Answers to Selected Questions and Problems

Chapter 2

2-1. (a) *Constant errors* are the same magnitude regardless of the sample size. *Proportional errors* are proportional in size to the sample size.

(c) The *mean* is the sum of the measurements in a set divided by the number of measurements. The *median* is the central value for a set of data; half of the measurements are larger and half are smaller than the median.

2-2. (1) Random temperature fluctuations causing random changes in the length of the metal rule; (2) uncertainties arising from having to move and position the rule twice; (3) personal judgment in reading the rule; (4) vibrations in the table and/or rule; (5) uncertainty in locating the rule perpendicular, to the edge of the table.

2-3. The three types of systematic error are *instrumental error, method error*, and *personal error.*

2-5. Constant errors.

	(a)	(c)
2-6.	−0.04%	−0.3%
2-7.	13 g	3 g
2-8.	+0.06%	+0.12%
2-9.	−1.0%	−0.10%

Chapter 3

3-1. (a) The *spread* or *range* for a set of replicate data is the numerical difference between the highest and lowest value.

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

3-2. (a) The *sample variance*, s^2, is given by the expression

$$s^2 = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}$$

where $\bar{x}$ is the sample mean.

The *sample standard deviation* is given by

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$$

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

3-3. (a) In statistics, a sample is a small set of replicate measurements. In chemistry, a sample is a portion of a material that is used for analysis.

3-5.

	Mean	Median	Spread	Standard Deviation	CV
A	2.08	2.1	0.9	0.35	17%
C	0.0918	0.0894	0.0116	0.0055	6.0%
E	69.53	69.635	0.44	0.22	0.31%

3-6.

	Absolute Error	Relative Error, ppt
A	+0.08	+40
C	−0.0012	−13
E	+0.48	+7.0

3-7.

	s_y	CV	y
(a)	0.030	5.2%	$0.57(\pm 0.03)$
(c)	0.14×10^{-16}	2.0%	$6.9(\pm 0.1) \times 10^{-1}$
(e)	5.1×10^{-3}	8.5%	$6.0(\pm 0.5) \times 10^{-2}$

3-8.

	s_y	CV	y
(a)	0.03×10^{-7}	2%	$-1.37(\pm 0.03) \times 10$
(c)	1.8	50%	4 ± 2
(e)	2×10^1	50%	$5(\pm 2) \times 10^1$

3-9.

	s_y	CV	y
(a)	0.0065	0.18%	$-3.70(\pm 0.01)$
(c)	0.11	0.7%	$15.8(\pm 0.1)$

3-10. (a) $s_y = 2.0$; CV = 1.9%; $y = 105(\pm 2)$

3-11. $2.2(\pm 0.1) \times 10^5$ L

3-13. $s_1 = 0.095$; $s_2 = 0.12$; $s_3 = 0.11$; $s_4 = 0.10$; $s_5 = 0.10$;
$s_{\text{pooled}} = 0.11\%$ K

3-15. $s_{\text{pooled}} = 0.29\%$

Chapter 4

4-1. Set A 2.1 ± 0.4; Set C 0.092 ± 0.009; Set E 69.5 ± 0.3

4-2. Set A 2.1 ± 0.2; Set C 0.092 ± 0.007; Set E 69.5 ± 0.2

4-3. Set A Retain; Set C Reject; Set E Reject

4-4. (a) 80% CL, 18 ± 3 μg/mL; 95% CL, 18 ± 5 μg/mL
(b) 80% CL, 18 ± 2 μg/mL; 95% CL, 18 ± 3 μg/mL
(c) 80% CL, 18 ± 2 μg/mL; 95% CL, 18 ± 2 μg/mL

4-6. 95%, 10 measurements; 99%, 17 measurements

4-8. (a) 3.22 ± 0.15 mmol/L (b) 3.22 ± 0.06 mmol/L

4-10. (a) 12 measurements

4-11. (a) Systematic error is indicated at 95% confidence.
(b) No systematic error is demonstrated.

4-13. At the 99% confidence level, the difference between the cobalt results should be no greater than ±0.053 ppm. The actual difference was −0.07 ppm. Similarly, the difference in the thorium results should be no greater than ±0.09 ppm. The actual difference was −0.12 ppm. Therefore, reasonable doubt exists as to the driver's guilt.

4-15. (a) 0.58 mg (b) 0.41 mg (c) 0.35 mg

4-16. (a) No difference demonstrated.
(c) No difference demonstrated.

4-17. (a) Outlier is retained.
(b) Outlier is rejected.

4-19. (a) $R = 0.162 + 0.232\,C_x$
(d) $C_x = 15.1$ mg SO_4^{2-}/L; $s = 1.4$ mg SO_4^{2-}/L; CV = 9.3%
(e) $s = 0.81$ mg SO_4^{2-}/L; CV = 5.4%

Chapter 5

5-1. (a) *Mass, m,* is an invariant measure of the amount of matter in an object. *Weight, w,* is the force of attraction between an object and earth.

(c) The individual particles of a *colloid* are smaller than about 10^{-5} mm in diameter, while those of a *crystalline precipitate* are larger. As a consequence, crystalline precipitates settle out of solution relatively rapidly, whereas colloidal particles do not unless they can be caused to agglomerate.

(e) *Precipitation* is the process by which a solid phase forms and is carried out of solution when the solubility product of a species is exceeded. *Coprecipitation* is the process in which a normally soluble species is carried out of solution during the formation of a precipitate.

(g) *Occlusion* is a type of coprecipitation in which an impurity is entrapped in a pocket formed by a rapidly growing crystal. *Mixed-crystal formation* is a type of coprecipitation in which a foreign ion is incorporated into a growing crystal in a lattice position that is ordinarily occupied by one of the ions of the precipitate.

5-2. (a) The dalton, which is synonymous with the atomic mass unit, is a relative mass unit that is equal to 1/12 of the mass of one neutral ^{12}C atom.

(c) Stoichiometry is the mass relationship among reacting chemical species.

(e) *Digestion* is a process for improving the purity and filterability of a precipitate by heating the solid in contact with the solution from which it is formed (the *mother liquor*).

(g) In *reprecipitation*, a precipitate is filtered, washed, redissolved, and then re-formed from the new solution. Because the concentration of contaminant is lower in this new solution than in the original, the second precipitate contains less coprecipitated impurity.

(i) The *electric double layer* consists of lattice ions adsorbed on the surface of a solid (the primary adsorption layer) and a volume of solution surrounding the particle (the counter-ion layer) in which an excess of ions of opposite charge exists.

(k) *Relative supersaturation* is given by the expression

$$\text{relative supersaturation} = \frac{Q - S}{S}$$

where Q is the concentration of a solute in a solution at any instant and S is its equilibrium solubility ($Q > S$).

