/2$, E_{appl} is the half-wave potential. With the added assumption that $k_{\mathrm{Q}} \approx k_{\mathrm{H_2Q}}$, this last equation becomes

$$E_{1/2} = E^{\mathrm{o}}_{\mathrm{Q}} - E_{\mathrm{ref}} - \frac{0.0592}{n}\log\left(\frac{1}{\left(c^{\mathrm{o}}_{\mathrm{H}^+}\right)^n}\right) \qquad (1)$$
$$= 0.599 - 0.244 - 0.0592\mathrm{pH}$$
$$= 0.0355 - 0.0592\mathrm{pH}$$

(a) At pH 7.00,

$E_{1/2}$ = 0.355 – 0.0592 × 7.00 = –0.059 V

(b) At pH 5.00,

$E_{1/2}$ = 0.355 – 0.0592 × 5.00 = +0.059 V

23-11. Here we develop the titration curve for 10, 25, 50, 75, 90, 95, 99, 100, 110, 125 and 150% titrated. The corresponding volumes of titrant are calculated in cells B8:B18 of the spreadsheet. We must find the concentration of Pb^{2+} at each volume and from it find the limiting current from

$$i_l = 10 \times c_{\mathrm{Pb}^{2+}}(\mathrm{mM}) = 10 \times 1000\left(\frac{\mathrm{mM}}{\mathrm{M}}\right)[\mathrm{Pb}^{2+}](\mathrm{M})$$

Pre-equivalence point region

At each titrant volume, we calculate the concentrations of sulfate and Pb^{2+} as follows:

$$[\mathrm{SO_4}^{2-}] = c_{\mathrm{SO_4}^{2-}} = \frac{\text{mmol SO}_4^{2-}\text{ initially present} - \text{mmol Pb}^{2+}\text{added}}{\text{total solution volume in mL}}$$

$$[\mathrm{Pb}^{2+}] = \frac{K_{\mathrm{sp}}}{[\mathrm{SO_4}^{2-}]}$$

The limiting current values are shown in the spreadsheet.

Equivalence point

Here, $[\mathrm{Pb}^{2+}] = [\mathrm{SO_4}^{2-}] = \sqrt{K_{\mathrm{sp}}}$

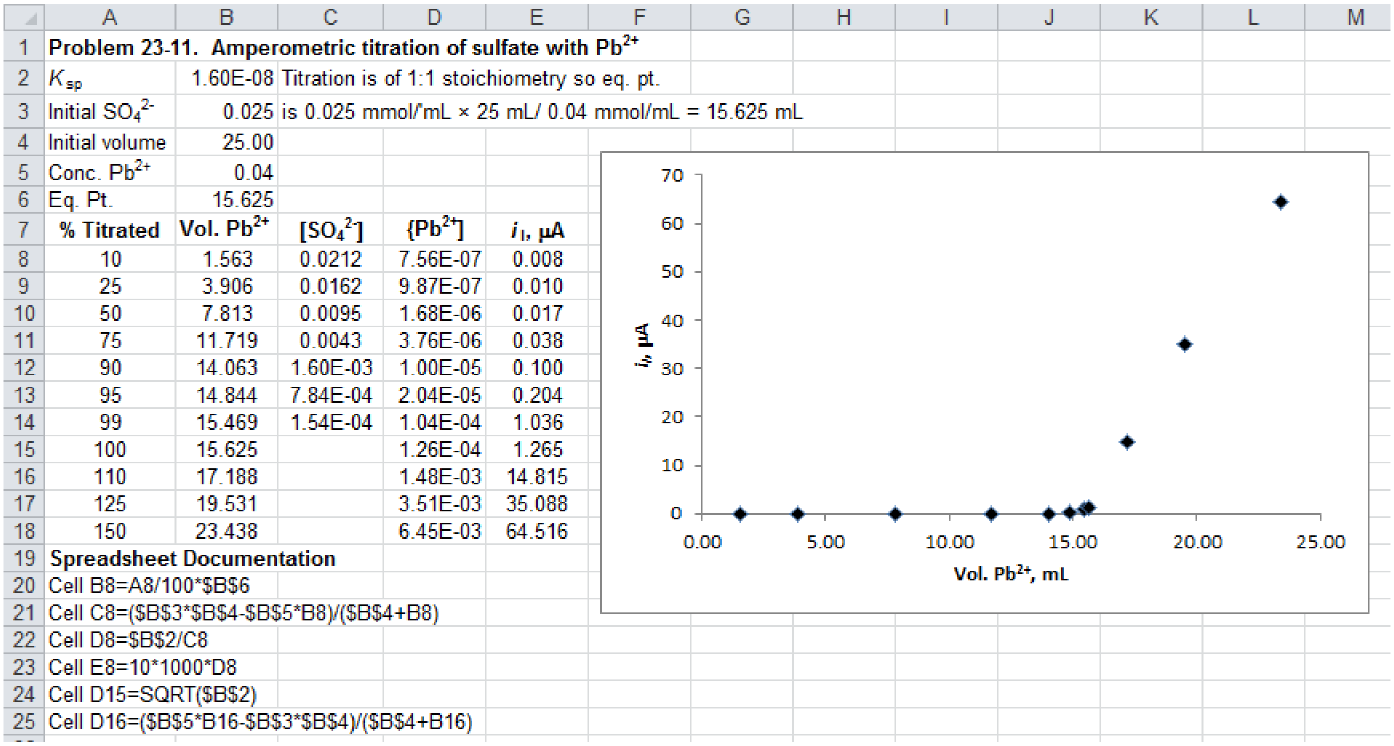
The result is shown in the spreadsheet.

Post-equivalence point region

Here we find the Pb^{2+} concentration from the excess titrant added.

$$[\mathrm{Pb}^{2+}] = c_{\mathrm{Pb}^{2+}} = \frac{\text{mmol Pb}^{2+}\text{ added} - \text{mmol SO}_4^{2-}\text{ initially present}}{\text{total solution volume in mL}}$$

The limiting current values are shown in the spreadsheet along with a plot i_l versus volume of Pb^{2+} added.



	A	B	C	D	E
1	**Problem 23-11. Amperometric titration of sulfate with Pb^{2+}**				
2	K_{sp}	1.60E-08	Titration is of 1:1 stoichiometry so eq. pt.		
3	Initial SO_4^{2-}	0.025	is 0.025 mmol/'mL × 25 mL/ 0.04 mmol/mL = 15.625 mL		
4	Initial volume	25.00			
5	Conc. Pb^{2+}	0.04			
6	Eq. Pt.	15.625			
7	**% Titrated**	**Vol. Pb^{2+}**	**[SO_4^{2-}]**	**{Pb^{2+}]**	**i_l, μA**
8	10	1.563	0.0212	7.56E-07	0.008
9	25	3.906	0.0162	9.87E-07	0.010
10	50	7.813	0.0095	1.68E-06	0.017
11	75	11.719	0.0043	3.76E-06	0.038
12	90	14.063	1.60E-03	1.00E-05	0.100
13	95	14.844	7.84E-04	2.04E-05	0.204
14	99	15.469	1.54E-04	1.04E-04	1.036
15	100	15.625		1.26E-04	1.265
16	110	17.188		1.48E-03	14.815
17	125	19.531		3.51E-03	35.088
18	150	23.438		6.45E-03	64.516
19	**Spreadsheet Documentation**				
20	Cell B8=A8/100*$B$6				
21	Cell C8=($B$3*$B$4-$B$5*B8)/($B$4+B8)				
22	Cell D8=$B$2/C8				
23	Cell E8=10*1000*D8				
24	Cell D15=SQRT($B$2)				
25	Cell D16=($B$5*B16-$B$3*$B$4)/($B$4+B16)				

23-12. Initally there are 60 mL × 0.08 mmol/mL = 4.8 mmol Cu^{2+} present.

Applying a current of 6.0 μA for 45 minutes represents a charge of

6.0×10^{-6} C/s × 45 min × 60 s/min = 0.0162 C

The number of moles of Cu^{2+} reduced by that amount of charge is:

$n_{\mathrm{Cu2+}} = Q/nF = 0.0162\ \mathrm{C}/(2 \times 96485\ \mathrm{C/mol}) = 8.4 \times 10^{-8}$ mol or 8.4×10^{-5} mmol

The percentage removed is thus (8.4×10^{-5} mmol/ 4.8 mmol) × 100% = 1.7×10^{-3}%

23-13. $i_1 = kc_u$ where $i_1 = 1.86$ μA and c_u is the concentration of the unknown.

$$i_2 = \frac{k\left(25.00c_u + 5.00 \times 2.12 \times 10^{-3}\right)}{25.00 + 5.00} = 5.27\ \mu\mathrm{A}$$

From above, $k = i_1/c_u$. Substituting this into the second equation and solving for c_u gives

$c_u = 1.77 \times 10^{-4}$ M

23-14. **(a)** The advantages include reaching steady-state currents rapidly, having very small charging currents which enables rapid potential scanning, having small *IR* drops, being able to respond to very small volumes and in flowing streams, and having large signal-to-noise ratios.

(b) The currents become very small as the electrode size decreases. Problems can also arise if the electrode dimensions become comparable to the double-layer thickness or to molecular dimensions. In some cases for nanoelectrodes, new theories and experimental approaches may be necessary.

Chapter 24

24-1. The yellow color comes about because the solution absorbs blue light in the wavelength region 435-480 nm and transmits its complementary color (yellow). The purple color comes about because green radiation (500-560 nm) is absorbed and its complementary color (purple) is transmitted.

24-2. (a) Absorbance A is the negative logarithm of transmittance T ($A = -\log T$).

(b) The molar absorptivity, ε, is given by A/bc where A is the absorbance of a medium having a pathlength of b cm and an analyte concentration of c molar. Molar absorptivity has the units of L mol^{-1} cm^{-1}. The absorptivity, a, is also given by A/bc where A is again the absorbance of the medium, but b may have any specified units of length and c may have any specified units of concentration.

24-3. Deviations from linearity can occur because of polychromatic radiation, unknown chemical changes such as association or dissociation reactions, stray light, and molecular or ionic interactions at high concentration.

24-4. A real deviation from Beer's law is a deviation due to a real limitation to the law. A real deviation occurs at high concentrations due to molecular or ionic interactions. Other deviations occur because of the imperfect manner in which measurements are made (instrumental deviations) or because of chemical changes that occur with concentration and are unknown to the user.

24-5. Both electronic and vibrational transitions are quantized, that is they occur at specific wavelengths and energies. Electronic transitions are much higher in energy, involving excitation or relaxation of electrons from one orbital to another, while vibrational transitions involve changes in the vibrational frequency of the atoms in a molecule. Both atoms and molecules can undergo electronic transitions while only molecules can undergo vibrational transitions.

24-6. $\nu = c/\lambda = 3.00 \times 10^{10}$ cm s^{-1}/λ(cm) = $(3.00 \times 10^{10}/\lambda)$ s^{-1} = $(3.00 \times 10^{10}/\lambda)$ Hz

(a) $\nu = 3.00 \times 10^{10}$ cm $s^{-1}/(2.65$ Å $\times 10^{-8}$ cm/Å) = 1.13×10^{18} Hz

(b) $\nu = 3.00 \times 10^{10}$ cm $s^{-1}/(211.0$ nm $\times 10^{-7}$ cm/nm) = 1.42×10^{15} Hz

(c) $\nu = 3.00 \times 10^{10}$ cm $s^{-1}/(694.3$ nm $\times 10^{-7}$ cm/nm) = 4.32×10^{14} Hz

(d) $\nu = 3.00 \times 10^{10}$ cm $s^{-1}/(10.6$ μm $\times 10^{-4}$ cm/μm) = 2.83×10^{13} Hz

(e) $\nu = 3.00 \times 10^{10}$ cm s^{-1} / (19.6 μm $\times 10^{-4}$ cm/μm) = 1.53×10^{13} Hz

(f) $\nu = 3.00 \times 10^{10}$ cm $s^{-1}/1.86$ cm = 1.61×10^{10} Hz

24-7. $\lambda = c/\nu = 3.00 \times 10^{10}$ cm s^{-1}/ν (s^{-1}) = $(3.00 \times 10^{10}/\nu)$ cm

(a) $\lambda = 3.00 \times 10^{10}$ cm $s^{-1}/(118.6$ MHz $\times 10^{6}$ Hz/MHz) = 253.0 cm

(b) $\lambda = 3.00 \times 10^{10}$ cm $s^{-1}/(114.10$ kHz $\times 10^{3}$ kHz/Hz) = 2.629×10^{5} cm

(c) $\lambda = 3.00 \times 10^{10}$ cm $s^{-1}/(105$ MHz $\times 10^{6}$ Hz/MHz) = 286 cm

(d) $\lambda = 1/1210$ $cm^{-1} = 8.264 \times 10^{-4}$ cm

24-8. $\bar{\nu} = 1/(185$ nm $\times 10^{-7}$ cm/nm) = 5.41×10^{4} cm^{-1} to

$1/(3000 \times 10^{-7}$ cm) = 3.33×10^{3} cm^{-1}

24-9. (a) $\bar{\nu} = 1/(3$ μm $\times 10^{-4}$ cm/μm) = 3.33×10^{3} cm^{-1} to

$1/(15 \times 10^{-4}$ cm) = 6.67×10^{2} cm^{-1}

(b) $\nu = 3.00 \times 10^{10}$ cm $s^{-1} \times 3.333 \times 10^{3}$ $cm^{-1} = 1.00 \times 10^{14}$ Hz to

$3.00 \times 10^{10} \times 6.67 \times 10^{2} = 2.00 \times 10^{13}$ Hz

24-10. $\nu = c/\lambda = 3.00 \times 10^{10}$ cm $s^{-1}/(2.70$ Å $\times 10^{-8}$ cm/Å) = 1.11×10^{18} Hz

$E = h\nu = 6.63 \times 10^{-34}$ J s $\times$ 1.11×10^{18} s^{-1} = 7.36×10^{-16} J

24-11. $\lambda = c/\nu = (3.00 \times 10^{10}\text{ cm s}^{-1}) / (220 \times 10^{6}\text{ s}^{-1})$ = 136 cm or 1.36 m

$E = h\nu = 6.63 \times 10^{-34}$ J s $\times$ 220×10^{6} s^{-1} = 1.46×10^{-25} J

24-12. (a) λ = 589 nm/1.35 = 436 nm

(b) λ = 694.3 nm/1.55 = 448 nm

24-13. (a) ppm^{-1} cm^{-1}

(b) L µg^{-1} cm^{-1}

(c) %$^{-1}$ cm^{-1}

(d) L g^{-1} cm^{-1}

24-14. (a) $\%T = 100 \times \text{antilog}(-0.0356) = 92.1\%$

Proceeding similarly, we obtain

(b) $\%T$ = 12.7; (c) $\%T$ = 41.8; (d) $\%T$ = 68.1; (e) $\%T$ = 32.7; (f) $\%T$ = 17.7%

24-15. (a) $A = -\log T = -\log(27.2\%/100\%) = 0.565$

Proceeding similarly,

(b) $A = -\log(0.579) = 0.237$; (c) A = 0.514; (d) A = 1.400; (e) A = 1.032; (f) A = 0.196

24-16. (a) $\%T = 100\% \times \text{antilog}(-2 \times 0.0356) = 100\% \times \text{antilog}(-0.0712) = 84.9\%$

Proceeding in the same way,

(b) $\%T$ = 1.62%; (c) $\%T$ = 17.5%; (d) $\%T$ = 46.3%; (e) $\%T$ = 10.7%; (f) $\%T$ = 3.12%

24-17. (a) $A = -\log T = -\log(0.2272/2) = 0.867$

Proceeding similarly,

(b) A = 0.538; (c) A = 0.815; (d) A = 1.701; (e) 1.333; (f) A = 0.497

24-18. (a) $\%T = \text{antilog}(-0.172) \times 100\% = 67.3\%$

$c = A/\varepsilon b = (0.172)/(4.23 \times 10^3 \times 1.00) = 4.07 \times 10^{-5}$ M

$$c = 4.07 \times 10^{-5}\frac{\text{mol}}{\text{L}}\times\frac{200\text{ g}}{\text{mol}}\times\frac{1\text{ L}}{1000\text{ g}}\times 10^{6}\text{ ppm} = 8.13\text{ ppm}$$

$a = A/bc = 0.172/(1.00 \times 8.13) = 0.0211\ \text{cm}^{-1}\ \text{ppm}^{-1}$

Using similar conversions and calculations, we can evaluate the missing quantities

			ε	***a***	***b***	***c***	
	A	***%T***	**L mol^{-1} cm^{-1}**	**cm^{-1} ppm^{-1}**	**cm**	**M**	**ppm**
*(a)	0.172	***67.3***	4.23×10^3	***0.0211***	1.00	***4.07×10^{-5}***	***8.13***
(b)	***0.348***	44.9	***5.16×10^3***	0.0258	***0.500***	1.35×10^{-4}	***27.0***
*(c)	0.520	***30.2***	7.95×10^3	***0.0397***	1.00	**6.54×10^{-5}**	***13.1***
(d)	***0.402***	39.6	***1.83×10^4***	0.0912	***2.50***	***8.80×10^{-6}***	1.76
*(e)	***0.638***	***23.0***	3.73×10^3	***0.0187***	0.100	1.71×10^{-3}	***342***
(f)	***0.0778***	83.6	***9.64×10^3***	***0.0483***	1.00	8.07×10^{-6}	***1.61***
*(g)	0.798	***15.9***	***3.17×10^3***	***0.0158***	1.50	***1.68×10^{-4}***	33.6
(h)	***0.955***	11.1	1.35×10^4	***0.0677***	***1.00***	7.07×10^{-5}	***14.1***
*(i)	***1.28***	5.23	9.78×10^3	***0.0489***	***5.00***	***2.62×10^{-5}***	5.24
(j)	0.179	***66.2***	***2.49×10^3***	***0.0124***	1.00	7.19×10^{-5}	***14.4***

24-19. molar mass $KMnO_4$ = 158.03 g/mol

$$c = \frac{4.48\text{ g KMnO}_4}{10^6\text{ g soln}} \times \frac{1000\text{ g soln}}{\text{L}} \times \frac{1\text{ mol}}{158.03\text{ g KMnO}_4} = 2.8349 \times 10^{-5}\text{ M}$$

$A = -\log(0.859) = 0.066$

$\varepsilon = A/bc = 0.066/(1.00 \times 2.8349 \times 10^{-5}) = 2.33 \times 10^3\ \text{L mol}^{-1}\ \text{cm}^{-1}$

24-20. $$c = \frac{2.25\text{ g Be(II) complex}}{10^6\text{ g soln}} \times \frac{1000\text{ g soln}}{\text{L}} \times \frac{\text{mol}}{166.2\text{ g Be(II)complex}} = 1.354 \times 10^{-5}\text{ M}$$

$A = -\log(37.5\%/100\%) = 0.426$

$\varepsilon = A/bc = = 0.426/1.354 \times 10^{-5} = 3.15 \times 10^4\ \text{L mol}^{-1}\ \text{cm}^{-1}$

24-21. (a) $A = 7.00 \times 10^3\ \text{L mol}^{-1}\ \text{cm}^{-1} \times 1.00\ \text{cm} \times 3.40 \times 10^{-5}\ \text{mol L}^{-1} = 0.238$

(b) $A = 7.00 \times 10^3 \times 1.00 \times 2 \times 3.40 \times 10^{-5} = 0.476$

(c) For part (a), T = antilog(–0.238) = 0.578

For part (b), T = antilog(–0.476) = 0.334

(d) $A = -\log(T) = -\log(0.578/2) = 0.539$

24-22.

$$c = \frac{4.33\ \cancel{\text{g Fe}}}{10^6\ \cancel{\text{g soln}}} \times \frac{1000\ \cancel{\text{g soln}}}{\text{L}} \times \frac{\cancel{\text{mol Fe}}}{55.847\ \cancel{\text{g Fe}}} \times \frac{1\ \text{mol FeSCN}^{2+}}{\cancel{\text{mol Fe}}} \times \frac{5.00\ \text{mL}}{50.00\ \text{mL}}$$

$$= 7.75 \times 10^{-6}\ \text{M}$$

$A = 7.00 \times 10^3 \times 2.50 \times 7.75 \times 10^{-6} = 0.136$

24-23. (a) $A = 9.32 \times 10^3$ L mol^{-1} cm^{-1} × 1.00 cm × 5.67 × 10^{-5} mol L^{-1} = 0.528

(b) %T = 100 × anitlog(–0.528) = 29.6%

(c) $c = A/\varepsilon b$ = 0.528/(9.32 × 10^3 L mol^{-1} cm^{-1} × 2.50 cm) = 2.27 × 10^{-5} M

24-24. (a) A = 7000 L mol^{-1} cm^{-1} × 1.00 cm × 6.17 × 10^{-5} mol L^{-1} = 0.439

(b) %T = 100 × anitlog(–0.439) = 36.4%

(c) $c = A/\varepsilon b$ = 0.439/(7000 L mol^{-1} cm^{-1} × 5.00 cm) = 1.25 × 10^{-5} M

(d) $b = A/\varepsilon c$ = 0.439/(7000 L mol^{-1} cm^{-1} × 3.13 × 10^{-5} mol L^{-1}) = 2.00 cm

24-25. $2.10 = -\log(P/P_0)$ $\qquad$ $P/P_0 = 0.0079433$

$P = 0.007943\ P_0$

$P_s/P_0 = 0.0075$

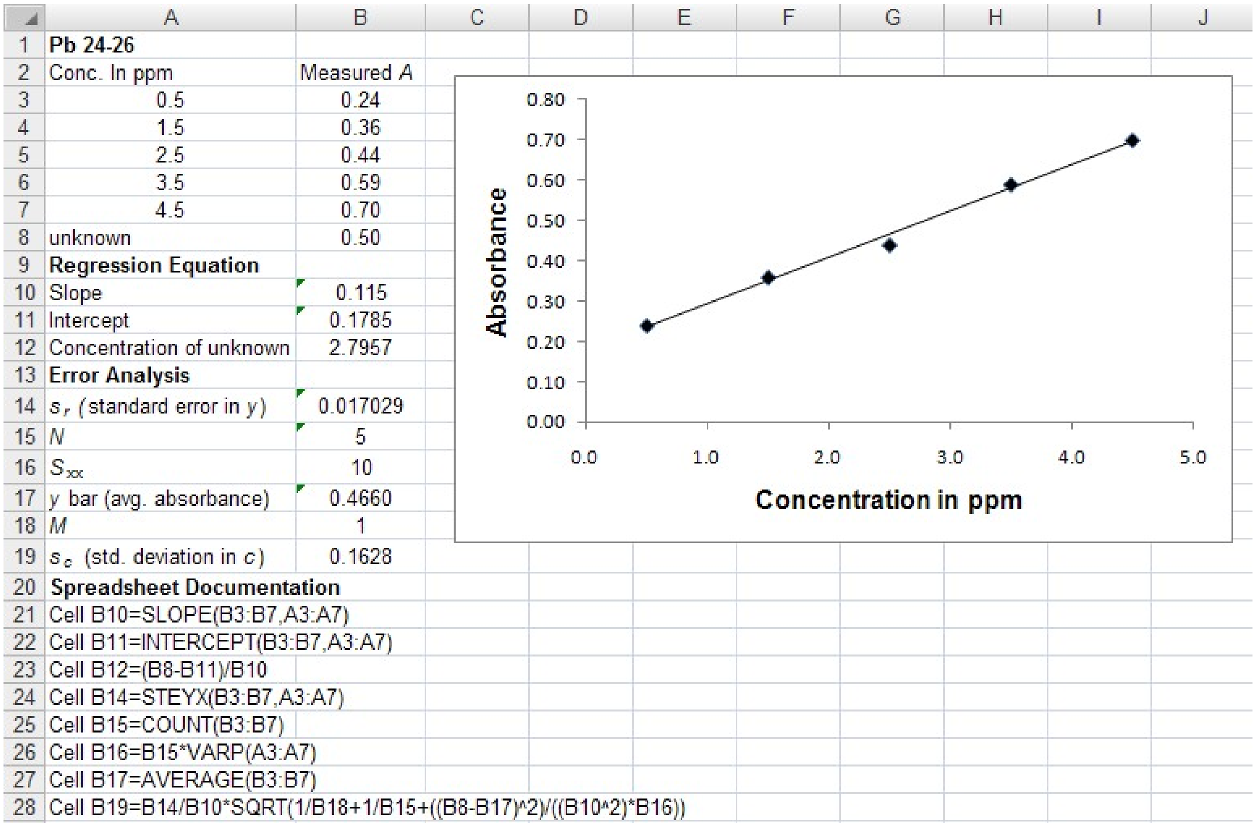
$P_s = 0.0075\ P_0$

$$A' = \left(\frac{P_0 + P_s}{P + P_s}\right) = \log\left(\frac{P_0 + 0.0075P_0}{0.007943P_0 + 0.0075P_0}\right) = \log\left(\frac{1.0075P_0}{0.015443P_0}\right) = \log(65.2139)$$

$= 1.81$

Error = [(1.81 – 2.10)/2.10] × %100 = –13.6%

24-26.

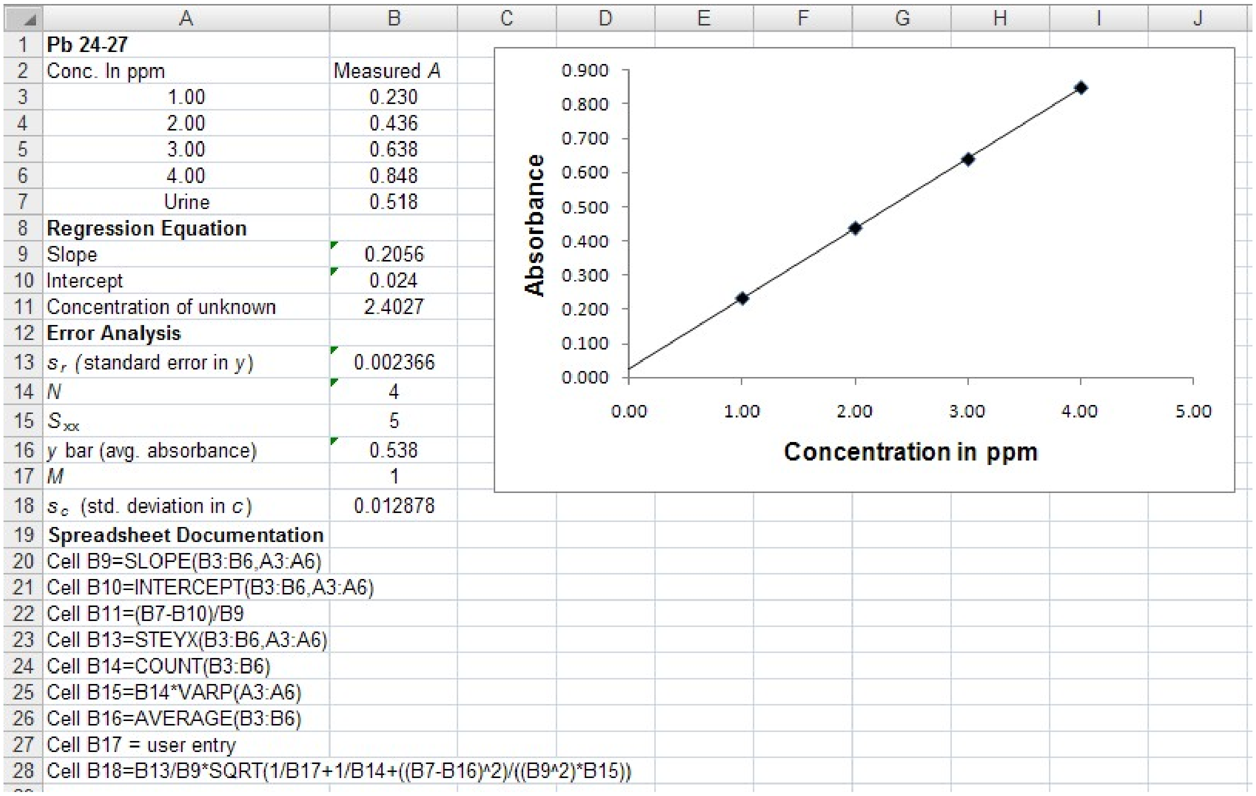


	A	B
1	**Pb 24-26**	
2	Conc. In ppm	Measured *A*
3	0.5	0.24
4	1.5	0.36
5	2.5	0.44
6	3.5	0.59
7	4.5	0.70
8	unknown	0.50
9	**Regression Equation**	
10	Slope	0.115
11	Intercept	0.1785
12	Concentration of unknown	2.7957
13	**Error Analysis**	
14	s_r (standard error in *y*)	0.017029
15	*N*	5
16	S_{xx}	10
17	*y* bar (avg. absorbance)	0.4660
18	*M*	1
19	s_c (std. deviation in *c*)	0.1628
20	**Spreadsheet Documentation**	
21	Cell B10=SLOPE(B3:B7,A3:A7)	
22	Cell B11=INTERCEPT(B3:B7,A3:A7)	
23	Cell B12=(B8-B11)/B10	
24	Cell B14=STEYX(B3:B7,A3:A7)	
25	Cell B15=COUNT(B3:B7)	
26	Cell B16=B15*VARP(A3:A7)	
27	Cell B17=AVERAGE(B3:B7)	
28	Cell B19=B14/B10*SQRT(1/B18+1/B15+((B8-B17)^2)/((B10^2)*B16))	

Rounding to keep only significant figures, we have

c_{unk} = 2.8 ± 0.2 ppm

24-27. (a)



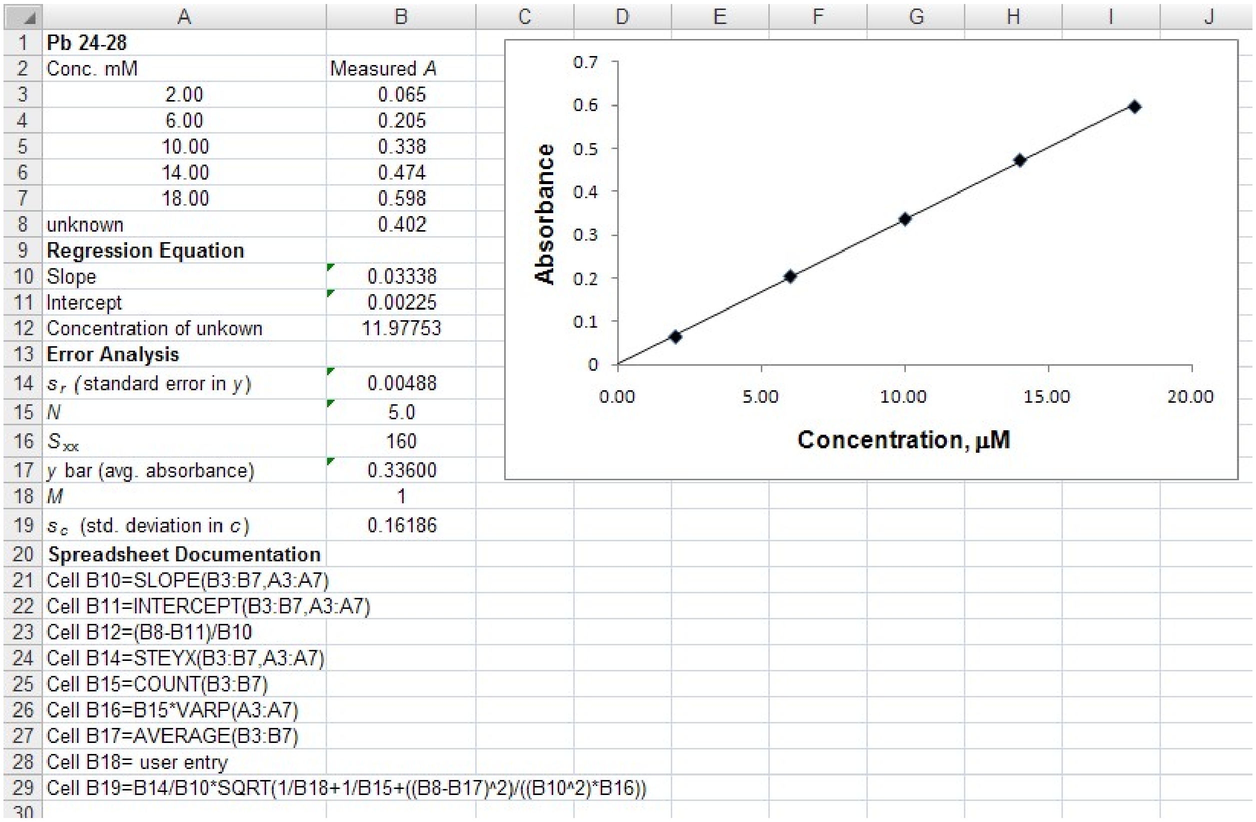
	A	B
1	**Pb 24-27**	
2	Conc. In ppm	Measured *A*
3	1.00	0.230
4	2.00	0.436
5	3.00	0.638
6	4.00	0.848
7	Urine	0.518
8	**Regression Equation**	
9	Slope	0.2056
10	Intercept	0.024
11	Concentration of unknown	2.4027
12	**Error Analysis**	
13	s_r (standard error in *y*)	0.002366
14	*N*	4
15	S_{xx}	5
16	*y* bar (avg. absorbance)	0.538
17	*M*	1
18	s_c (std. deviation in *c*)	0.012878
19	**Spreadsheet Documentation**	
20	Cell B9=SLOPE(B3:B6,A3:A6)	
21	Cell B10=INTERCEPT(B3:B6,A3:A6)	
22	Cell B11=(B7-B10)/B9	
23	Cell B13=STEYX(B3:B6,A3:A6)	
24	Cell B14=COUNT(B3:B6)	
25	Cell B15=B14*VARP(A3:A6)	
26	Cell B16=AVERAGE(B3:B6)	
27	Cell B17 = user entry	
28	Cell B18=B13/B9*SQRT(1/B17+1/B14+((B7-B16)^2)/((B9^2)*B15))	

(b) $\text{mass P} = 1123\ \text{mL} \times 1122\ \cancel{\text{mL}} \times \dfrac{2.4\ \text{mg P}}{1000\ \cancel{\text{mL}}} \times \dfrac{50.0\ \cancel{\text{mL}}}{1.00\ \cancel{\text{mL}}} = 135\ \text{mg P}$

(c) conc. PO_4^{3-} =

$$\frac{2.4\ \cancel{\text{mg P}}}{\text{L}} \times \frac{50.0\ \cancel{\text{mL}}}{1\ \cancel{\text{mL}}} \times \frac{\cancel{\text{mmol P}}}{30.9738\ \cancel{\text{mg P}}} \times \frac{1\ \text{mmol PO}_4^{3-}}{\cancel{\text{mmol P}}} = 3.87\ \text{mM}$$

24-28.



