Complete Solutions Manual

GENERAL CHEMISTRY

NINTH EDITION

Ebbing/Gammon

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Contents

PREFACE XI

CHAPTER 1 – CHEMISTRY AND MEASUREMENT 1

Solutions To Exercises *1*

Answers To Concept Checks *3*

Answers To Self-Assessment And Review Questions *4*

Answers To Concept Explorations *7*

Answers To Conceptual Problems *8*

Solutions To Practice Problems *11*

Solutions To General Problems *20*

Solutions To Strategy Problems *29*

Solutions To Cumulative-Skills Problems *30*

CHAPTER 2 – ATOMS, MOLECULES, AND IONS 36

Solutions To Exercises *36*

Answers To Concept Checks *38*

Answers To Self-Assessment And Review Questions *39*

Answers To Concept Explorations *42*

Answers To Conceptual Problems *43*

Solutions To Practice Problems *45*

Solutions To General Problems *56*

Solutions To Strategy Problems *63*

Solutions To Cumulative-Skills Problems *64*

CHAPTER 3 – CALCULATIONS WITH CHEMICAL FORMULAS AND EQUATIONS 66

Solutions To Exercises *66*

Answers To Concept Checks *71*

Answers To Self-Assessment And Review Questions *73*

Answers To Concept Explorations *75*

Answers To Conceptual Problems *77*

Solutions To Practice Problems *79*

Solutions To General Problems *103*

Solutions To Strategy Problems *109*

Solutions To Cumulative-Skills Problems *113*

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CHAPTER 4 – CHEMICAL REACTIONS 116
Solutions To Exercises *116*
Answers To Concept Checks *120*
Answers To Self-Assessment And Review Questions *122*
Answers To Concept Explorations *124*
Answers To Conceptual Problems *127*
Solutions To Practice Problems *129*
Solutions To General Problems *145*
Solutions To Strategy Problems *155*
Solutions To Cumulative-Skills Problems *157*
CHAPTER 5 – THE GASEOUS STATE 164
Solutions To Exercises *164*
Answers To Concept Checks *170*
Answers To Self-Assessment And Review Questions *172*
Answers To Concept Explorations *176*
Answers To Conceptual Problems *177*
Solutions To Practice Problems *179*
Solutions To General Problems *192*
Solutions To Strategy Problems *200*
Solutions To Cumulative-Skills Problems *202*
CHAPTER 6 – THERMOCHEMISTRY 207
Solutions To Exercises *207*
Answers To Concept Checks *209*
Answers To Self-Assessment And Review Questions *210*
Answers To Concept Explorations *213*
Answers To Conceptual Problems *214*
Solutions To Practice Problems *216*
Solutions To General Problems *225*
Solutions To Strategy Problems *233*
Solutions To Cumulative-Skills Problems *235*
CHAPTER 7 – QUANTUM THEORY OF THE ATOM 242
Solutions To Exercises *242*
Answers To Concept Checks *243*
Answers To Self-Assessment And Review Questions *244*
Answers To Concept Explorations *246*

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Answers To Conceptual Problems *248*
Solutions To Practice Problems *250*
Solutions To General Problems *257*
Solutions To Strategy Problems *262*
Solutions To Cumulative-Skills Problems *264*
CHAPTER 8 – ELECTRON CONFIGURATIONS AND PERIODICITY 268
Solutions To Exercises *268*
Answers To Concept Checks *269*
Answers To Self-Assessment And Review Questions *270*
Answers To Concept Explorations *273*
Answers To Conceptual Problems *274*
Solutions To Practice Problems *276*
Solutions To General Problems *279*
Solutions To Strategy Problems *282*
Solutions To Cumulative-Skills Problems *283*
CHAPTER 9 – IONIC AND COVALENT BONDING 286
Solutions To Exercises *286*
Answers To Concept Checks *289*
Answers To Self-Assessment And Review Questions *291*
Answers To Concept Explorations *294*
Answers To Conceptual Problems *295*
Solutions To Practice Problems *298*
Solutions To General Problems *317*
Solutions To Strategy Problems *328*
Solutions To Cumulative-Skills Problems *330*
CHAPTER 10 – MOLECULAR GEOMETRY AND CHEMICAL BONDING THEORY 336
Solutions To Exercises *336*
Answers To Concept Checks *340*
Answers To Self-Assessment And Review Questions *341*
Answers To Concept Explorations *344*
Answers To Conceptual Problems *345*
Solutions To Practice Problems *348*
Solutions To General Problems *361*
Solutions To Strategy Problems *368*
Solutions To Cumulative-Skills Problems *370*

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CHAPTER 11 – STATES OF MATTER; LIQUIDS AND SOLIDS 375
Solutions To Exercises *375*
Answers To Concept Checks *377*
Answers To Self-Assessment And Review Questions *379*
Answers To Concept Explorations *381*
Answers To Conceptual Problems *384*
Solutions To Practice Problems *387*
Solutions To General Problems *399*
Solutions To Strategy Problems *407*
Solutions To Cumulative-Skills Problems *410*
CHAPTER 12 – SOLUTIONS 413
Solutions To Exercises *413*
Answers To Concept Checks *417*
Answers To Self-Assessment And Review Questions *418*
Answers To Concept Explorations *421*
Answers To Conceptual Problems *422*
Solutions To Practice Problems *424*
Solutions To General Problems *435*
Solutions To Strategy Problems *445*
Solutions To Cumulative-Skills Problems *448*
CHAPTER 13 – RATES OF REACTION 453
Solutions To Exercises *453*
Answers To Concept Checks *455*
Answers To Self-Assessment And Review Questions *457*
Answers To Concept Explorations *460*
Answers To Conceptual Problems *461*
Solutions To Practice Problems *464*
Solutions To General Problems *478*
Solutions To Strategy Problems *490*
Solutions To Cumulative-Skills Problems *492*
CHAPTER 14 – CHEMICAL EQUILIBRIUM 496
Solutions To Exercises *496*
Answers To Concept Checks *500*
Answers To Self-Assessment And Review Questions *501*
Answers To Concept Explorations *504*

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Answers To Conceptual Problems *505*
Solutions To Practice Problems *507*
Solutions To General Problems *521*
Solutions To Strategy Problems *536*
Solutions To Cumulative-Skills Problems *541*
CHAPTER 15 – ACIDS AND BASES 543
Solutions To Exercises *543*
Answers To Concept Checks *545*
Answers To Self-Assessment And Review Questions *545*
Answers To Concept Explorations *548*
Answers To Conceptual Problems *549*
Solutions To Practice Problems *550*
Solutions To General Problems *561*
Solutions To Strategy Problems *568*
Solutions To Cumulative-Skills Problems *571*
CHAPTER 16 – ACID-BASE EQUILIBRIA 572
Solutions To Exercises *572*
Answers To Concept Checks *582*
Answers To Self-Assessment And Review Questions *583*
Answers To Concept Explorations *587*
Answers To Conceptual Problems *589*
Solutions To Practice Problems *591*
Solutions To General Problems *624*
Solutions To Strategy Problems *648*
Solutions To Cumulative-Skills Problems *655*
CHAPTER 17 – SOLUBILITY AND COMPLEX-ION EQUILIBRIA 657
Solutions To Exercises *657*
Answers To Concept Checks *661*
Answers To Self-Assessment And Review Questions *662*
Answers To Concept Explorations *664*
Answers To Conceptual Problems *666*
Solutions To Practice Problems *667*
Solutions To General Problems *683*
Solutions To Strategy Problems *698*
Solutions To Cumulative-Skills Problems *702*