5-3. A *chelating agent* is an organic compound or ion that contains two or more electron-donor groups located in such a way that five- or six-membered rings are formed when the donor groups complex a cation.

5-5. (a) positive charge (b) adsorbed Ag^+ (c) NO_3^-

5-7. *Peptization* is the process in which a coagulated colloid returns to its original dispersed state as a consequence of a decrease in the electrolyte concentration of the solution in contact with the precipitate. Peptization of a coagulated colloid can be avoided by washing with an electrolyte solution rather than with pure water.

5-9. (a) Generate hydroxide ions from urea.
(c) Generate hydrogen sulfide from thioacetamide.

5-10. The atomic mass of iron is 55.85 daltons, or 55.85 amu. Its molar mass is 55.85 grams.

5-12. (a) 0.0982 mol B_2O_3
(b) 7.76×10^{-4} mol $Na_2B_4O_7 \cdot 10H_2O$
(c) 0.0382 mol Mn_3O_4
(d) 5.26×10^{-4} mol CaC_2O_4

5-14. (a) 4.20×10^4 mg HNO_3
(b) 1.21×10^4 mg MgO
(c) 1.52×10^6 mg NH_4NO_3
(d) 2.92×10^6 mg $(NH_4)_2Ce(NO_3)_6$

5-16. (a) $\dfrac{1 \text{ mol } CO_2}{\text{mol } BaCO_3}$

(c) $\dfrac{1 \text{ mol } K_2O}{2 \times \text{mol } (C_6H_5)_4BK}$

(e) $\dfrac{1 \text{ mol } H_2S}{\text{mol } CdSO_4}$

(g) $\dfrac{1 \text{ mol } C_8H_6O_3Cl_2}{2 \times \text{mol } AgCl}$

(i) $\dfrac{1 \text{ mol } CoSiF_6 \cdot 6H_2O}{6 \times \text{mol } H_2O}$

5-18. (a) 1.172 g Ag_2CrO_4 (b) 2.050 g Ag_2CrO_4
5-20. (a) 0.318 g AgCl (c) 0.438 g AgCl
5-21. (a) 0.369 g $Ba(IO_3)_2$ (b) 0.0149 g $BaCl_2 \cdot 2H_2O$
5-24. 95.35% KCl
5-26. 18.99% C
5-29. 46.40% NH_3
5-30. 0.03219 g $C_{21}H_{29}NH_2$/tablet
5-31. 1.867% P_2O_5
5-33. 96.12% $C_6H_5NO_2$
5-35. (a) 0.239 g sample (b) 0.494 g AgCl
(c) 0.4065 g sample
5-37. 4.72% Cl^- 27.05% I^-
5-39. 1.80% KI
5-40. (a) 80.00% Ag and 20.00% Cu
(c) 90.00% Ag and 10.00% Cu
(e) 50.00% Ag and 50.00% Cu

Chapter 6

6-2. (a) The *millimole* is the amount of an elementary species, such as an atom, an ion, a molecule, or an electron. A millimole contains

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

(c) The *stoichiometric factor* is the molar ratio of two species that appear in a balanced chemical equation.

6-3. (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.

(c) A *primary standard* is a highly purified substance that serves as the basis for a titrimetric method. It is used either (1) to prepare a standard solution directly by mass or (2) to standardize a solution to be used in a titration.

A *secondary standard* is a 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.

6-4. $\frac{\text{mg}}{\text{L}} = \frac{10^{-3}\text{ g solute}}{10^{3}\text{ g solution}} = \frac{1\text{ g solute}}{10^{6}\text{ g solution}} = 1\text{ ppm}$

6-5. (a) $\frac{1\text{ mol }H_2NNH_2}{2\text{ mol }I_2}$

(c) $\frac{1\text{ mol }Na_2B_4O_7 \cdot 10H_2O}{2\text{ mol }H^+}$

6-6. (a) 5.52 mmol
(b) 31.2 mmol
(c) 6.58×10^{-3} mmol
(d) 966 mmol
6-8. (a) 1.33×10^{3} mg (b) 520 mg
6-9. (a) 2.51 g (b) 2.88×10^{-3} g
6-10. 19.0 M
6-12. (a) 6.161 M (c) 4.669 M
6-13. (a) Dilute 80 g ethanol to 500 mL with water.
(b) Dilute 80.0 mL ethanol to 500 mL with water.
(c) Dilute 80.0 g ethanol with 420 g water.
6-15. Dilute 26 mL of the concentrated reagent to 2.0 L.
6-17. (a) Dissolve 6.37 g of $AgNO_3$ in water and dilute to 500 mL.
(b) Dilute 52.5 mL of 6.00 M HCl to 1.00 L.
(c) Dissolve 4.56 g $K_4Fe(CN)_6$ in water and dilute to 600 mL.
(d) Dilute 144 mL of 0.400 M $BaCl_2$ to a volume of 400 mL.
(e) Dilute 25 mL of the commercial reagent to a volume of 2.0 L.
(f) Dissolve 1.67 g Na_2SO_4 in water and dilute to 9.00 L.
6-19. 9.151×10^{-2} M
6-21. 0.06114 M $BaCl_2$
6-22. 0.2970 M $HClO_4$; 0.3259 M NaOH
6-24. 0.08411 M
6-25. 345.8 ppm S
6-27. 5.471% As_2O_3
6-28. 7.317% $(NH_2)_2CS$
6-30. (a) 9.36×10^{-3} M $Ba(OH)_2$
(b) 1.9×10^{-5} M
(c) −3 ppt
6-32. (a) $\frac{0.02966\text{ mmol }KMnO_4}{\text{g soln}}$
(b) 31.68% Fe_2O_3
6-34. (a) 1.821×10^{-2} M
(b) 1.821×10^{-2} M
(c) 5.463×10^{-2} M
(d) 0.506% (w/v)
(e) 1.366 mmol Cl^-
(f) 712 ppm K^+

Chapter 7

7-1. (a) A weak electrolyte is a substance that ionizes only partially in a solvent.
(c) The conjugate base of a Brønsted-Lowry acid is the species formed when the acid has donated a proton.
(e) An amphiprotic solute is one that can act either as an acid or as a base when dissolved in a solvent.
(g) Autoprotolysis is self-ionization of a solvent to give a conjugate acid and a conjugate base.
(i) The Le Châtelier principle states that the position of equilibrium in a system always shifts in a direction that tends to relieve an applied stress to the system.
7-2. (a) An amphiprotic solvent is a solvent that acts as a base with acidic solutes and as an acid with basic solutes.

(c) A leveling solvent is one in which a series of acids (or bases) all dissociate completely.