	A	B
1	**Pb 24-28**	
2	Conc. mM	Measured *A*
3	2.00	0.065
4	6.00	0.205
5	10.00	0.338
6	14.00	0.474
7	18.00	0.598
8	unknown	0.402
9	**Regression Equation**	
10	Slope	0.03338
11	Intercept	0.00225
12	Concentration of unkown	11.97753
13	**Error Analysis**	
14	s_r (standard error in *y*)	0.00488
15	*N*	5.0
16	S_{xx}	160
17	*y* bar (avg. absorbance)	0.33600
18	*M*	1
19	s_c (std. deviation in *c*)	0.16186
20	**Spreadsheet Documentation**	
21	Cell B10=SLOPE(B3:B7,A3:A7)	
22	Cell B11=INTERCEPT(B3:B7,A3:A7)	
23	Cell B12=(B8-B11)/B10	
24	Cell B14=STEYX(B3:B7,A3:A7)	
25	Cell B15=COUNT(B3:B7)	
26	Cell B16=B15*VARP(A3:A7)	
27	Cell B17=AVERAGE(B3:B7)	
28	Cell B18= user entry	
29	Cell B19=B14/B10*SQRT(1/B18+1/B15+((B8-B17)^2)/((B10^2)*B16))	
30		

Rounding to keep only significant figures

$c_{\text{unk}} = 12.0 \pm 0.2$ μM

24-29. $[Cr_2O_7^{2-}]/\{[CrO_4^{2-}][H^+]^2 = 4.2 \times 10^{14}$

$[H^+] =$ antilog $(-5.60) = 2.51 \times 10^{-6}$

$[Cr_2O_7^{2-}] = c_{K_2Cr_2O_7} - [CrO_4^{2-}]/2$

$$\frac{c_{K_2Cr_2O_7} - 0.500[CrO_4^{2-}]}{[CrO_4^{2-}]^2 \times \left(2.51 \times 10^{-6}\right)^2} = 4.2 \times 10^{14}$$

$c_{K_2Cr_2O_7} - 0.500\,[CrO_4^{2-}] = 2.65 \times 10^3[CrO_4^{2-}]^2$

$[CrO_4^{2-}]^2 + 1.887\times10^{-4}[CrO_4^{2-}] - 3.774 \times 10^{-4}\,c_{K_2Cr_2O_7} = 0$

When $c_{K_2Cr_2O_7} = 4.00\times10^{-4}$

$[CrO_4^{2-}]^2 + 1.887\times10^{-4}[CrO_4^{2-}] - 1.510 \times 10^{-7} = 0$

$[CrO_4^{2-}] = 3.055 \times 10^{-4}$ M

$[Cr_2O_7^{2-}] = 4.00\times10^{-4} - 3.055 \times 10^{-4}/2 = 2.473 \times 10^{-4}$

$A_{345} = 1.84 \times 10^3 \times 3.055 \times 10^{-4} + 10.7 \times 10^2 \times 2.473 \times 10^{-4} = 0.827$

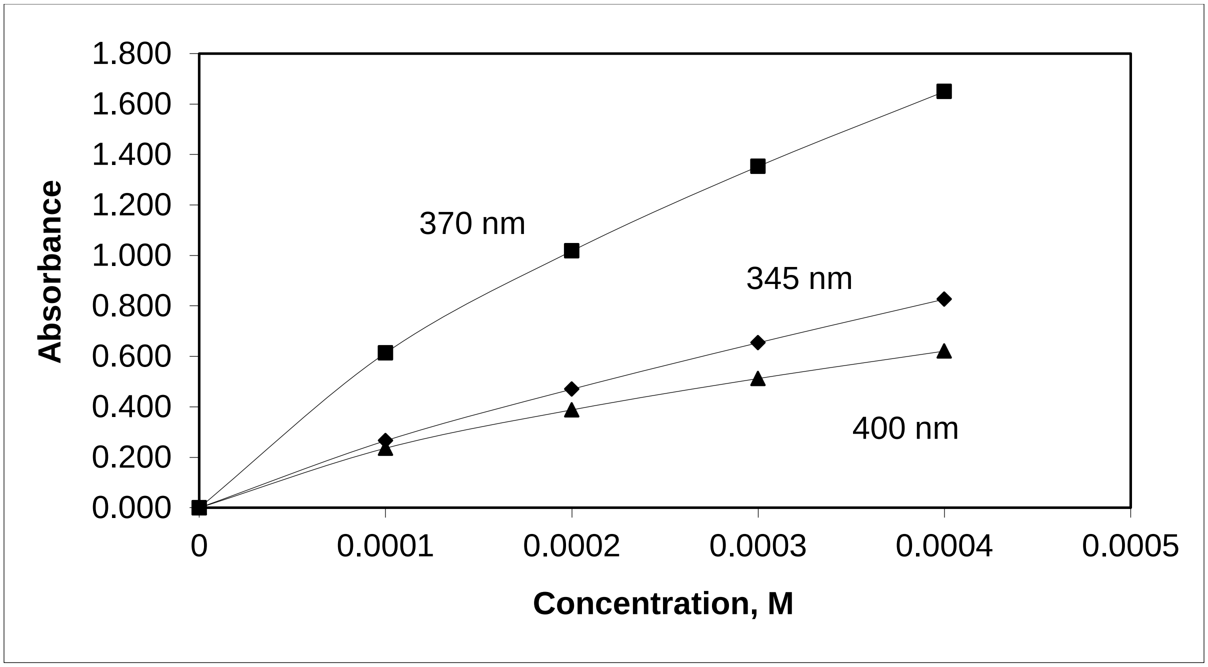
$A_{370} = 4.81 \times 10^3 \times 3.055 \times 10^{-4} + 7.28 \times 10^2 \times 2.473 \times 10^{-4} = 1.649$

$A_{400} = 1.88 \times 10^3 \times 3.055 \times 10^{-4} + 1.89 \times 10^2 \times 2.473 \times 10^{-4} = 0.621$

Proceeding in the same way, we obtain

$c_{K_2Cr_2O_7^{2-}}$	$[CrO_4^{2-}]$	$[Cr_2O_7^{2-}]$	A_{345}	A_{370}	A_{400}
4.00×10^{-4}	3.055×10^{-4}	2.473×10^{-4}	0.827	1.649	0.621
3.00×10^{-4}	2.551×10^{-4}	1.725×10^{-4}	0.654	1.353	0.512
2.00×10^{-4}	1.961×10^{-4}	1.019×10^{-4}	0.470	1.018	0.388
1.00×10^{-4}	1.216×10^{-4}	3.920×10^{-4}	0.266	0.613	0.236
0.0	0.0	0.0	0.000	0.000	0.000

Plotting these data clearly shows the deviations from linearity that occur



Chapter 25

25-1. **(a)** *Phototubes* consist of a single photoemissive surface (cathode) and an anode in an evacuated envelope. They exhibit low dark current, but have no inherent amplification. *Solid-state photodiodes* are semiconductor *pn*-junction devices that respond to incident light by forming electron-hole pairs. They are more sensitive than phototubes but less sensitive than photomultiplier tubes.

(b) *Phototubes* consist of a single photoemissive surface (cathode) and an anode in an evacuated envelope. They exhibit low dark current, but have no inherent amplification. *Photomultipliers* have built-in gains and thus have very high sensitivities. They suffer from somewhat larger dark currents.

(c) *Filters* isolate a single band of wavelengths. They provide low resolution wavelength selection suitable for quantitative work. *Monochromators* produce high resolution for qualitative and quantitative work. With monochromators, the wavelength can be varied continuously, whereas this is not possible with filters.

(d) A *conventional spectrophotometer* monitors a given narrow range of wavelengths determined by the orientation of the grating in the monochromator and the openings of the slits. This device can provide very high resolution wavelength selection, but is relatively slow when acquiring an absorption spectrum over a range of wavelengths due to the necessity of scanning the monochromator. A *diode-array spectrophotometer* simultaneously monitors a range of wavelengths determined by the dispersion of the grating monochromator and the width of the diode-array. This device allows very high-speed acquisition of an absorption spectrum over a range of wavelengths, but the wavelength resolution is limited by the dispersion of the monochromator and the separation between the detecting elements in the diode-array.

25-2. The *effective bandwidth of a monochromator* is the width in units of wavelength of the band of transmitted radiation measured at one half the height of the band.

25-3. Quantitative analyses can tolerate rather wide slits since measurements are usually carried out at a wavelength maximum where the slope of the spectrum $dA/d\lambda$ is relatively constant. On the other hand, qualitative analyses require narrow slits so that any fine structure in the spectrum will be resolved. This can allow differentiation of one compound from another.

25-4. Photons in the infrared region of the spectrum do not have sufficient energy to cause photoemission from the cathode of a photomultiplier.

25-5. *Tungsten/halogen lamps* contain a small amount of iodine in the evacuated quartz envelope that contains the tungsten filament. The iodine prolongs the life of the lamp and permits it to operate at a higher temperature. The iodine combines with gaseous tungsten that sublimes from the filament and causes the metal to be redeposited, thus adding to the life of the lamp.

25-6. **(a)** *Spectrophotometers* have monochromators for multiple wavelength operation and for procuring spectra while *photometers* utilize filters for fixed wavelength operation. While offering the advantage of multiple wavelength operation, spectrophotometers are substantially more complex and more expensive than photometers.

(b) A *spectrograph* uses a diffraction grating to disperse the spectrum, but contains no exit slit, allowing the dispersed spectrum to strike a multi-wavelength detector. A *polychromator* uses a diffraction grating to disperse the spectrum, but contains multiple exit slits, allowing several discrete wavelengths to be monitored simultaneously.

(c) Both a *monochromator* and a *polychromator* use a diffraction grating to disperse the spectrum, but a monochromator contains only one exit slit and detector while a polychromator contains multiple exit slits and detectors. A monochromator can be used to monitor one wavelength at a time while a polychromator can monitor several discrete wavelengths simultaneously.

(d) A *single-beam spectrophotometer* employs a fixed beam of radiation that irradiates first the solvent and then the analyte solution. In a *double-beam instrument* the solvent and solution are irradiated simultaneously or nearly so. The advantages of the double-beam instruments are freedom from problems arising from fluctuations in the source intensity due to drift in electronic circuits and easier adaptation to automatic spectral recording. The single-beam instrument offers the advantages of simplicity and lower cost.

25-7. **(a)** $\lambda_{\text{max}} = 2.90 \times 10^3 / T = 2.90 \times 10^3 / 4000 = 0.73\ \mu\text{m}$

(b) $\lambda_{\text{max}} = 2.90 \times 10^3 / 3000 = 0.97\ \mu\text{m}$

(c) $\lambda_{\text{max}} = 2.90 \times 10^3 / 2000 = 1.45\ \mu\text{m}$

(d) $\lambda_{\text{max}} = 2.90 \times 10^3 / 1000 = 2.90\ \mu\text{m}$

25-8. **(a)** $E_\text{t} = 5.69 \times 10^{-8}\ (4000)^4 = 1.46 \times 10^7\ \text{W/m}^2$

(b) $E_\text{t} = 5.69 \times 10^{-8}\ (3000)^4 = 4.61 \times 10^6\ \text{W/m}^2$

(c) $E_\text{t} = 5.69 \times 10^{-8}\ (2000)^4 = 9.10 \times 10^5\ \text{W/m}^2$

(d) $E_\text{t} = 5.69 \times 10^{-8}\ (1000)^4 = 5.69 \times 10^4\ \text{W/m}^2$

25-9. **(a)** $\lambda_{\max} = 2.90 \times 10^3 / 2870 = 1.01\ \mu\text{m}$ (1010 nm)

$\lambda_{\max} = 2.90 \times 10^3 / 3000 = 0.967\ \mu\text{m}$ (967 nm)

(b) $E_t = 5.69 \times 10^{-8}\ (2870)^4 \times (1\text{ m} / 100\text{ cm})^2 = 386\text{ W/cm}^2$

$E_t = 5.69 \times 10^{-8}\ (3000)^4 \times (1\text{ m} / 100\text{ cm})^2 = 461\text{ W/cm}^2$

25-10. As a minimum requirement, the radiation emitted by the source of a single-beam instrument must be stable for however long it takes to make the 0% *T* adjustment, the 100% *T* adjustment, and the measurement of *T* for the sample.

25-11. **(a)** The 0% transmittance is measured with no light reaching the detector and is a measure of the dark current.

(b) The 100% transmittance adjustment is made with a blank in the light path and measures the unattenuated source. It compensates for any absorption or reflection losses in the cell and optics.

25-12. Electrolyte concentration, pH, temperature.

25-13. Fourier transform IR spectrometers have the advantages over dispersive instruments of higher speed and sensitivity, better light-gathering power, more accurate and precise wavelength settings, simpler mechanical design, and elimination of stray light and IR emission.

25-14. **(a)** $\%T = (149 / 625) \times 100\% = 23.84\%$

$A = -\log(23.84\% / 100\%) = 0.623$

(b) Since A is proportional to concentration, at ½ concentration $A = 0.623 / 2 = 0.311$

$T = \text{antilog}(-A) = \text{antilog}(-0.311) = 0.488$

(c) Since A is proportional to light path, at twice the light path $A = 2 \times 0.623 = 1.246$

$T = \text{antilog}(-A) = \text{antilog}(-1.246) = 0.057$; %T = 5.7

25-15. **(a)** $\%T = (23.5/75.9) \times 100\% = 30.96\%$

(b) $A = -\log(30.96\%/100\%) = 0.509$

(c) Since A is proportional to concentration, at 1/3 concentration $A = 0.509/3 = 0.170$

$T = \text{antilog}(-A) = \text{antilog}(-0.170) = 0.677$

(d) $A = 2 \times 0.509 = 1.018$

$T = \text{antilog}(-A) = \text{antilog}(-1.018) = 0.096$

25-16. In a *deuterium lamp,* the input energy from the power source produces an excited deuterium molecule that dissociates into two atoms in the ground state and a photon of radiation. As the excited deuterium molecules relaxes, the quantized energy is distributed between the energy of the photon and the kinetic energies of the two deuterium atoms. The latter can vary from nearly zero to the original energy of the excited molecule. Therefore, the energy of the radiation, which is the difference between the quantized energy of the excited molecule and the kinetic energies of the atoms, can also vary continuously over the same range. Consequently, the emission spectrum is a continuum.

25-17. A *photon detector* produces a current or voltage as a result of the emission of electrons from a photosensitive surface when struck by photons. A *thermal detector* consists of a darkened surface to absorb infrared radiation and produce a temperature increase. A *thermal transducer* produces an electrical signal whose magnitude is related to the temperature and thus the intensity of the infrared radiation.

25-18. An *absorption spectrometer* requires a separate radiation source and a sample compartment that holds containers for the sample and blank. With an *emission spectrometer,* the sample is introduced directly into a hot plasma or flame where excitation and emission occur.

25-19. Basically, an *absorption photometer* and a *fluorescence photometer* consist of the same components. The basic difference is in the location of the detector. The detector in a fluorometer is positioned at an angle of 90^o to the direction of the beam from the source so that emission is detected rather than transmisson. In addition, a filter is often positioned in front of the detector to remove radiation from the excitation beam that may result from scattering or other nonfluorescence processes. In a transmission photometer, the detector is positioned in a line with the source, the filter, and the detector.

25-20. The performance characteristics of an interference filter include the wavelength of its transmittance peak, the percent transmission at the peak, and the effective bandwidth.

25-21. **(a)** *Transducer* indicates the type of detector that converts quantities, such as light intensity, pH, mass, and temperature, into electrical signals that can be subsequently amplified, manipulated, and finally converted into numbers proportional to the magnitude of the original quantity.

(b) The *dark current* is the small current that develops in a radiation transducer in the absence of radiation.

(c) A semiconductor containing unbonded electrons (e.g. produced by doping silicon with a Group V element) is termed an *n*-type semiconductor.

(d) The *majority carrier* in a semiconductor is the mobile charge carrier in either *n*-type or *p*-type materials. For *n*-type, the majority carrier is the electron, while in *p*-type, the majority carrier is a positively charged hole.

(e) A *depletion layer* results when a reverse bias is applied to a *pn*-junction type device. Majority carriers are drawn away from the junction leaving a nonconductive depletion layer.

(f) *Scattered radiation* in a monochromator is unwanted radiation that reaches the exit slit as a result of reflection and scattering. Its wavelength usually differs from that of the radiation reaching the slit from the dispersing element.

25-22. **(a)** $\lambda_{\max} = 2t\eta/\mathbf{n}$

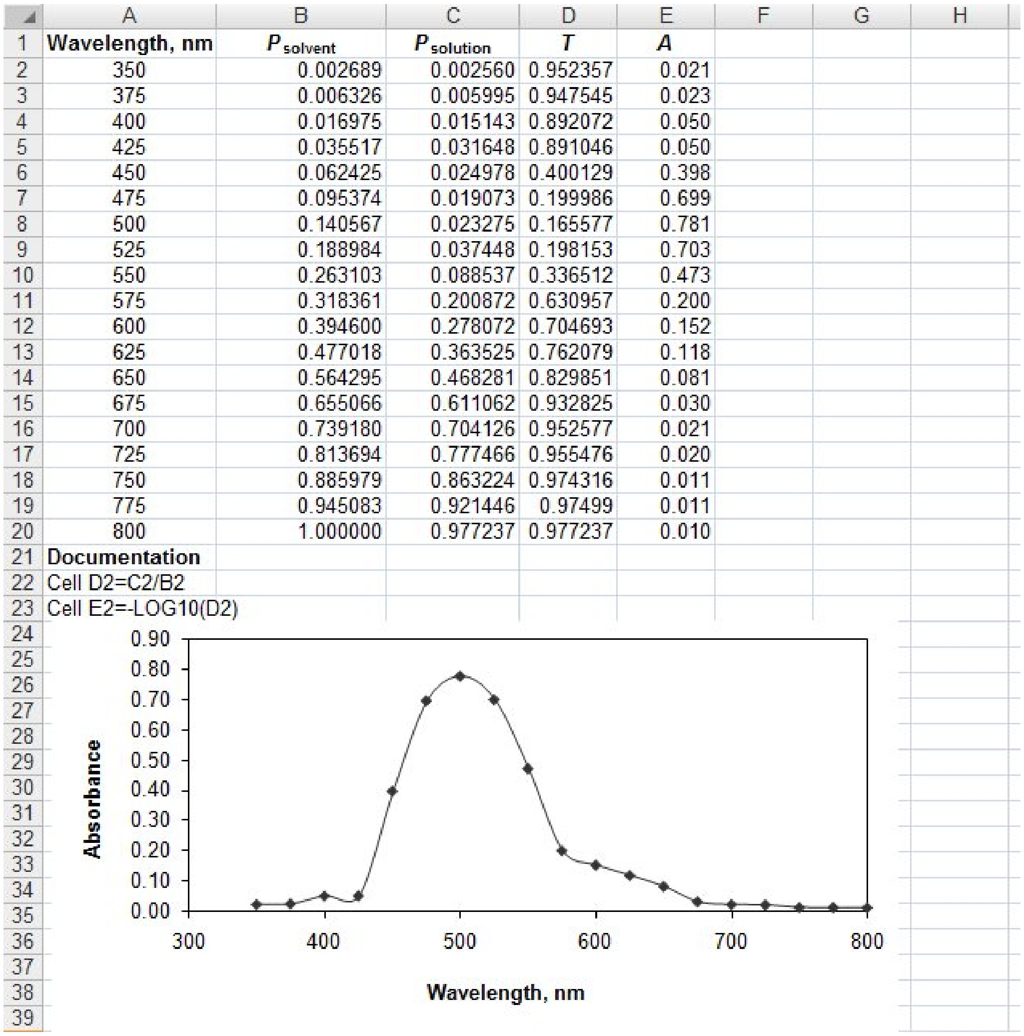
$t = \lambda_{\max}\,\mathbf{n}/(2\eta) = 4.54\ \mu\text{m}\ \times 1 / (2 \times 1.34) = 1.69\ \mu\text{m}$

(b) $\lambda_{\text{n}} = 2t\eta\ \mathbf{n}$

For $\mathbf{n} = 1, 2, 3, \ldots$

$\lambda_1 = 4.54\ \mu\text{m}$, $\lambda_2 = 2.27\ \mu\text{m}$, $\lambda_3 = 1.51\ \mu\text{m}$, etc.

25-23.



	A	B	C	D	E	F	G	H
1	**Wavelength, nm**	***P*$_{solvent}$**	***P*$_{solution}$**	***T***	***A***			
2	350	0.002689	0.002560	0.952357	0.021			
3	375	0.006326	0.005995	0.947545	0.023			
4	400	0.016975	0.015143	0.892072	0.050			
5	425	0.035517	0.031648	0.891046	0.050			
6	450	0.062425	0.024978	0.400129	0.398			
7	475	0.095374	0.019073	0.199986	0.699			
8	500	0.140567	0.023275	0.165577	0.781			
9	525	0.188984	0.037448	0.198153	0.703			
10	550	0.263103	0.088537	0.336512	0.473			
11	575	0.318361	0.200872	0.630957	0.200			
12	600	0.394600	0.278072	0.704693	0.152			
13	625	0.477018	0.363525	0.762079	0.118			
14	650	0.564295	0.468281	0.829851	0.081			
15	675	0.655066	0.611062	0.932825	0.030			
16	700	0.739180	0.704126	0.952577	0.021			
17	725	0.813694	0.777466	0.955476	0.020			
18	750	0.885979	0.863224	0.974316	0.011			
19	775	0.945083	0.921446	0.97499	0.011			
20	800	1.000000	0.977237	0.977237	0.010			
21	**Documentation**							
22	Cell D2=C2/B2							
23	Cell E2=-LOG10(D2)							

Chapter 26

26-1. **(a)** *Spectrophotometers* use a grating or a prism to provide narrow bands of radiation while *photometers* use filters for this purpose. The advantages of spectrophotometers are greater versatility and the ability to obtain entire spectra. The advantages of photometers are simplicity, ruggedness, higher light throughput and low cost.

(b) A *single-beam spectrophotometer* employs a fixed beam of radiation that irradiates first the solvent and then the analyte solution. In a *double-beam instrument* the solvent and solution are irradiated simultaneously or nearly so. The advantages of the double-beam instruments are freedom from problems arising from fluctuations in the source intensity due to drift in electronic circuits and easier adaptation to automatic spectral recording. The single-beam instrument offers the advantages of simplicity and lower cost.

(c) *Diode-array spectrophotometers* detect the entire spectral range essentially simultaneously and can produce a spectrum in less than a second. *Conventional spectrophotometers* require several minutes to scan the spectrum. Accordingly, diode-array instruments can be used to monitor processes that occur on fast time scales. Their resolution is usually lower than that of a conventional spectrophotometer.

26-2. As a minimum requirement, the radiation emitted by the source of a single-beam instrument must be stable for however long it takes to make the 0% T adjustment, the 100% T adjustment, and the measurement of T for the sample.

26-3. Electrolyte concentration, pH, temperature, nature of solvent, and interfering substances.

26-4. The multiple standard-addition method provides a built-in test for Beer's law adherence (linearity), whereas the single point method assumes adherence to Beer's law.

26-5. $A = \varepsilon\, b\, c$

$c_{\mathrm{min}} = A/\varepsilon b = 0.10/(9.32 \times 10^{3} \times 1.00) = 1.1 \times 10^{-5}$ M

$c_{\mathrm{max}} = A/\varepsilon b = 0.90/(9.32 \times 10^{3} \times 1.00) = 9.7 \times 10^{-5}$ M

26-6. $A = -\log(\%T/100\%) = \varepsilon bc$

$c_{\mathrm{min}} = -\log(\%T/100\%) / \varepsilon b = -\log(85\%/100\%)/(6.17 \times 10^{3} \times 1.00) = 1.1 \times 10^{-5}$ M

$c_{\mathrm{max}} = -\log(\%T/100\%)/\varepsilon b = -\log(7\%/100\%) / (6.17 \times 10^{3} \times 1.00) = 1.9 \times 10^{-4}$ M

26-7. $\log \varepsilon = 2.75$ $\varepsilon = 5.6 \times 10^{2}$

$c_{\mathrm{min}} = A/\varepsilon b = 0.100/(5.6 \times 10^{2} \times 1.50) = 1.2 \times 10^{-4}$ M

$c_{\mathrm{max}} = A/\varepsilon b = 2.000/(5.6 \times 10^{2} \times 1.50) = 2.4 \times 10^{-3}$ M

26-8. $\log \varepsilon = 3.812$ $\varepsilon = 6.49 \times 10^{3}$

$c_{\mathrm{min}} = A/\varepsilon b = 0.150/(6.49 \times 10^{3} \times 1.25) = 1.85 \times 10^{-5}$ M

$c_{\mathrm{max}} = A/\varepsilon b = 1.500/(6.49 \times 10^{3} \times 1.25) = 1.85 \times 10^{-4}$ M

26-9. **(a)** $T = 169$ mV/690 mV = 0.245

$A = -\log(0.245) = 0.611$

(b) Since A is proportional to concentration, at ½ concentration $A = 0.611/2 = 0.305$

$T = \mathrm{antilog}(-A) = \mathrm{antilog}(-0.305) = 0.495$

(c) Since A is proportional to light path, at twice the light path $A = 2 \times 0.611 = 1.222$

$T = \mathrm{antilog}(-A) = \mathrm{antilog}(-1.222) = 0.060$

26-10. **(a)** $\%T = (23.7 / 75.5) \times 100\% = 31.4\%$

(b) $A = -\log(31.4\% / 100\%) = 0.503$

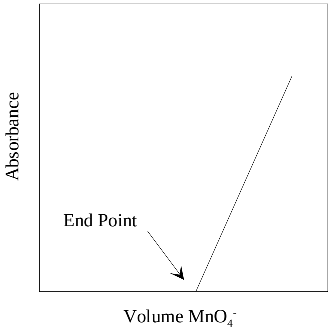
(c) Since A is proportional to concentration, at 1/3 concentration $A = 0.503/3 = 0.168$

$T = \mathrm{antilog}(-A) = \mathrm{antilog}(-0.168) = 0.679$

(d) $A = 2 \times 0.503 = 1.006$

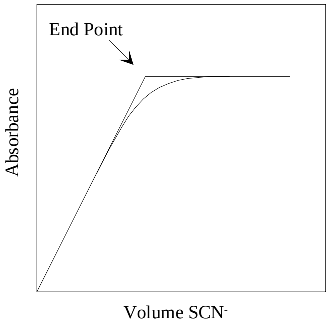
$T = \text{antilog}(-A) = \text{antilog}(-1.006) = 0.099$

26-11.



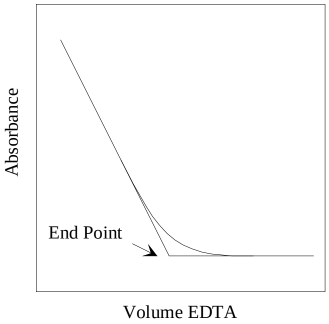
A green filter should be used because the red permanganate solution absorbs green light.

26-12.



A green filter is used because the red $Fe(SCN)^{2+}$ absorbs green light.

26-13.



The absorbance should decrease approximately linearly with titrant volume until the end point.

After the end point the absorbance becomes independent of titrant volume.

26-14. The data must be corrected for dilution so

$$A_{\text{corr}} = A_{500} \times \frac{10.00\ \text{mL} + V}{10.00\ \text{mL}}$$

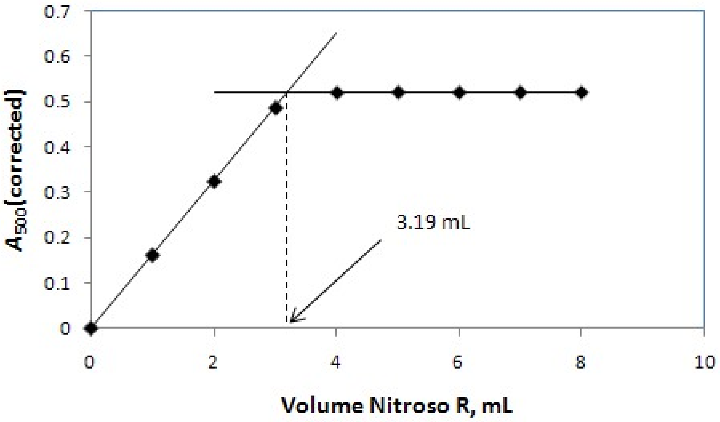
For 1.00 mL

$$A_{\text{corr}} = 0.147 \times \frac{10.00\ \text{mL} + 1.00\ \text{mL}}{10.00\ \text{mL}} = 0.162$$

A_{corr} is calculated for each volume in the same way and the following results are obtained.

Vol, mL	$\boldsymbol{A_{500}}$	$\boldsymbol{A_{\text{corr}}}$
0	0	0
1.00	0.147	0.162
2.00	0.271	0.325
3.00	0.375	0.488
4.00	0.371	0.519
5.00	0.347	0.521
6.00	0.325	0.520
7.00	0.306	0.520
8.00	0.289	0.520

A plot of these data is shown below.