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CHAPTER 18 – THERMODYNAMICS AND EQUILIBRIUM 706
Solutions To Exercises *706*
Answers To Concept Checks *710*
Answers To Self-Assessment And Review Questions *710*
Answers To Concept Explorations *713*
Answers To Conceptual Problems *714*
Solutions To Practice Problems *716*
Solutions To General Problems *728*
Solutions To Strategy Problems *738*
Solutions To Cumulative-Skills Problems *743*
CHAPTER 19 – ELECTROCHEMISTRY 750
Solutions To Exercises *750*
Answers To Concept Checks *756*
Answers To Self-Assessment And Review Questions *757*
Answers To Concept Explorations *760*
Answers To Conceptual Problems *761*
Solutions To Practice Problems *764*
Solutions To General Problems *795*
Solutions To Strategy Problems *808*
Solutions To Cumulative-Skills Problems *811*
CHAPTER 20 – NUCLEAR CHEMISTRY 816
Solutions To Exercises *816*
Answers To Concept Checks *819*
Answers To Self-Assessment And Review Questions *820*
Answers To Conceptual Problems *822*
Solutions To Practice Problems *824*
Solutions To General Problems *836*
Solutions To Strategy Problems *844*
Solutions To Cumulative-Skills Problems *848*
CHAPTER 21 – CHEMISTRY OF THE MAIN-GROUP ELEMENTS 852
Answers To Concept Checks *852*
Answers To Self-Assessment And Review Questions *852*
Answers To Conceptual Problems *860*
Solutions To Practice Problems *861*
Solutions To General Problems *880*

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Solutions To Strategy Problems *887*
CHAPTER 22 – THE TRANSITION ELEMENTS AND COORDINATION COMPOUNDS 894
Solutions To Exercises *894*
Answers To Concept Checks *896*
Answers To Self-Assessment And Review Questions *896*
Answers To Conceptual Problems *900*
Solutions To Practice Problems *901*
Solutions To General Problems *912*
Solutions To Strategy Problems *915*
CHAPTER 23 – ORGANIC CHEMISTRY 918
Solutions To Exercises *918*
Answers To Concept Checks *922*
Answers To Self-Assessment And Review Questions *922*
Answers To Conceptual Problems *925*
Solutions To Practice Problems *927*
Solutions To General Problems *938*
Solutions To Strategy Problems *943*
CHAPTER 24 – POLYMER MATERIALS: SYNTHETIC AND BIOLOGICAL 946
Solutions To Exercises *946*
Answers To Concept Checks *946*
Answers To Self-Assessment And Review Questions *947*
Answers To Conceptual Problems *949*
Solutions To Practice Problems *951*
Solutions To General Problems *956*
Solutions To Strategy Problems *959*
APPENDIX A – MATHEMATICAL SKILLS 967
Solutions To Exercises *967*

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Preface

This Complete Solutions Manual provides worked-out answers to all of the problems that appear in *General Chemistry, 9th Edition*, by Darrell D. Ebbing and Steven D. Gammon. The solutions follow the same order as the textbook:

Exercises

Concept Checks

Self-Assessment and Review Questions

Concept Explorations

Conceptual Problems

Practice Problems

General Problems

Strategy Problems

Cumulative-Skills Problems

For convenience, the short answers for all in-chapter Exercises, Concept Checks, and Self-Assessment and Review Questions, as well as for selected odd-numbered problems are provided at the back of the textbook. This Complete Solutions Manual provides detailed solutions for all in-chapter Exercises, as well as in-depth answers to the Concept Checks, Self-Assessment and Review Questions, Concept Explorations, and Conceptual Problems. Step-by-step worked-out solutions are provided for all Practice Problems, General Problems, Strategy Problems, and Cumulative-Skills Problems.

For each chapter of the text, six additional interactive Self-Assessment and Review Questions are available at the student website (**college.hmco.com/pic/ebbing9e**). Their in-depth answers are available online, and are not included in this manual. In addition, a Strategies and Solutions Guide for the Concept Checks and Conceptual Problems is also available at the website.

Please note the following:

> **Significant figures:** The answer is first shown with 1 to 2 nonsignificant figures and no units, and the least significant digit is underlined. The answer is then rounded off to the correct number of significant figures, and the units are added. No attempt has been made to round off intermediate answers, but the least significant digit has been underlined wherever possible.

Great effort and care have gone into the preparation of this manual. The solutions have been checked and rechecked for accuracy and completeness several times. I would like to express my thanks to Tsun-Mei Chang of the University of Wisconsin-Parkside for her assistance and for her careful work in accuracy reviewing this manuscript.

D. B.

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CHAPTER 1

Chemistry and Measurement

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

1.1. From the law of conservation of mass,

Mass of wood + mass of air = mass of ash + mass of gases

Substituting, you obtain

1.85 grams + 9.45 grams = 0.28 grams + mass of gases

or,

Mass of gases = (1.85 + 9.45 − 0.28) grams = 11.02 grams

Thus, the mass of gases in the vessel at the end of the experiment is 11.02 grams.

1.2. Physical properties: soft, silvery-colored metal; melts at 64°C.

Chemical properties: reacts vigorously with water; reacts with oxygen; reacts with chlorine.

1.3.

a. The factor 9.1 has the fewest significant figures, so the answer should be reported to two significant figures.

$$\frac{5.61 \times 7.891}{9.1} = 4.\underline{8}6 = 4.9$$

b. The number with the least number of decimal places is 8.91. Therefore, round the answer to two decimal places.

$$8.91 - 6.435 = 2.47\underline{5} = 2.48$$

c. The number with the least number of decimal places is 6.81. Therefore, round the answer to two decimal places.

$$6.81 - 6.730 = 0.0\underline{8}0 = 0.08$$

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d. You first do the subtraction within parentheses. In this step, the number with the least number of decimal places is 6.81, so the result of the subtraction has two decimal places. The least significant figure for this step is underlined.

$$38.91 \text{ x } (6.81 - 6.730) = 38.91 \text{ x } 0.0\underline{8}0$$

Next, perform the multiplication. In this step, the factor 0.0$\underline{8}$0 has the fewest significant figures, so round the answer to one significant figure.

$$38.91 \text{ x } 0.0\underline{8}0 = \underline{3}.11 = 3$$

1.4.