7-3. For an aqueous equilibrium in which water is a reactant or a product, the concentration of water is normally so much larger than the concentrations of the reactants and products that its concentration can be assumed to be constant and independent of the position of the equilibrium. Thus, its concentration is assumed to be constant and is included in the equilibrium constant. For a solid reactant or product, it is the concentration of that reactant in the solid phase that would influence the position of equilibrium. However, the concentration of a species in the solid phase is constant. Thus, as long as some solid exists as a second phase, its effect on the equilibrium is constant, and its concentration is included in the equilibrium constant.

7-4.

Acid	Conjugate Base
(a) HCN	CN^-
(c) NH_4^+	NH_3
(e) $H_2PO_4^-$	HPO_4^{2-}

7-6. (a) $2H_2O \rightleftharpoons H_3O^+ + OH^-$
(c) $2CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + CH_3NH^-$

7-7. (a) $K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$
(c) $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 1.2 \times 10^{-12}$

7-8. (a) $K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{2.31 \times 10^{-11}} = 4.33 \times 10^{-4}$

$$= \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]}$$

(c) $K_a = 5.90 \times 10^{-6} = \frac{[H_3O^+][C_5H_5N]}{[C_5H_5NH^+]}$

(e) $\beta_3 = K_1K_2K_3 = 2 \times 10^{-21} = \frac{[H_3O^+]^3[AsO_4^{3-}]}{[H_3AsO_4]}$

7-9. (a) $K_{sp} = [Ag^+][IO_3^-] = 3.1 \times 10^{-8}$
(b) $K_{sp} = [Ag^+]^2[SO_3^{2-}]$
(c) $K_{sp} = [Ag^+]^3[AsO_4] = 6 \times 10^{-23}$
(d) $K_{sp} = [Pb^{2+}][Cl^-][F^-]$

7-10. (a) $K_{sp} = S^2$ (b) $K_{sp} = 4S^3$ (c) $K_{sp} = 27S^4$
(d) $K_{sp} = S^3$

7-11. (a) 4.0×10^{-16}
(c) 3.1×10^{-6}
(e) 3.5×10^{-10}

7-12. (a) 8.0×10^{-15} M (c) 3.9×10^{-3} M
(e) 6.4×10^{-4} M

7-13. (a) 8.0×10^{-15} M (c) 1.2×10^{-3} M
(e) 2.8×10^{-6} M

7-14. (a) 2.18×10^{-7} M (b) 0.98 M

7-16. (a) 0.0250 M Ce^{3+} (b) 1.7×10^{-2} M
(c) 1.9×10^{-3} M (d) 7.6×10^{-7} M

7-18. (a) $PbI_2 > TlI > BiI_3 > AgI$
(b) $PbI_2 > TlI > AgI > BiI_3$
(c) $PbI_2 > TlI > BiI_3 > AgI$

7-21. (a) $[H_3O^+] = 2.4 \times 10^{-5}$ M; $[OH^-] = 4.1 \times 10^{-10}$ M
(c) $[H_3O^+] = 1.1 \times 10^{-12}$ M; $[OH^-] = 9.3 \times 10^{-3}$ M
(e) $[H_3O^+] = 5.0 \times 10^{-11}$ M; $[OH^-] = 2.0 \times 10^{-4}$ M
(g) $[H_3O^+] = 3.32 \times 10^{-4}$ M; $[OH^-] = 3.02 \times 10^{-11}$ M

7-22. (a) $[H_3O^+] = 1.10 \times 10^{-2}$ M
(b) $[H_3O^+] = 1.17 \times 10^{-8}$ M
(e) $[H_3O^+] = 1.46 \times 10^{-4}$ M

Chapter 8

8-1. (a) *Activity, a,* is the effective concentration of a species A in solution. The *activity coefficient,* γ_A, is the factor needed to convert a molar concentration to activity:

$$a_A = \gamma_A[A]$$

(b) The *thermodynamic equilibrium constant* refers to an ideal system within which each species is unaffected by any others. A *concentration equilibrium constant* takes account of the influence exerted by solute species upon one another. A thermodynamic constant is based upon activities of reactants and products; a concentration constant is based upon molar concentrations of reactants and products.

8-3. (a) Ionic strength should decrease.
(b) Ionic strength should be unchanged.
(c) Ionic strength should increase.

8-5. For a given ionic strength, activity coefficients for ions with multiple charge show greater departures from ideality.

8-7. (a) 0.16 (c) 1.2

8-8. (a) 0.20 (c) 0.073

8-9. (a) 0.21 (c) 0.079

8-10. (a) 1.7×10^{-12} (c) 7.6×10^{-11}

8-11. (a) 5.2×10^{-6} M (b) 6.2×10^{-6} M
(c) 9.5×10^{-12} M (d) 1.5×10^{-7} M

8-12. (a) (1) 1.4×10^{-6} M (2) 1.0×10^{-6} M
(b) (1) 2.1×10^{-3} M (2) 1.3×10^{-3} M
(c) (1) 2.8×10^{-5} M (2) 1.0×10^{-5} M
(d) (1) 1.4×10^{-5} M (2) 2.0×10^{-6} M

Chapter 9

9-1. In the calculation of the molar solubility of $Fe(OH)_2$, the hydronium ion concentration may be assumed to be negligibly small. This assumption cannot be made in the case of $Fe(OH)_3$. In the latter case we assume $[H_3O^+] = [OH^-] \approx 1.00 \times 10^{-7}$.

9-4. A charge-balance equation is derived by relating the concentration of cations and anions in such a way that no. mol/L positive charge = no. mol/L negative charge. For a doubly charged ion such as Ba^{2+}, the concentration of electrons 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.

9-5. (a) $0.10 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$
(c) $0.100 + 0.0500 = [HNO_2] + [NO_2^-]$
(e) $0.100 = [Na^+] = [OH^-] + 2[Zn(OH)_4^{2-}]$
(g) $[Ca^{2+}] = \frac{1}{2}([F^-] + [HF])$

9-7. (a) 5.2×10^{-3} M (c) 3.6×10^{-4} M

9-8. (a) 1.47×10^{-4} M (c) 7.42×10^{-5} M

9-9. (a) 2.5×10^{-9} M (b) 2.5×10^{-12} M

9-11. (a) 5×10^{-2} M

9-12. (a) 1.4×10^{-5} M (b) 2.53×10^{-6} M

9-14. (a) $Cu(OH)_2$ forms first
(b) 9.8×10^{-10} M (c) 9.6×10^{-9} M

9-16. (a) 8.3×10^{-11} M (b) 1.6×10^{-11} M
(c) 5.2×10^{6} M (d) 1.3×10^{4}
9-17. (a) not feasible (c) feasible
9-18. 1.877 g
9-20. (a) 0.0095 M; 48% (b) 6.6×10^{-3} M; 70%

Chapter 10

In the answers to this chapter, (Q) indicates that the answer was obtained by solving a quadratic equation.