The point of intersection of the linear portion of the plot can be determined graphically or evaluated by performing least-squares on the linear portions and solving the two linear simultaneous equations. Least-squares analysis gives the following results.

Points 1 to 4	Points 5 to 9
b_1 = slope = 1.626×10^{-1}	$b_2 = 1.300 \times 10^{-4}$
a_1 = intercept = 3.000×10^{-4}	$a_2 = 5.1928 \times 10^{-1}$
$y = a_1 + b_1x$	$y = a_2 + b_2x$

$$x = \frac{a_2 - a_1}{b_1 - b_2} = 3.19 \text{ mL}$$

$$\frac{3.19\text{ mL} \times 2.44 \times 10^{-4}\ \frac{\text{mmol Nitroso R}}{\text{mL}} \times \frac{1\text{ mmol Pd(II)}}{2\text{ mmol Nitroso R}}}{10.00\text{ mL solution}} = 3.89 \times 10^{-5}\text{ M}$$

26-15. For the unknown alone, we can write Beer's law in the form

$A_x = \varepsilon b c_x V_x / V_t$ where V_t is the total volume of solution.

For the solution after standard addition

$$A_s = \varepsilon b\,(c_xV_x + c_sV_s) / V_t$$

Dividing the first equation by the second gives

$$\frac{A_x}{A_s} = \frac{c_xV_x}{c_xV_x + c_sV_s}$$

$$A_xc_xV_x + A_xc_sV_s = A_sc_xV_x$$

This equation can be rearranged to give

$$c_x\,(A_sV_x - A_xV_x) = A_xc_sV_s$$

$$c_x = \frac{A_xc_sV_s}{V_x(A_s - A_x)}$$

We can substitute numerical values to give

$$c_x = \frac{0.398 \times 3.00 \times 5.00}{25.00(0.510 - 0.398)} = 2.132 \text{ ppm Co}$$

$$\frac{2.132 \text{ g Co}}{10^6 \text{ g soln}} \times 500 \text{ g soln} = 1.066 \times 10^{-3} \text{ g Co}$$

$$\text{percent Co} = \frac{1.066 \times 10^{-3} \text{ g Co}}{4.97 \text{ g sample}} \times 100\% = 0.0214\%$$

26-16. Applying the equation we developed in Solution 26-15 we write

$$c_x = \frac{0.231 \times 2.75 \times 5.00}{50.0(0.549 - 0.231)} = 0.200 \text{ ppm Fe}$$

26-17. $A_{365} = 3529 \times 1.00 \times c_{\text{Co}} + 3228 \times 1.00 \times c_{\text{Ni}}$

$A_{700} = 428.9 \times 1.00 \times c_{\text{Co}} + 0.00 \times 1.00 \times c_{\text{Ni}}$

$c_{\text{Co}} = A_{700}/ 428.9$ $\qquad$ $c_{\text{Ni}} = (A_{365} - 3529\ c_{\text{Co}}) / 3228$

Soln 1

$c_{\text{Co}} = 0.0235/428.9 = 5.48 \times 10^{-5}$ M

$c_{\text{Ni}} = (0.617 - 3529 \times 5.48 \times 10^{-5})/3228 = 1.31 \times 10^{-4}$ M

Proceeding in the same way, we obtain,

Soln 2

$c_{\text{Co}} = 1.66 \times 10^{-4}$ M $\qquad$ $c_{\text{Ni}} = 5.19 \times 10^{-5}$ M

Soln 3

$c_{\text{Co}} = 2.20 \times 10^{-4}$ M $\qquad$ $c_{\text{Ni}} = 4.41 \times 10^{-5}$ M

Soln 4

$c_{\text{Co}} = 3.43 \times 10^{-5}$ M $\qquad$ $c_{\text{Ni}} = 1.46 \times 10^{-4}$ M

Soln 5

$c_{\text{Co}} = 1.26 \times 10^{-4}$ M $\qquad$ $c_{\text{Ni}} = 7.46 \times 10^{-5}$ M

26-18.

$$A_{510} = 0.446 = 36400 \times 1.00 \times c_{\mathrm{Co}} + 5520 \times 1.00 \times c_{\mathrm{Ni}}$$

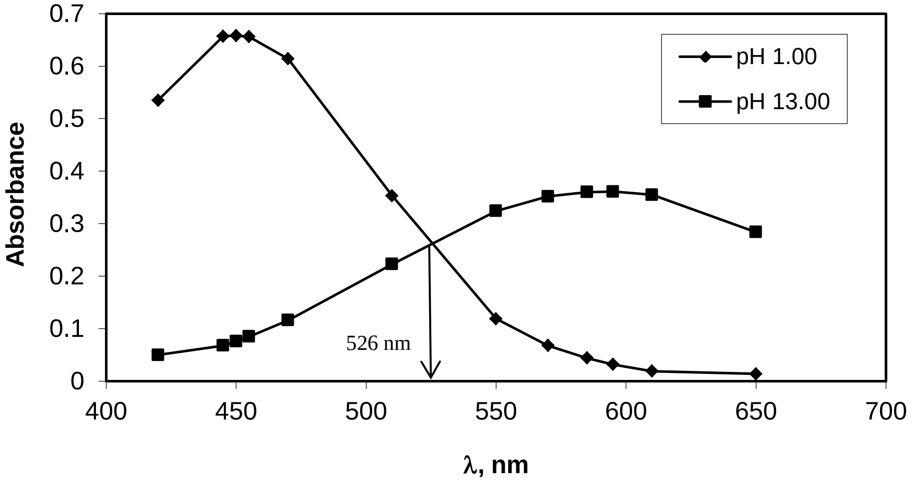
$$A_{656} = 0.326 = 1240 \times 1.00 \times c_{\mathrm{Co}} + 17500 \times 1.00 \times c_{\mathrm{Ni}}$$

$$c_{\mathrm{Co}} = 9.530\times10^{-6}\ \mathrm{M} \qquad c_{\mathrm{Ni}} = 1.795\times10^{-5}\ \mathrm{M}$$

$$c_{\mathrm{Co}} = \frac{50.0\ \mathrm{mL} \times 9.530 \times 10^{-6}\,\dfrac{\mathrm{mmol}}{\mathrm{mL}} \times \dfrac{50.0\ \mathrm{mL}}{25.0\ \mathrm{mL}} \times \dfrac{0.05893\ \mathrm{g\ Co}}{\mathrm{mmol}}}{0.425\ \mathrm{g}} \times 10^6\ \mathrm{ppm} = 132\ \mathrm{ppm}$$

$$c_{\mathrm{Ni}} = \frac{50.0\ \mathrm{mL} \times 1.795 \times 10^{-5}\,\dfrac{\mathrm{mmol}}{\mathrm{mL}} \times \dfrac{50.0\ \mathrm{mL}}{25.0\ \mathrm{mL}} \times \dfrac{0.05869\ \mathrm{g\ Ni}}{\mathrm{mmol}}}{0.425\ \mathrm{g}} \times 10^6\ \mathrm{ppm} = 248\ \mathrm{ppm}$$

26-19. The data are plotted in the figure that follows. The isosbestic point is estimated to be at 526 nm.



26-20. $\alpha_0 = \dfrac{[H_3O^+]}{[H_3O^+]+K_{HIn}}$ $\alpha_1 = 1 - \alpha_0$

$A_{450} = \varepsilon_{HIn} \times 1.00 \times [HIn] + \varepsilon_{In} \times 1.00 \times [In^-]$

$= \varepsilon_{HIn}\alpha_0 c_{In} + \varepsilon_{In}\alpha_1 c_{In}$

$= (\varepsilon_{HIn}\alpha_0 + \varepsilon_{In}\alpha_1)c_{In}$

where c_{In} is the analytical concentration of the indicator ($c_{In} = [HIn] + [In^-]$).

We may assume at pH 1.00 all of the indicator is present as HIn; at pH 13.0 it is all present as In^-. Therefore, from the data in Problem 26-19 we may write

$$\varepsilon_{HIn} = \frac{A_{450}}{bc_{HIn}} = \frac{0.658}{1.00 \times 8.00 \times 10^{-5}} = 8.22 \times 10^3 \text{ L mol}^{-1}\text{ cm}^{-1}$$

$$\varepsilon_{In} = \frac{A_{450}}{bc_{In}} = \frac{0.076}{1.00 \times 8.00 \times 10^{-5}} = 9.5 \times 10^2 \text{ L mol}^{-1}\text{ cm}^{-1}$$

(a) At pH = 4.92, $[H_3O^+] = 1.20\times10^{-5}$ M

$$\alpha_0 = \frac{1.20 \times 10^{-5}}{1.20 \times 10^{-5} + 4.80 \times 10^{-6}} = 0.714$$

$\alpha_1 = 1.000 - 0.714 = 0.286$

$A_{450} = (8.22 \times 10^3 \times 0.714 + 9.5 \times 10^2 \times 0.286) \times 8.00 \times 10^{-5} = 0.492$

	pH	**$[H_3O^+]$**	**α_0**	**α_1**	**A_{450}**
(a)	4.92	1.20×10^{-5}	0.714	0.286	0.492
(b)	5.46	3.47×10^{-6}	0.419	0.581	0.320
(c)	5.93	1.18×10^{-6}	0.197	0.803	0.190
(d)	6.16	6.92×10^{-7}	0.126	0.874	0.149

26-21. The approach is identical to that of Solution 26-20. At 595 nm and

at pH = 1.00, $\varepsilon_{HIn} = \dfrac{A_{595}}{bc_{HIn}} = \dfrac{0.032}{1.00 \times 8.00 \times 10^{-5}} = 4.0 \times 10^2 \text{ L mol}^{-1}\text{ cm}^{-1}$

at pH = 13.00, $\varepsilon_{\mathrm{In}} = \dfrac{A_{595}}{bc_{\mathrm{In}}} = \dfrac{0.361}{1.00 \times 8.00 \times 10^{-5}} = 4.51 \times 10^{3}\ \mathrm{L\ mol^{-1}\ cm^{-1}}$

(a) At pH = 5.30 and with 1.00-cm cells, $[H_3O^+] = 5.01 \times 10^{-6}$ M and

$$\alpha_0 = \frac{[H_3O^+]}{[H_3O^+] + K_{\mathrm{HIn}}} = \frac{5.01 \times 10^{-6}}{5.01 \times 10^{-6} + 4.80 \times 10^{-6}} = 0.511$$

$$\alpha_1 = 1 - \alpha_0 = 0.489$$

$$A_{595} = (\varepsilon_{\mathrm{HIn}}\alpha_0 + \varepsilon_{\mathrm{In}}\alpha_1)c_{\mathrm{In}}$$

$$A_{595} = (4.0 \times 10^{2} \times 0.511 + 4.51 \times 10^{3} \times 0.489) \times 1.25 \times 10^{-4} = 0.301$$

Similarly for parts (b) and (c)

	pH	**$[H_3O^+]$**	**α_0**	**α_1**	**A_{595}**
(a)	5.30	5.01×10^{-6}	0.511	0.489	0.301
(b)	5.70	2.00×10^{-6}	0.294	0.706	0.413
(c)	6.10	7.94×10^{-7}	0.142	0.858	0.491

26-22. In these solutions the concentrations of the two absorbers HIn and In^- must be determined by the analysis of mixtures, so

$$A_{450} = \varepsilon'_{\mathrm{HIn}}b[\mathrm{HIn}] + \varepsilon'_{\mathrm{In}}b[\mathrm{In}^-]$$

$$A_{595} = \varepsilon''_{\mathrm{HIn}}b[\mathrm{HIn}] + \varepsilon''_{\mathrm{In}}b[\mathrm{In}^-]$$

From the solutions to 26-20 and 26-21

$\varepsilon'_{\mathrm{HIn}} = 8.22\times10^{3}$ $\varepsilon'_{\mathrm{In}} = 9.5\times10^{2}$ $\varepsilon''_{\mathrm{HIn}} = 4.0\times10^{2}$ $\varepsilon''_{\mathrm{In}} = 4.51\times10^{3}$

Thus, $A_{450} = 0.344 = (8.22\times10^{3})[\mathrm{HIn}] + (9.5\times10^{2})[\mathrm{In}^-]$

$$A_{595} = 0.310 = (4.0\times10^{2})[\mathrm{HIn}] + (4.51\times10^{3})[\mathrm{In}^-]$$

Solving these equations gives

$[\mathrm{HIn}] = 3.42 \times 10^{-5}$ M and $[\mathrm{In}^-] = 6.57 \times 10^{-5}$ M

$$K_{\text{HIn}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}_3\text{O}^+] = K_{\text{HIn}}\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{(4.80\times10^{-6})(3.42\times10^{-5})}{6.57\times10^{-5}} = 2.50\times10^{-6}\text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.50\times10^{-6}) = 5.60$$

The results for all solutions are shown in the table that follows.

Solution	**[HIn]**	**[In$^-$]**	**pH**
A	3.42×10^{-5}	6.57×10^{-5}	5.60
B	5.69×10^{-5}	4.19×10^{-5}	5.19
C	7.70×10^{-5}	2.33×10^{-5}	4.80
D	1.72×10^{-5}	8.27×10^{-5}	6.00

26-23. **(a)** In this case,

$[\text{HIn}]/[\text{In}^-] = 3.00$ and $([\text{HIn}] + [\text{In}^-]) = 7.00\times10^{-5}$ M

so $[\text{HIn}] = 5.25\times10^{-5}$ M and $[\text{In}^-] = 1.75\times10^{-5}$ M

For each wavelength λ

$$A_\lambda = \varepsilon_{\text{HIn}}b[\text{HIn}] + \varepsilon_{\text{In}}b[\text{In}^-]$$

At λ = 595 nm, for example,

$\varepsilon_{\text{HIn}} = 4.0\times10^2$ and $\varepsilon_{\text{In}} = 4.51\times10^3$ (see solution 26-21)

$$A_{595} = 4.0\times10^2\times1.00\times5.25\times10^{-5} + 4.51\times10^3\times1.00\times1.75\times10^{-5} = 0.0999$$

Results for the other wavelengths are tabulated and plotted as follows after part (c)

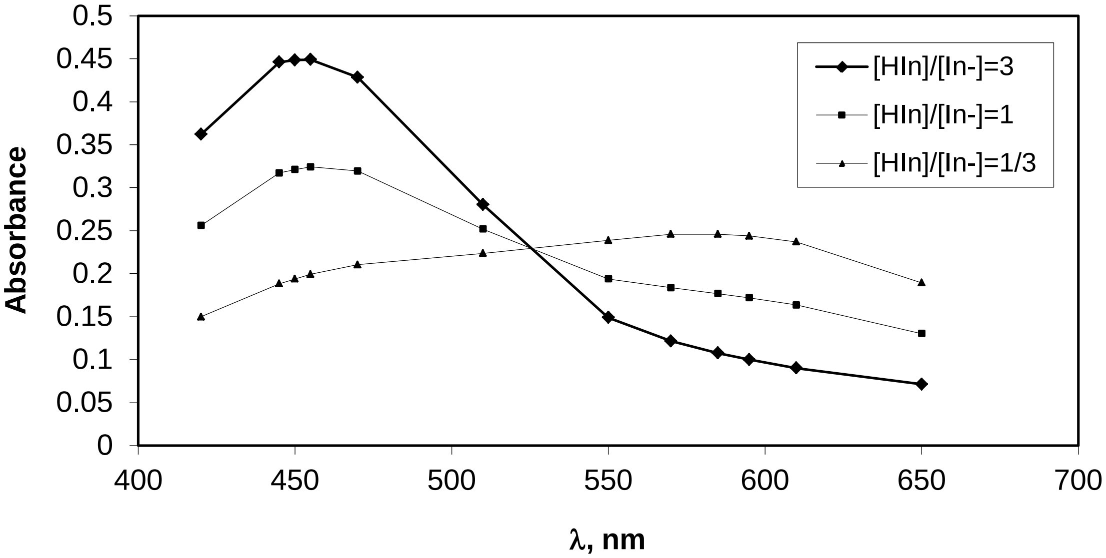
(b) Here, $[\text{HIn}] = [\text{In}^-] = 3.50\times10^{-5}$ M

Absorbance data are computed in the same way as in part (a), tabulated and plotted after part (c).

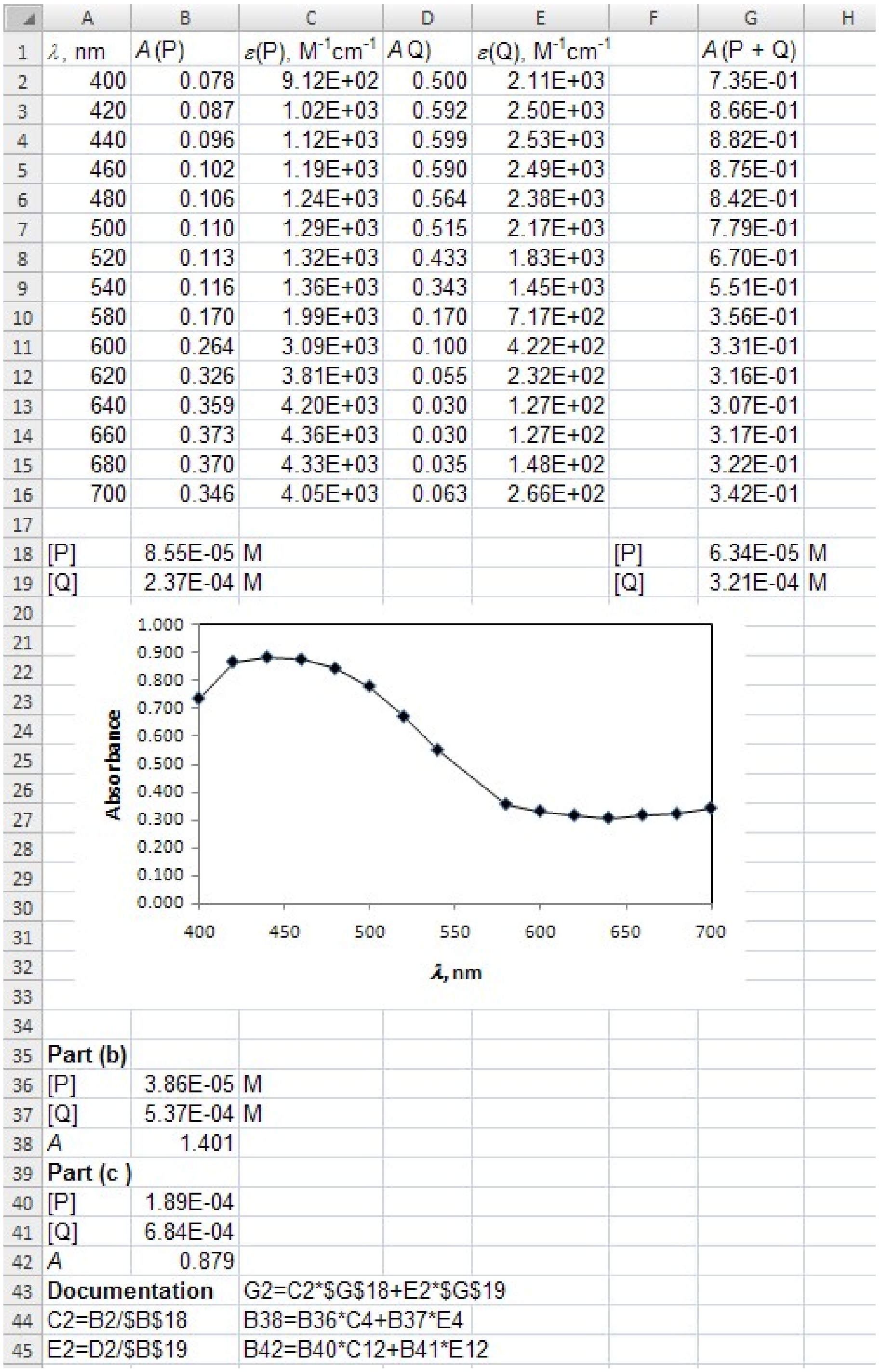
(c) Here, [HIn] = 1.75×10^{-5} M and $[\text{In}^-] = 5.25 \times 10^{-5}$ M

Absorbance data are computed in the same way as in part (a), tabulated and plotted.

λ, nm	ε_{HIn}	ε_{In}	*A* (3:1)	*A* (1:1)	*A* (1:3)
420	6688	625	0.362	0.256	0.150
445	8212	850	0.446	0.317	0.188
450	8225	950	0.448	0.321	0.194
455	8200	1062	0.449	0.324	0.199
470	7675	1450	0.428	0.319	0.210
510	4412	2788	0.280	0.252	0.224
550	1488	4050	0.149	0.194	0.239
570	850	4400	0.122	0.184	0.246
585	550	4500	0.108	0.177	0.244
595	400	4512	0.100	0.171	0.237
610	238	4438	0.090	0.164	0.189
650	175	3550	0.071	0.130	0.216



26-24.



	A	B	C	D	E	F	G	H
1	λ, nm	*A* (P)	ε(P), $M^{-1}cm^{-1}$	*A* Q)	ε(Q), $M^{-1}cm^{-1}$		*A* (P + Q)	
2	400	0.078	9.12E+02	0.500	2.11E+03		7.35E-01	
3	420	0.087	1.02E+03	0.592	2.50E+03		8.66E-01	
4	440	0.096	1.12E+03	0.599	2.53E+03		8.82E-01	
5	460	0.102	1.19E+03	0.590	2.49E+03		8.75E-01	
6	480	0.106	1.24E+03	0.564	2.38E+03		8.42E-01	
7	500	0.110	1.29E+03	0.515	2.17E+03		7.79E-01	
8	520	0.113	1.32E+03	0.433	1.83E+03		6.70E-01	
9	540	0.116	1.36E+03	0.343	1.45E+03		5.51E-01	
10	580	0.170	1.99E+03	0.170	7.17E+02		3.56E-01	
11	600	0.264	3.09E+03	0.100	4.22E+02		3.31E-01	
12	620	0.326	3.81E+03	0.055	2.32E+02		3.16E-01	
13	640	0.359	4.20E+03	0.030	1.27E+02		3.07E-01	
14	660	0.373	4.36E+03	0.030	1.27E+02		3.17E-01	
15	680	0.370	4.33E+03	0.035	1.48E+02		3.22E-01	
16	700	0.346	4.05E+03	0.063	2.66E+02		3.42E-01	
17								
18	[P]	8.55E-05	M			[P]	6.34E-05	M
19	[Q]	2.37E-04	M			[Q]	3.21E-04	M
35	**Part (b)**							
36	[P]	3.86E-05	M					
37	[Q]	5.37E-04	M					
38	*A*	1.401						
39	**Part (c)**							
40	[P]	1.89E-04						
41	[Q]	6.84E-04						
42	*A*	0.879						
43	**Documentation**		G2=C2*$G$18+E2*$G$19					
44	C2=B2/$B$18		B38=B36*C4+B37*E4					
45	E2=D2/$B$19		B42=B40*C12+B41*E12					

26-25. $A_{440} = \varepsilon'_{\mathrm{P}} b c_{\mathrm{P}} + \varepsilon'_{\mathrm{Q}} b c_{\mathrm{Q}}$ $\quad b = 1.00$ cm

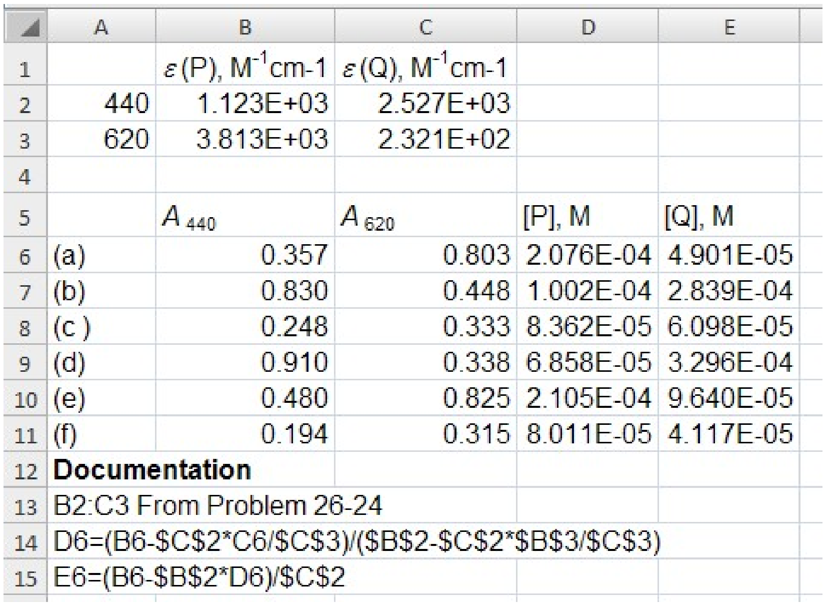
$$A_{620} = \varepsilon''_{\mathrm{P}} b c_{\mathrm{P}} + \varepsilon''_{\mathrm{Q}} b c_{\mathrm{Q}}$$

$$c_{\mathrm{P}} = \frac{A_{440} - \varepsilon'_{\mathrm{Q}} c_{\mathrm{Q}}}{\varepsilon'_{\mathrm{P}}}$$

Substituting for c_{P} in the second equation gives

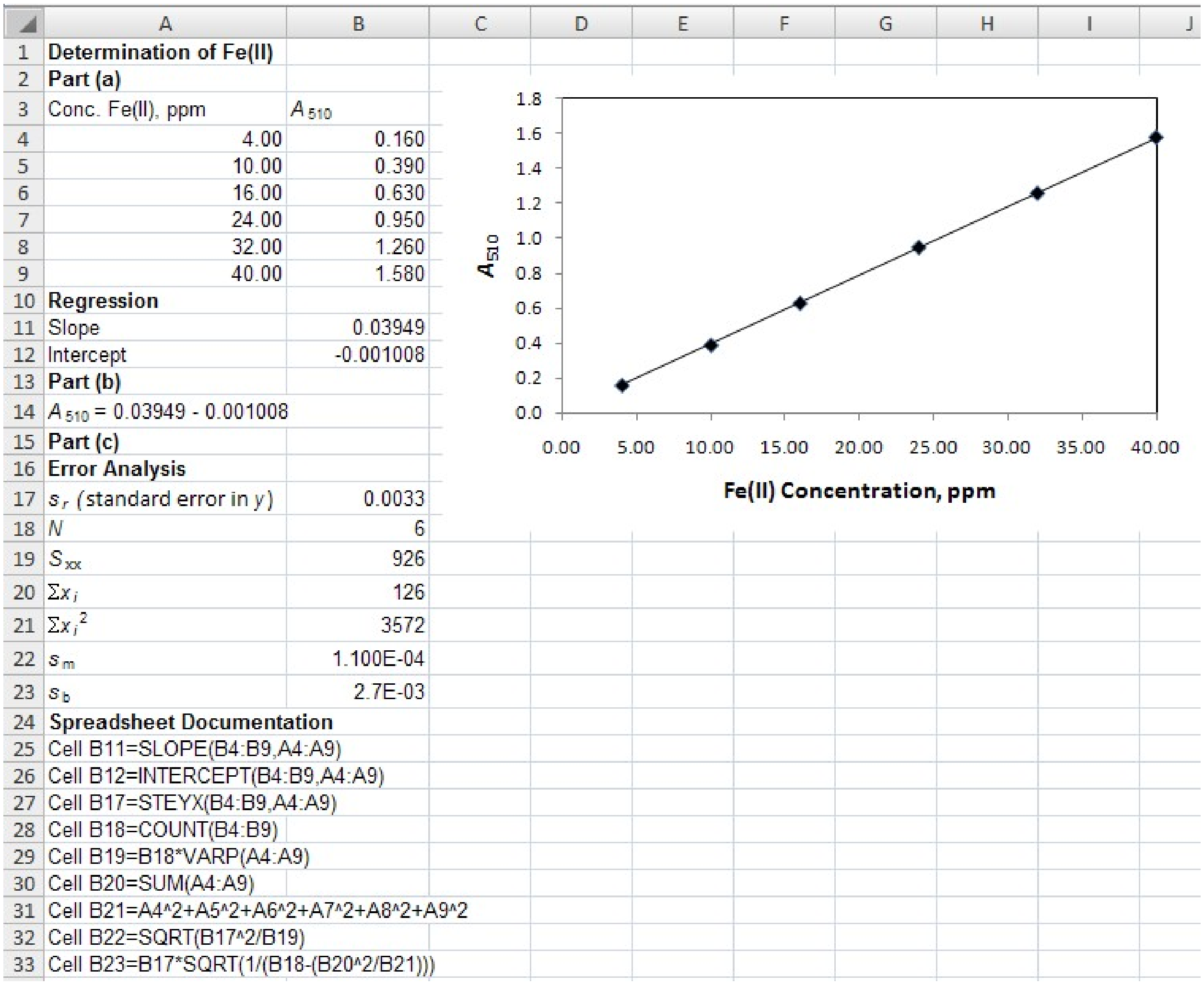
$$A_{620} = \varepsilon''_{\mathrm{P}} \left[\frac{A_{440} - \varepsilon'_{\mathrm{Q}} c_{\mathrm{Q}}}{\varepsilon'_{\mathrm{P}}} \right] + \varepsilon''_{\mathrm{Q}} c_{\mathrm{Q}}$$

We then solve for c_{Q} and c_{P} as in the spreadsheet



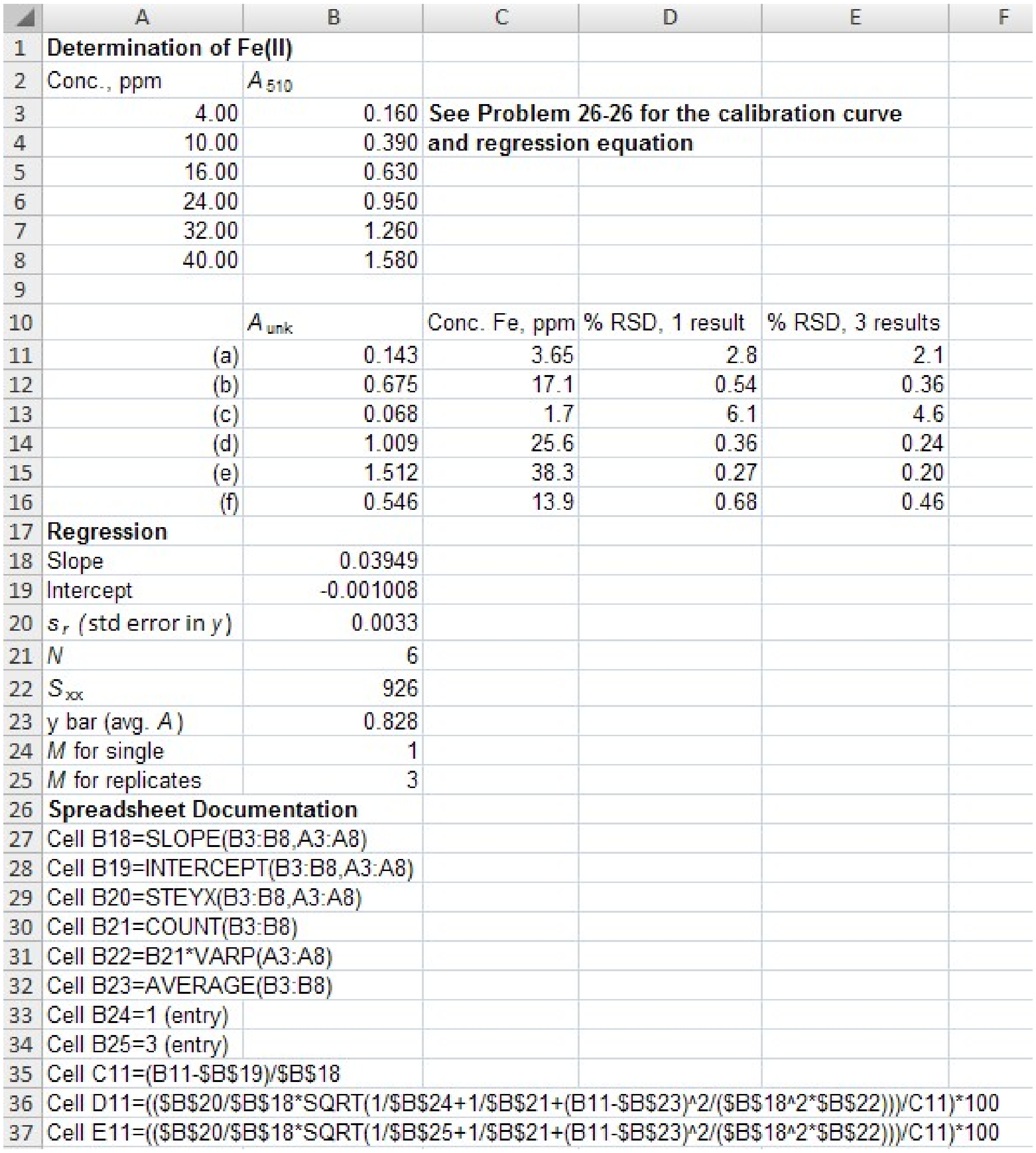
	A	B	C	D	E
1		ε(P), M^{-1}cm-1	ε(Q), M^{-1}cm-1		
2	440	1.123E+03	2.527E+03		
3	620	3.813E+03	2.321E+02		
4					
5		A_{440}	A_{620}	[P], M	[Q], M
6	(a)	0.357	0.803	2.076E-04	4.901E-05
7	(b)	0.830	0.448	1.002E-04	2.839E-04
8	(c)	0.248	0.333	8.362E-05	6.098E-05
9	(d)	0.910	0.338	6.858E-05	3.296E-04
10	(e)	0.480	0.825	2.105E-04	9.640E-05
11	(f)	0.194	0.315	8.011E-05	4.117E-05
12	**Documentation**				
13	B2:C3 From Problem 26-24				
14	D6=(B6-$C$2*C6/$C$3)/($B$2-$C$2*$B$3/$C$3)				
15	E6=(B6-$B$2*D6)/$C$2				

26-26.