a. $1.84 \text{ x } 10^{-9} \text{ m} = 1.84 \text{ nm}$

b. $5.67 \text{ x } 10^{-12} \text{ s} = 5.67 \text{ ps}$

c. $7.85 \text{ x } 10^{-3} \text{ g} = 7.85 \text{ mg}$

d. $9.7 \text{ x } 10^{3} \text{ m} = 9.7 \text{ km}$

e. $0.000732 \text{ s} = 0.732 \text{ ms, or } 732 \text{ } \mu\text{s}$

f. $0.000000000154 \text{ m} = 0.154 \text{ nm, or } 154 \text{ pm}$

1.5.

a. Substituting, we find that

$$t_C = \frac{5°C}{9°F} \text{ x } (t_F - 32°F) = \frac{5°C}{9°F} \text{ x } (102.5°F - 32°F) = 39.\underline{1}67°C$$

$$= 39.2°C$$

b. Substituting, we find that

$$T_K = \left(t_c \text{ x } \frac{1 \text{ K}}{1°C}\right) + 273.15 \text{ K} = \left(-78°C \text{ x } \frac{1 \text{ K}}{1°C}\right) + 273.15 \text{ K} = 19\underline{5}.15 \text{ K}$$

$$= 195 \text{ K}$$

1.6. Recall that density equals mass divided by volume. You substitute 159 g for the mass and 20.2 g/cm^3 for the volume.

$$d = \frac{m}{V} = \frac{159 \text{ g}}{20.2 \text{ cm}^3} = 7.8\underline{7}1 \text{ g/cm}^3 = 7.87 \text{ g/cm}^3$$

The density of the metal equals that of iron.

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1.7. Rearrange the formula defining the density to obtain the volume.

$$V = \frac{m}{d}$$

Substitute 30.3 g for the mass and 0.789 g/cm^3 for the density.

$$V = \frac{30.3\ \text{g}}{0.789\ \text{g/cm}^3} = 38.\underline{4}0\ \text{cm}^3 = 38.4\ \text{cm}^3$$

1.8. Since one pm $= 10^{-12}$ m, and the prefix milli- means 10^{-3}, you can write

$$121\ \text{pm} \times \frac{10^{-12}\ \text{m}}{1\ \text{pm}} \times \frac{1\ \text{mm}}{10^{-3}\ \text{m}} = 1.21 \times 10^{-7}\ \text{mm}$$

1.9. $$67.6\ \text{Å}^3 \times \left(\frac{10^{-10}\ \text{m}}{1\ \text{Å}}\right)^3 \times \left(\frac{1\ \text{dm}}{10^{-1}\ \text{m}}\right)^3 = 6.76 \times 10^{-26}\ \text{dm}^3$$

1.10. From the definitions, you obtain the following conversion factors:

$$1 = \frac{36\ \text{in}}{1\ \text{yd}} \quad 1 = \frac{2.54\ \text{cm}}{1\ \text{in}} \quad 1 = \frac{10^{-2}\ \text{m}}{1\ \text{cm}}$$

Then,

$$3.54\ \text{yd} \times \frac{36\ \text{in}}{1\ \text{yd}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{10^{-2}\ \text{m}}{1\ \text{cm}} = 3.2\underline{3}6\ \text{m} = 3.24\ \text{m}$$

■ ANSWERS TO CONCEPT CHECKS

1.1. Box A contains a collection of identical units; therefore, it must represent an element. Box B contains a compound because a compound is the chemical combination of two or more elements (two elements in this case). Box C contains a mixture because it is made up of two different substances.

1.2.

a. For a person who weighs less than 100 pounds, two significant figures are typically used, although one significant figure is possible (for example, 60 pounds). For a person who weighs 100 pounds or more, three significant figures are typically used to report the weight (given to the whole pound), although people often round to the nearest unit of 10, which may result in reporting the weight with two significant figures (for example, 170 pounds).

b. 165 pounds rounded to two significant figures would be reported as 1.7×10^2 pounds.

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c. For example, 165 lb weighed on a scale that can measure in 100-lb increments would be 200 lb. Using the conversion factor 1 lb = 0.4536 kg, 165 lb is equivalent to 74.8 kg. Thus, on a scale that can measure in 50-kg increments, 165 lb would be 50 kg.

1.3.

a. If your leg is approximately 32 inches long, this would be equivalent to 0.81 m, 8.1 dm, or 81 cm.

b. One story is approximately 10 feet, so three stories is 30 feet. This would be equivalent to approximately 9 m.

c. Normal body temperature is 98.6°F, or 37.0°C. Thus, if your body temperature were 39°C (102°F), you would feel as if you had a moderate fever.

d. Room temperature is approximately 72°F, or 22°C. Thus, if you were sitting in a room at 23°C (73°F), you would be comfortable in a short-sleeve shirt.

1.4. Gold is a very unreactive substance, so comparing physical properties is probably your best option. However, color is a physical property you cannot rely on in this case to get your answer.

One experiment you could perform is to determine the densities of the metal and the chunk of gold. You could measure the mass of the nugget on a balance and the volume of the nugget by water displacement. Using this information, you could calculate the density of the nugget. Repeat the experiment and calculations for the sample of gold. If the nugget is gold, the two densities should be equal and be 19.3 g/cm^3.

Also, you could determine the melting points of the metal and the chunk of pure gold. The two melting points should be the same (1338 K) if the metal is gold.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

1.1. One area of technology that chemistry has changed is the characteristics of materials. The liquid-crystal displays (LCDs) in devices such as watches, cell phones, computer monitors, and televisions are materials made of molecules designed by chemists. Electronics and communications have been transformed by the development of optical fibers to replace copper wires. In biology, chemistry has changed the way scientists view life. Biochemists have found that all forms of life share many of the same molecules and molecular processes.

1.2. An experiment is an observation of natural phenomena carried out in a controlled manner so that the results can be duplicated and rational conclusions obtained. A theory is a tested explanation of basic natural phenomena. They are related in that a theory is based on the results of many experiments and is fruitful in suggesting other, new experiments. Also, an experiment can disprove a theory but can never prove it absolutely. A hypothesis is a tentative explanation of some regularity of nature.

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1.3. Rosenberg conducted controlled experiments and noted a basic relationship that could be stated as a hypothesis—that is, that certain platinum compounds inhibit cell division. This led him to do new experiments on the anticancer activity of these compounds.

1.4. Matter is the general term for the material things around us. It is whatever occupies space and can be perceived by our senses. Mass is the quantity of matter in a material. The difference between mass and weight is that mass remains the same wherever it is measured, but weight is proportional to the mass of the object divided by the square of the distance between the center of mass of the object and that of the earth.

1.5. The law of conservation of mass states that the total mass remains constant during a chemical change (chemical reaction). To demonstrate this law, place a sample of wood in a sealed vessel with air, and weigh it. Heat the vessel to burn the wood, and weigh the vessel after the experiment. The weight before the experiment and that after it should be the same.