10-1. (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.

10-3. The limited sensitivity of the eye to small color differences requires that there be a roughly tenfold excess of one or the other form of the indicator to be present in order for the color change to be seen. This change corresponds to a pH range of ± 1 pH unit about the pK of the indicator.

10-5. The standard reagents in neutralization titrations are always strong acids or strong bases because the reactions with this type of reagent are more complete than with those of their weaker counterparts. Sharper end points are the consequence of this difference.

10-7. The *buffer capacity* of a solution is the number of moles of hydronium ion or hydroxide ion needed to cause 1.00 L of the buffer to undergo a unit change in pH.

10-9. The three solutions will have the same pH, since the ratios of the amounts of weak acid to conjugate base are identical. They will differ in buffer capacity, however, with (a) having the greatest and (c) the least.

10-10. (a) Malic acid/sodium hydrogen malate
(c) NH_4Cl/NH_3
10-11. (a) NaOCl (c) CH_3NH_2
10-12. (a) HIO_3 (c) $CH_3COCOOH$
10-14. 3.24
10-16. (a) 14.94
10-17. (a) 12.94
10-18. −0.607
10-20. 7.04 (Q)
10-22. (a) 1.05 (b) 1.05 (c) 1.81
(d) 1.81 (e) 12.60
10-24. (a) 1.30 (b) 1.37
10-26. (a) 4.26 (b) 4.76 (c) 5.76
10-28. (a) 11.12 (b) 10.62 (c) 9.53 (Q)
10-30. (a) 12.04 (Q) (b) 11.48 (Q) (c) 9.97 (Q)
10-32. (a) 1.94 (b) 2.45 (c) 3.52
10-34. (a) 2.41 (Q) (b) 8.35 (c) 12.35
(d) 3.84
10-37. (a) 3.85 (b) 4.06 (c) 2.63 (Q)
(d) 2.10 (Q)
10-39. (a) 0.00 (c) −1.000 (e) −0.500
(g) 0.000
10-40. (a) −5.00 (c) −0.097
(e) −3.369 (g) −0.017
10-41. (a) 5.00
(c) 0.079
(e) 3.272
(g) 0.017
10-42. (b) −0.141
10-43. 15.5 g sodium formate
10-45. 194 mL HCl

10-47.

V_{HCl}	pH	V_{HCl}	pH
0.00	13.00	49.00	11.00
10.00	12.82	50.00	7.00
25.00	12.52	51.00	3.00
40.00	12.05	55.00	2.32
45.00	11.72	60.00	2.04

10-48. The theoretical pH at 24.95 mL is 6.44; at 25.05 mL it is 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 10-1) would be quite suitable.

10-50.

	(a)	(c)
Vol, mL	pH	pH
0.00	2.09 (Q)	3.12
5.00	2.38 (Q)	4.28
15.00	2.82 (Q)	4.86
25.00	3.17 (Q)	5.23
40.00	3.76 (Q)	5.83
45.00	4.11 (Q)	6.18
49.00	4.85 (Q)	6.92
50.00	7.92	8.96
51.00	11.00	11.00
55.00	11.68	11.68
60.00	11.96	11.96

10-51.

	(a)
Vol HCl, mL	pH
0.00	11.12
5.00	10.20
15.00	9.61
25.00	9.24
40.00	8.64
45.00	8.29
49.00	7.55
50.00	5.27
51.00	3.00
55.00	2.32
60.00	2.04

10-52.

Vol, mL	(a) pH	(c) pH
0.00	2.80	4.26
5.00	3.65	6.57
15.00	4.23	7.15
25.00	4.60	7.52
40.00	5.20	8.12
49.00	6.29	9.21
50.00	8.65	10.11
51.00	11.00	11.00
55.00	11.68	11.68
60.00	11.96	11.96

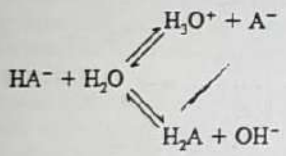
10-53. (a) $\alpha_0 = 0.215$; $\alpha_1 = 0.785$
(c) $\alpha_0 = 0.769$; $\alpha_1 = 0.231$
(e) $\alpha_0 = 0.917$; $\alpha_1 = 0.083$

10-54. 6.61×10^{-2} M

10-56. (a) Lactic; pH = 3.61; [HA] = 0.0768; $[A^-] = 0.0432$; $\alpha_1 = 0.360$
(b) Sulfamic; [HA] = 0.095; $[A^-] = 0.155$; $\alpha_0 = 0.380$; $\alpha_1 = 0.620$

Chapter 11

11-1. Not only is NaHA a proton donor, it is also the conjugate base of the parent acid H_2A.



Solutions of acid salts are acidic or alkaline, depending upon which of these equilibria predominates. In order to compute the pH of this type, it is necessary to take both equilibria into account.

11-3. The HPO_4^{2-} is such a weak acid ($K_a = 4.5 \times 10^{-13}$) that the change in pH in the vicinity of the third equivalence point is too small to be observable.

11-4. (a) Since the *K*s are essentially identical, the solution should be approximately neutral. (c) neutral
(e) basic (g) acidic

11-6. phenolphthalein

11-8. (a) cresol purple (c) cresol purple
(e) bromocresol green (g) phenolphthalein

11-9. (a) 1.86 (Q) (c) 1.64 (Q) (e) 4.21

11-10. (a) 4.71 (c) 4.28 (e) 9.80

11-11. (a) 12.32 (Q) (c) 9.70 (e) 12.58 (Q)

11-12. (a) 2.07 (Q) (b) [illegible].18 (c) 10.63
(d) 2.55 (Q) (e) 2.06

11-14. (a) 1.54 (b) 1.99 (c) 12.07 (d) 12.01

11-16. (a) $[SO_3^{2-}]/[HSO_3^-] = 15.2$
(b) $[HCit^{2-}][Cit^{3-}] = 2.5$
(c) $[HM^-][M^{2-}] = 0.498$
(d) $[HT^-][T^{2-}] = 0.0232$

11-18. 50.2 g

11-20. (a) 2.11 (Q) (b) 7.38

11-22. Mix 442 mL of 0.300 M Na_2CO_3 with 558 mL of 0.200 M HCl.

11-24. Mix 704 mL of the HCl with 296 mL of the Na_3AsO_4.

11-28.