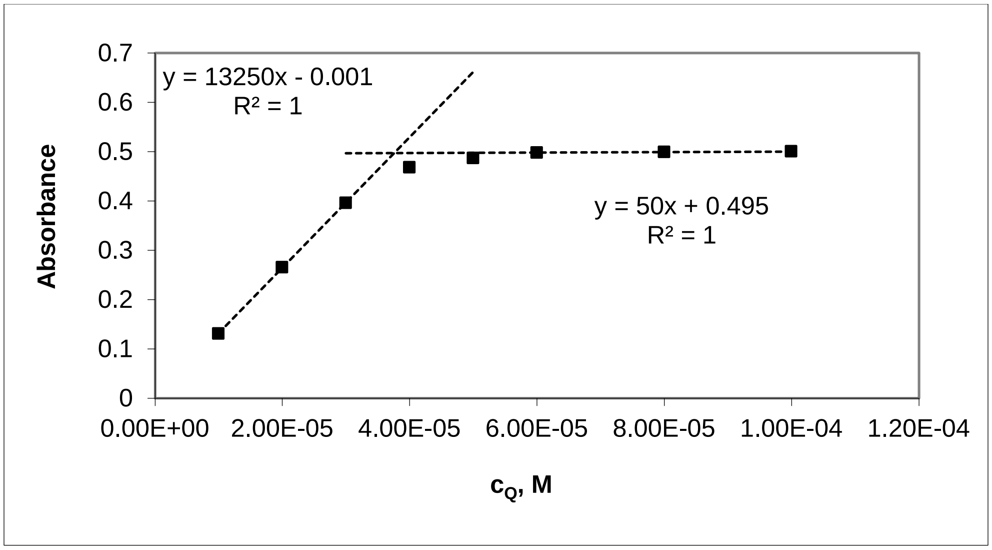
	A	B
1	**Determination of Fe(II)**	
2	**Part (a)**	
3	Conc. Fe(II), ppm	A_{510}
4	4.00	0.160
5	10.00	0.390
6	16.00	0.630
7	24.00	0.950
8	32.00	1.260
9	40.00	1.580
10	**Regression**	
11	Slope	0.03949
12	Intercept	-0.001008
13	**Part (b)**	
14	A_{510} = 0.03949 - 0.001008	
15	**Part (c)**	
16	**Error Analysis**	
17	s_r (standard error in y)	0.0033
18	N	6
19	S_{xx}	926
20	Σx_i	126
21	Σx_i^2	3572
22	s_m	1.100E-04
23	s_b	2.7E-03
24	**Spreadsheet Documentation**	
25	Cell B11=SLOPE(B4:B9,A4:A9)	
26	Cell B12=INTERCEPT(B4:B9,A4:A9)	
27	Cell B17=STEYX(B4:B9,A4:A9)	
28	Cell B18=COUNT(B4:B9)	
29	Cell B19=B18*VARP(A4:A9)	
30	Cell B20=SUM(A4:A9)	
31	Cell B21=A4^2+A5^2+A6^2+A7^2+A8^2+A9^2	
32	Cell B22=SQRT(B17^2/B19)	
33	Cell B23=B17*SQRT(1/(B18-(B20^2/B21)))	

26-27.



	A	B	C	D	E	F
1	**Determination of Fe(II)**					
2	Conc., ppm	A_{510}				
3	4.00	0.160	**See Problem 26-26 for the calibration curve**			
4	10.00	0.390	**and regression equation**			
5	16.00	0.630				
6	24.00	0.950				
7	32.00	1.260				
8	40.00	1.580				
9						
10		A_{unk}	Conc. Fe, ppm	% RSD, 1 result	% RSD, 3 results	
11	(a)	0.143	3.65	2.8	2.1	
12	(b)	0.675	17.1	0.54	0.36	
13	(c)	0.068	1.7	6.1	4.6	
14	(d)	1.009	25.6	0.36	0.24	
15	(e)	1.512	38.3	0.27	0.20	
16	(f)	0.546	13.9	0.68	0.46	
17	**Regression**					
18	Slope	0.03949				
19	Intercept	-0.001008				
20	s_r (std error in y)	0.0033				
21	N	6				
22	S_{xx}	926				
23	y bar (avg. A)	0.828				
24	M for single	1				
25	M for replicates	3				
26	**Spreadsheet Documentation**					
27	Cell B18=SLOPE(B3:B8,A3:A8)					
28	Cell B19=INTERCEPT(B3:B8,A3:A8)					
29	Cell B20=STEYX(B3:B8,A3:A8)					
30	Cell B21=COUNT(B3:B8)					
31	Cell B22=B21*VARP(A3:A8)					
32	Cell B23=AVERAGE(B3:B8)					
33	Cell B24=1 (entry)					
34	Cell B25=3 (entry)					
35	Cell C11=(B11-$B$19)/$B$18					
36	Cell D11=(($B$20/$B$18*SQRT(1/$B$24+1/$B$21+(B11-$B$23)^2/($B$18^2*$B$22)))/C11)*100					
37	Cell E11=(($B$20/$B$18*SQRT(1/$B$25+1/$B$21+(B11-$B$23)^2/($B$18^2*$B$22)))/C11)*100					

26-28. Plotting the data in the problem gives

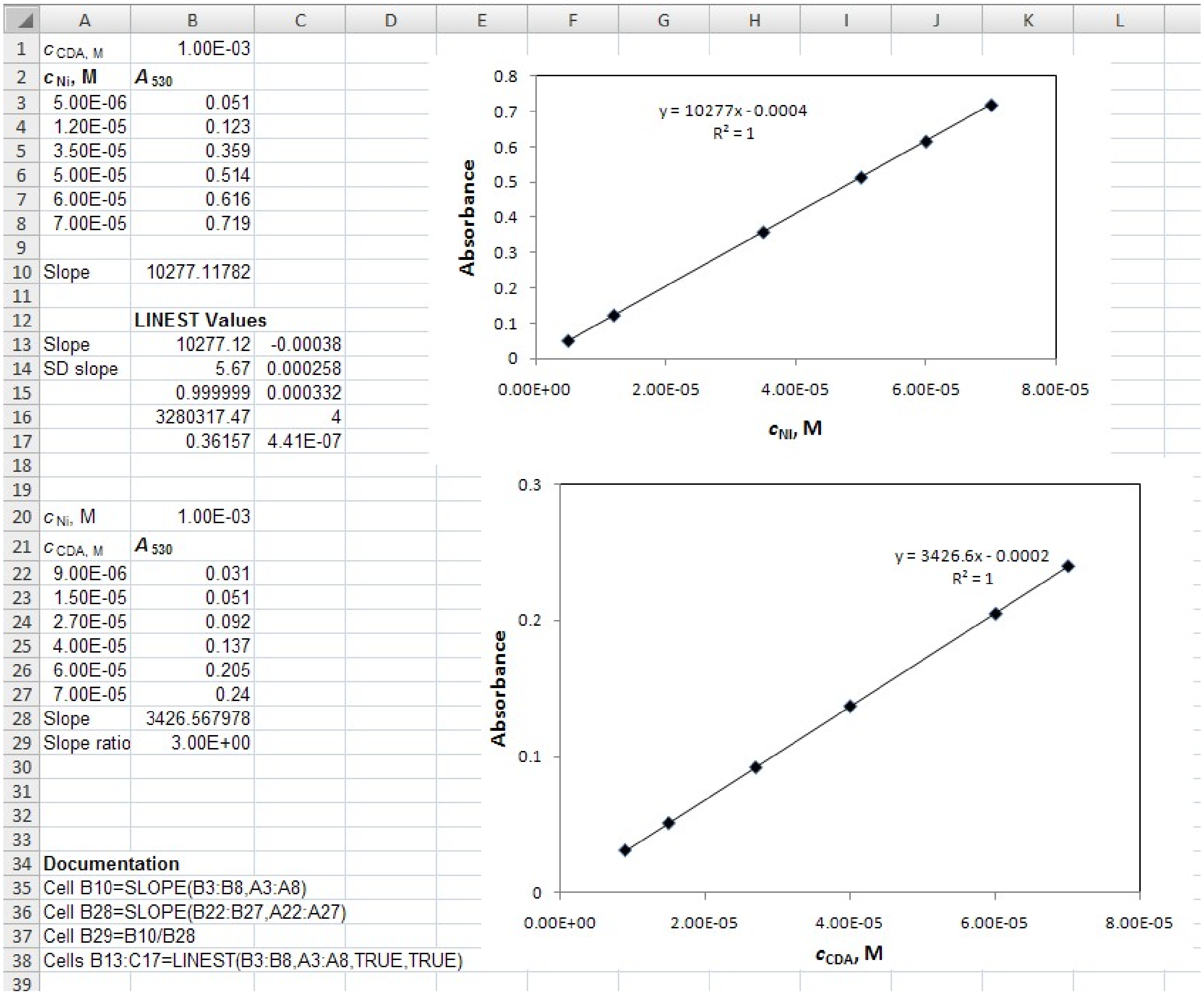


Solving for the crossing point by using the 2 best fit equations gives, $c_Q = 3.76 \times 10^{-5}$ M.

(a) Since $c_{Al} = 3.7\times10^{-5}$ M and no more complex forms after $c_Q = 3.76\times10^{-5}$ M, the complex must be 1:1, or AlQ^{2+}.

(b) ε for $AlQ^{2+} = (0.500)/(3.7 \times 10^{-5}) = 1.4 \times 10^4$ L mol^{-1} cm^{-1}

26-29.

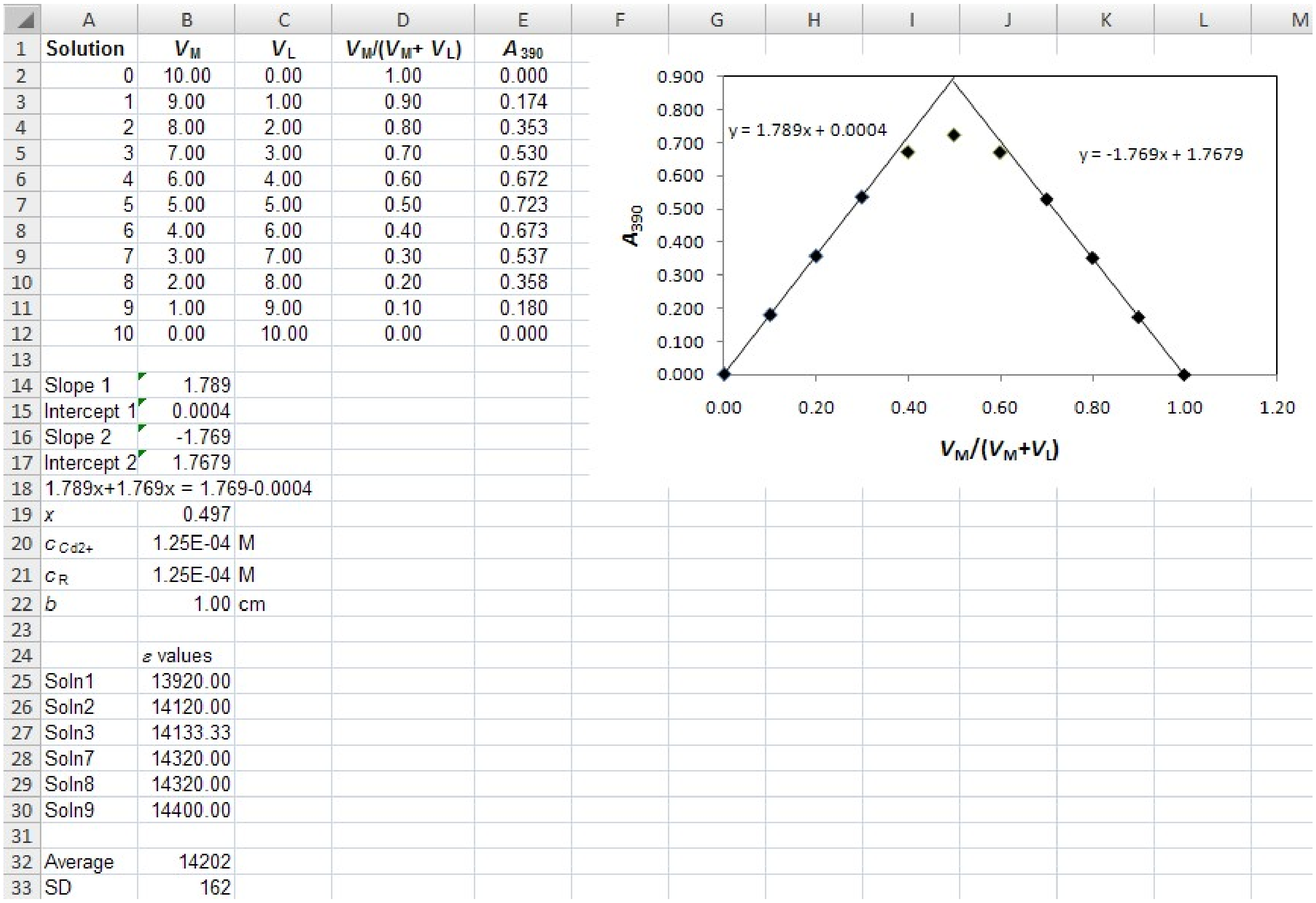


	A	B	C
1	$c_{CDA, M}$	1.00E-03	
2	c_{Ni}, M	A_{530}	
3	5.00E-06	0.051	
4	1.20E-05	0.123	
5	3.50E-05	0.359	
6	5.00E-05	0.514	
7	6.00E-05	0.616	
8	7.00E-05	0.719	
9			
10	Slope	10277.11782	
11			
12		LINEST Values	
13	Slope	10277.12	-0.00038
14	SD slope	5.67	0.000258
15		0.999999	0.000332
16		3280317.47	4
17		0.36157	4.41E-07
18			
19			
20	c_{Ni}, M	1.00E-03	
21	$c_{CDA, M}$	A_{530}	
22	9.00E-06	0.031	
23	1.50E-05	0.051	
24	2.70E-05	0.092	
25	4.00E-05	0.137	
26	6.00E-05	0.205	
27	7.00E-05	0.24	
28	Slope	3426.567978	
29	Slope ratio	3.00E+00	
30			
31			
32			
33			
34	Documentation		
35	Cell B10=SLOPE(B3:B8,A3:A8)		
36	Cell B28=SLOPE(B22:B27,A22:A27)		
37	Cell B29=B10/B28		
38	Cells B13:C17=LINEST(B3:B8,A3:A8,TRUE,TRUE)		
39			

(a) Based on the slope ratio, the complex ratio is 1:3 and the formula is $Ni(CDA)_3^{2+}$

(b) The molar absorptivity is obtained directly from the LINEST values (Slope and SD slope) for the first plot. Thus, $\varepsilon = 10277 \pm 6$

26-30.



	A	B	C	D	E
1	Solution	V_M	V_L	$V_M/(V_M+ V_L)$	A_{390}
2	0	10.00	0.00	1.00	0.000
3	1	9.00	1.00	0.90	0.174
4	2	8.00	2.00	0.80	0.353
5	3	7.00	3.00	0.70	0.530
6	4	6.00	4.00	0.60	0.672
7	5	5.00	5.00	0.50	0.723
8	6	4.00	6.00	0.40	0.673
9	7	3.00	7.00	0.30	0.537
10	8	2.00	8.00	0.20	0.358
11	9	1.00	9.00	0.10	0.180
12	10	0.00	10.00	0.00	0.000
13					
14	Slope 1	1.789			
15	Intercept 1	0.0004			
16	Slope 2	-1.769			
17	Intercept 2	1.7679			
18	1.789x+1.769x = 1.769-0.0004				
19	*x*	0.497			
20	c_{Cd2+}	1.25E-04	M		
21	c_R	1.25E-04	M		
22	*b*	1.00	cm		
23					
24		ε values			
25	Soln1	13920.00			
26	Soln2	14120.00			
27	Soln3	14133.33			
28	Soln7	14320.00			
29	Soln8	14320.00			
30	Soln9	14400.00			
31					
32	Average	14202			
33	SD	162			

(a) The two lines intercept at V_M / (V_M + V_L) = 0.5 (Cell B19). The Cd^{2+} to R ratio is 1:1.

(b) The molar absorptivities can be obtained from solutions 1-3 where the reagent is limiting and solutions 7-9 where the metal is limiting. Rounding the results in Cells B32 and B33 the average $\varepsilon = 1400 \pm 200$ L mol^{-1} cm^{-1}

(c) The absorbance at the volume ratio where the lines intersect is $A = 0.723$. Thus,

$[CdR] = (0.723)/(14202) = 5.09 \times 10^{-5}$ M

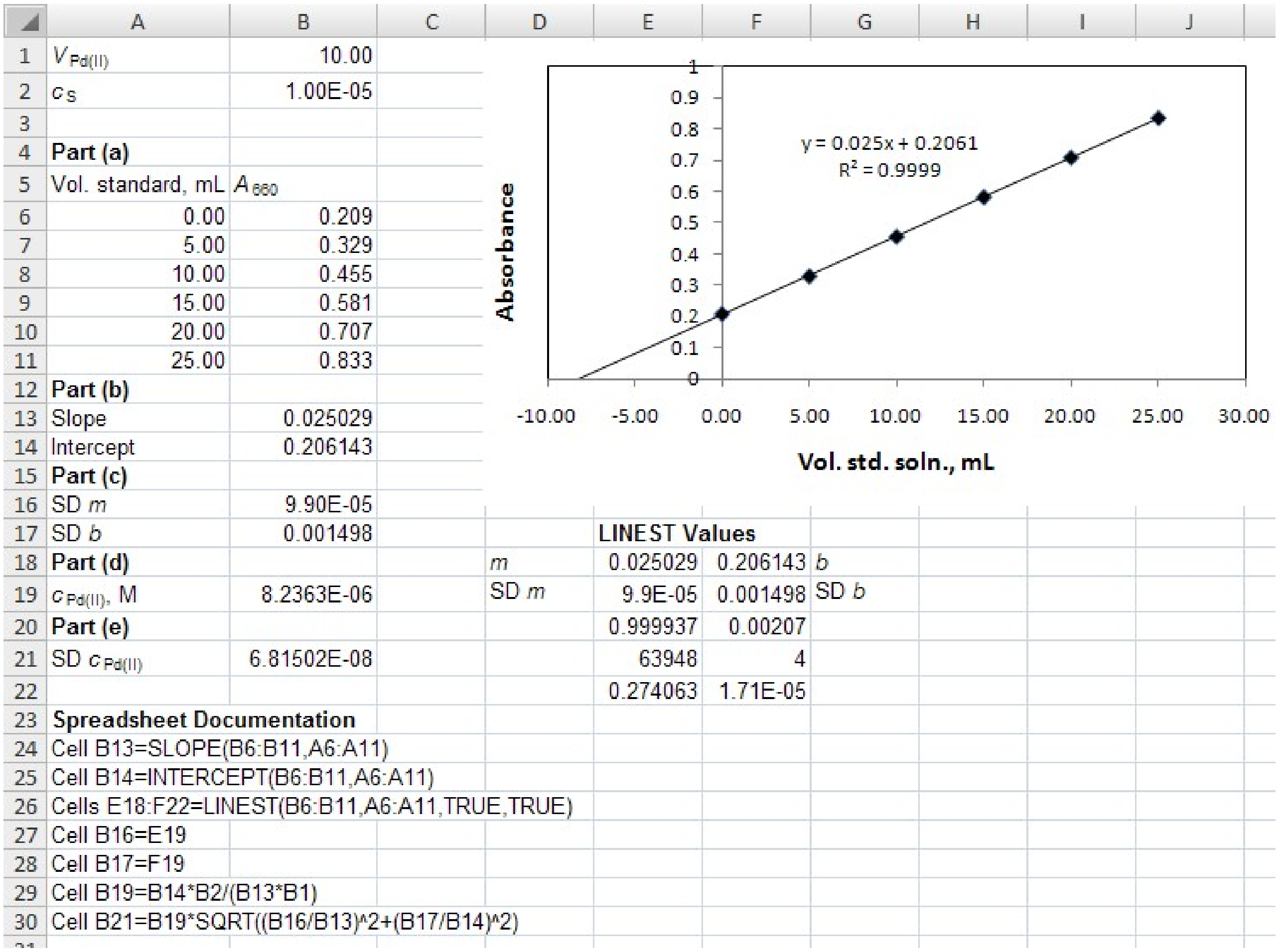
$[Cd^{2+}] = [(5.00 \text{ mL})(1.25 \times 10^{-4} \text{ mmol/mL}) - (10.00 \text{ mL})(5.09 \times 10^{-5} \text{ mmol/mL})]/(10.00 \text{ mL})$

$= 1.16 \times 10^{-5}$ M

$$[\text{R}] = [\text{Cd}^{2+}] = 1.16 \times 10^{-5}\ \text{M}$$

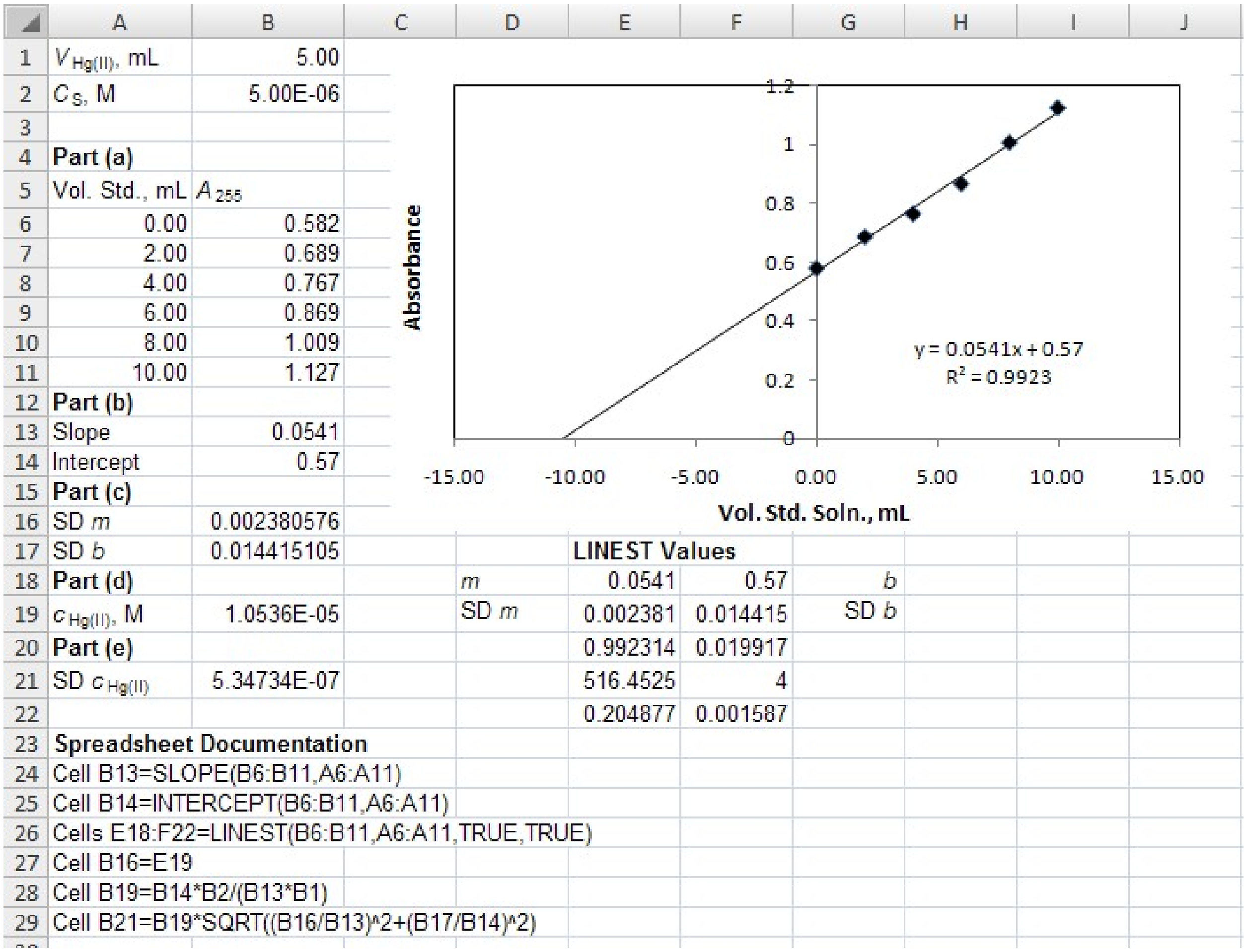
$$K_\text{f} = \frac{[\text{CdR}]}{[\text{Cd}^{2+}][\text{R}]} = \frac{\left(5.09 \times 10^{-5}\right)}{\left(1.16 \times 10^{-5}\right)^2} = 3.78 \times 10^5$$

26-31.



	A	B	C	D	E	F	G	H	I	J
1	$V_{\text{Pd(II)}}$	10.00								
2	c_S	1.00E-05								
3										
4	**Part (a)**									
5	Vol. standard, mL	A_{660}								
6	0.00	0.209								
7	5.00	0.329								
8	10.00	0.455								
9	15.00	0.581								
10	20.00	0.707								
11	25.00	0.833								
12	**Part (b)**									
13	Slope	0.025029								
14	Intercept	0.206143								
15	**Part (c)**									
16	SD *m*	9.90E-05								
17	SD *b*	0.001498			**LINEST Values**					
18	**Part (d)**			*m*	0.025029	0.206143	*b*			
19	$c_{\text{Pd(II)}}$, M	8.2363E-06		SD *m*	9.9E-05	0.001498	SD *b*			
20	**Part (e)**				0.999937	0.00207				
21	SD $c_{\text{Pd(II)}}$	6.81502E-08			63948	4				
22					0.274063	1.71E-05				
23	**Spreadsheet Documentation**									
24	Cell B13=SLOPE(B6:B11,A6:A11)									
25	Cell B14=INTERCEPT(B6:B11,A6:A11)									
26	Cells E18:F22=LINEST(B6:B11,A6:A11,TRUE,TRUE)									
27	Cell B16=E19									
28	Cell B17=F19									
29	Cell B19=B14*B2/(B13*B1)									
30	Cell B21=B19*SQRT((B16/B13)^2+(B17/B14)^2)									

26-32.



	A	B	C	D	E	F	G
1	$V_{Hg(II)}$, mL	5.00					
2	c_S, M	5.00E-06					
3							
4	**Part (a)**						
5	Vol. Std., mL	A_{255}					
6	0.00	0.582					
7	2.00	0.689					
8	4.00	0.767					
9	6.00	0.869					
10	8.00	1.009					
11	10.00	1.127					
12	**Part (b)**						
13	Slope	0.0541					
14	Intercept	0.57					
15	**Part (c)**						
16	SD *m*	0.002380576					
17	SD *b*	0.014415105			**LINEST Values**		
18	**Part (d)**			*m*	0.0541	0.57	*b*
19	$c_{Hg(II)}$, M	1.0536E-05		SD *m*	0.002381	0.014415	SD *b*
20	**Part (e)**				0.992314	0.019917	
21	SD $c_{Hg(II)}$	5.34734E-07			516.4525	4	
22					0.204877	0.001587	
23	**Spreadsheet Documentation**						
24	Cell B13=SLOPE(B6:B11,A6:A11)						
25	Cell B14=INTERCEPT(B6:B11,A6:A11)						
26	Cells E18:F22=LINEST(B6:B11,A6:A11,TRUE,TRUE)						
27	Cell B16=E19						
28	Cell B19=B14*B2/(B13*B1)						
29	Cell B21=B19*SQRT((B16/B13)^2+(B17/B14)^2)						

26-33. From Figure 26F-2, the frequencies of the band maxima are estimated to be:

(1) 740 cm^{-1} C-Cl stretch

(2) 1270 cm^{-1} CH_2 wagging

(3) 2900 cm^{-1} Aliphatic C-H stretch.

Chapter 27

27-1. **(a)** *Fluorescence* is a photoluminescence process in which atoms or molecules are excited by absorption of electromagnetic radiation and then relax to the ground state, giving up their excess energy as photons. The transition is from the lowest lying excited singlet state to the ground singlet state.

(b) *Vibrational relaxation* occurs when excited species collide with molecules, such as the solvent, and in doing so lose energy without emission of electromagnetic radiation. The energy of the excited species is decreased by an amount equal to the quantity of vibrational energy transferred.

(c) *Internal conversion* is the nonradiative relaxation of a molecule from a low energy vibrational level of an excited electronic state to a high energy vibrational level of a lower electronic state.

(d) *Phosphorescence* is a photoluminescence process in which atoms or molecules are excited by absorption of electromagnetic radiation. An excited triplet state is produced and the transition is from the excited triplet state to the ground singlet state.

(e) The *Stokes shift* is the difference in wavelength between the radiation used to excite fluorescence and the wavelength of the emitted radiation.

(f) The *quantum yield* of fluorescence is the ratio of the number of fluorescing molecules to the total number of excited molecules.

(g) An *inner filter effect* is a result of excessive absorption of the incident beam (primary absorption) or absorption of the emitted beam (secondary absorption).

(h) An *excitation spectrum* is a plot of fluorescence or phosphorescence emission intensity as a function of the excitation wavelength.

27-2. For spectrofluorometry, the analytical signal, *F*, is given by $F = 2.3K'\varepsilon bcP_0$. The magnitude of *F*, and thus sensitivity, can be enhanced by increasing the source intensity, $P_{0,}$ or the transducer sensitivity. For spectrophotometry, the analytical *A* is given by $A = P/P_0$. Increasing P_0 or the detector's response to P_0 is accompanied by a corresponding increase in *P*. Thus, the ratio does not change nor does the analytical signal. Consequently, no improvement in sensitivity accompanies such changes.

27-**3**. **(a)** Fluorescein because of its greater structural rigidity due to the bridging –O– groups.

(b) *o,o'*-dihdroxyazobenzene because the –N=N– group provides rigidity that is absent in the –NH–NH– group.