1.6. Mercury metal, which is a liquid, reacts with oxygen gas to form solid mercury(II) oxide. The color changes from that of metallic mercury (silvery) to a color that varies from red to yellow depending on the particle size of the oxide.

1.7. Gases are easily compressible and fluid. Liquids are relatively incompressible and fluid. Solids are relatively incompressible and rigid.

1.8. An example of a substance is the element sodium. Among its physical properties: It is a solid, and it melts at 98°C. Among its chemical properties: It reacts vigorously with water, and it burns in chlorine gas to form sodium chloride.

1.9. An example of an element: sodium; of a compound: sodium chloride, or table salt; of a heterogeneous mixture: salt and sugar; of a homogeneous mixture: sodium chloride dissolved in water to form a solution.

1.10. A glass of bubbling carbonated beverage with ice cubes contains three phases: gas, liquid, and solid.

1.11. A compound may be decomposed by chemical reactions into elements. An element cannot be decomposed by any chemical reaction. Thus, a compound cannot also be an element in any case.

1.12. The precision refers to the closeness of the set of values obtained from identical measurements of a quantity. The number of digits reported for the value of a measured or calculated quantity (significant figures) indicates the precision of the value.

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1.13. Multiplication and division rule: In performing the calculation 100.0 x 0.0634 ÷ 25.31, the calculator display shows 0.2504938. We would report the answer as 0.250 because the factor 0.0634 has the least number of significant figures (three).

Addition and subtraction rule: In performing the calculation 184.2 + 2.324, the calculator display shows 186.524. Because the quantity 184.2 has the least number of decimal places (one), the answer is reported as 186.5.

1.14. An exact number is a number that arises when you count items or sometimes when you define a unit. For example, a foot is defined to be 12 inches. A measured number is the result of a comparison of a physical quantity with a fixed standard of measurement. For example, a steel rod measures 9.12 centimeters, or 9.12 times the standard centimeter unit of measurement.

1.15. For a given unit, the SI system uses prefixes to obtain units of different sizes. Units for all other possible quantities are obtained by deriving them from any of the seven base units. You do this by using the base units in equations that define other physical quantities.

1.16. An absolute temperature scale is a scale in which the lowest temperature that can be attained theoretically is zero. Degrees Celsius and kelvins have units of equal and are related by the formula

$$t_C = (T_K - 273.15\ \text{K}) \times \frac{1^\circ\text{C}}{1\ \text{K}}$$

1.17. The density of an object is its mass per unit volume. Because the density is characteristic of a substance, it can be helpful in identifying it. Density can also be useful in determining whether a substance is pure. It also provides a useful relationship between mass and volume.

1.18. Units should be carried along because (1) the units for the answers will come out in the calculations, and (2), if you make an error in arranging factors in the calculation, this will become apparent because the final units will be nonsense.

1.19. The answer is c, three significant figures.

1.20. The answer is a, 4.43×10^2 mm.

1.21. The answer is e, 75 mL.

1.22. The answer is c, 0.23 mg.

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ANSWERS TO CONCEPT EXPLORATIONS

1.23.

a. First, check the physical appearance of each sample. Check the particles that make up each sample for consistency and hardness. Also, note any odor. Then perform on each sample some experiments to measure physical properties such as melting point, density, and solubility in water. Compare all of these results and see if they match.

b. It is easier to prove that the compounds were different by finding one physical property that is different, say different melting points. To prove the two compounds were the same would require showing that every physical property was the same.

c. Of the properties listed in part a, the melting point would be most convincing. It is not difficult to measure, and it is relatively accurate. The density of a powder is not as easy to determine as the melting point, and solubility is not reliable enough on its own.

d. No. Since neither solution reached a saturation point, there is not enough information to tell if there was a difference in behavior. Many white powders dissolve in water. Their chemical compositions are not the same.

1.24. Part 1

a. 3 g + 1.4 g + 3.3 g = 7.7 g = 8 g

b. First, 3 g + 1.4 g = 4.4 g = 4 g. Then, 4 g + 3.3 g = 7.3 g = 7 g.

c. Yes, the answer in part a is more accurate. When you round off intermediate steps, you accumulate small errors and your answer is not as accurate.

d. The answer 29 g is correct.

e. This answer is incorrect. It should be 3×10^1 with only one significant figure in the answer. The student probably applied the rule for addition (instead of for multiplication) after the first step.

f. The answer 28.5 g is correct.

g. Don't round off intermediate answers. Indicate the round-off position after each step by underlining the least significant digit.

Part 2

a. The calculated answer is incorrect. It should be 11 cm^3. The answer given has too many significant figures. There is also a small round off error due to using a rounded-off value for the density.

b. This is a better answer. It is reported with the correct number of significant figures (three). It can be improved by using all of the digits given for the density.

c. $$V = \frac{10 \text{ ball bearings}}{1} \times \frac{1.234 \text{ g}}{1 \text{ ball bearing}} \times \frac{1 \text{ cm}^3}{3.1569 \text{ g}} = 3.90\underline{8}89 = 3.909 \text{ cm}^3$$

d. There was no rounding off of intermediate steps; all the factors are as accurate as possible.

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■ ANSWERS TO CONCEPTUAL PROBLEMS

1.25.

a. Two phases: liquid and solid.

b. Three phases: liquid water, solid quartz, and solid seashells.

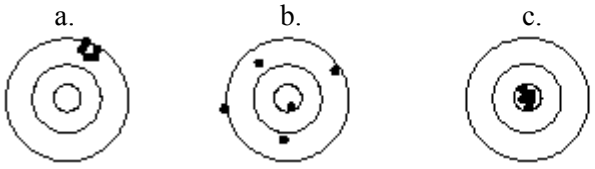
1.26. If the material is a pure compound, all samples should have the same melting point, the same color, and the same elemental composition. If it is a mixture, these properties should differ depending on the composition.

1.27.

a. You need to establish two points on the thermometer with known (defined) temperatures—for example, the freezing point (0°C) and boiling point (100°C) of water. You could first immerse the thermometer in an ice-water bath and mark the level at this point as 0°C. Then, immerse the thermometer in boiling water, and mark the level at this point as 100°C. As long as the two points are far enough apart to obtain readings of the desired accuracy, the thermometer can be used in experiments.

b. You could make 19 evenly spaced marks on the thermometer between the two original points, each representing a difference of 5°C. You may divide the space between the two original points into fewer spaces as long as you can read the thermometer to obtain the desired accuracy.

1.28.



1.29.

a. To answer this question, you need to develop an equation that converts between °F and °YS. To do so, you need to recognize that one degree on the Your Scale does not correspond to one degree on the Fahrenheit scale and that −100°F corresponds to 0° on Your Scale (different "zero" points). As stated in the problem, in the desired range of 100 Your Scale degrees, there are 120 Fahrenheit degrees. Therefore, the relationship can be expressed as 120°F = 100°YS, since it covers the same temperature range. Now you need to "scale" the two systems so that they correctly convert from one scale to the other. You could set up an equation with the known data points and then employ the information from the relationship above.