Vol reagent, mL	(a) pH	(c) pH
0.00	11.66	0.96
12.50	10.33	1.28
20.00	9.73	1.50
24.00	8.95	1.63
25.00	8.34	1.67
26.00	7.73	1.70
37.50	6.35	2.19
45.00	5.75	2.70
49.00	4.97	3.46
50.00	3.83	7.35
51.00	2.70	11.30
60.00	1.74	12.26

11-29. 0.00 mL, pH = 13.00; 26.00 mL, pH = 9.26
10.00 mL, pH = 12.70; 35.00 mL, pH = 7.98
20.00 mL, pH = 12.15; 44.00 mL, pH = 6.70
24.00 mL, pH = 11.43; 45.00 mL, pH = 4.68
25.00 mL, pH = 10.35; 46.00 mL, pH = 2.68
50.00 mL, pH = 2.00

11-31. (a) $\dfrac{[H_3AsO_4][HAsO_4^{2-}]}{[H_2AsO_4^-]^2} = 1.9 \times 10^{-5}$

11-32. $\dfrac{[NH_3][HOAc]}{[NH_4^+][OAc^-]} = 3.26 \times 10^{-5}$

11-33.

	pH	*D*	α_0	α_1	α_2	α_3
(a)	2.00	1.112×10^{-4}	0.899	0.101	3.94×10^{-5}	
	6.00	5.500×10^{-9}	1.82×10^{-4}	0.204	0.796	
	10.00	4.379×10^{-9}	2.28×10^{-12}	2.56×10^{-5}	1.000	
(c)	2.00	1.075×10^{-6}	0.931	6.93×10^{-2}	1.20×10^{-4}	4.82×10^{-9}
	6.00	1.882×10^{-14}	5.31×10^{-5}	3.96×10^{-2}	0.685	0.275
	10.00	5.182×10^{-15}	1.93×10^{-16}	1.44×10^{-9}	2.49×10^{-4}	1.000
(e)	2.00	4.000×10^{-4}	0.250	0.750	1.22×10^{-5}	
	6.00	3.486×10^{-9}	2.87×10^{-5}	0.861	0.139	
	10.00	4.863×10^{-9}	2.06×10^{-12}	6.17×10^{-4}	0.999	

Chapter 12

12-1. Carbon dioxide is not strongly bonded by water molecules, and thus is readily volatilized from aqueous media. Gaseous HCl molecules, on the other hand, are fully dissociated into H_3O^+ and Cl^- when dissolved in water; neither of these species is volatile.

12-3. Primary-standard Na_2CO_3 can be obtained by heating primary-standard-grade $NaHCO_3$ for about an hour at 270° to 300°C. The reaction is

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

12-5. For, let us say, a 40-mL titration

mass $KH(IO_3)_2$ required = 0.16 g

mass HBz required = 0.049 g

The $KH(IO_3)_2$ is preferable because the relative weighing error would be less with a 0.16-g sample than with a 0.049-g sample. A second advantage of $KH(IO_3)_2$ is that it acts as a strong acid, which makes the choice of indicator simpler.

12-8. (a) Dissolve 17 g KOH in water and dilute to 2.0 L.
(b) Dissolve 9.5 g of $Ba(OH)_2 \cdot 2H_2O$ in water and dilute to 2.0 L.
(c) Dilute about 120 mL of the reagent HCl to 2.0 L.

12-10. (a) 0.1026 M
(b) $s = 0.00039$ and CV = 0.38%

12-12. (a) 0.1388 M (b) 0.1500 M

12-14. (a) 0.08387 M (b) 0.1007 M (c) 0.1311 M

12-16. (a) 0.28 to 0.36 g Na_2CO_3 (c) 0.85 to 1.1 g HBz
(e) 0.17 to 0.22 g TRIS

12-17. (a) 0.067% (b) 0.16% (c) 0.043%

12-19. (a) 0.1217 g H_2T/100 mL

12-21. (a) 46.25% $Na_2B_4O_7$
(b) 87.67% $Na_2B_4O_7 \cdot 10H_2O$
(c) 32.01% B_2O_3
(d) 9.94% B

12-23. 24.4% HCHO

12-25. 7.079% RS_4

12-27. $MgCO_3$ with a molar mass of 84.31 seems a likely candidate.

12-29. 3.35×10^3 ppm CO_2

12-31. 6.333% P

12-32. 13.86% analyte

12-33. 22.08% RN_4

12-35. 3.885% N

12-37. (a) 10.09% N (c) 47.61% $(NH_4)_2SO_4$

12-39. 15.23% $(NH_4)_2SO_4$ and 24.39% NH_4NO_3

12-40. 69.84% KOH; 21.04% K_2CO_3; 9.12% H_2O

12-42. (a) 18.15 mL HCl (b) 45.37 mL HCl
(c) 38.28 mL HCl (d) 12.27 mL HCl

12-44. (a) 4.314 mg NaOH/mL
(b) 7.985 mg Na_2CO_3/mL and 4.358 mg $NaHCO_3$/mL
(c) 3.455 mg Na_2CO_3/mL and 4.396 mg NaOH/mL
(d) 8.215 mg Na_2CO_3/mL
(e) 13.46 mg $NaHCO_3$/mL

12-46. The equivalent weight of an acid is that weight of the pure material that contains one mole of titratable protons in a specified reaction. The equivalent weight of base is that weight of a pure compound that consumes one mole of protons in a specified reaction.

Chapter 13

13-1. The Fajan determination of chloride involves a direct titration, while the Volhard approach requires two standard solutions and a filtration step to eliminate AgCl.

13-3. In contrast to Ag_2CO_3 and AgCN, the solubility of AgI is unaffected by the acidity and additionally is less soluble than AgSCN. The filtration step is thus unnecessary, whereas it is with the other two compounds.

13-5. Potassium is determined by precipitation with an excess of a standard solution of sodium tetraphenylboron. An excess of standard $AgNO_3$ is then added, which precipitates the excess tetraphenylboron 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.

13-7. (a) 51.78 mL $AgNO_3$ (c) 10.64 mL $AgNO_3$
(e) 46.24 mL $AgNO_3$

13-9. (a) 44.70 mL $AgNO_3$ (c) 14.87 mL $AgNO_3$

13-11. 28.5% Cl

13-13. 18.9 ppm H_2S

13-15. 1.472% P_2O_5

13-16. 116.7 mg analyte

13-19. 0.07052 M

13-20. Only one of the chlorines in the heptachlor reacts with $AgNO_3$.