27-4. Compounds that fluoresce have structures that slow the rate of nonradiative relaxation to the point where there is time for fluorescence to occur. Compounds that do not fluoresce have structures that permit rapid relaxation by nonradiative processes.

27-5. Organic compounds containing aromatic rings often exhibit fluorescence. Rigid molecules or multiple ring systems tend to have large quantum yields of fluorescence while flexible molecules generally have lower quantum yields.

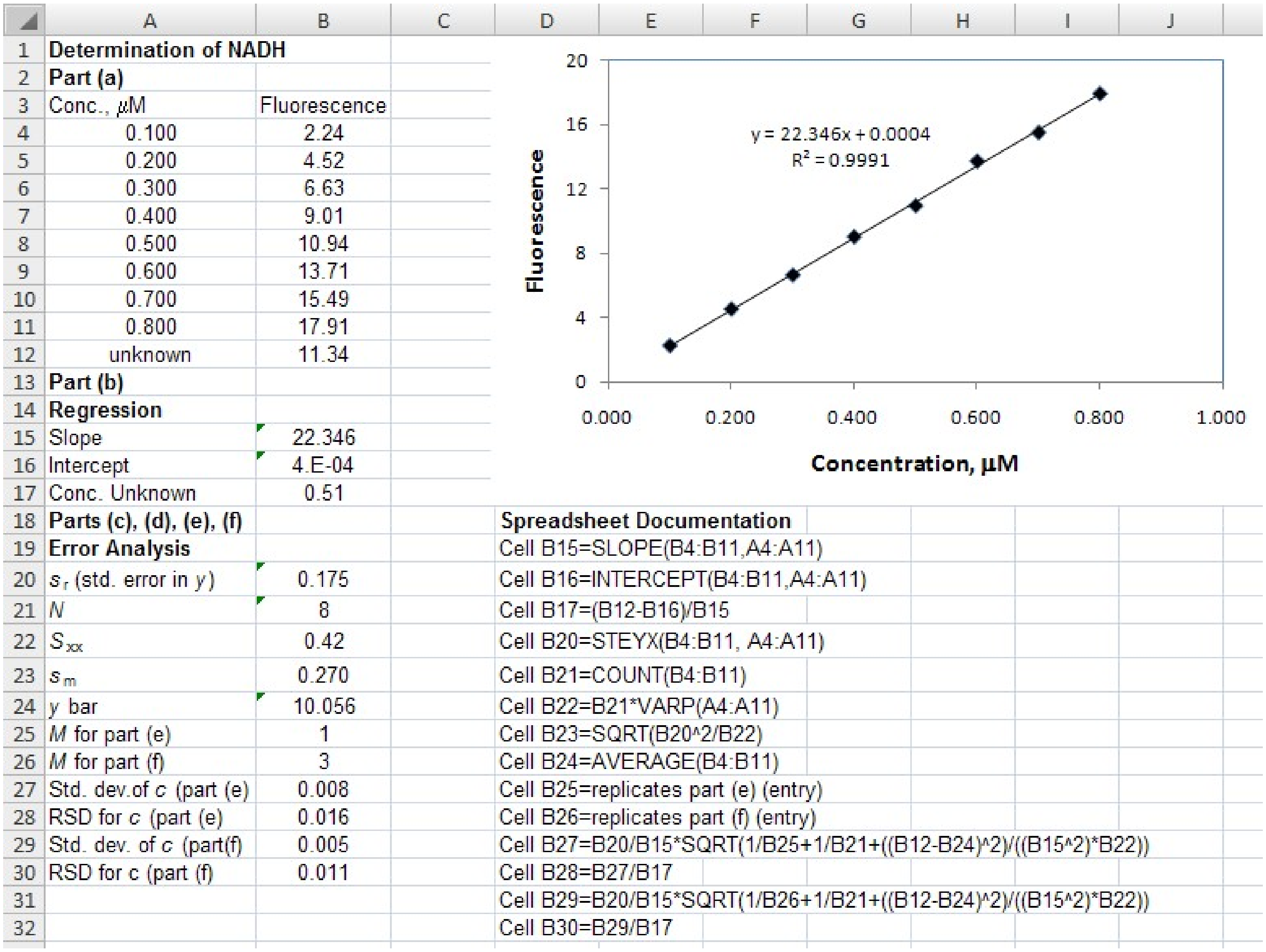
27-6. Excitation of fluorescence usually involves transfer of an electron to a high vibrational state of an upper electronic state. Relaxation to a lower vibrational state of this electronic state goes on much more rapidly than fluorescence relaxation. Fluorescence almost always occurs from the lowest vibrational level of the excited electronic state to various vibrational levels of the ground electronic state. Such transitions involve less energy than the excitation energy. Therefore, the emitted radiation is longer in wavelength than the excitation wavelength.

27-7. See Figure 27-8. A filter fluorometer usually consists of a light source, a filter for selecting the excitation wavelength, a sample container, an emission filter and a transducer/readout device. A spectrofluorometer has two monochromators that are the wavelength selectors.

27-8. Most fluorescence instruments are double beam to compensate for fluctuations in the analytical signal due to variations in source intensity.

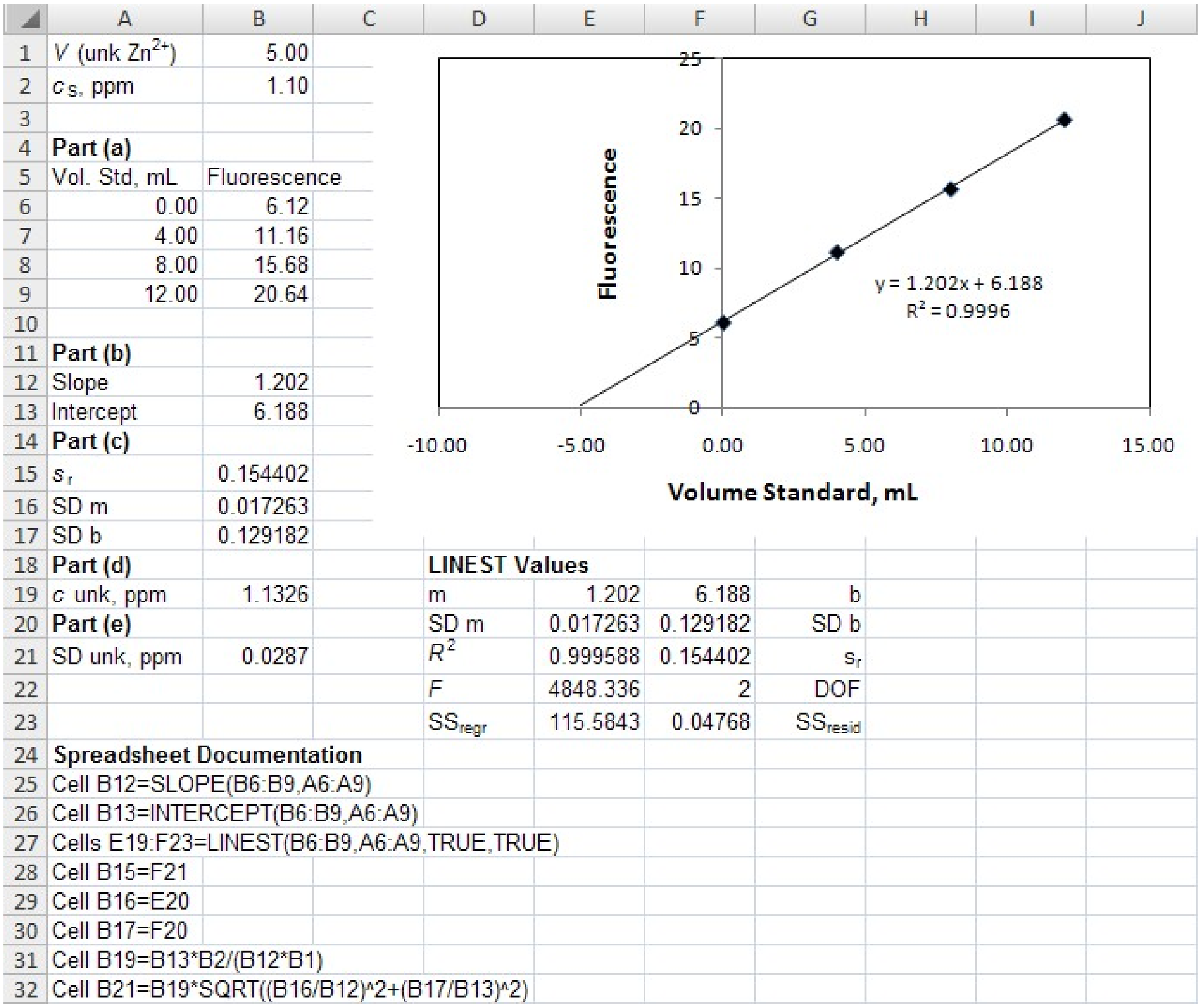
27-9. Fluorometers are more sensitive because filters allow more excitation radiation to reach the sample and more emitted radiation to reach the transducer. Thus, a fluorometer can provide lower limits of detection than a spectrofluorometer. In addition, fluorometers are substantially less expensive and more rugged than spectrofluorometer, making them particularly well suited for routine quantitation and remote analysis applications.

27-10.



	A	B	C	D
1	**Determination of NADH**			
2	**Part (a)**			
3	Conc., µM	Fluorescence		
4	0.100	2.24		
5	0.200	4.52		
6	0.300	6.63		
7	0.400	9.01		
8	0.500	10.94		
9	0.600	13.71		
10	0.700	15.49		
11	0.800	17.91		
12	unknown	11.34		
13	**Part (b)**			
14	**Regression**			
15	Slope	22.346		
16	Intercept	4.E-04		
17	Conc. Unknown	0.51		
18	**Parts (c), (d), (e), (f)**			**Spreadsheet Documentation**
19	**Error Analysis**			Cell B15=SLOPE(B4:B11,A4:A11)
20	s_r (std. error in y)	0.175		Cell B16=INTERCEPT(B4:B11,A4:A11)
21	N	8		Cell B17=(B12-B16)/B15
22	S_{xx}	0.42		Cell B20=STEYX(B4:B11, A4:A11)
23	s_m	0.270		Cell B21=COUNT(B4:B11)
24	y bar	10.056		Cell B22=B21*VARP(A4:A11)
25	M for part (e)	1		Cell B23=SQRT(B20^2/B22)
26	M for part (f)	3		Cell B24=AVERAGE(B4:B11)
27	Std. dev.of c (part (e)	0.008		Cell B25=replicates part (e) (entry)
28	RSD for c (part (e)	0.016		Cell B26=replicates part (f) (entry)
29	Std. dev. of c (part(f)	0.005		Cell B27=B20/B15*SQRT(1/B25+1/B21+((B12-B24)^2)/((B15^2)*B22))
30	RSD for c (part (f)	0.011		Cell B28=B27/B17
31				Cell B29=B20/B15*SQRT(1/B26+1/B21+((B12-B24)^2)/((B15^2)*B22))
32				Cell B30=B29/B17

27-11.



	A	B	C	D	E	F	G	H	I	J
1	V (unk Zn^{2+})	5.00								
2	c_S, ppm	1.10								
3										
4	**Part (a)**									
5	Vol. Std, mL	Fluorescence								
6	0.00	6.12								
7	4.00	11.16								
8	8.00	15.68								
9	12.00	20.64								
10										
11	**Part (b)**									
12	Slope	1.202								
13	Intercept	6.188								
14	**Part (c)**									
15	s_r	0.154402								
16	SD m	0.017263								
17	SD b	0.129182								
18	**Part (d)**			**LINEST Values**						
19	c unk, ppm	1.1326		m	1.202	6.188	b			
20	**Part (e)**			SD m	0.017263	0.129182	SD b			
21	SD unk, ppm	0.0287		R^2	0.999588	0.154402	s_r			
22				F	4848.336	2	DOF			
23				SS_{regr}	115.5843	0.04768	SS_{resid}			
24	**Spreadsheet Documentation**									
25	Cell B12=SLOPE(B6:B9,A6:A9)									
26	Cell B13=INTERCEPT(B6:B9,A6:A9)									
27	Cells E19:F23=LINEST(B6:B9,A6:A9,TRUE,TRUE)									
28	Cell B15=F21									
29	Cell B16=E20									
30	Cell B17=F20									
31	Cell B19=B13*B2/(B12*B1)									
32	Cell B21=B19*SQRT((B16/B12)^2+(B17/B13)^2)									

27-12. $c_{\mathrm{Q}} = 100\ \mathrm{ppm} \times 288/180 = 160\ \mathrm{ppm}$

$$160\ \mathrm{ppm} \times \frac{100\ \mathrm{mL}}{15\ \mathrm{mL}} \times \frac{1\ \mathrm{mg\ quinine}}{1 \times 10^{3}\ \mathrm{g\ solution}} \times \frac{1\ \mathrm{g\ solution}}{1\ \mathrm{mL}} \times 500\ \mathrm{mL} = 533\ \mathrm{mg\ quinine}$$

27-13. $c_{\mathrm{Q}} = \dfrac{A_1 c_{\mathrm{s}} V_{\mathrm{s}}}{(A_2 - A_1)V_{\mathrm{Q}}} = \dfrac{(540)(50\ \mathrm{ppm})(10.0\ \mathrm{mL})}{(600 - 540)(20.0\ \mathrm{mL})} = 225\ \mathrm{ppm}$

$$225\ \mathrm{ppm} \times \frac{1\ \mathrm{mg\ quinine}}{1 \times 10^{3}\ \mathrm{g\ solution}} \times \frac{1\ \mathrm{g\ solution}}{1\ \mathrm{mL}} \times 1000\ \mathrm{mL} = 225\ \mathrm{mg\ quinine}$$

$$\frac{0.225\ \mathrm{g\ Q}}{2.196\ \mathrm{g\ tablet}} \times 10^{6} = 1.02 \times 10^{5}\ \mathrm{ppm}$$

Chapter 28

28-1. In *atomic emission spectroscopy* the radiation source is the sample itself. The energy for excitation of analyte atoms is supplied by a plasma, a flame, an oven, or an electric arc or spark. The signal is the measured intensity of the source at the wavelength of interest. In *atomic absorption spectroscopy* the radiation source is usually a line source such as a hollow cathode lamp, and the signal is the absorbance. The latter is calculated from the radiant power of the source and the resulting power after the radiation has passed through the atomized sample. In *atomic fluorescence spectroscopy,* an external radiation source is used, and the fluorescence emitted, usually at right angles to the source, is measured. The signal is the intensity of the fluorescence emitted.

28-**2**. **(a)** *Atomization* is a process in which a sample, often in solution, is volatilized and decomposed to form an atomic vapor.

(b) *Collisiional broadening* is an increase in the widths of atomic emission or absorption lines brought about by collisions between atoms and molecules in the gas phase. These collisions lead to slight changes in the energies of the states involved in emission or absorption and thus broadening of the spectral line. The amount of broadening increases with the increasing concentration (pressure) of the collision partners and with increasing temperature.

(c) *Doppler broadening* is an increase in the width of the atomic lines caused by the Doppler effect in which atoms moving toward a detector absorb or emit wavelengths that are slightly shorter than those absorbed or emitted b atoms moving at right angles to the detector. The reverse effect is observed for atoms moving away from the detector.

(d) *Nebulization* is the process that converts a liquid into a mist or an aerosol by the flow of gas around the end of a capillary tube the other end of which is immersed in the liquid.

(e) A *plasma* is a conducting gas that contains a large concentration of ions and/or electrons.

(f) A *laminar flow burner* is a premixed burner that provides a fairly quiet blame and a relatively long path length.

(g) A *hollow cathode lamp* consists of a tungsten wire anode and a cylindrical cathode sealed in a glass tube that contains argon at a pressure of 1 to 5 torr. The cathode is constructed from or supports the element whose emission spectrum is desired.

(h) *Sputtering* is a process in which atoms of an element are dislodged from the surface of a cathode by bombardment by a stream of inert gas ions that have been accelerated toward the cathode by a high electric potential.

(i) An *additive interference*, also called a blank interference, produces an effect that is independent of the analyte concentration. It could be eliminated with a perfect blank solution.

(j) A *spectral interference* in atomic spectroscopy occurs when a spectral line of an element in the sample matrix overlaps that of the analyte. It is an example of an additive interference.

(k) A *chemical interference* in atomic spectroscopy is encountered when a species interacts with the analyte in such a way as to alter the spectral emission or absorption characteristics of the analyte.

(l) A *radiation buffer* is a substance that is added in large excess to both standards and samples in atomic spectroscopy to prevent the presence of that substance in the sample matrix from having an appreciable effect on the results.

(m) A *protective agent* prevents interference by forming a stable, but volatile, compound with the analyte. It protects the analyte from forming non-volatile, but less stable interfering compounds.

(n) An *ionization suppressor* is a compound containing an easily ionized cation, such as potassium; it is introduced into a solution of an analyte to provide a high concentration of electrons during atomization. In this way, interference due to ionization of the analyte is minimized.

28-3. In atomic emission spectroscopy, the analytical signal is produced by the relatively small number of *excited* atoms or ions, whereas in atomic absorption the signal results from absorption by the much larger number of *unexcited* species. Any small change in flame conditions dramatically influences the number of *excited species,* whereas such changes have a much smaller effect on the number of *unexcited species.*

28-4. Ionization interference effects are less severe in the ICP because the large concentration of electrons from the ionization of argon maintains a more-or-less constant electron concentration in the plasma. In the flame, ionization of matrix elements can change the electron concentration and thus the extent of ionization of the analyte.

28-5. In atomic absorption spectroscopy the source radiation is modulated to create an ac signal at the detector. The detector is made to reject the dc signal from the flame and measure the modulated signal from the source. In this way, background emission from the flame and atomic emission from the analyte is discriminated against and prevented from causing an interference effect.

28-6. The resolution and selectivity in ICP emission comes primarily from the monochromator. As a result, a high resolution monochromator can isolate the analyte spectral line from lines of concomitants and background emission. It can thus reduce spectral interferences. In atomic absorption spectrometry, the resolution comes primarily from the very narrow hollow cathode lamp emission. The monochromator must only isolate the emission line of the analyte element from lines of impurities and the fill gas, and from background emission from the atomizer. A much lower resolution is needed for this purpose.

28-7. The temperature and pressure in a hollow cathode lamp are much less than those in an ordinary flame. As a result, Doppler and collisional broadening effects are much less, and narrower lines results.

28-8. **(a)** Sulfate ion forms complexes with Fe(III) that are not readily volatilized and converted to free atoms. Thus, the concentration of iron atoms is lower in the presence of sulfate.

(b) A releasing agent that forms more stable complexes with sulfate than iron forms could be added. A protective agent, such as EDTA, that forms a stable, but volatile complex with Fe(III) could be introduced. A higher temperature flame could be used.

28-9. The temperatures are high which favors the formation of atoms and ions. Sample residence times are long so that desolvation and vaporization are essentially complete. The atoms and ions are formed in a nearly chemically inert environment. The high and relatively constant electron concentration leads to fewer ionization interferences.

28-10. The ICP is rarely used for atomic absorption measurements because the short optical path length of the ICP means that absorbances are small, which leads to lower sensitivity than longer path length flames. Also, the high temperature of the plasma reduces the population of atoms in the ground state substantially.

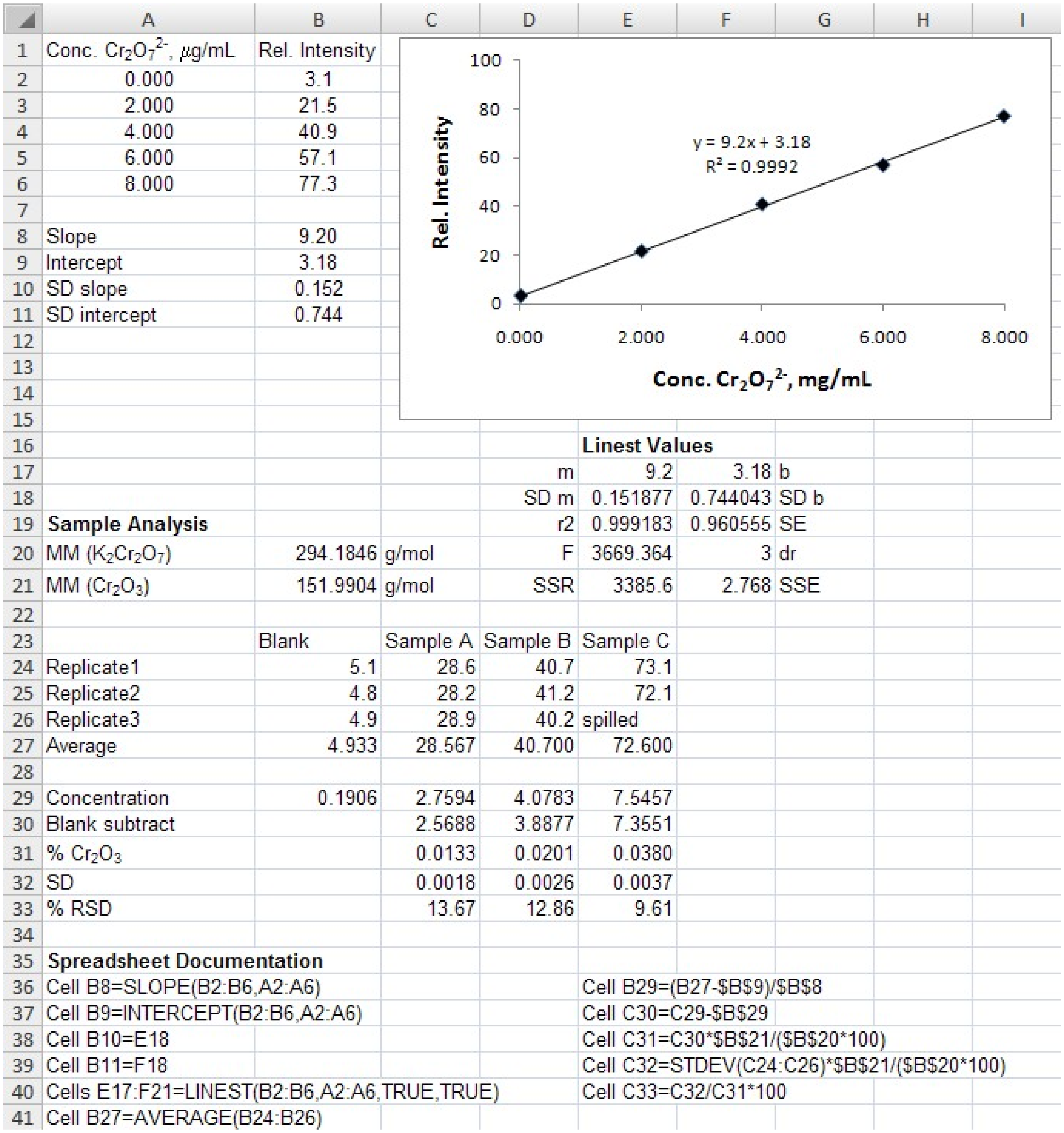
28-11. The radial geometry provides better stability and precision while the axial geometry can achieve lower detection limits. Many ICP emission systems allow both geometries.

28-12. Deviations from linearity at low concentrations are often the result of significant ionization of the analyte. When a high concentration of an easily ionized metal salt is added, the ionization of the analyte is suppressed because of the electrons produced by ionization of the metal.

28-13. By linear interpolation

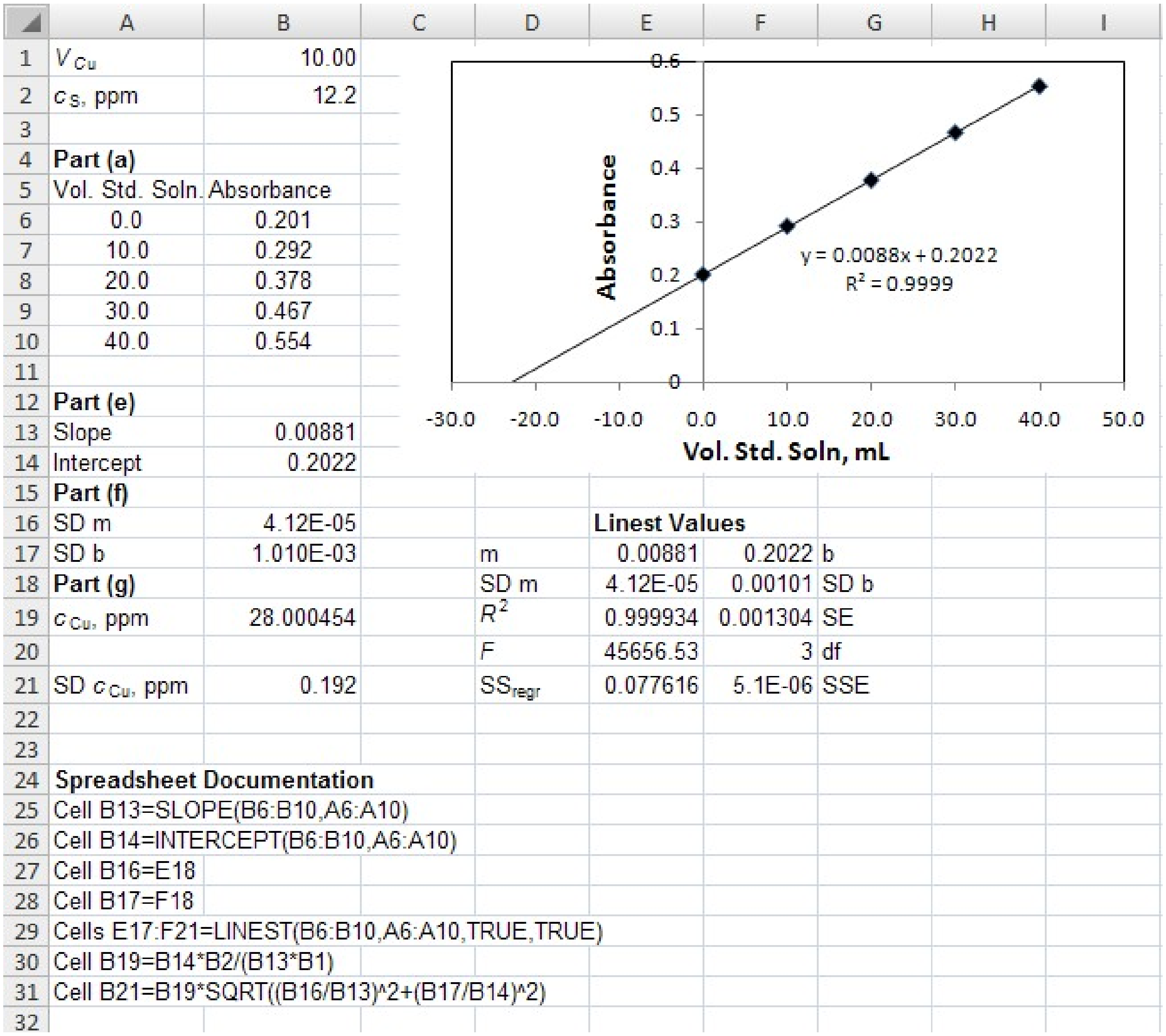
$$0.400 + (0.502 - 0.396)\frac{(0.600\ -\ 0.400)}{(0.599\ -\ 0.396)} = 0.504 \text{ ppm Pb}$$

28-14.



	A	B	C	D	E	F	G	H	I
1	Conc. $Cr_2O_7^{2-}$, µg/mL	Rel. Intensity							
2	0.000	3.1							
3	2.000	21.5							
4	4.000	40.9							
5	6.000	57.1							
6	8.000	77.3							
7									
8	Slope	9.20							
9	Intercept	3.18							
10	SD slope	0.152							
11	SD intercept	0.744							
12									
13									
14									
15									
16					**Linest Values**				
17				m	9.2	3.18	b		
18				SD m	0.151877	0.744043	SD b		
19	**Sample Analysis**			r2	0.999183	0.960555	SE		
20	MM ($K_2Cr_2O_7$)	294.1846	g/mol	F	3669.364	3	dr		
21	MM (Cr_2O_3)	151.9904	g/mol	SSR	3385.6	2.768	SSE		
22									
23		Blank	Sample A	Sample B	Sample C				
24	Replicate1	5.1	28.6	40.7	73.1				
25	Replicate2	4.8	28.2	41.2	72.1				
26	Replicate3	4.9	28.9	40.2	spilled				
27	Average	4.933	28.567	40.700	72.600				
28									
29	Concentration	0.1906	2.7594	4.0783	7.5457				
30	Blank subtract		2.5688	3.8877	7.3551				
31	% Cr_2O_3		0.0133	0.0201	0.0380				
32	SD		0.0018	0.0026	0.0037				
33	% RSD		13.67	12.86	9.61				
34									
35	**Spreadsheet Documentation**								
36	Cell B8=SLOPE(B2:B6,A2:A6)				Cell B29=(B27-$B$9)/$B$8				
37	Cell B9=INTERCEPT(B2:B6,A2:A6)				Cell C30=C29-$B$29				
38	Cell B10=E18				Cell C31=C30*$B$21/($B$20*100)				
39	Cell B11=F18				Cell C32=STDEV(C24:C26)*$B$21/($B$20*100)				
40	Cells E17:F21=LINEST(B2:B6,A2:A6,TRUE,TRUE)				Cell C33=C32/C31*100				
41	Cell B27=AVERAGE(B24:B26)								

28-15.



	A	B	C	D	E	F	G	H	I
1	V_{Cu}	10.00							
2	c_S, ppm	12.2							
3									
4	**Part (a)**								
5	Vol. Std. Soln.	Absorbance							
6	0.0	0.201							
7	10.0	0.292							
8	20.0	0.378							
9	30.0	0.467							
10	40.0	0.554							
11									
12	**Part (e)**								
13	Slope	0.00881							
14	Intercept	0.2022							
15	**Part (f)**								
16	SD m	4.12E-05			**Linest Values**				
17	SD b	1.010E-03		m	0.00881	0.2022	b		
18	**Part (g)**			SD m	4.12E-05	0.00101	SD b		
19	c_{Cu}, ppm	28.000454		R^2	0.999934	0.001304	SE		
20				F	45656.53	3	df		
21	SD c_{Cu}, ppm	0.192		SS_{regr}	0.077616	5.1E-06	SSE		
22									
23									
24	**Spreadsheet Documentation**								
25	Cell B13=SLOPE(B6:B10,A6:A10)								
26	Cell B14=INTERCEPT(B6:B10,A6:A10)								
27	Cell B16=E18								
28	Cell B17=F18								
29	Cells E17:F21=LINEST(B6:B10,A6:A10,TRUE,TRUE)								
30	Cell B19=B14*B2/(B13*B1)								
31	Cell B21=B19*SQRT((B16/B13)^2+(B17/B14)^2)								
32									

(a) See plot in spreadsheet

(b) $$A_s = \frac{\varepsilon b V_s c_s}{V_t} + \frac{\varepsilon b V_x c_x}{V_t} = kV_s c_s + kV_x c_x$$

(c) For the plot of A_s versus V_s, $A_s = mV_s + b$ where $m = kc_s$

and $b = kV_x c_x$

(d) From the equations in **(c)**: $k = \dfrac{m}{c_s} = \dfrac{b}{V_x c_x}$

Rearranging and solving for c_x: $c_x = \dfrac{bc_s}{mV_x}$

(e) From the values in the spreadsheet: $m = 0.00881$ and $b = 0.2022$

(f) From the values in the spreadsheet: $s_m = 4.1 \times 10^{-5}$ and $s_b = 1.0 \times 10^{-3}$

(g) From the values in the spreadsheet: $c_{\mathrm{Cu}} = 28.0\ (\pm 0.2)$ ppm

Chapter 29

29-1. **(a)** The *Dalton* is one unified atomic mass unit and equal to 1/12 the mass of a neutral $^{12}_{6}\text{C}$ atom.

(b) A *quadrupole mass filter* consists of 4 cylindrical rods that only allow ions of a certain mass-to-charge (*m/z*) ratio to pass. With proper adjustment of the voltages applied to the rods, a stable path is created for ions of a certain *m/z* ratio to pass through the analyzer to the detector.