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For example, to construct the conversion between °YS and °F, you could perform the following steps:

Step 1: $°F = °YS$

Not a true statement, but one you would like to make true.

Step 2: $°F = °YS \times \frac{120°F}{100°YS}$

This equation takes into account the difference in the size between the temperature unit on the two scales but will not give you the correct answer because it doesn't take into account the different zero points.

Step 3: By subtracting 100°F from your equation from Step 2, you now have the complete equation that converts between °F and °YS.

$$°F = (°YS \times \frac{120°F}{100°YS}) - 100°F$$

b. Using the relationship from part a, 66°YS is equivalent to

$$(66°YS \times \frac{120°F}{100°YS}) - 100°F = -2\underline{0}.8°F = -21°F$$

1.30. Some physical properties you could measure are density, hardness, color, and conductivity. Chemical properties of sodium would include reaction with air, reaction with water, reaction with chlorine, reaction with acids, bases, etc.

1.31. The empty boxes are identical, so they do not contribute to any mass or density difference. Since the edge of the cube and the diameter of the sphere are identical, they will occupy the same volume in each of the boxes; therefore, each box will contain the same number of cubes or spheres. If you view the spheres as cubes that have been rounded by removing wood, you can conclude that the box containing the cubes must have a greater mass of wood; hence, it must have a greater density.

1.32.

a. Since the bead is less dense than any of the liquids in the container, the bead will float on top of all the liquids.

b. First, determine the density of the plastic bead. Since density is mass divided by volume, you get

$$d = \frac{m}{V} = \frac{3.92 \times 10^{-2}\ g}{0.043\ mL} = 0.9\underline{1}1\ g/mL = 0.91\ g/mL$$

Thus, the glass bead will pass through the top three layers and float on the ethylene glycol layer, which is more dense.

c. Since the bead sinks all the way to the bottom, it must be more dense than 1.114 g/mL.

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1.33.

a. A paper clip has a mass of about 1 g.

b. Answers will vary depending on your particular sample. Keeping in mind that the SI unit for mass is kg, the approximate weights for the items presented in the problem are as follows: a grain of sand, 1×10^{-5} kg; a paper clip, 1×10^{-3} kg; a nickel, 5×10^{-3} kg; a 5.0-gallon bucket of water, 2.0×10^{1} kg; a brick, 3 kg; a car, 1×10^{3} kg.

1.34. When taking measurements, never throw away meaningful information even if there is some uncertainty in the final digit. In this case, you are certain that the nail is between 5 and 6 cm. The uncertain, yet still important, digit is between the 5 and 6 cm measurements. You can estimate with reasonable precision that it is about 0.7 cm from the 5 cm mark, so an acceptable answer would be 5.7 cm. Another person might argue that the length of the nail is closer to 5.8 cm, which is also acceptable given the precision of the ruler. In any case, an answer of 5.7 or 5.8 should provide useful information about the length of the nail. If you were to report the length of the nail as 6 cm, you would be discarding potentially useful length information provided by the measuring instrument. If a higher degree of measurement precision were needed (more significant figures), you would need to switch to a more precise ruler—for example, one that had mm markings.

1.35.

a. The number of significant figures in this answer follows the rules for multiplication and division. Here, the measurement with the fewest significant figures is the reported volume 0.310 m^3, which has three. Therefore, the answer will have three significant figures. Since Volume = $L \times W \times H$, you can rearrange and solve for one of the measurements, say the length.

$$L = \frac{V}{W \times H} = \frac{0.310\ \text{m}^3}{(0.7120\ \text{m})\ (0.52145\ \text{m})} = 0.83\underline{4}96\ \text{m} = 0.835\ \text{m}$$

b. The number of significant figures in this answer follows the rules for addition and subtraction. The measurement with the least number of decimal places is the result 1.509 m, which has three. Therefore, the answer will have three decimal places. Since the result is the sum of the three measurements, the third length is obtained by subtracting the other two measurements from the total.

$$\text{Length} = 1.509\ \text{m} - 0.7120\ \text{m} - 0.52145\ \text{m} = 0.27\underline{5}55\ \text{m} = 0.276\ \text{m}$$

1.36. The mass of something (how heavy it is) depends on how much of the item, material, substance, or collection of things you have. The density of something is the mass of a specific amount (volume) of an item, material, substance, or collection of things. You could use 1 kg of feathers and 1 kg of water to illustrate that they have the same mass yet have very different volumes; therefore, they have different densities.

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SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

1.37. By the law of conservation of mass:

Mass of sodium carbonate + mass of acetic acid solution = mass of contents of reaction vessel + mass of carbon dioxide

Plugging in gives

15.9 g + 20.0 g = 29.3 g + mass of carbon dioxide

Mass of carbon dioxide = 15.9 g + 20.0 g − 29.3 g = 6.6 g

1.38. By the law of conservation of mass:

Mass of iron + mass of acid = mass of contents of beaker + mass of hydrogen

Plugging in gives

5.6 g + 15.0 = 20.4 g + mass of hydrogen

Mass of hydrogen = 5.6 g + 15.0 g − 20.4 g = 0.2 g

1.39. By the law of conservation of mass:

Mass of zinc + mass of sulfur = mass of zinc sulfide

Rearranging and plugging in give

Mass of zinc sulfide = 65.4 g + 32.1 g = 97.5 g

For the second part, let x = mass of zinc sulfide that could be produced. By the law of conservation of mass:

20.0 g + mass of sulfur = x

Write a proportion that relates the mass of zinc reacted to the mass of zinc sulfide formed, which should be the same for both cases.

$$\frac{\text{mass zinc}}{\text{mass zinc sulfide}} = \frac{65.4\text{ g}}{97.5\text{ g}} = \frac{20.0\text{ g}}{x}$$

Solving gives $x = 29.\underline{8}1\text{ g} = 29.8\text{ g}$

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1.40. By the law of conservation of mass:

Mass of aluminum + mass of bromine = mass of aluminum bromide

Plugging in and solving give

27.0 g + Mass of bromine = 266.7 g

Mass of bromine = 266.7 g − 27.0 g = 239.7 g

For the second part, let x = mass of bromine that reacts. By the law of conservation of mass:

15.0 g + x = mass of aluminum bromide

Write a proportion that relates the mass of aluminum reacted to the mass of bromine reacted, which should be the same for both cases.

$$\frac{\text{mass aluminum}}{\text{mass bromine}} = \frac{27.0\text{ g}}{239.7\text{ g}} = \frac{15.0\text{ g}}{x}$$

Solving gives x = 133.1 g = 133 g

1.41.

a. Solid
b. Liquid
c. Gas
d. Solid

1.42.

a. Solid
b. Solid
c. Solid
d. Liquid

1.43.

a. Physical change
b. Physical change
c. Chemical change
d. Physical change

1.44.

a. Physical change
b. Chemical change
c. Chemical change

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d. Physical change

1.45. Physical change: Liquid mercury is cooled to solid mercury.

Chemical changes: (1) Solid mercury oxide forms liquid mercury metal and gaseous oxygen; (2) glowing wood and oxygen form burning wood (form ash and gaseous products).