13-23. 15.60 mg saccharin/tablet

13-24. 21.5% CH_2O

13-25. 0.4348% $C_{19}H_{16}O_4$

13-28. 10.60% Cl^-; 55.65% ClO_4^-

13-29. (a)

V_{NH_4SCN} (mL)	$[Ag^+]$	$[SCN^-]$	pAg
30.00	9.09×10^{-3}	1.2×10^{-10}	2.04
40.00	3.85×10^{-3}	2.9×10^{-10}	2.42
49.00	3.38×10^{-4}	3.3×10^{-9}	3.47
50.00	1.05×10^{-6}	1.05×10^{-6}	5.98
51.00	3.3×10^{-9}	3.3×10^{-4}	8.48
60.00	3.7×10^{-10}	2.94×10^{-3}	9.43
70.00	2.1×10^{-10}	5.26×10^{-3}	9.68

(c)

V_{NaCl} (mL)	$[Ag^+]$	$[Cl^-]$	pAg
10.00	3.75×10^{-2}	4.85×10^{-9}	1.43
20.00	1.50×10^{-2}	1.21×10^{-8}	1.82
29.00	1.27×10^{-3}	1.43×10^{-7}	2.90
30.00	1.35×10^{-5}	1.35×10^{-5}	4.87
31.00	1.48×10^{-7}	1.23×10^{-3}	6.83
40.00	1.70×10^{-8}	1.07×10^{-2}	7.77
50.00	9.71×10^{-9}	1.88×10^{-2}	8.01

(e)

$V_{Na_2SO_4}$ (mL)	$[Ba^{2+}]$	$[SO_4^{2-}]$	pBa
0.00	2.50×10^{-2}	0.0	1.60
10.00	1.00×10^{-2}	1.1×10^{-8}	2.00
19.00	8.48×10^{-4}	1.3×10^{-7}	3.07
20.00	1.05×10^{-5}	1.05×10^{-5}	4.98
21.00	1.3×10^{-7}	8.20×10^{-4}	6.87
30.00	1.5×10^{-8}	7.14×10^{-3}	7.81
40.00	8.8×10^{-9}	1.25×10^{-2}	8.06

13-30.

V_{AgNO_3} (mL)	$[Ag^+]$
5.00	1.57×10^{-11}
40.00	7.07×10^{-7}
45.00	2.63×10^{-3}

Chapter 14

14-1. (a) A *chelate* is a cyclic complex consisting of a 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 *ligand* is a species that contains one or more electron pair donor groups that tend to form bonds with metal ions.

(e) 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) *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.

14-2. Three general methods for performing EDTA titrations are (1) direct titration, (2) back-titration, and (3) displacement titration. Method (1) is simple, rapid, and requires but one standard reagent. Method (2) is advantageous for those metals that react so slowly with EDTA as to make direct titration inconvenient. In addition, the 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 the analytical conditions. Method (3) is particularly useful in situations where no satisfactory indicators are available for direct titration.

14-4. (a) $Ag^+ + S_2O_3^{2-} \rightleftharpoons AgS_2O_3^-$

$$K_1 = \frac{[AgS_2O^-]}{[Ag^+][S_2O_3^{2-}]}$$

$$AgS_2O_3^- + S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-}$$

$$K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[AgS_2O_3^-][S_2O_3^{2-}]}$$

14-5. The overall formation constant β_n is equal to the product of the individual stepwise constants. Thus, the overall constant for formation of $Ni(SCN)_3^-$ in Problem 14-4(b) is

$$\beta_3 = K_1K_2K_3 = \frac{[Ni(SCN)_3^-]}{[Ni^{2+}][SCN^-]^3}$$

which is the equilibrium constant for the reaction

$$Ni^{2+} + 3SCN^- \rightleftharpoons Ni(SCN)_3^-$$

and

$$\beta_2 = K_1K_2 = \frac{Ni(SCN)_2}{[Ni^{2+}][SCN^-]^2}$$

where the overall constant β_2 is for the reaction

$$Ni^{2+} + 2SCN^- \rightleftharpoons Ni(SCN)_2$$

14-8. 0.01032 M EDTA
14-10. (a) 39.1 mL EDTA (c) 41.6 mL EDTA
(e) 31.2 mL EDTA
14-12. 3.028% Zn
14-14. 1.228% Tl_2SO_4
14-16. 184.0 ppm Fe^{3+}; 213.0 ppm Fe^{2+}
14-18. 55.16% Pb; 44.86% Cd
14-20. 99.7% ZnO; 0.256% Fe_2O_3
14-22. 64.68 ppm K^+
14-24. 8.518% Pb; 24.86% Zn: 64.08% Cu; 2.54% Sn
14-25. (a) 4.6×10^9; (b) 1.1×10^{12}; (c) 7.4×10^{13}

14.27.

Vol, mL	pSr	Vol, mL	pSr
0.00	2.00	25.00	5.37
10.00	2.30	25.10	6.16
24.00	3.57	26.00	7.16
24.90	4.57	30.00	7.86

Chapter 15

15-1. (a) *Oxidation* is a process in which a species loses one or more electrons.

(c) A *salt bridge* is a device that provides electrical contact but prevents mixing of dissimilar solutions in an electrochemical cell.

(e) The *Nernst equation* relates the potential to the concentrations (strictly, activities) of the participants in an electrochemical reaction.

15-2. (a) The *electrode potential* is the potential of an electrochemical cell in which a standard hydrogen electrode acts as anode and the half-cell of interest is the cathode.

(c) The *standard electrode potential* for a half-reaction is the potential of a *cell* consisting of a cathode at which that half-reaction is occurring and a standard hydrogen electrode behaving as the anode. The activities of all of the participants in the half-reaction are specified as having a value of unity. The additional specification that the standard hydrogen electrode is the anode implies that the standard potential for a half-reaction is always a *reduction potential*.

(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.

15-3. (a) *Reduction* is the process whereby a substance acquires electrons; a *reducing agent* is a supplier of electrons.

(c) The *anode* of an electrochemical cell is the electrode at which oxidation occurs. The *cathode* is the electrode at which reduction occurs.

(e) The *standard electrode potential* is the potential of an electrochemical cell in which the standard hydrogen electrode acts as an anode and all participants in the cathode process have unit activity. The formal potential differs in that the molar *concentrations* of the reactants and products are unity and the concentration of other species in the solution are carefully specified.

15-4. The first standard potential is for a solution that is 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. Such a half-cell, if it existed, would have a greater potential, since the driving force for the reduction would be greater at the higher I_2 concentration. The second half-cell potential, although hypothetical, is nevertheless useful for calculating electrode potentials for solutions that are undersaturated in I_2.

15-5. It is necessary to bubble hydrogen through the electrolyte in a hydrogen electrode in order to keep the solution saturated with the gas. Only under these circumstances is the hydrogen activity constant so that the electrode potential is constant and reproducible.