(c) The *mass number* is the atomic or molecular mass expressed without units.

(d) A *sector analyzer* consists of either a magnetic sector that deflects ions in a magnetic field or an electric sector in which the deflection is by means of an electrostatic field. In a double-focusing spectrometer, an electic sector precedes the magnetic sector.

(e) In a *time-of-flight* analyzer ions with nearly the same kinetic energy traverse a field-free region. The time required for an ion to reach a detector at the end of the field-free region is inversely proportional to the mass of the ion.

(f) An *electron multiplier* is a common transducer for mass spectrometry and consists of a cathode which when struck by ions produces secondary electrons. These electrons are attracted to dynodes that are each held at successively higher positive voltage and collisions with the dynodes yields additional cascading electrons.

29-2. The temperatures are high which favors the formation of ions. Spectra consist of a simple series of isotope peaks for each element present along with some background ionic peaks. Sample residence times are long so that desolvation and vaporization are essentially complete.

29-3. The ICP torch serves both as an atomizer and ionizer.

29-4. In an ordinary mass spectrum, the ordinate is ion abundance (number of ions, ion current, or counts) and the abscissa is the mass-to-charge ratio or sometimes just mass assuming singly charged ions.

29-5. Interferences fall into two categories: spectroscopic interferences and matrix interferences. In a spectroscopic interference, the interfering species has the same mass-to-charge ratio as the analyte. Matrix effects occur at high concentrations where interfering species can interact chemically or physically to change the analyte signal.

29-6. Internal standards are used in ICP-MS to compensate for instrument drifts, instabilities, and matrix effects when performing quantitative analysis.

29-7. The higher resolution of the double focusing spectrometer allows the ions of interest to be better separated from background ions than with a relative low resolution quadrupole spectrometer. The higher signal-to-background ratio of the double focusing instrument leads to lower detection limits than with the quadrupole instrument.

29-8. With a gaseous ionization source, the sample is first vaporized and then ionized. With a desorption source, the solid or liquid sample is converted directly into gas-phase ions. Desorption sources have the advantage that they can be used to ionize nonvolatile and thermally unstable compounds. Gas-phase sources are often more reliable and reproducible. Many mass spectral libraries have spectra collected with gas-phase sources like the electron-impact source.

29-9. The high energy of the beam of electrons used in EI sources is enough to break some chemical bonds and produce fragment ions. Such fragment ions can be useful in qualitative identification of molecular species.

29-10. A gas-phase sample is needed for mass spectrometry. The output of the LC column is a solute dissolved in a solvent, whereas the output of the GC column is a gas and thus directly compatible. As a first step in LC/MS, the solvent must be vaporized. When vaporized, however, the LC solvent produces a gas volume that is 10-1000 times greater than the carrier gas in GC. Hence, most of the solvent must also be removed.

29-11. The ion selected by the first analyzer is called the precursor ion. It then undergoes thermal decomposition, reaction with a collision gas, or photodecomposition to form product ions that are analyzed by a second mass analyzer.

29-12. A hard ionization source, such as an EI source, is often more useful for structural elucidation because the many fragments provide information about bonding in the molecule. A soft ionization source can provide accurate information about the molecular mass because the molecular ion is often the most abundant ion produced. Hard ionization sources provide many fragment ions which allows the mass spectrum to be used in qualitative identification. Most mass spectral libraries used in identifying compounds are based on electron-impact ionization, a hard ionization method.

Chapter 30

30-1. **(a)** The *order of a reaction* is the numerical sum of the exponents of the concentration terms in the rate law for the reaction.

(b) A reaction is pseudo-first-order when all reactants but one are in large excess so that their concentrations are essentially constant during the course of the reaction. The rate of the reaction then depends upon the concentration of the isolated reactant A. Under these conditions, rate = $k[A]$ where k contains the concentration(s) of the reagents that are in excess.

(c) *Enzymes* are high molecular mass organic molecules that catalyze reactions of biological importance.

(d) A *substrate* is the reagent that is acted on by an enzyme.

(e) The *Michaelis constant* K_m is an equilibrium-like constant for the dissociation of the enzyme-substrate complex. It is defined by the equation $K_m = (k_{-1} + k_2)/k_1$, where k_1 and k_{-1} are the rate constants for the forward and reverse reactions in the formation of the enzyme-substrate complex. The term k_2 is the rate constant for the dissociation of the complex to give products.

(f) *Differential methods* are those in which the concentration of the analyte is determined from a differential form of the rate law. For example, the expression $-d[A]/dt = k[A]_0e^{-kt}$ allows the computation of $[A]_0$ if the rate is measured at time t and k is known from other experiments.

(g) *Integral methods* use integrated forms of the rate equations to calculate concentrations from kinetic data.

(h) An *indicator reaction* (or *follow-up reaction*) is one used to monitor the appearance of a reactant or the disappearance of a product. For example, the reaction of 1,10-phenanthroline with Fe^{2+} is often used to monitor the progress of reactions that produce Fe^{2+}. The indicator reaction must not affect the rate of the reaction of interest.

30-2. The "separation" of the components of a mixture is essentially carried out by finding the differences in their rates of reaction with a common reagent.

30-3. Advantages would include; (1) measurements are made relatively early in the reaction before side reactions can occur; (2) measurements do not depend upon the determination of absolute concentration but rather depend upon differences in concentration; (3) selectivity is often enhanced in reaction-rate methods, particularly in enzyme-based methods. Limitations would include; (1) lower sensitivity, since reaction is not allowed to proceed to equilibrium; (2) greater dependence on conditions such as temperature, ionic strength, pH and concentration of reagents; (3) lower precision since the analytical signal is lower.

30-4. *Pseudo-first order* conditions are used in kinetic methods because under these conditions the reaction rate is directly proportional to the concentration of the analyte.

30-5. $[A]_t = [A]_0 e^{-kt}$ $\qquad \ln\frac{[A]_t}{[A]_0} = -kt$

For $t = t_{1/2}$, $\qquad [A]_t = [A]_0/2 \quad \ln\frac{[A]_0/2}{[A]_0} = \ln(1/2) = -kt_{1/2}$

$\ln 2 = kt_{1/2}$

$t_{1/2} = \ln 2/k = 0.693/k$

30-6. **(a)** $\tau = 1/k = 1/0.497\ s^{-1} = 2.01\ s$

(b) $\tau = 1/k = 1/6.62\ \text{h}^{-1} = 0.151\ \text{h}$

$$0.151\ \text{h} \times \frac{60\ \text{min}}{\text{h}} \times \frac{60\ \text{s}}{\text{min}} = 544\ \text{s}$$

(c) $\ln\frac{[\text{A}]_0}{[\text{A}]_t} = kt$ $\tau = 1/k = t/\ln([\text{A}]_0/[\text{A}]_t) = 3876\ \text{s}/\ln(3.16/0.496) = 2.093 \times 10^3\ \text{s}$

(d) Since 1 mole of product is formed for each mole of analyte reacted,

$[\text{P}]_\infty = [\text{A}]_0$

$$[\text{P}]_t = [\text{P}]_\infty(1 - e^{-kt})$$

$$[\text{P}]_t/[\text{P}]_\infty = 1 - e^{-kt}$$

$$1 - [\text{P}]_t/[\text{P}]_\infty = e^{-kt}$$

$$\ln\left(1 - \frac{[\text{P}]_t}{[\text{P}]_\infty}\right) = -kt$$

$\tau = 1/k = -t\ /\ln(1-[\text{P}]_t/[\text{P}]_\infty) = -9.54\ \text{s}/\ln((1-0.0423)/0.176) = 34.7\ \text{s}$

(e) $t_{1/2} = 26.5\ \text{yr} \times \frac{365\ \text{d}}{1\ \text{yr}} \times \frac{24\ \text{h}}{1\ \text{d}} \times \frac{60\ \text{min}}{1\ \text{h}} \times \frac{60\ \text{s}}{1\ \text{min}} = 8.36 \times 10^8\ \text{s}$

$$\tau = 1/k = t_{1/2}/0.693 = 8.36 \times 10^8\ \text{s}/0.693 = 1.2 \times 10^9\ \text{s}$$

(f) $\tau = 1/k = t_{1/2}/0.693 = 0.583/0.693 = 0.841\ \text{s}$

30-7. **(a)** $\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$ $k = -\frac{1}{t}\ln\frac{[\text{A}]_t}{[\text{A}]_0}$

$$k = -\frac{1}{0.0100}\ln(0.75) = 28.8\ \text{s}^{-1}$$

(b) $k = -\frac{1}{0.100}\ln(0.75) = 2.88\ \text{s}^{-1}$

Proceeding in the same way, except for different *t* values, we have

(c) $k = 0.288\ \text{s}^{-1}$

(d) $k = 5.45 \times 10^{-5}\ \text{s}^{-1}$

(e) $k = 1.07 \times 10^{4}\ \text{s}^{-1}$

(f) $k = 3.25 \times 10^{7}\ \text{s}^{-1}$

30-8. Let m = no. half-lives = $$\frac{t}{t_{1/2}} = \frac{-\frac{1}{k}\ln\frac{[\text{A}]}{[\text{A}]_0}}{-\frac{1}{k}\ln\frac{[\text{A}]_0/2}{[\text{A}]_0}}$$

$$m = \frac{\ln[\text{A}]/[\text{A}]_0}{\ln 1/2} = -1.4427\ \ln([\text{A}]/[\text{A}]_0)$$

(a) $m = -1.4427 \ln 0.90 = 0.152$

(b) $m = -1.4427 \ln 0.50 = 1.00$

(c) $m = -1.4427 \ln 0.10 = 3.3$

(d) $m = -1.4427 \ln 0.01 = 6.6$

(e) $m = -1.4427 \ln 0.001 = 10$

(f) $m = -1.4427 \ln 0.0001 = 13$

30-9. **(a)** $\ln([\text{A}]/[\text{A}]_0) = -kt = -t/\tau$, where $\tau = 1/k$

At 10% completion $[\text{A}]/[\text{A}]_0 = 0.90$

n = no. lifetimes = $t/\tau = -\ln([\text{A}]/[\text{A}]_0) = -\ln 0.90 = 0.105$

(b) $n = -\ln 0.50 = 0.69$

(c) $n = -\ln 0.10 = 2.3$

(d) $n = -\ln 0.01 = 4.6$

(e) $n = -\ln 0.001 = 6.9$

(f) $n = -\ln 0.0001 = 9.2$

30-10. **(a)** $[R]_0 = 5.00[A]_0$ where 5.00 is the ratio of the initial reagent concentration to the initial concentration of the analyte.

At 1% reaction, $[A] = 0.99[A]_0$

$[R]_{1\%} = [R] - 0.01[A]_0 = 5.00[A]_0 - 0.01[A]_0 = 4.99[A]_0$

$\text{Rate}_{\text{assumed}} = k[R][A] = k(5.00[A]_0 \times 0.99[A]_0)$

$\text{Rate}_{\text{true}} = k(4.99[A]_0 \times 0.99[A]_0)$

$$\text{relative error} = \frac{k(5.00[A]_0 \times 0.99[A]_0) - k(4.99[A]_0 \times 0.99[A]_0)}{k(4.99[A]_0 \times 0.99[A]_0)}$$

$$= \frac{(5.00 \times 0.99) - (4.99 \times 0.99)}{(4.99 \times 0.99)} = 0.00200$$

relative error × 100% = 0.2%

(b) $\text{relative error} = \dfrac{(10.00 \times 0.99) - (9.99 \times 0.99)}{(9.99 \times 0.99)} = 0.00100$

relative error × 100% = 0.1%

(c) (50.00 – 49.99)/49.99 = 0.000200 or 0.02%

(d) 0.01/99.99 = 0.0001 or 0.01%

(e) (5.00 – 4.95)/4.95 = 0.0101 or 1.0%

(f) (10.00 – 9.95)/9.95 = 0.00502 or 0.5%

(g) (100.00 – 99.95)/99.95 = 0.0005002 or 0.05%

(h) (5.000 – 4.368)/4.368 = 0.145 or 14%

(i) (10.000 – 9.368)/9.368 = 0.06746 or 6.7%

(j) (50.000 – 49.368)/49.368 = 0.0128 or 1.3%

(k) (100.00 – 99.368)/99.368 = 0.00636 or 0.64%

30-11. $\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \mathrm{K}_m}$

At ν_{max}, $\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{E}]_0$, Thus, at $\nu_{\mathrm{max}}/2$, we can write

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_0}{2} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m}$$

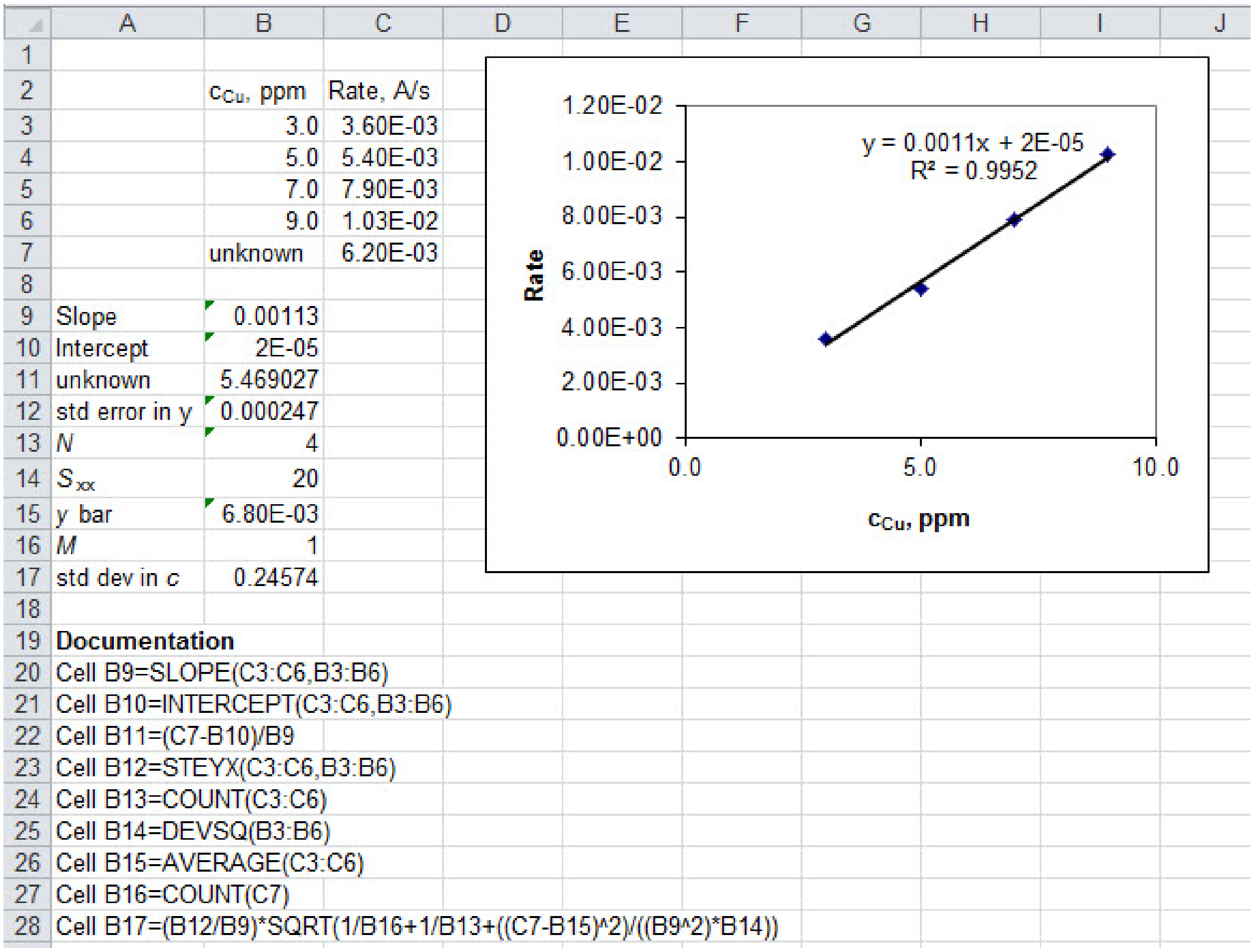
$[\mathrm{S}] + K_m = 2[\mathrm{S}]$

$K_m = [\mathrm{S}]$

30-12. **(a)** Plot 1/Rate versus 1/[S] for known [S] to give a linear calibration curve. Measure rate for unknown [S], calculate 1/Rate and $1/[\mathrm{S}]_{\mathrm{unknown}}$ from the working curve and find $[\mathrm{S}]_{\mathrm{unknown}}$.

(b) The intercept of the calibration curve is $1/v_{\mathrm{max}}$ and the slope is $K_{\mathrm{m}}/v_{\mathrm{max}}$. Use the intercept to calculate K_{m} = slope/intercept, and v_{max} = 1/intercept.

30-13.



	A	B	C
1			
2		c_{Cu}, ppm	Rate, A/s
3		3.0	3.60E-03
4		5.0	5.40E-03
5		7.0	7.90E-03
6		9.0	1.03E-02
7		unknown	6.20E-03
8			
9	Slope	0.00113	
10	Intercept	2E-05	
11	unknown	5.469027	
12	std error in y	0.000247	
13	*N*	4	
14	S_{xx}	20	
15	*y* bar	6.80E-03	
16	*M*	1	
17	std dev in *c*	0.24574	
18			
19	**Documentation**		
20	Cell B9=SLOPE(C3:C6,B3:B6)		
21	Cell B10=INTERCEPT(C3:C6,B3:B6)		
22	Cell B11=(C7-B10)/B9		
23	Cell B12=STEYX(C3:C6,B3:B6)		
24	Cell B13=COUNT(C3:C6)		
25	Cell B14=DEVSQ(B3:B6)		
26	Cell B15=AVERAGE(C3:C6)		
27	Cell B16=COUNT(C7)		
28	Cell B17=(B12/B9)*SQRT(1/B16+1/B13+((C7-B15)^2)/((B9^2)*B14))		

We report the concentration of the unknown as 5.5 ± 0.2 ppm

30-14. $R = 1.74\, c_{\mathrm{Al}} - 0.225$ $\qquad c_{\mathrm{Al}} = (R + 0.225) / 1.74$

$c_{\mathrm{Al}} = (0.76 + 0.225)/1.74 = 0.57\ \mu\mathrm{M}$

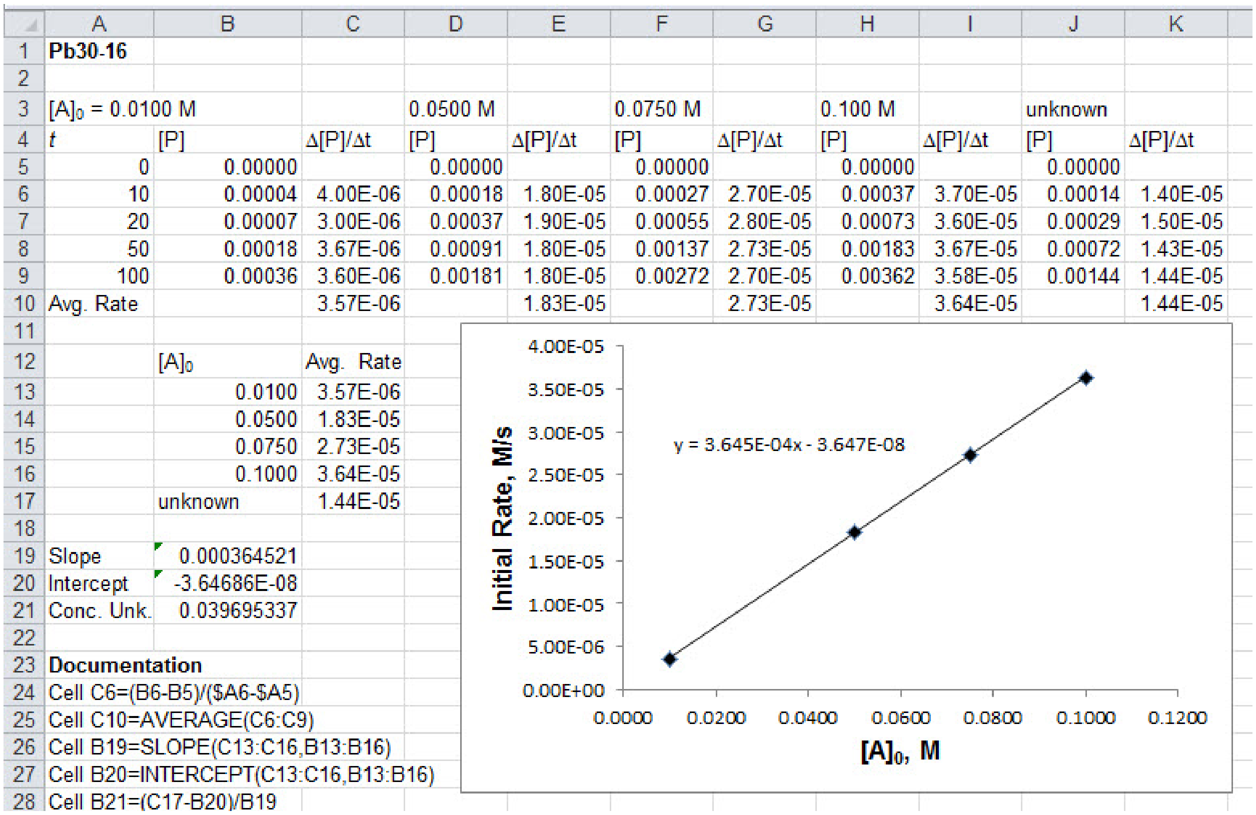
30-15. $\text{Rate} = R = \dfrac{k_2[\mathrm{E}]_0[\mathrm{tryp}]_t}{[\mathrm{tryp}]_t + K_m}$

Assume $K_m >> [\mathrm{tryp}]_t$

$$R = \frac{v_{\max}[\text{tryp}]_t}{K_m} \qquad \text{and } [\text{tryp}]_t = K_m/v_{\max}$$

$$[\text{tryp}]_t = (0.18\ \mu\text{M/min})(4.0 \times 10^{-4}\ \text{M})/(1.6 \times 10^{-3}\ \mu\text{M/min}) = 0.045\ \text{M}$$

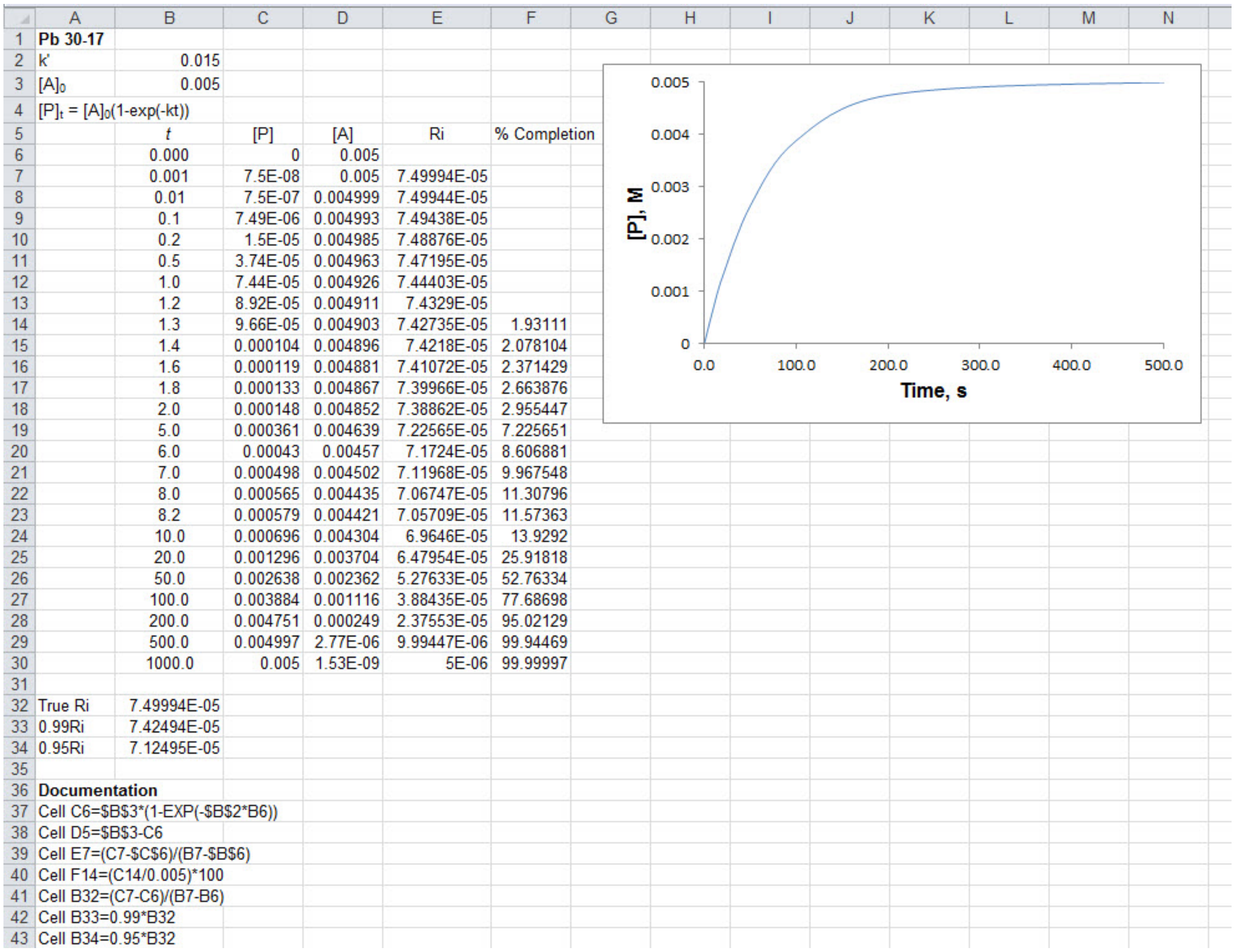
30-16.



	A	B	C	D	E	F	G	H	I	J	K
1	**Pb30-16**										
2											
3	$[A]_0$ = 0.0100 M			0.0500 M		0.0750 M		0.100 M		unknown	
4	*t*	[P]	Δ[P]/Δt	[P]	Δ[P]/Δt	[P]	Δ[P]/Δt	[P]	Δ[P]/Δt	[P]	Δ[P]/Δt
5	0	0.00000		0.00000		0.00000		0.00000		0.00000	
6	10	0.00004	4.00E-06	0.00018	1.80E-05	0.00027	2.70E-05	0.00037	3.70E-05	0.00014	1.40E-05
7	20	0.00007	3.00E-06	0.00037	1.90E-05	0.00055	2.80E-05	0.00073	3.60E-05	0.00029	1.50E-05
8	50	0.00018	3.67E-06	0.00091	1.80E-05	0.00137	2.73E-05	0.00183	3.67E-05	0.00072	1.43E-05
9	100	0.00036	3.60E-06	0.00181	1.80E-05	0.00272	2.70E-05	0.00362	3.58E-05	0.00144	1.44E-05
10	Avg. Rate		3.57E-06		1.83E-05		2.73E-05		3.64E-05		1.44E-05
11											
12		$[A]_0$	Avg. Rate								
13		0.0100	3.57E-06								
14		0.0500	1.83E-05								
15		0.0750	2.73E-05								
16		0.1000	3.64E-05								
17		unknown	1.44E-05								
18											
19	Slope	0.000364521									
20	Intercept	-3.64686E-08									
21	Conc. Unk.	0.039695337									
22											
23	**Documentation**										
24	Cell C6=(B6-B5)/($A6-$A5)										
25	Cell C10=AVERAGE(C6:C9)										
26	Cell B19=SLOPE(C13:C16,B13:B16)										
27	Cell B20=INTERCEPT(C13:C16,B13:B16)										
28	Cell B21=(C17-B20)/B19										

We would report the unknown concentration as 0.0397 M or 0.040 M

30-17.



	A	B	C	D	E	F
1	**Pb 30-17**					
2	k'	0.015				
3	$[A]_0$	0.005				
4	$[P]_t = [A]_0(1-\exp(-kt))$					
5		*t*	[P]	[A]	Ri	% Completion
6		0.000	0	0.005		
7		0.001	7.5E-08	0.005	7.49994E-05	
8		0.01	7.5E-07	0.004999	7.49944E-05	
9		0.1	7.49E-06	0.004993	7.49438E-05	
10		0.2	1.5E-05	0.004985	7.48876E-05	
11		0.5	3.74E-05	0.004963	7.47195E-05	
12		1.0	7.44E-05	0.004926	7.44403E-05	
13		1.2	8.92E-05	0.004911	7.4329E-05	
14		1.3	9.66E-05	0.004903	7.42735E-05	1.93111
15		1.4	0.000104	0.004896	7.4218E-05	2.078104
16		1.6	0.000119	0.004881	7.41072E-05	2.371429
17		1.8	0.000133	0.004867	7.39966E-05	2.663876
18		2.0	0.000148	0.004852	7.38862E-05	2.955447
19		5.0	0.000361	0.004639	7.22565E-05	7.225651
20		6.0	0.00043	0.00457	7.1724E-05	8.606881
21		7.0	0.000498	0.004502	7.11968E-05	9.967548
22		8.0	0.000565	0.004435	7.06747E-05	11.30796
23		8.2	0.000579	0.004421	7.05709E-05	11.57363
24		10.0	0.000696	0.004304	6.9646E-05	13.9292
25		20.0	0.001296	0.003704	6.47954E-05	25.91818
26		50.0	0.002638	0.002362	5.27633E-05	52.76334
27		100.0	0.003884	0.001116	3.88435E-05	77.68698
28		200.0	0.004751	0.000249	2.37553E-05	95.02129
29		500.0	0.004997	2.77E-06	9.99447E-06	99.94469
30		1000.0	0.005	1.53E-09	5E-06	99.99997
31						
32	True Ri	7.49994E-05				
33	0.99Ri	7.42494E-05				
34	0.95Ri	7.12495E-05				
35						
36	**Documentation**					
37	Cell C6=$B$3*(1-EXP(-$B$2*B6))					
38	Cell D5=$B$3-C6					
39	Cell E7=(C7-$C$6)/(B7-$B$6)					
40	Cell F14=(C14/0.005)*100					
41	Cell B32=(C7-C6)/(B7-B6)					
42	Cell B33=0.99*B32					
43	Cell B34=0.95*B32					

(a) The initial rate drops to $0.99R_\text{i}$ between times 1.3 and 1.4 s, which is ≈ 2% of the reaction.

(b) Between 6.0 and 7.0 s so a little over 9% of the reaction is completed.

Chapter 31

31-1. A *collector ion* is an ion added to a solution that forms a precipitate with the reagent which carries the desired minor species out of solution.

31-2. A high concentration of salt added to a solution that leads to precipitation of a protein is a *salting-out* effect. At low salt concentrations, protein solubility is often increased with increasing salt concentration, termed a *salting-in* effect.

31-3. The two events are transport of material and a spatial redistibrution of the components.

31-4. Precipitation, extraction, distillation, ion exchange.

31-5. **(a)** *Elution* is a process in which species are washed through a chromatographic column by additions of fresh mobile phase.

(b) The *mobile phase* in chromatography is the one that moves over or through an immobilized phase that is fixed in place in a column or on the surface of a flat plate.

(c) The *stationary phase* in chromatography is a solid or liquid phase that is fixed in place. The mobile phase then passes over or through the stationary phase.

(d) The *distribution constant* is an equilibrium constant for the distribution of a species between two phases.

(e) The *retention time* for an analyte is the time interval between its injection onto a column and its appearance at the detector at the other end of the column.

(f) The *retention factor k* is defined by the equation $k = K_A V_S / V_M$ where K_A is the partition ratio for the species A and V_S and V_M are the volumes of the stationary and mobile phases, respectively

(g) The *selectivity factor* α of a column toward two species is given by the equation $\alpha = K_B/K_A$, where K_B is the distribution constant for the more strongly retained species B and K_A is the constant for the less strongly held or more rapidly eluting species A.