1.46. Physical changes: (1) Solid iodine is heated to gaseous iodine; (2) gaseous iodine is cooled to form solid iodine.

Chemical change: Solid iodine and zinc metal are ignited to form a white powder.

1.47.

a. Physical property
b. Chemical property
c. Physical property
d. Physical property
e. Chemical property

1.48.

a. Physical property
b. Chemical property
c. Physical property
d. Chemical property
e. Physical property

1.49. Physical properties: (1) Iodine is solid; (2) the solid has lustrous blue-black crystals; (3) the crystals vaporize readily to a violet-colored gas.

Chemical properties: (1) Iodine combines with many metals, such as with aluminum to give aluminum iodide.

1.50. Physical properties: (1) is a solid; (2) has an orange-red color; (3) has a density of 11.1 g/cm^3; (4) is insoluble in water.

Chemical property: Mercury(II) oxide decomposes when heated to give mercury and oxygen.

1.51.

a. Physical process
b. Chemical reaction
c. Physical process

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d. Chemical reaction
e. Physical process

1.52.

a. Chemical reaction
b. Physical process
c. Physical process
d. Physical process
e. Chemical reaction

1.53.

a. Solution
b. Substance
c. Substance
d. Homogeneous or Heterogeneous mixture

1.54.

a. Heterogeneous mixture
b. Substance
c. Solution
d. Substance

1.55.

a. A pure substance with two phases present, liquid and gas.
b. A mixture with two phases present, solid and liquid.
c. A pure substance with two phases present, solid and liquid.
d. A mixture with two phases present, solid and solid.

1.56.

a. A mixture with two phases present, solid and liquid.
b. A mixture with two phases present, solid and liquid.
c. A mixture with two phases present, solid and solid.
d. A pure substance with two phases present, liquid and gas.

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1.57.

a. six
b. three
c. four
d. five
e. three
f. four

1.58.

a. three
b. four
c. six
d. four
e. four
f. four

1.59. 4<u>0</u>,000 km = 4.0×10^4 km

1.60. 15<u>0</u>,000,000 km = 1.50×10^8 km

1.61.

a. $\dfrac{8.71 \times 0.0301}{0.031} = 8.\underline{4}57 = 8.5$

b. $0.71 + 92.2 = 92.\underline{9}1 = 92.9$

c. $934 \times 0.00435 + 107 = 4.0\underline{6}29 + 107 = 11\underline{1}.06 = 111$

d. $(847.89 - 847.73) \times 14673 = 0.1\underline{6} \times 14673 = 2\underline{3}47 = 2.3 \times 10^3$

1.62.

a. $\dfrac{0.871 \times 0.57}{5.871} = 0.08\underline{4}56 = 0.085$

b. $8.937 - 8.930 = 0.007$

c. $8.937 + 8.930 = 17.867$

d. $0.00015 \times 54.6 + 1.002 = 0.008\underline{1}9 + 1.002 = 1.01\underline{0}1 = 1.010$

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1.63. The volume of the first sphere is

$$V_1 = (4/3)\pi r^3 = (4/3)\pi \text{ x } (5.10 \text{ cm})^3 = 55\underline{5}.64 \text{ cm}^3$$

The volume of the second sphere is

$$V_2 = (4/3)\pi r^3 = (4/3)\pi \text{ x } (5.00 \text{ cm})^3 = 52\underline{3}.60 \text{ cm}^3$$

The difference in volume is

$$V_1 - V_2 = 55\underline{5}.64 \text{ cm}^3 - 52\underline{3}.60 \text{ cm}^3 = 3\underline{2}.04 \text{ cm}^3 = 32 \text{ cm}^3$$

1.64. The length of the cylinder between the two marks is

$$l = 3.50 \text{ cm} - 3.10 \text{ cm} = 0.4\underline{0} \text{ cm}$$

The volume of iron contained between the marks is

$$V = \pi r^2 l = \pi \text{ x } (1.500 \text{ cm})^2 \text{ x } 0.4\underline{0} \text{ cm} = 2.\underline{8}2 \text{ cm}^3 = 2.8 \text{ cm}^3$$

1.65.

a. $5.89 \text{ x } 10^{-12} \text{ s} = 5.89 \text{ ps}$

b. $0.2010 \text{ m} = 20.10 \text{ cm}$

c. $2.560 \text{ x } 10^{-9} \text{ g} = 2.560 \text{ ng}$

d. $6.05 \text{ x } 10^{3} \text{ m} = 6.05 \text{ km}$

1.66.

a. $4.851 \text{ x } 10^{-6} \text{ g} = 4.851 \text{ µg}$

b. $3.16 \text{ x } 10^{-2} \text{ m} = 3.16 \text{ cm}$

c. $2.591 \text{ x } 10^{-9} \text{ s} = 2.591 \text{ ns}$

d. $8.93 \text{ x } 10^{-12} \text{ g} = 8.93 \text{ pg}$

1.67.

a. $6.15 \text{ ps} = 6.15 \text{ x } 10^{-12} \text{ s}$

b. $3.781 \text{ µm} = 3.781 \text{ x } 10^{-6} \text{ m}$

c. $1.546 \text{ Å} = 1.546 \text{ x } 10^{-10} \text{ m}$

d. $9.7 \text{ mg} = 9.7 \text{ x } 10^{-3} \text{ g}$

1.68.

a. $6.20 \text{ km} = 6.20 \text{ x } 10^{3} \text{ m}$

b. $1.98 \text{ ns} = 1.98 \text{ x } 10^{-9} \text{ s}$

c. $2.54 \text{ cm} = 2.54 \text{ x } 10^{-2} \text{ m}$

d. $5.23 \text{ µg} = 5.23 \text{ x } 10^{-6} \text{ g}$

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1.69.

a. $t_C = \frac{5°C}{9°F} \times (t_F - 32°F) = \frac{5°C}{9°F} \times (68°F - 32°F) = 2\underline{0}.0°C = 20.°C$

b. $t_C = \frac{5°C}{9°F} \times (t_F - 32°F) = \frac{5°C}{9°F} \times (-23°F - 32°F) = -3\underline{0}.55°C = -31°C$

c. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (26°C \times \frac{9°F}{5°C}) + 32°F = 7\underline{8}.8°F = 79°F$

d. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (-70°C \times \frac{9°F}{5°C}) + 32°F = -9\underline{4}.0°F = -94°F$

1.70.