15-7. (a) $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$

(c) $2NO_3^- + Cu(s) + 4H^+ \rightarrow 2NO_2(g) + 2H_2O + Cu^{2+}$

(e) $Ti^{3+} + Fe(CN)_6^{3-} + H_2O \rightarrow TiO^{2+} + Fe(CN)_6^{4-} + 2H^+$

(g) $2Ag(s) + 2I^- + Sn^{4+} \rightarrow 2AgI(s) + Sn^{2+}$

(i) $5HNO_2 + 2MnO_4^- + H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$

15-8. (a) Oxidizing agent Fe^{3+}; $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
Reducing agent Sn^{2+}; $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$

(c) Oxidizing agent NO_3^-;
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2(g) + H_2O$
Reducing agent Cu; $Cu(s) \rightleftharpoons Cu^{2+} + 2e^-$

(e) Oxidizing agent $Fe(CN)_6^{3-}$;
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$
Reducing agent Ti^{3+};
$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$

(g) Oxidizing agent Sn^{4+}; $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$
Reducing agent Ag;
$Ag(s) + I^- \rightleftharpoons AgI(s) + e^-$

(i) Oxidizing agent MnO_4^-;
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$
Reducing agent HNO_2;
$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$

15-9. (a) $MnO_4^- + 5VO^{2+} + 11H_2O \rightarrow Mn^{2+} + 5V(OH)_4^+ + 2H^+$

(c) $Cr_2O_7^{2-} + 3U^{4+} + 2H^+ \rightarrow 2Cr^{3+} + 3UO_2^{2+} + H_2O$

(e) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + H_2O$

(g) $HPO_3^{2-} + 2MnO_4^- + 3OH^- \rightarrow PO_4^{3-} + 2MnO_4^{2-} + 2H_2O$

(i) $V^{2+} + 2V(OH)_4^+ + 2H^+ \rightarrow 3VO^{2+} + 5H_2O$

15-10. (a) Oxidizing agent MnO_4^-;
$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$
Reducing agent VO^{2+};
$VO^{2+} + 3H_2O \rightleftharpoons V(OH)_4^+ + 2H^+ + e^-$

(c) Oxidizing agent $Cr_2O_7^{2-}$;
$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 7H_2O$
Reducing agent U^{4+};
$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2e^- + 4H^+$

(e) Oxidizing agent IO_3^-;
$IO_3^- + 5e^- + 6H^+ \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$
Reducing agent I^-; $I^- \rightleftharpoons \frac{1}{2}I_2 + e^-$

(g) Oxidizing agent MnO_4^-;
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$
Reducing agent HPO_3^{2-};
$HPO_3^{2-} + H_2O \rightleftharpoons PO_4^{3-} + 2e^- + 3H^+$

(i) Oxidizing agent $V(OH)_4^+$;
$V(OH)_4^+ + e^- + 2H^+ \rightleftharpoons VO^{2+} + 3H_2O$
Reducing agent V^{2+};
$V^{2+} + H_2O \rightleftharpoons VO^{2+} + 2e^- + 2H^+$

15-11. (a) $AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$; $V^{2+} \rightleftharpoons V^{3+} + e^-$
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$; $Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^-$
$V^{3+} + e^- \rightleftharpoons V^{2+}$; $Zn \rightleftharpoons Zn^{2+} + 2e^-$
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$;
$Ag(s) + Br^- \rightleftharpoons AgBr(s) + e^-$
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$; $Tl^+ \rightleftharpoons Tl^{3+} + 2e^-$

(b), (c)	E^0
$S_2O_8^{2-} \rightleftharpoons 2SO_4^{2-}$	2.01
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	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

15-13. (a) 0.297 V (b) 0.190 V (c) −0.152 V
(d) 0.047 V (e) 0.007 V

15-15. −0.121 V

15-16. (a) 0.78 V (b) 0.198 V (c) −0.355 V
(d) 0.210 V (e) 0.177 V (f) 0.86 V

15-18. (a) −0.280 anode (b) −0.090 anode
(c) 1.003 cathode
(d) 0.171 V cathode (e) −0.009 V anode

15-20. 0.390 V

15-22. −0.964 V

15-24. −1.25 V

Chapter 16

16-1. The electrode potential of a system is the electrode potential of all half-cell processes at equilibrium in the system.

16-2. (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.

16-4. For points before equivalence, potential data are computed from the analyte standard potential and the analytical concentrations of the analyte and its product. Postequivalence 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.

16-6. An asymmetric titration curve will be encountered whenever the titrant and the analyte react in a ratio that is not 1:1.

16-8. (a) 0.452 V, galvanic (d) −0.401 V, electrolytic
(b) 0.031 V, galvanic (e) −0.208 V, electrolytic
(c) 0.414 V, galvanic (f) 0.724 V, galvanic

16-9. (a) 0.631 V (c) 0.331 V (e) −0.620 V

16-11. (a) 2.2×10^{17} (c) 3.2×10^{22}
(e) 9×10^{37} (g) 2.4×10^{10}

16-13. (a) Phenosafranine (e) Erioglaucin A
(c) Indigo tetrasulfonate or Methylene blue (g) None

16-14.

	E, V		
Vol, mL	(a)	(c)	(e)
10.00	−0.292	0.32	0.316
25.00	−0.256	0.36	0.334
49.00	−0.156	0.46	0.384
49.90	−0.097	0.52	0.414
50.00	0.017	0.95	1.17
50.10	0.074	1.17	1.48
51.00	0.104	1.20	1.49
60.00	0.133	1.23	1.50

Chapter 17

17-1. (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) $ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O$

17-3. 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^- ion, the half-reaction occurring in the Walden reductor is

$$Ag(s) + Cl^- \longrightarrow AgCl(s) + e^-$$

The excess HCl increases the tendency of this reaction to occur by the common ion effect.

17-5. $UO_2^{2+} + 2Ag(s) + 4H^+ + 2Cl^- \rightleftharpoons U^{4+} + 2AgCl(s) + H_2O$

17-7. Standard solutions of reductants find somewhat limited use because of their susceptibility to air oxidation.

17-8. Standard $KMnO_4$ solutions are seldom used to titrate solutions containing HCl because of the tendency of MnO_4^- to oxidize Cl^- to Cl_2, thus causing an overconsumption of MnO_4^-.

17-10. $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$

17-13. $4MnO_4^- + 2H_2O \rightarrow \underset{\text{brown}}{4MnO_2(s)} + 3O_2 + 4OH^-$

17-15. Iodine is not sufficiently soluble in water to produce a useful standard reagent. It is quite soluble in solutions that contain an excess of iodide, however, as a consequence of the formation of the triiodide complex. The rate at which iodine dissolves in iodide solutions increases as the concentration of iodide ion becomes greater. For this reason, iodine is always dissolved in a very concentrated solution of potassium iodide and diluted only after solution is complete.

17-17. $S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S(s)$

17-19. $BrO_3^- + \underset{\text{excess}}{6I^-} + 6H^+ \rightarrow Br^- + 3I_2 + 3H_2O$

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

17-21. $2I_2 + N_2H_4 \rightarrow N_2 + 4H^+ + 4I^-$

17-23. (a) 0.1122 M Ce^{4+} (c) 0.02245 M MnO_4^-
(e) 0.02806 M IO_3^-

17-24. Dissolve 2.574 g $K_2Cr_2O_7$ in sufficient water to give 250.0 mL of solution.