(h) The *plate height*, H, of a chromatographic is defined by the relationship $H = \sigma^2 / L$ where σ^2 is the variance obtained from the Gaussian shaped chromatographic peak and L is the length of the column packing in centimeters.

31-6. *Strong acid type exchangers* have sulfonic acid groups ($-SO_3^-H^+$)attached to the polymeric matrix and have wider application than *weak acid type exchangers*, which owe their action to carboxylic acid (–COOH) groups.

31-7. The variables that lead to *band broadening* include: (1) large particle diameters for stationary phases; (2) large column diameters; (3) high temperatures (important only in gas chromatography); (4) for liquid stationary phases, thick layers of the immobilized liquid; and (5) very rapid or very slow flow rates.

31-8. In gas-liquid chromatography, the mobile phase is a gas, whereas in liquid-liquid chromatography, it is a liquid.

31-9. Determine the retention time t_R for a solute and the width of the solute peak at its base, W. The number of plates N is then $N = 16(t_R/W)^2$.

31-10. Two general methods for improving the resolution of a column are to increase the column length and to reduce the plate height.

31-11. $[X]_i = \left(\dfrac{V_{aq}}{V_{org}K + V_{aq}}\right)^i [X]_0$

(a) $[X]_1 = \left(\dfrac{50.0}{40.0 \times 8.9 + 50.0}\right)(0.200) = 0.0246 \text{ M}$

(b) $[\mathrm{X}]_2 = \left(\dfrac{50.0}{20.0\ \times\ 8.9 + 50.0}\right)^2 (0.200)$ = 9.62 × 10^{-3} M

(c) $[\mathrm{X}]_4 = \left(\dfrac{50.0}{10.0\ \times\ 8.9 + 50.0}\right)^4 (0.200)$ = 3.35 × 10^{-3} M

(d) $[\mathrm{X}]_8 = \left(\dfrac{50.0}{5.0\ \times\ 8.9 + 50.0}\right)^8 (0.200)$ = 1.23 × 10^{-3}M

31-12. **(a)** $[\mathrm{Z}]_1 = \left(\dfrac{25.0}{25.0\ \times\ 5.85 + 25.0}\right)(0.0550)$ = 8.029 × 10^{-3} M

% Z = 8.029 × 10^{-3} × 100%/0.0550 = 14.6%

(b) $[\mathrm{Z}]_2 = \left(\dfrac{25.0}{12.5\ \times\ 5.85 + 25.0}\right)^2 (0.0550)$ = 3.57 × 10^{-3} M

% Z = 3.57 × 10^{-3} × 100%/0.0550 = 6.49%

(c) $[\mathrm{Z}]_5 = \left(\dfrac{25.0}{5.0\ \times\ 5.85 + 25.0}\right)^5 (0.0550)$ = 1.14 × 10^{-3} M

% Z = 1.14 × 10^{-3} × 100%/0.0550 = 6.49% = 2.08%

(d) $[\mathrm{Z}]_{10} = \left(\dfrac{25.0}{2.50\ \times\ 5.85 + 25.0}\right)^{10} (0.0550)$ = 5.5 × 10^{-4} M

% Z = 5.5 × 10^{-4} × 100%/0.0550 = 6.49% = 1.0%

31-13. $[\mathrm{A}]_i = \left(\dfrac{V_{\mathrm{aq}}}{V_{\mathrm{org}}K + V_{\mathrm{aq}}}\right)^i [\mathrm{A}]_0$ $\qquad$ $i = \dfrac{\log\left([\mathrm{A}]_i / [\mathrm{A}]_0\right)}{\log\left(\dfrac{V_{\mathrm{aq}}}{V_{\mathrm{org}}K + V_{\mathrm{aq}}}\right)}$

(a) $i = \dfrac{\log\left(\dfrac{1.00\times10^{-4}}{0.0500}\right)}{\log\left(\dfrac{25.0}{25.0\times8.9 + 25.0}\right)}$ = 2.7 extractions. So 3 extractions are needed.

The total volume would be 75 mL with 3 extractions.

(b) As in part (a), *i* = 4.09 extractions, so 5 extractions are needed.

The total volume would be 5 × 10 mL = 50 mL

(c) *i* = 11.6 so 12 extractions are needed

The total volume would be 12 × 2 mL = 24 mL

31-14. **(a)**

$$i = \frac{\log\left(\frac{1.00\times10^{-5}}{0.0200}\right)}{\log\left(\frac{40.0}{50.0\times5.85+40.0}\right)} = 3.6 \text{ so 4 extractions are needed or } 4 \times 50 \text{ ml} = 200 \text{ mL}$$

(b) As in part (a), *i* = 4.94 or 5 extractions. A total volume of 5 × 25 mL = 125 mL.

(c) *i* = 8.4 so 9 extractions. A total volume of 9 × 10 mL = 90 mL.

31.15. If 99% of the solute is removed then 1% of solute remains and $[A]_i / [A]_0 = 0.01$.

(a) $$\frac{[A]_i}{[A]_0} = \left(\frac{50.0}{25.0K+50.0}\right)^2 = 0.01$$

$(0.01)^{1/2}(25.0K + 50.0) = 50.0$

$2.5K + 5.0 = 50.0$

$K = (50.0 - 5.0)/2.5 = 18.0$

(b) $$\frac{[A]_i}{[A]_0} = \left(\frac{50.0}{10.0K+50.0}\right)^5 = 0.01$$

$(0.01)^{1/5}(10.0K + 50.0) = 50.0$

$3.98K + 19.9 = 50.0$

$K = (50.0 - 19.9)/3.98 = 7.56$

31-16. **(a)** If 1.00×10^{-4} % of the solute remains, $[A]_i / [A]_0 = 1.00\times10^{-6}$.

$$\frac{[\mathrm{A}]_i}{[\mathrm{A}]_0} = \left(\frac{30.0}{10.0K + 30.0}\right)^4 = 1.00 \times 10^{-6}$$

$(1\times10^{-6})^{1/4}(10.0K + 30.0) = 30.0$

$0.316K + 0.949 = 30.0$

$K = (30.0 - 0.949)/0.31 = 91.9$

(b) For 1.00 × 10^{-3} %, $[\mathrm{A}]_i / [\mathrm{A}]_0 = 1.00\times10^{-5}$.

$$\frac{[\mathrm{A}]_i}{[\mathrm{A}]_0} = \left(\frac{30.0}{10.0K + 30.0}\right)^4 = 1.00 \times 10^{-5}$$

$(1\times10^{-5})^{1/4}(10.0K + 30.0) = 30.0$

$0.562K + 1.69 = 30.0$

$K = (30.0 - 1.69)/0.562 = 50.3$

(c) $\frac{[\mathrm{A}]_i}{[\mathrm{A}]_0} = \left(\frac{30.0}{10.0K + 30.0}\right)^4 = 1.00 \times 10^{-4}$

$(1\times10^{-4})^{1/4}(10.0K + 30.0) = 30.0$

$1.00K + 3.00 = 30.0$

$K = (30.0 - 3.00)/1.00 = 27.0$

31-17. **(a)** Recognizing that in each of the solutions [HA] = 0.0750 due to dilution, from the data for solution 1,

$[\mathrm{HA}]_{\mathrm{org}} = 0.0454$ M

$$[\mathrm{HA}]_{\mathrm{aq}} = \frac{25.0(0.0750) - 25.0(0.0454)}{25.0} = 0.0296 \text{ M}$$

$K = [\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{aq}} = 0.0454/0.0296 = 1.53$

(b) For solution 3, after extraction

$[HA]_{aq} = [HA]_{org} / K = 0.0225 / 1.53 = 0.0147$ M

$[A^-] = (\text{mols } HA_{tot} - \text{mols } HA_{aq} - \text{mols } HA_{org})/(25.0 \text{ mL})$

$$[A^-] = \frac{(25.0)(0.0750) - (25.0)(0.0147) - (25.0)(0.0225)}{25.0} = 0.0378 \text{ M}$$

(c) Since $[H^+] = [A^-]$, $K_a = (0.0378)^2/(0.0147) = 0.0972$

31-18. $[I_2]_{aq} = 1.12\times10^{-4}$ M

$[I_2]_{org} = (\text{mols } I_{2tot} - \text{mols } I_{2aq})/(10.0 \text{ mL})$

$$[I_2]_{org} = \frac{(25.0)(0.0100) - (25.0)(1.12\times10^{-4})}{10.0} = 0.0378 \text{ M}$$

$[I_2]_{org} = 0.0247$ M

$K = [I_2]_{org} / [I_2]_{aq} = 0.0247 / (1.12\times10^{-4}) = 221$

(b) after extraction, $[I_2]_{aq} = [I_2]_{org}/K = (1.02\times10^{-3})/221 = 4.62\times10^{-6}$ M

$[I(SCN)_2^-] = [I^-] = (\text{mmols } I_{2tot} - \text{mmols } I_{2aq} - \text{mmols } I_{2org})/(25.0 \text{ mL})$

$$[I(SCN)_2^-] = [I^-] = \frac{(25.0)(0.0100) - (25.0)(4.62\times10^{-6}) - (10.0)(1.02\times10^{-3})}{25.0} = 0.0095874 \text{ M}$$

$[SCN^-] = (\text{mmols } SCN^-_{tot} - 2\times\text{mmols } I(SCN)_2^-)/(25.0 \text{ mL})$

$$[SCN^-] = \frac{(25.0)(0.100) - 2\times(25.0)(0.0095874)}{25.0} = 0.080825$$

$$K_f = \frac{[I(SCN)_2^-][I^-]}{[I_2][SCN^-]^2} = (0.0095874)^2/(4.62\times10^{-6}\times(0.080825)^2) = 3.05\times10^3$$

31-19. (a) amount H^+ resulting from exchange = 15.3 mL × 0.0202 mmol/mL = 0.3091 mmol

mmols H^+ = mol cation = 0.3091 in 0.0250 L sample

0.3091 mmol cation/0.0250 L = 12.36 mmol cation/L

(b) $\dfrac{12.36\text{ mmol cation}}{\text{L}}\times\dfrac{1\text{ mmol CaCO}_3}{2\text{ mmol cation}}\times\dfrac{100.087\text{ mg CaCO}_3}{\text{mmol CaCO}_3}$ = 619 mg $CaCO_3$/L

31-20. $2.00\text{ L}\times\dfrac{0.1500\text{ mol HCl}}{\text{L}}\times\dfrac{1\text{ mol NaCl}}{1\text{ mol HCl}}\times\dfrac{58.4425\text{ g NaCl}}{\text{mol NaCl}}$ = 17.53 g NaCl

Dissolve 17.53 g of NaCl in about 100 mL water and pass through the column packed with a cation exchange resin in its acid form. Wash with several hundred milliliters of water, collecting the liquid from the original solution and washings in a 2.00-L volumetric flask. Dilute to the mark and mix well.

31-21. [HCl] = $17.53\text{ mL}\times\dfrac{0.02932\text{ mmol NaOH}}{\text{mL}}\times\dfrac{1\text{ mmol HCl}}{1\text{ mmol NaOH}}\times\dfrac{1}{25.00\text{ mL}}$

= 0.02056 mmol/mL

amount H_3O^+/mL from exchange = 35.94 mL×0.02932 mmol/mL/10.00 mL = 0.10538

= (no. mmol HCl + 2 × no. mmol $MgCl_2$)/mL

mmol $MgCl_2$/mL = (0.10536 – 0.02056)/2 = 0.0424

The solution is thus 0.02056 M in HCl and 0.0424 M in $MgCl_2$.

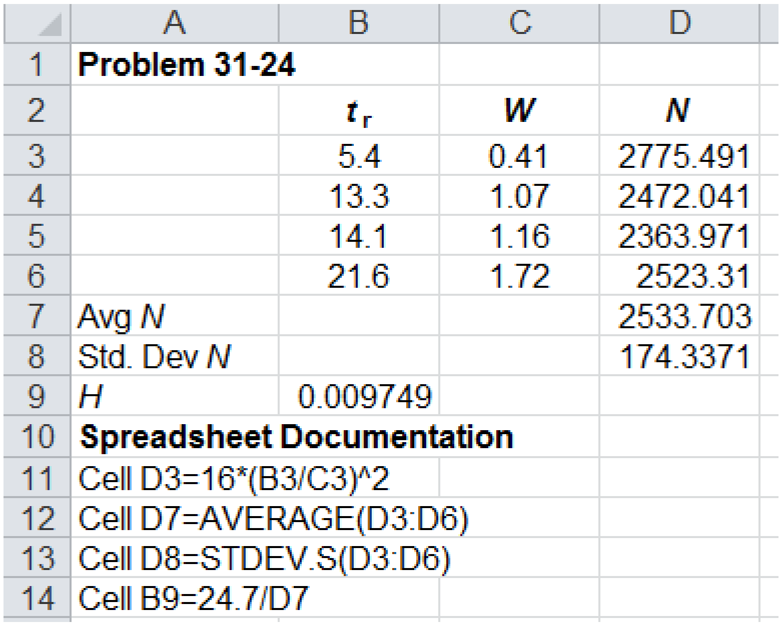
31-22. From Equation 31-12,

$$u_0 = F/\pi r^2 = F/\pi(d/2)^2 = \frac{0.95\text{ cm}^3\text{/min}}{3.1415\times\left(\dfrac{0.025\text{ cm}}{2}\right)^2}\left(\frac{1\text{ min}}{60\text{ s}}\right) = 32.3\text{ cm/s}$$

31-23. From equation 31-13,

$$u_0 = F/\varepsilon\pi r^2 = F/\varepsilon\pi(d/2)^2 = \frac{48\text{ cm}^3\text{/min}}{0.43\times3.1415\times\left(\dfrac{0.50\text{ cm}}{2}\right)^2}\left(\frac{1\text{ min}}{60\text{ s}}\right) = 9.5\text{ cm/s}$$

31-24. $N = 16(t_R/W)^2$



	A	B	C	D
1	**Problem 31-24**			
2		t_r	W	N
3		5.4	0.41	2775.491
4		13.3	1.07	2472.041
5		14.1	1.16	2363.971
6		21.6	1.72	2523.31
7	Avg *N*			2533.703
8	Std. Dev *N*			174.3371
9	*H*	0.009749		
10	**Spreadsheet Documentation**			
11	Cell D3=16*(B3/C3)^2			
12	Cell D7=AVERAGE(D3:D6)			
13	Cell D8=STDEV.S(D3:D6)			
14	Cell B9=24.7/D7			

(a) See column D in the spreadsheet

(b) $\overline{N} = 2534 \approx 2.5 \times 10^3$

$s = 174 \approx 0.2 \times 10^3$

$\overline{N} = 2.5\ (\pm 0.2) \times 10^3$

(c) $H = L/N = 0.0097$ cm

31-25. (a) $k = (t_R - t_M)/t_M$

For A, $k_A = (5.4 - 3.1)/3.1 = 0.742 = 0.74$

For B, $k_B = (13.3 - 3.1)/3.1 = 3.29 = 3.3$

For C, $k_C = (14.1 - 3.1)/3.1 = 3.55 = 3.5$

For D, $k_D = (21.6 - 3.1)/3.1 = 5.97 = 6.0$

(b) $K = k\, V_M/V_S$

For A, $K_A = 0.742 \times 1.37 / 0.164 = 6.2$

For compound B, $K_B = 3.29 \times 1.37\ 0.164 = 27$

For compound C, $K_C = 3.55 \times 1.37/0.164 = 30$

For compound D, $K_D = 5.97 \times 1.37/0.164 = 50$

31-26. (a) $R_S = 2[(t_R)_C - (t_R)_B]/(W_B + W_C)$

$R_S = 2(14.1 - 13.3)/(1.07 + 1.16) = 0.717 = 0.72$

(b) $\alpha_{C,B} = \dfrac{(t_R)_C - t_M}{(t_R)_B - t_M} = \dfrac{14.1 - 3.1}{13.3 - 3.1} = 1.08 = 1.1$

(c) $\dfrac{(R_S)_1}{(R_S)_2} = \dfrac{\sqrt{N_1}}{\sqrt{N_2}} = \dfrac{0.717}{1.5} = \dfrac{\sqrt{2534}}{\sqrt{N_2}}$

$N_2 = 2534 \times (1.5)^2 / (0.717)^2 = 11090 = 1.11 \times 10^4$

From solution 31-24 (c), $H = 9.75 \times 10^{-3}$ cm/plate

$L = 11090 \times 9.75 \times 10^{-3} = 108$ cm

(d) $\dfrac{(t_R)_1}{(t_R)_2} = \dfrac{(R_S)_1}{(R_S)_2} = \dfrac{14.1}{(t_R)_2} = \dfrac{(0.717)^2}{(1.5)^2}$

$(t_R)_2 = [14.1 \times (1.5)^2]/(0.717)^2 = 61.7 = 62$ min

31-27. (a) $R_S = 2[(t_R)_D - (t_R)_C] / (W_D + W_C)$

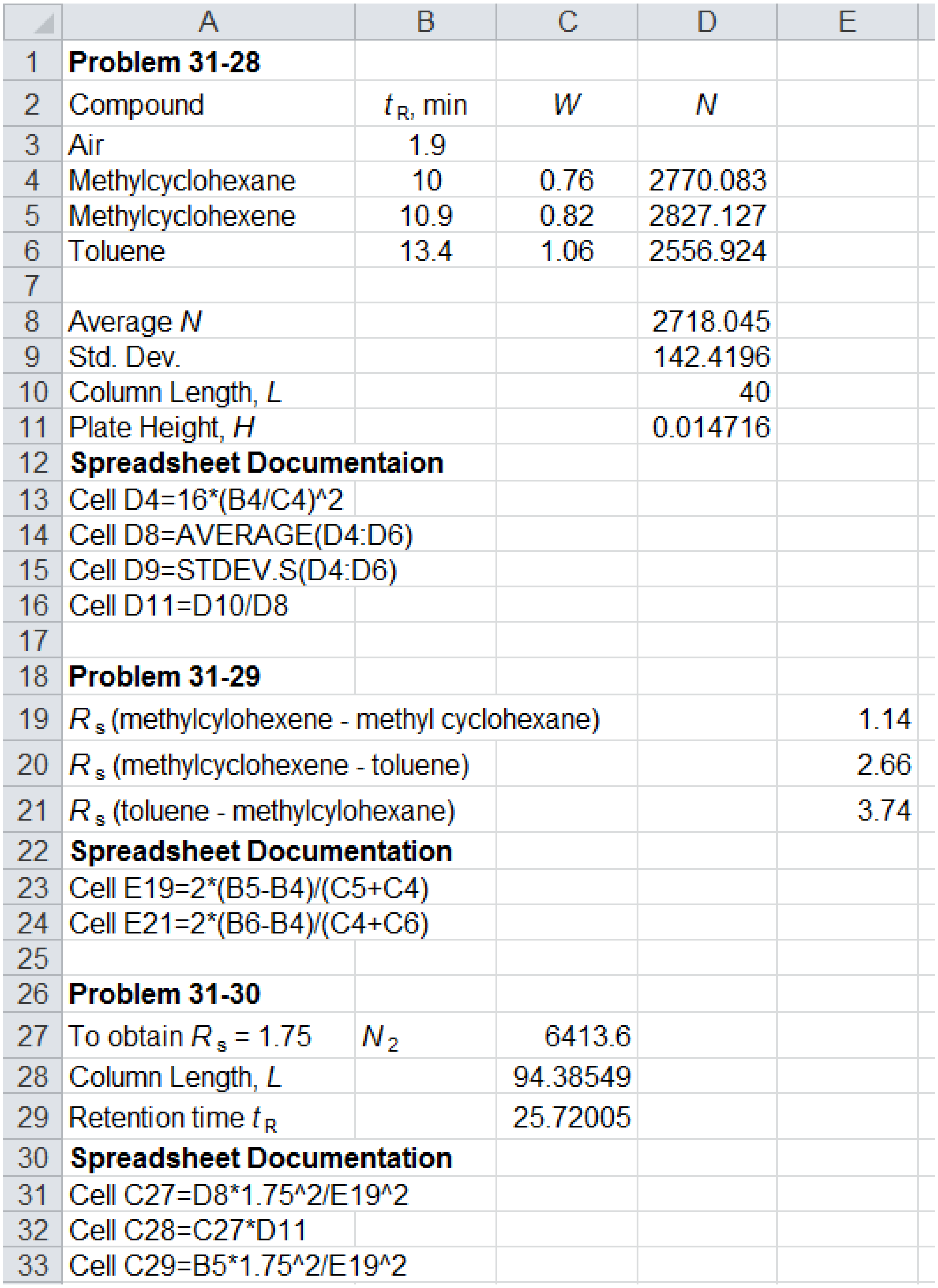
$R_S = 2(21.6 - 14.1)/(1.72 + 1.16) = 5.21 = 5.2$

(b) $\dfrac{(R_S)_1}{(R_S)_2} = \dfrac{\sqrt{N_1}}{\sqrt{N_2}} = \dfrac{1.5}{5.21} = \dfrac{\sqrt{N_1}}{\sqrt{2534}}$

$N_1 = 2534 \times (1.5)^2/(5.21)^2 = 210$

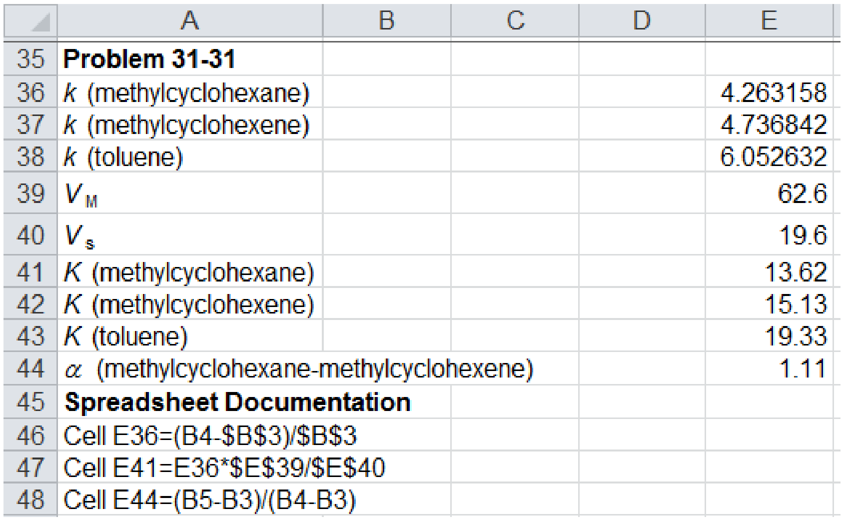
$L = 210 \times 9.75 \times 10^{-3} = 2.0$ cm

Problems 31-28 through 31-31: See next two spreadsheets



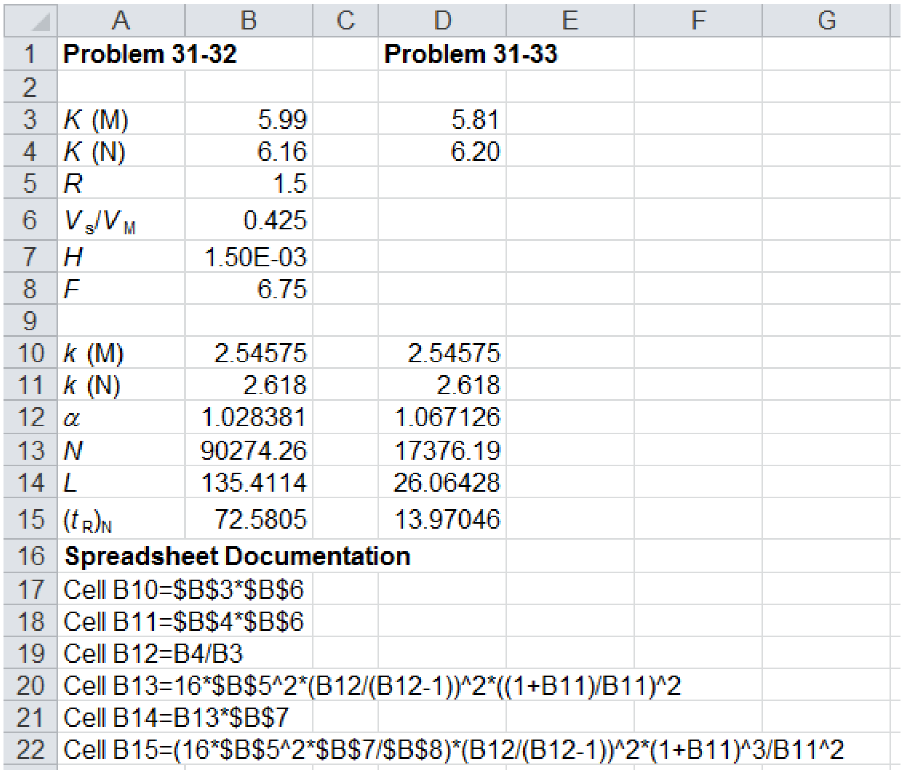
	A	B	C	D	E
1	**Problem 31-28**				
2	Compound	t_R, min	*W*	*N*	
3	Air	1.9			
4	Methylcyclohexane	10	0.76	2770.083	
5	Methylcyclohexene	10.9	0.82	2827.127	
6	Toluene	13.4	1.06	2556.924	
7					
8	Average *N*			2718.045	
9	Std. Dev.			142.4196	
10	Column Length, *L*			40	
11	Plate Height, *H*			0.014716	
12	**Spreadsheet Documentaion**				
13	Cell D4=16*(B4/C4)^2				
14	Cell D8=AVERAGE(D4:D6)				
15	Cell D9=STDEV.S(D4:D6)				
16	Cell D11=D10/D8				
17					
18	**Problem 31-29**				
19	R_s (methylcylohexene - methyl cyclohexane)				1.14
20	R_s (methylcyclohexene - toluene)				2.66
21	R_s (toluene - methylcylohexane)				3.74
22	**Spreadsheet Documentation**				
23	Cell E19=2*(B5-B4)/(C5+C4)				
24	Cell E21=2*(B6-B4)/(C4+C6)				
25					
26	**Problem 31-30**				
27	To obtain R_s = 1.75	N_2	6413.6		
28	Column Length, *L*		94.38549		
29	Retention time t_R		25.72005		
30	**Spreadsheet Documentation**				
31	Cell C27=D8*1.75^2/E19^2				
32	Cell C28=C27*D11				
33	Cell C29=B5*1.75^2/E19^2				

The following spreadsheet is a continuation of the previous spreadsheet.



	A	B	C	D	E
35	**Problem 31-31**				
36	k (methylcyclohexane)				4.263158
37	k (methylcyclohexene)				4.736842
38	k (toluene)				6.052632
39	V_M				62.6
40	V_s				19.6
41	K (methylcyclohexane)				13.62
42	K (methylcyclohexene)				15.13
43	K (toluene)				19.33
44	α (methylcyclohexane-methylcyclohexene)				1.11
45	**Spreadsheet Documentation**				
46	Cell E36=(B4-$B$3)/$B$3				
47	Cell E41=E36*$E$39/$E$40				
48	Cell E44=(B5-B3)/(B4-B3)				

Problems 31-32 and 31-33



	A	B	C	D	E	F	G
1	**Problem 31-32**			**Problem 31-33**			
2							
3	K (M)	5.99		5.81			
4	K (N)	6.16		6.20			
5	R	1.5					
6	V_s/V_M	0.425					
7	H	1.50E-03					
8	F	6.75					
9							
10	k (M)	2.54575		2.54575			
11	k (N)	2.618		2.618			
12	α	1.028381		1.067126			
13	N	90274.26		17376.19			
14	L	135.4114		26.06428			
15	$(t_R)_N$	72.5805		13.97046			
16	**Spreadsheet Documentation**						
17	Cell B10=$B$3*$B$6						
18	Cell B11=$B$4*$B$6						
19	Cell B12=B4/B3						
20	Cell B13=16*$B$5^2*(B12/(B12-1))^2*((1+B11)/B11)^2						
21	Cell B14=B13*$B$7						
22	Cell B15=(16*$B$5^2*$B$7/$B$8)*(B12/(B12-1))^2*(1+B11)^3/B11^2						

Chapter 32

32-1. In *gas-liquid chromatography*, the stationary phase is a liquid that is immobilized on a solid. Retention of sample constituents involves equilibria between a gaseous and a liquid phase. In *gas-solid chromatography,* the stationary phase is a solid surface that retains analytes by physical adsorption. Here separation involves adsorption equilibria.

32-2. Gas-solid chromatography has limited application because active or polar compounds are retained more or less permanently on the packings. In addition severe tailing is often observed owing to the nonlinear character of the physical adsorption process.

32-3. Gas-solid chromatography is used primarily for separating low molecular mass gaseous species, such as carbon dioxide, carbon monoxide and oxides of nitrogen.

32-4. Electronic, bubble, bubble with digital readout, digital mass or volume flow meters are used.

32-5. A chromatogram is a plot of detector response versus time. The peak position, retention time, can reveal the identity of the compound eluting. The peak area is related to the concentration of the compound.

32-6. *Temperature programming* involves increasing the temperature of a gas-chromatographic column as a function of time. This technique is particularly useful for samples that contain constituents whose boiling points differ significantly. Low boiling point constituents are separated initially at temperatures that provide good resolution. As the separation proceeds the column temperature is increased so that the higher boiling constituents come off the column with good resolution and at reasonable lengths of time.

32-7. In *open tubular or capillary columns,* the stationary phase is held on the inner surface of a capillary, whereas in *packed columns,* the stationary phase is supported on particles that are contained in a glass or metal tube. Open tubular columns contain an enormous number of plates that permit rapid separations of closely related species. They suffer from small sample capacities.

32-8. For satisfactory qualitative data, carrier gas flow rate, column temperature, injection port temperature, and injection volume (sample size) are among the most important variables.

32-9. Sample injection volume, carrier gas flow rate and column condition are among the parameters which must be controlled for highest precision quantitative GC. The use of an internal standard can minimize the impact of variations in these parameters.

32-10. **(a)** The *thermal conductivity detector* is based on the decrease in thermal conductivity of the helium or hydrogen carrier gas brought about by the presence of analyte molecules.

(b) The *flame ionization detector* is based on measuring the current that results from ions and electrons produced when organic compounds are combusted in a small air/hydrogen flame.

(c) The *electron capture detector* is based on the affinity of halogen-containing organic compounds for electrons emitted by nickel-63 leading to a reduction in the monitored current.

(d) The *thermionic detector* is based on the ion currents produced when the mobile phase is combusted in a hydrogen flame and then passed over a heated rubidium silicate bead. It is used primarily for detecting analytes that contain phosphorus or nitrogen.

(e) The *photoionization detector* is based on the ion currents that develop when analyte molecules are irradiated with an intense beam of far-ultraviolet radiation.

32-11. **(a)** Advantages of thermal conductivity: general applicability, large linear range, simplicity, nondestructive.

Disadvantage: low sensitivity.

(b) Advantages of flame ionization: high sensitivity, large linear range, low noise, ruggedness, ease of use, and response that is largely independent of flow rate.

Disadvantage: destructive.

(c) Advantages of electron capture: high sensitivity selectivity towards halogen-containing compounds and several others, nondestructive.

Disadvantage: small linear range.

(d) Advantages of thermionic detector: high sensitivity for compounds containing nitrogen and phosphorus, good linear range.

Disadvantages: destructive, not applicable for many analytes.

(e) Advantages of photoionization: versatility, nondestructive, large linear range.

Disadvantages: not widely available, expensive.

32-12. A *hyphenated gas chromatographic method* is a method in which the analytes exiting from a column are identified by one of the selective techniques such as mass spectrometry, absorption or emission spectroscopy or voltammetry.

32-13. Megabore columns are open tubular columns that have a greater inside diameter (530 μm) than typical open tubular columns (150 to 320 μm). Megabore columns can tolerate sample sizes similar to those for packed columns, but with significantly improved performance characteristics. Thus, megabore columns can be used for preparative scale GC purification of mixtures where the compound of interest is to be collected and further analyzed using other analytical techniques.