a. $t_C = \frac{5°C}{9°F} \times (t_F - 32°F) = \frac{5°C}{9°F} \times (51°F - 32°F) = 1\underline{0}.555°C = 11°C$

b. $t_C = \frac{5°C}{9°F} \times (t_F - 32°F) = \frac{5°C}{9°F} \times (-7°F - 32°F) = -2\underline{1}.6°C = -22°C$

c. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (-41°C \times \frac{9°F}{5°C}) + 32°F = -4\underline{1}.8°F = -42°F$

d. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (22°C \times \frac{9°F}{5°C}) + 32°F = 7\underline{1}.6°F = 72°F$

1.71. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (-21.1°C \times \frac{9°F}{5°C}) + 32°F = -5.\underline{9}8°F = -6.0°F$

1.72. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (-196°C \times \frac{9°F}{5°C}) + 32°F = -32\underline{0}.8°F = -321°F$

1.73. $d = \frac{m}{V} = \frac{12.4\ g}{1.64\ cm^3} = 7.5\underline{6}0\ g/cm^3 = 7.56\ g/cm^3$

1.74. $d = \frac{m}{V} = \frac{17.84\ g}{25.0\ mL} = 0.71\underline{3}6\ g/mL = 0.714\ g/mL$

1.75. First, determine the density of the liquid.

$$d = \frac{m}{V} = \frac{6.71\ g}{8.5\ mL} = 0.7\underline{8}94 = 0.79\ g/mL$$

The density is closest to ethanol (0.789 g/cm^3).

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1.76. First, determine the density of the mineral sample.

$$d = \frac{m}{V} = \frac{59.5\text{ g}}{7.9\text{ cm}^3} = 7.\underline{5}31 = 7.5\text{ g/cm}^3$$

The density is closest to cassiterite (6.99 g/cm^3).

1.77. The mass of platinum is obtained as follows.

$$\text{Mass} = d \times V = 21.4\text{ g/cm}^3 \times 5.9\text{ cm}^3 = 1\underline{2}6\text{ g} = 1.3 \times 10^2\text{ g}$$

1.78. The mass of gasoline is obtained as follows.

$$\text{Mass} = d \times V = 0.70\text{ g/mL} \times 43.8\text{ mL} = 3\underline{0}.66\text{ g} = 31\text{ g}$$

1.79. The volume of ethanol is obtained as follows. Recall that 1 mL = 1 cm^3.

$$\text{Volume} = \frac{m}{d} = \frac{19.8\text{ g}}{0.789\text{ g/cm}^3} = 25.\underline{0}9\text{ cm}^3 = 25.1\text{ cm}^3 = 25.1\text{ mL}$$

1.80. The volume of bromine is obtained as follows.

$$\text{Volume} = \frac{m}{d} = \frac{88.5\text{ g}}{3.10\text{ g/mL}} = 28.\underline{5}4\text{ mL} = 28.5\text{ mL}$$

1.81. Since 1 kg = 10^3 g, and 1 mg = 10^{-3} g, you can write

$$0.480\text{ kg} \times \frac{10^3\text{ g}}{1\text{ kg}} \times \frac{1\text{ mg}}{10^{-3}\text{ g}} = 4.80 \times 10^5\text{ mg}$$

1.82. Since 1 mg = 10^{-3} g, and 1 μg = 10^{-6} g, you can write

$$501\text{ mg} \times \frac{10^{-3}\text{ g}}{1\text{ mg}} \times \frac{1\text{ μg}}{10^{-6}\text{ g}} = 5.01 \times 10^5\text{ μg}$$

1.83. Since 1 nm = 10^{-9} m, and 1 cm = 10^{-2} m, you can write

$$555\text{ nm} \times \frac{10^{-9}\text{ m}}{1\text{ nm}} \times \frac{1\text{ cm}}{10^{-2}\text{ m}} = 5.55 \times 10^{-5}\text{ cm}$$

1.84. Since 1 Å = 10^{-10} m, you can write

$$0.96\text{ Å} \times \frac{10^{-10}\text{ m}}{1\text{ Å}} = 9.6 \times 10^{-11}\text{ m}$$

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1.85. Since 1 km = 10^3 m, you can write

$$3.73 \times 10^8 \text{ km}^3 \times \left(\frac{10^3 \text{ m}}{1 \text{ km}}\right)^3 = 3.73 \times 10^{17} \text{ m}^3$$

Now, 1 dm = 10^{-1} m. Also, note that 1 dm^3 = 1 L. Therefore, you can write

$$3.73 \times 10^{17} \text{ m}^3 \times \left(\frac{1 \text{ dm}}{10^{-1} \text{ m}}\right)^3 = 3.73 \times 10^{20} \text{ dm}^3 = 3.73 \times 10^{20} \text{ L}$$

1.86. 1 μm = 10^{-6} m, and 1 dm = 10^{-1} m. Also, note that 1 dm^3 = 1 L. Therefore, you can write

$$1.3 \text{ } \mu\text{m}^3 \times \left(\frac{10^{-6} \text{ m}}{1 \text{ } \mu\text{m}}\right)^3 \times \left(\frac{1 \text{ dm}}{10^{-1} \text{ m}}\right)^3 = 1.3 \times 10^{-15} \text{ dm}^3 = 1.3 \times 10^{-15} \text{ L}$$

1.87. $$3.58 \text{ short ton} \times \frac{2000 \text{ lb}}{1 \text{ short ton}} \times \frac{16 \text{ oz}}{1 \text{ lb}} \times \frac{1 \text{ g}}{0.03527 \text{ oz}} = 3.2\underline{4}8 \times 10^6 \text{ g} = 3.25 \times 10^6 \text{ g}$$

1.88. $$3.15 \text{ Btu} \times \frac{252.0 \text{ cal}}{1 \text{ Btu}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 33\underline{2}1 \text{ J} = 3.32 \times 10^3 \text{ J}$$

1.89. $$2425 \text{ fathoms} \times \frac{6 \text{ ft}}{1 \text{ fathom}} \times \frac{12 \text{ in.}}{1 \text{ ft}} \times \frac{2.54 \times 10^{-2} \text{ m}}{1 \text{ in.}} = 443\underline{4}.8 \text{ m} = 4.435 \times 10^3 \text{ m}$$

1.90. $$1.3 \times 10^{10} \text{ barrels} \times \frac{42 \text{ gal}}{1 \text{ barrel}} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{9.46 \times 10^{-4} \text{ m}^3}{1 \text{ qt}} = 2.\underline{0}66 \times 10^9 \text{ m}^3 = 2.1 \times 10^9 \text{ m}^3$$

1.91. $$(20.0 \text{ in.})(20.0 \text{ in.})(10.0 \text{ in.}) \times \left(\frac{2.54 \text{ cm}}{1 \text{ in.}}\right)^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 65.\underline{5}4 \text{ L} = 65.5 \text{ L}$$

1.92. $$(1.00 \text{ km})(2.0 \text{ km})(1 \text{ m}) \times \left(\frac{1000 \text{ m}}{1 \text{ km}}\right)^2 \times \frac{25 \text{ worms}}{1 \text{ m}^3} = 5.\underline{0}0 \times 10^7 = 5.0 \times 10^7 \text{ worms}$$

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■ SOLUTIONS TO GENERAL PROBLEMS

1.93. From the law of conservation of mass,

Mass of sodium + mass of water = mass of hydrogen + mass of solution

Substituting, you obtain

19.70 g + 126.22 g = mass of hydrogen + 145.06 g

or,

Mass of hydrogen = 19.70 g + 126.22 g − 145.06 g = 0.8<u>6</u> g

Thus, the mass of hydrogen produced was 0.86 g.