17-26. Dissolve about 24 g of $KMnO_4$ in 1.5 L of water.

17-28. 0.01518 M $KMnO_4$

17-30. 0.06711 M $Na_2S_2O_3$

17-32. (a) 14.72% Sb (b) 20.54% Sb_2S_3

17-34. 9.38% analyte

17-35. (a) 32.08% Fe (b) 45.86% Fe_2O_3

17-37. 0.03074 M

17-39. 56.53% $KClO_3$

~~17-41. 0.701% As_2O_3~~

17-43. 3.64% C_2H_5SH

17-45. 2.635% KI

17-46. 69.07% Fe and 21.07% Cr

17-48. 0.5554 g Tl

17-49. 10.4 ppm SO_2

17-51. 19.5 ppm H_2S

Chapter 18

18-1. (a) An indicator electrode is an electrode used in potentiometry that responds to variations in the activity of an analyte ion or molecule.

(c) An electrode of the first kind is a metal electrode that is used to determine the concentration of the cation of that metal in a solution.

18-2. (a) A liquid-junction potential is the potential that develops across the interface between two solutions having different electrolyte compositions.

18-3. (a) An electrode of the first kind for Hg(II) would take the form

$$\|Hg^{2+}(xM)|Hg$$

$$E_{Hg} = E^0_{Hg} - \frac{0.0592}{2}\log\frac{1}{[Hg^{2+}]}$$

$$= E^0_{Hg} + \frac{0.0592}{2}\,pHg$$

(b) An electrode of the second kind for EDTA would take the form

$$\|\mathrm{HgY}^{2-}(y\mathrm{M}),\ \mathrm{Y}^{4-}(x\mathrm{M})|\mathrm{Hg}$$

where a small and fixed amount of HgY^{2-} is introduced into the analyte solution so that its concentration is xM. Here the potential of the mercury electrode is given by

$$E_{\mathrm{Hg}} = K - \frac{0.0592}{2}\log[\mathrm{Y}^{4-}] = K + \frac{0.0592}{2}\mathrm{pY}$$

where

$$K = E^0_{\mathrm{HgY}^{2-}} - \frac{0.0592}{2}\log\frac{1}{a_{\mathrm{HgY}^{2-}}}$$
$$\sim 0.21 - \frac{0.0592}{2}\log\frac{1}{[\mathrm{HgY}^{2-}]}$$

18-5. The pH-dependent potential that develops across a glass membrane arises from the difference in positions of dissociation equilibria that arise on each of the two surfaces. These equilibria are described by the equation

$$\underset{\text{membrane}}{\mathrm{H^+Gl^-}} \rightleftharpoons \underset{\text{soln}}{\mathrm{H^+}} + \underset{\text{membrane}}{\mathrm{Gl^-}}$$

The surface exposed to the solution having the higher hydrogen ion activity then 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.

18-7. Uncertainties that may be encountered in pH measurements 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 differ from that of the analyte solution, (4) uncertainties in the pH of the standard buffers, (5) nonreproducible junction potentials when samples of low ionic strength are measured, and (6) dehydration of the working surface.

18-9. 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 both hydrogen and alkali ions. Low pH values arise as a consequence.

18-11. (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^+:

$$\underset{\text{membrane}_1}{\mathrm{A^+M^-}} \rightleftharpoons \underset{\text{soln}_1}{\mathrm{A^+}} + \underset{\text{membrane}_1}{\mathrm{M^-}}$$

$$\underset{\text{membrane}_2}{\mathrm{A^+M^-}} \rightleftharpoons \underset{\text{soln}_2}{\mathrm{A^+}} + \underset{\text{membrane}_2}{\mathrm{M^-}}$$

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 on 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^+.

(d) The membrane in a solid state electrode for F^- is crystalline $\mathrm{LaF_3}$, which when immersed in aqueous solution $\mathrm{LaF_3}$ dissociates according to the equation

$$\mathrm{LaF_3}(s) \rightleftharpoons \mathrm{La^{3+}} + 3\mathrm{F^-}$$

Thus, a boundary potential develops across this membrane when it separates two solutions of different F^- ion concentration. The source of this potential is described in part (b) of this answer.

Chapter 19

19-1. The direct potentiometric measurement of pH provides a measure of the equilibrium activity of hydronium ions present in a solution of the sample. A potentiometric titration provides information on the amount of reactive protons, both ionized and nonionized, that are present in a sample.

19-2. (a) 0.354 V
(b) $\mathrm{SCE}\|\mathrm{IO_3^-}(x\mathrm{M}),\ \mathrm{AgIO_3}(\text{sat'd})|\mathrm{Ag}$
(c) $\mathrm{pIO_3} = \dfrac{E_{\text{cell}} - 0.110}{0.0592}$
(d) 3.11

19-4. (a) $\mathrm{SCE}\|\mathrm{SCN^-}(x\mathrm{M}),\ \mathrm{AgSCN}(\text{sat'd})|\mathrm{Ag}$
(c) $\mathrm{SCE}\|\mathrm{SO_3^{2-}}(x\mathrm{M}),\ \mathrm{Ag_2SO_3}(\text{sat'd})|\mathrm{Ag}$

19-5. (a) $\mathrm{pSCN} = \dfrac{E_{\text{cell}} + 0.153}{0.0592}$
(c) $\mathrm{pSO_3} = \dfrac{2(E_{\text{cell}} - 0.146)}{0.0592}$

19-6. (a) 4.65 (c) 5.20

19-7. 6.76

19-9. (a) 0.157 V (b) −0.026 V

19-11. (a) $\mathrm{pH} = 12.629;\ a_{\mathrm{H}^+} = 2.35 \times 10^{-13}$
(b) $\mathrm{pH} = 5.579;\ a_{\mathrm{H}^+} = 2.64 \times 10^{-6}$
(c) $\mathrm{pH} = 12.596;\ a_{\mathrm{H}^+} = 2.54 \times 10^{-13}$
$\mathrm{pH} = 12.663;\ a_{\mathrm{H}^+} = 2.17 \times 10^{-13}$
and
$\mathrm{pH} = 5.545$ and 5.612
$a_{\mathrm{H}^+} = 2.85 \times 10^{-6}$ and 2.44×10^{-6}

19-13. 2.0×10^{-6}

19-15. 136 g HA/mol

19-17.

(a) mL Reagent	E vs. SCE, V	mL Reagent	E vs. SCE, V
5.00	0.58	49.00	0.66
10.00	0.59	50.00	0.80
15.00	0.60	51.00	1.10
25.00	0.61	55.00	1.14
40.00	0.63	60.00	1.15