32-14. **a)** A PLOT column is a porous layer open tubular column, which is also called a support coated open-tubular (SCOT) column. The inner surface of a PLOT column is lined with a thin film of a support material, such as a diatomaceous earth. This type of column holds several times as much stationary phase as does a wall-coated column.

(b) A WCOT column is simply a capillary tubing fashioned from fused silica, stainless steel, aluminum, copper, plastic or glass. Its inner walls are coated with a thin layer of the mobile phase.

32-15. Currently, liquid stationary phases are generally bonded and/or cross-linked in order to provide thermal stability and a more permanent stationary phase that will not leach off the column. Bonding involves attaching a monomolecular layer of the stationary phase to the packing surface by means of chemical bonds. Cross linking involves treating the stationary phase while it is in the column with a chemical reagent that creates cross links between the molecules making up the stationary phase.

32-16. The stationary phase liquid should have low volatility, good thermal stability, chemical inertness and solvent characteristics that provide suitable retention factor and selectivity for the separation.

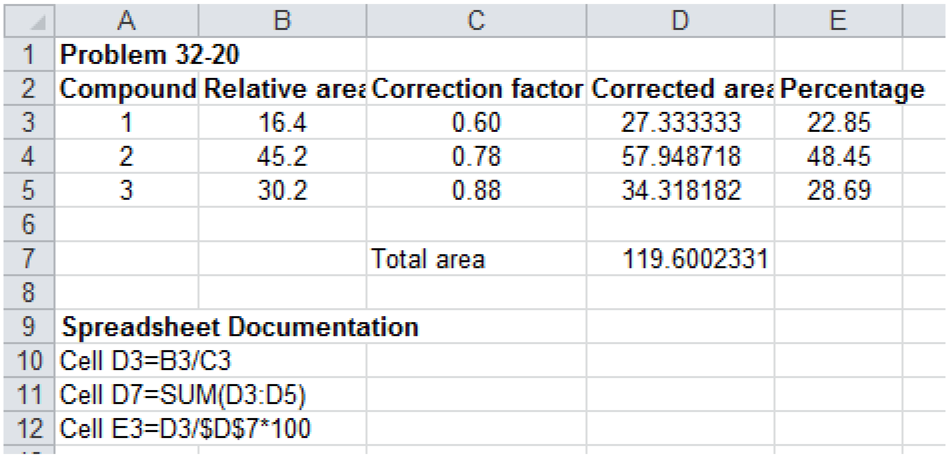
32-17. Fused silica columns have greater physical strength and flexibility than glass open tubular columns and are less reactive toward analytes than either glass or metal columns.

32-18. Film thickness influences the rate at which analytes are carried through the column, with the rate increasing as the thickness is decreased. Less band broadening is encountered with thin films.

32-19. **(a)** Band broadening arises from very high or very low flow rates, large particles making up packing, thick layers of stationary phase, low temperature, and slow injection rates.

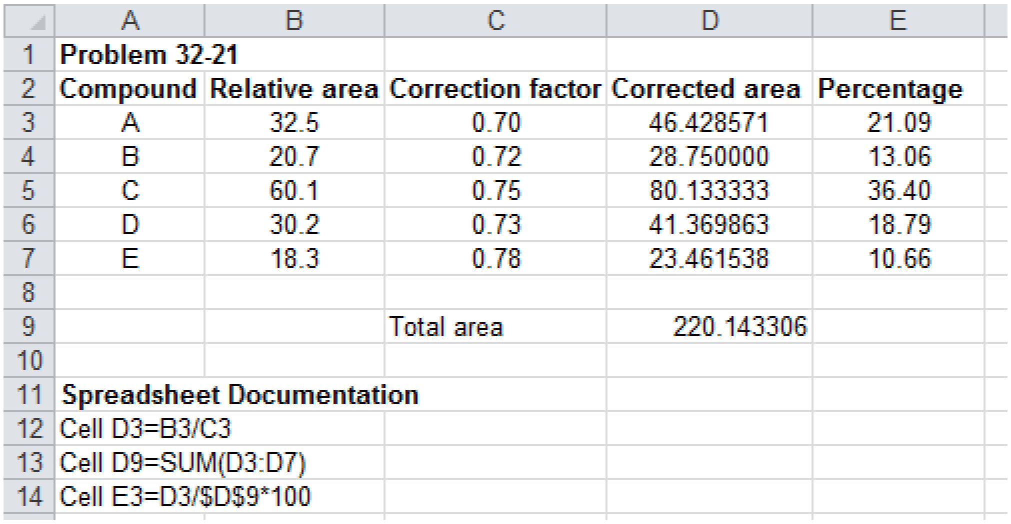
(b) Band separation is enhanced by maintaining conditions so that *k* lies in the range of 1 to 10, using small particles for packing, limiting the amount of stationary phase so that particle coatings are thin, and injecting the sample rapidly.

32-20.



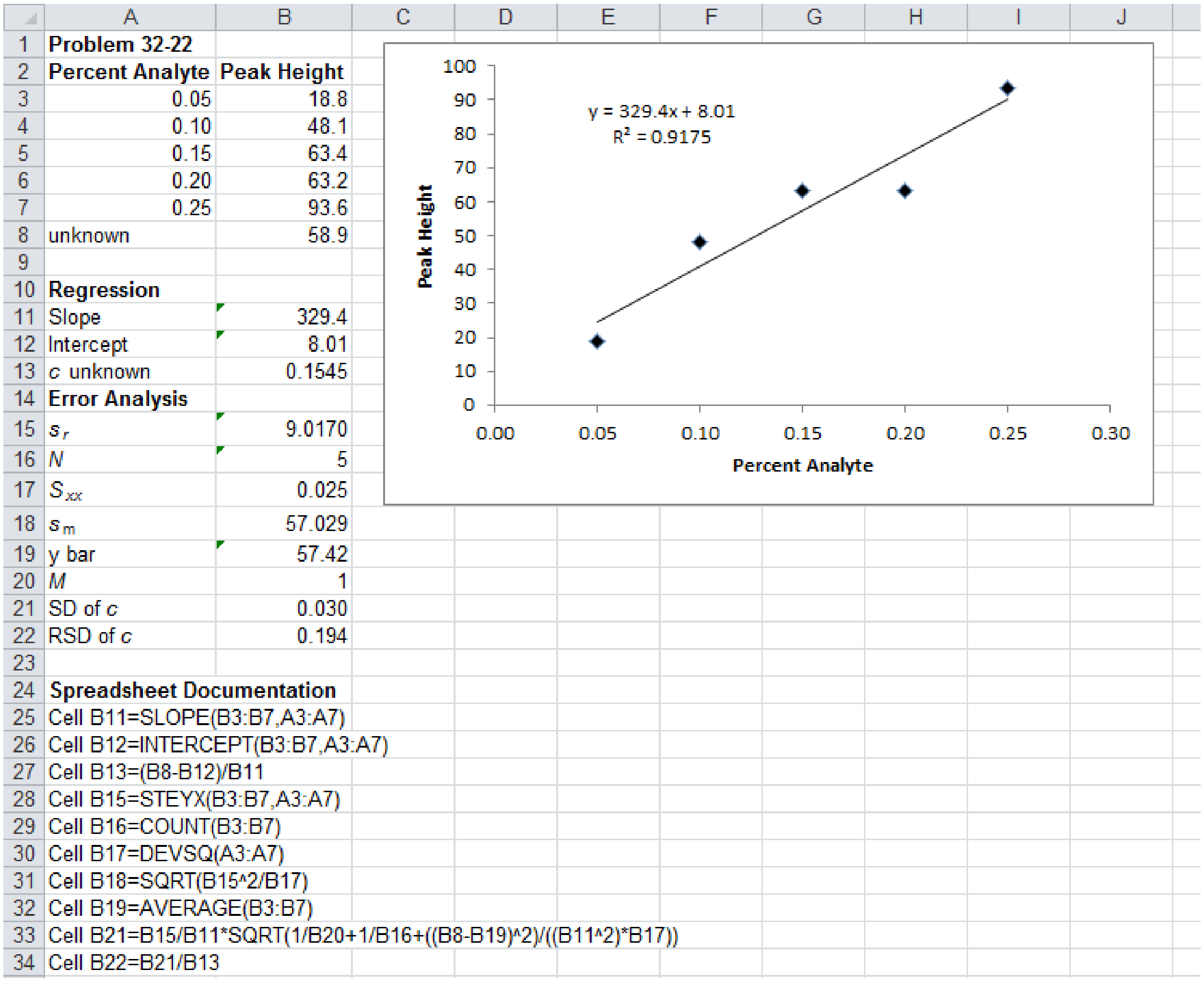
	A	B	C	D	E
1	**Problem 32-20**				
2	**Compound**	**Relative are**	**Correction factor**	**Corrected are**	**Percentage**
3	1	16.4	0.60	27.333333	22.85
4	2	45.2	0.78	57.948718	48.45
5	3	30.2	0.88	34.318182	28.69
6					
7			Total area	119.6002331	
8					
9	**Spreadsheet Documentation**				
10	Cell D3=B3/C3				
11	Cell D7=SUM(D3:D5)				
12	Cell E3=D3/$D$7*100				

32-21.



	A	B	C	D	E
1	**Problem 32-21**				
2	**Compound**	**Relative area**	**Correction factor**	**Corrected area**	**Percentage**
3	A	32.5	0.70	46.428571	21.09
4	B	20.7	0.72	28.750000	13.06
5	C	60.1	0.75	80.133333	36.40
6	D	30.2	0.73	41.369863	18.79
7	E	18.3	0.78	23.461538	10.66
8					
9			Total area	220.143306	
10					
11	**Spreadsheet Documentation**				
12	Cell D3=B3/C3				
13	Cell D9=SUM(D3:D7)				
14	Cell E3=D3/$D$9*100				

32-22.



	A	B
1	**Problem 32-22**	
2	**Percent Analyte**	**Peak Height**
3	0.05	18.8
4	0.10	48.1
5	0.15	63.4
6	0.20	63.2
7	0.25	93.6
8	unknown	58.9
9		
10	**Regression**	
11	Slope	329.4
12	Intercept	8.01
13	c unknown	0.1545
14	**Error Analysis**	
15	s_r	9.0170
16	N	5
17	S_{xx}	0.025
18	s_m	57.029
19	y bar	57.42
20	M	1
21	SD of c	0.030
22	RSD of c	0.194
23		
24	**Spreadsheet Documentation**	
25	Cell B11=SLOPE(B3:B7,A3:A7)	
26	Cell B12=INTERCEPT(B3:B7,A3:A7)	
27	Cell B13=(B8-B12)/B11	
28	Cell B15=STEYX(B3:B7,A3:A7)	
29	Cell B16=COUNT(B3:B7)	
30	Cell B17=DEVSQ(A3:A7)	
31	Cell B18=SQRT(B15^2/B17)	
32	Cell B19=AVERAGE(B3:B7)	
33	Cell B21=B15/B11*SQRT(1/B20+1/B16+((B8-B19)^2)/((B11^2)*B17))	
34	Cell B22=B21/B13	

The percentage of the analyte in the unknown by the method of external standards is 0.15 ± 0.03, which is substantially less precise than the value determined using the method of internal standards which obtained an unknown concentration of 0.163 ± 0.008. The internal standards compensate for variations in sample injection volume, carrier gas flow rate, and column conditions.

Chapter 33

33-1. **(a)** Substances that are somewhat volatile and are thermally stable.

(b) Molecular species that are nonvolatile and are thermally stable.

(c) Substances that are ionic.

(d) Molecules that selectively bind the affinity ligand usually biomolecules.

(e) High molecular mass compounds that are soluble in nonpolar solvents.

(f) High molecular mass hydrophilic compounds.

(g) Chiral compounds (enantiomers).

33-2. **(a)** In an *isocratic elution,* the solvent composition is held constant throughout the elution.

(b) In a *gradient elution*, two or more solvents are employed and the composition of the eluent is changed continuously or in steps as the separation proceeds.

(c) In a *normal-phase packing*, the stationary phase is quite polar and the mobile phase is relatively nonpolar.

(d) A *reversed-phase packing* is a nonpolar packing that is used in partition chromatography with a relatively polar mobile phase.

(e) In a *bonded-phase packing*, the stationary phase liquid is held in place by chemically bonding it to the solid support.

(f) In *chiral chromatography,* enantiomers are separated based on their different interactions with a chiral resolving agent.

(g) In *ion-pair chromatography* a large organic counter-ion is added to the mobile phase as an ion-pairing reagent. Separation is achieved either through partitioning of the neutral ion-pair or as a result of electrostatic interactions between the ions in solution and charges on the stationary phase resulting from adsorption of the organic counter-ion.

(h) An *eluent-suppressor column* is located after the ion-exchange column in ion chromatography. It converts the ionized species used to elute analyte ions to largely undissociated molecules that do not interfere with conductometric detection.

(i) *Gel filtration* is a type of size-exclusion chromatography in which the packings are hydrophilic, and eluents are aqueous. It is used for separating high molecular mass polar compounds.

(j) *Gel permeation* is a type of size-exclusion chromatography in which the packings are hydrophobic and the eluents are nonaqueous. It is used for separating high molecular mass nonpolar species.

33-3. **(a)** diethyl ether, benzene, *n*-hexane.

(b) acetamide, acetone, dichloroethane.

33-4. **(a)** ethyl acetate, dimethylamine, acetic acid.

(b) hexane, propylene, benzene, dichlorobenzene.

33-5. In *adsorption chromatography,* separations are based on adsorption equilibria between the components of the sample and a solid surface. In *partition chromatography,* separations are based on distribution equilibria between two immiscible liquids.

33-6. In *size-exclusion chromatography* separations are based on the size, and to some extent the shape, of molecules with little interactions between the stationary phase and the sample components occurring. In *ion-exchange chromatography,* in contrast, separations are based on ion-exchange reactions between the stationary phase and the components of the sample in the mobile phase.

33-7. *Gel filtration* is a type of size-exclusion chromatography in which the packings are hydrophilic and eluents are aqueous. It is used for separating high molecular mass polar compounds. *Gel permeation chromatography* is a type of size-exclusion chromatography in which the packings are hydrophobic and the eluents are nonaqueous. It is used for separating high molecular mass nonpolar species.

33-8. Nonvolatile and thermally unstable compounds.

33-9. In an *isocratic elution,* the solvent composition is held constant throughout the elution. Isocratic elution works well for many types of samples and is simplest to implement. In a *gradient elution*, two or more solvents are employed and the composition of the eluent is changed continuously or in steps as the separation proceeds. Gradient elution is best used for samples in which there are some compounds separated well and others with inordinately long retention times.

33-10. *Pneumatic pumps* are simple, inexpensive and pulse free. They consist of a collapsible solvent container housed in a vessel that can be pressurized by a compressed gas. This pump has limited capacity and pressure output and is not adaptable to gradient elution. The pumping rate depends on solvent viscosity. *Screw-driven syringe pumps* consist of a large syringe in which the piston is moved by a motor-driven screw. They are pulse free and the rate of delivery is easily varied. They suffer from lack of capacity and are inconvenient when solvents must be changed. *Reciprocating pumps* are versatile and widely used. They consist of a small cylindrical chamber that is filled and then emptied by the back-and-forth motion of a piston. Advantages include small internal volume, high output pressures, adaptability to gradient elution, and constant flow rates that are independent of viscosity and back pressure. The pulsed output must be damped.

33-11. In *suppressor-column ion chromatography* the chromatographic column is followed by a column whose purpose is to convert the ions used for elution to molecular species that are largely nonionic and thus do not interfere with conductometric detection of the analyte species. In *single-column ion chromatography*, low capacity ion exchangers are used so that the concentrations of ions in the eluting solution can be kept low. Detection then is based on the small differences in conductivity caused by the presence of eluted sample components.

33-12. A gas-phase sample is needed for mass spectrometry. The output of the LC column is a solute dissolved in a solvent, whereas the output of the GC column is a gas and thus directly compatible. As a first step in LC/MS, the solvent must be vaporized. When vaporized, however, the LC solvent produces a gas volume that is 10-1000 times greater than the carrier gas in GC. Hence, most of the solvent must also be removed.

33-13. Comparison of Table 33-1 with Table 32-1 suggests that the GC detectors that are suitable for HPLC are the mass spectrometer, FTIR and possible photoionization. Many of the GC detectors are unsuitable for HPLC because they require the eluting analyte components to be in the gas-phase.

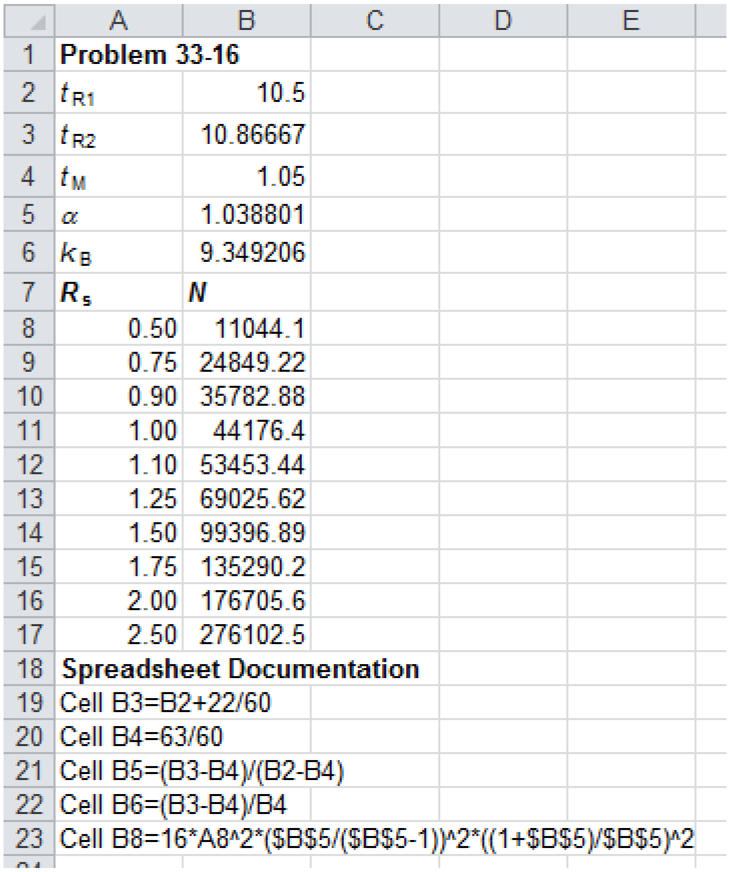
33-14. The ideal HPLC detector would have all the same characteristics as listed for the ideal GC detector. In addition, the HPLC detector should have low dead volume and be compatible with the liquid flows and pressures encountered in HPLC.

33-15. A number of factors that influence separation are clearly temperature dependent including distribution constants and diffusion rates. In addition, temperature changes can influence selectivity if components A and B are influenced differently by changes in temperature. Because resolution depends on all these factors, resolution will also be temperature dependent.

(a) For a reversed phase chromatographic separation of a steroid mixture, selectivity and, as a consequence, separation could be influenced by temperature dependent changes in distribution coefficients.

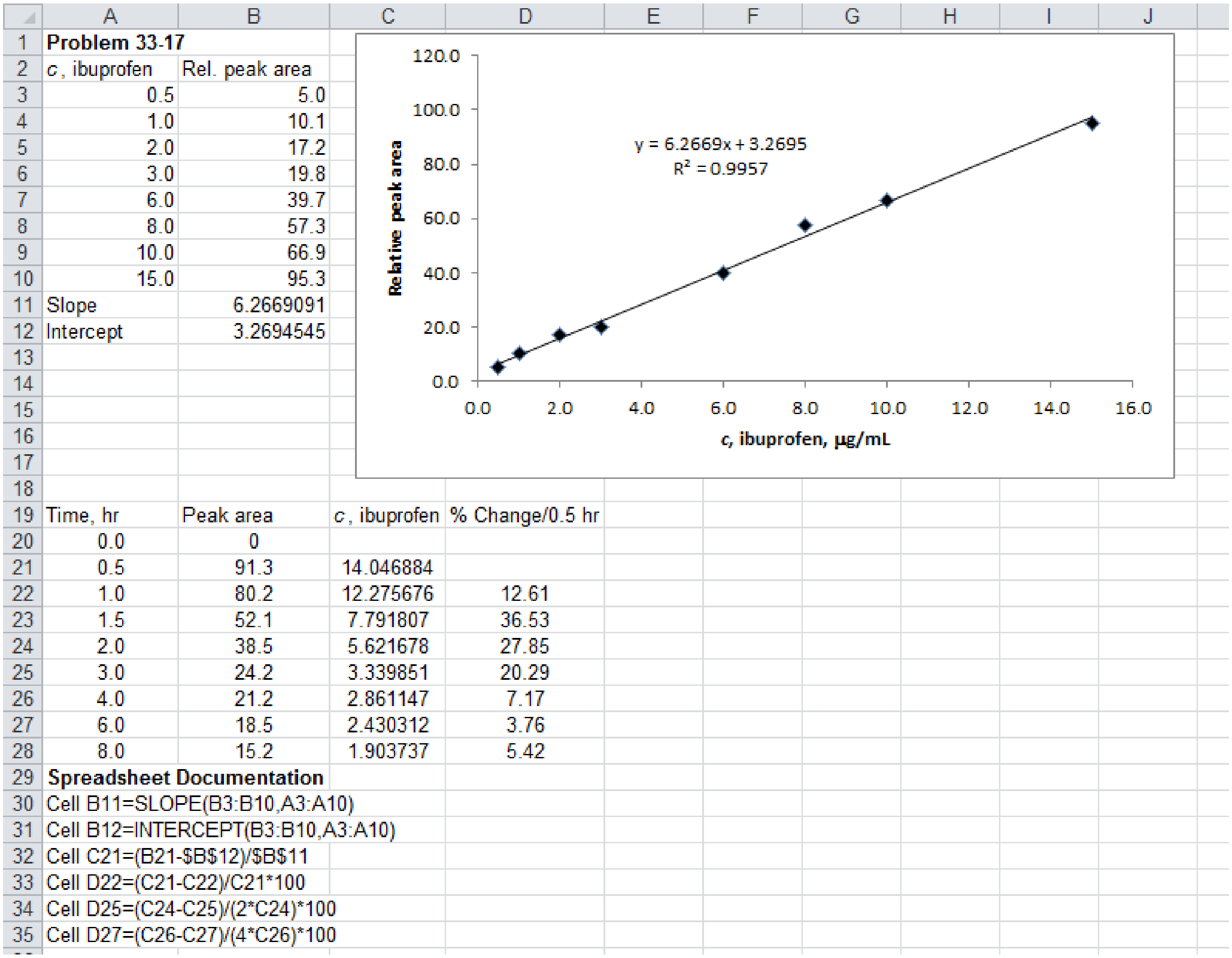
(b) For an adsorption chromatographic separation of a mixture of isomers, selectivity and, as a consequence, separation could be influenced by temperature dependent changes in distribution coefficients.

33-16.



	A	B	C	D	E
1	**Problem 33-16**				
2	t_{R1}	10.5			
3	t_{R2}	10.86667			
4	t_M	1.05			
5	α	1.038801			
6	k_B	9.349206			
7	R_s	N			
8	0.50	11044.1			
9	0.75	24849.22			
10	0.90	35782.88			
11	1.00	44176.4			
12	1.10	53453.44			
13	1.25	69025.62			
14	1.50	99396.89			
15	1.75	135290.2			
16	2.00	176705.6			
17	2.50	276102.5			
18	**Spreadsheet Documentation**				
19	Cell B3=B2+22/60				
20	Cell B4=63/60				
21	Cell B5=(B3-B4)/(B2-B4)				
22	Cell B6=(B3-B4)/B4				
23	Cell B8=16*A8^2*($B$5/($B$5-1))^2*((1+$B$5)/$B$5)^2				

33-17.



	A	B	C	D
1	**Problem 33-17**			
2	*c*, ibuprofen	Rel. peak area		
3	0.5	5.0		
4	1.0	10.1		
5	2.0	17.2		
6	3.0	19.8		
7	6.0	39.7		
8	8.0	57.3		
9	10.0	66.9		
10	15.0	95.3		
11	Slope	6.2669091		
12	Intercept	3.2694545		
13				
14				
15				
16				
17				
18				
19	Time, hr	Peak area	*c*, ibuprofen	% Change/0.5 hr
20	0.0	0		
21	0.5	91.3	14.046884	
22	1.0	80.2	12.275676	12.61
23	1.5	52.1	7.791807	36.53
24	2.0	38.5	5.621678	27.85
25	3.0	24.2	3.339851	20.29
26	4.0	21.2	2.861147	7.17
27	6.0	18.5	2.430312	3.76
28	8.0	15.2	1.903737	5.42
29	**Spreadsheet Documentation**			
30	Cell B11=SLOPE(B3:B10,A3:A10)			
31	Cell B12=INTERCEPT(B3:B10,A3:A10)			
32	Cell C21=(B21-$B$12)/$B$11			
33	Cell D22=(C21-C22)/C21*100			
34	Cell D25=(C24-C25)/(2*C24)*100			
35	Cell D27=(C26-C27)/(4*C26)*100			

The largest loss of ibuprofen as a percentage occurs between 1.0 and 1.5 hours.

Chapter 34

34-1. **(a)** Nonvolatile or thermally unstable species that contain no chromophoric groups.

(b) Particularly important for drug purity determination and in clinical laboratories.

(c) Inorganic anions and cations, amino acids, catecholamines, drugs, vitamins, carbohydrates, peptides, proteins, nucleic acids, nucleotides, and polynucleotides.

(d) Molecules with molecular masses exceeding 10^6 like polymers, biological macromolecules, natural and industrial colloids, emulsions and subcelluar particles.

(e) Proteins, synthetic polymers, and colloidal particles.

(f) Low molecular mass aromatic phenols and nitro compounds.

34-2. **(a)** A *supercritical fluid* is a substance that is maintained above its critical temperature so that it cannot be condensed into a liquid no matter how great the pressure.

(b) The *critical point* is the point on a temperature / pressure phase diagram above which the gas acquires supercritical fluid properties.

(c) In *two-dimensional thin layer chromatography,* development is carried out with two solvents that are applied successively at right angles to one another.

(d) The *electrophoretic mobility* is the ratio of the migration rate of an ion to the applied electric field.

(e) The *critical micelle concentration* is the level above which surfactant molecules begin to form spherical aggregates made up to 40 to 100 ions with their hydrocarbon tails in the interior of the aggregate and their charged ends exposed to water on the outside.

(f) In *electrical* FFF, an electric field is applied perpendicular to the flow direction. Retention and separation occur based on electrical charge.

34-3. The properties of a supercritical fluid that are important in chromatography include its density, its viscosity, and the rates at which solutes diffuse in it. The magnitude of each of these lies intermediate between a typical gas and a typical liquid.

34-4. Pressure increases the density of a supercritical fluid, which causes the retention factor k for analytes to change. Generally, increases in pressure reduce the retention times of solutes.

34-5. (a) Instruments for supercritical-fluid chromatography are very similar to those for HPLC except that in SFC there are provisions for controlling and measuring the column pressure. (b) SFC instruments differ substantially from those used for GC in that SFC instruments must be capable of operating at much higher mobile phase pressures than are typically encountered in GC’

34-6. It is an excellent solvent for a variety of nonpolar organic molecules. It transmits in the UV range and is odorless, nontoxic, readily available, and remarkably inexpensive relative to other chromatographic solvents. In addition, its critical temperature and pressure are relatively low allowing a wide selection of temperatures and pressures to be used without exceeding the operating limits of modern instrumentation.

34-7. Their ability to dissolve large nonvolatile molecules, such as large *n*-alkanes and polycyclic aromatic hydrocarbons.

34-8. Like GC, SFC is inherently faster than liquid chromatography because of the lower viscosity and higher diffusion rates in the mobile phase. Unlike GC, however, the intermediate diffusivities and viscosities of supercritical fluids reduce longitudinal band spreading, similar to the situation encountered in HPLC.

34-9. **(a)** An increase in flow rate results in a decrease in retention time.

(b) An increase in pressure results in a decrease in retention time.

(c) An increase in temperature results in a decrease in density of supercritical fluids and thus an increase in retention time.

34-10. In solution, amino acids exist as zwitterions that bear both a positive and a negative charge. At low pH values, the net effective charge is positive owing to the interaction of hydrogen ions with the amine groups of the amino acid, whereas at high pH values the net charge is negative due to the dissociation of the carboxylic acid groups. Thus, at low pH values the protein molecules will be strongly attracted toward the negative electrode, while in basic solutions the reverse will be the case.

34-11. *Electroosmotic flow* is the migration of the solvent towards the cathode in an electrophoretic separation. This flow is due to the electrical double layer that develops at the silica/solution interface. At pH values higher than 3 the inside wall of the silica capillary becomes negatively charged leading to a build-up of buffer cations in the electrical double layer adjacent to the wall. The cations in this double layer are attracted to the cathode and, since they are solvated they drag the bulk solvent along with them.

34-12. Electroosmotic flow can be repressed by reducing the charge on the interior of the capillary by chemical treatment of the surface. Sometimes, species elute from the capillary before they are resolved because of electroosmotic flow. Flow rates can also be erratic due to surface capillary conditions such non-uniform charge distributions and adsorption of ions.

34-13. Under the influence of an electric field, mobile ions in solution are attracted or repelled by the negative potential of one of the electrodes. The rate of movement toward or away from a negative electrode is dependent on the net charge on the analyte and the size and shape of analyte molecules. These properties vary from species to species. Hence, the rate at which molecules migrate under the influence of the electric field vary, and the time it takes them to traverse the capillary varies, making separations possible.

34-14. **(a)** $N = \dfrac{\mu_e V}{2D} = \dfrac{(5.13 \times 10^{-4})(5000)}{2(9.1 \times 10^{-6})} = 1.41 \times 10^5$

(b) $N = (5.13 \times 10^{-4})(10000)/(2 \times 9.1 \times 10^{-6}) = 2.8 \times 10^5$

(c) $N = (5.13 \times 10^{-4})(20000)/(2 \times 9.1 \times 10^{-6}) = 5.6 \times 10^5$

(d) $N = (5.13 \times 10^{-4})(30000)/(2 \times 9.1 \times 10^{-6}) = 8.4 \times 10^5$

34-15. The electrophoretic mobility is given by

$$v = \frac{\mu_e V}{L} = \frac{5.13 \times 10^{-4}\ \text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1} \times 20000\ \text{V}}{50} = 0.2052\ \text{cm s}^{-1}$$

The electroosmotic flow rate is given as 0.65 mm s^{-1} = 0.065 cm s^{-1}

Thus, the total flow rate = 0.2052 + 0.065 = 0.2702 cm s^{-1}, and

$t = [(40.0\ \text{cm})/0.2702\ \text{cm s}^{-1})] \times (1\ \text{min}/60\ \text{s}) = 2.5\ \text{min}$

34-16. In *micellar electrokinetic capillary chromatography* surfactants are added to the operating buffer in amounts that exceed the critical micelle concentration. The components of a sample added to this system distribute themselves between the aqueous phase and the hydrocarbon phase in the interior of the micelles according to their partition coefficients, similar to partition chromatography. The negatively charged micelles do exhibit electrophoretic flow but at a much slower rate than the buffer. Thus, MEKC is a true chromatography, where CZE separates sample components simply on the basis of ion mobility in a homogeneous buffer solution.

34-17. Higher column efficiencies and the ease with which pseudostationary phase can be altered.

34-18. Particle size and mass.

34-19. B^+ followed by A^{2+} followed by C^{3+}.

34-20. FFF methods are particularly well suited to high molecular mass materials such as polymers, large particles and colloids. In addition, no packing material or stationary phase is needed for separation to occur avoiding undesirable interactions between the packing material and the sample constituents. Finally, the geometry and flow profiles in FFF are well characterized allowing fairly exact theoretical predictions of retention and plate height to be made.