1.94. From the law of conservation of mass,

Mass of tablet + mass of acid solution = mass of carbon dioxide + mass of solution

Substituting, you obtain

0.853 g + 56.519 g = mass of carbon dioxide + 57.152 g

Mass of carbon dioxide = 0.853 g + 56.519 g − 57.152 g = 0.22<u>0</u> g

Thus, the mass of carbon dioxide produced was 0.220 g.

1.95. From the law of conservation of mass,

Mass of aluminum + mass of iron(III) oxide = mass of iron + mass of aluminum oxide + mass of unreacted iron(III) oxide

5.40 g + 18.50 g = 11.17 g + 10.20 g + mass of iron(III) oxide unreacted

Mass of iron(III) oxide unreacted = 5.40 g + 18.50 g − 11.17 g − 10.20 g = 2.53 g

Thus, the mass of unreacted iron(III) oxide is 2.53 g.

1.96. From the law of conservation of mass,

Mass of sodium bromide + mass of chlorine reacted = mass of bromine + mass of sodium chloride

20.6 g + mass of chlorine reacted = 16.0 g + 11.7 g

Mass of chlorine reacted = 16.0 g + 11.7 g − 20.6 g = 7.<u>1</u> g

Thus, the mass of chlorine that reacted is 7.1 g.

1.97. 53.10 g + 5.348 g + 56.1 g = 114.<u>5</u>4 g = 114.5 g total

1.98. 68.1 g + 58.2 g + 5.279 g = 131.<u>5</u>79 g = 131.6 g total

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1.99.

a. Chemical

b. Physical

c. Physical

d. Chemical

1.100.

a. Physical

b. Chemical

c. Physical

d. Chemical

1.101. Compounds always contain the same proportions of the elements by mass. Thus, if we let X be the proportion of iron in a sample, we can calculate the proportion of iron in each sample as follows.

$$\text{Sample A: } X = \frac{\text{mass of iron}}{\text{mass of sample}} = \frac{1.094\text{ g}}{1.518\text{ g}} = 0.720\underline{6}8 = 0.7207$$

$$\text{Sample B: } X = \frac{\text{mass of iron}}{\text{mass of sample}} = \frac{1.449\text{ g}}{2.056\text{ g}} = 0.704\underline{7}6 = 0.7048$$

$$\text{Sample C: } X = \frac{\text{mass of iron}}{\text{mass of sample}} = \frac{1.335\text{ g}}{1.873\text{ g}} = 0.712\underline{7}6 = 0.7128$$

Since each sample has a different proportion of iron by mass, the material is not a compound.

1.102. Compounds always contain the same proportions of the elements by mass. Thus, if we let X be the proportion of mercury in a sample, we can calculate the proportion of mercury in each sample as follows.

$$\text{Sample A: } X = \frac{\text{mass of mercury}}{\text{mass of sample}} = \frac{0.9641\text{ g}}{1.0410\text{ g}} = 0.926\underline{1}2 = 0.9261$$

$$\text{Sample B: } X = \frac{\text{mass of mercury}}{\text{mass of sample}} = \frac{1.4293\text{ g}}{1.5434\text{ g}} = 0.926\underline{0}7 = 0.9261$$

$$\text{Sample C: } X = \frac{\text{mass of mercury}}{\text{mass of sample}} = \frac{1.1283\text{ g}}{1.2183\text{ g}} = 0.926\underline{1}2 = 0.9261$$

Since each sample has the same proportion of mercury by mass, the data are consistent with the hypothesis that the material is a compound.

1.103. $V = (\text{edge})^3 = (39.3\text{ cm})^3 = 6.06\underline{9} \times 10^4\text{ cm}^3 = 6.07 \times 10^4\text{ cm}^3$

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1.104. $V = \pi r^2 l = \pi \text{ x } (2.56 \text{ cm})^2 \text{ x } 56.32 \text{ cm} = 1159 \text{ cm}^3 = 1.16 \text{ x } 10^3 \text{ cm}^3$

1.105. $V = LWH = 47.8 \text{ in. x } 12.5 \text{ in. x } 19.5 \text{ in. x } \dfrac{1 \text{ gal}}{231 \text{ in}^3} = 50.43 \text{ gal} = 50.4 \text{ gal}$

1.106. The volume in cubic inches is

$$V = (4/3)\pi r^3 = (4/3)\pi \text{ x } (175.0 \text{ in.})^3 = 2.24492 \text{ x } 10^7 \text{ in}^3 = 2.245 \text{ x } 10^7 \text{ in}^3$$

The volume in imperial gallons is

$$V = 2.24492 \text{ x } 10^7 \text{ in}^3 \text{ x } \frac{1 \text{ gal}}{277.4 \text{ in}^3} = 8.09275 \text{ x } 10^4 \text{ gal} = 8.093 \text{ x } 10^4 \text{ gal}$$

1.107. The volume of the first sphere is given by

$$V_1 = (4/3)\pi r^3 = (4/3)\pi \text{ x } (5.61 \text{ cm})^3 = 739.5 \text{ cm}^3$$

The volume of the second sphere is given by

$$V_2 = (4/3)\pi r^3 = (4/3)\pi \text{ x } (5.85 \text{ cm})^3 = 838.6 \text{ cm}^3$$

The difference in volume between the two spheres is given by

$$V = V_2 - V_1 = 838.6 \text{ cm}^3 - 739.5 \text{ cm}^3 = 9.91 \text{ x } 10^1 = 9.9 \text{ x } 10^1 \text{ cm}^3$$

1.108. The surface area of the first circle is given by

$$S_1 = \pi r^2 = \pi \text{ x } (7.98 \text{ cm})^2 = 200.0 \text{ cm}^2$$

The surface area of the second circle is given by

$$S_2 = \pi r^2 = \pi \text{ x } (8.50 \text{ cm})^2 = 226.9 \text{ cm}^2$$

The difference in surface area between the two circles is

$$\text{Difference} = S_2 - S_1 = 226.9 \text{ cm}^2 - 200.0 \text{ cm}^2 = 26.9 \text{ cm}^2 = 27 \text{ cm}^2$$

1.109.

a. $\dfrac{56.1 - 51.1}{6.58} = 7.59 \text{ x } 10^{-1} = 7.6 \text{ x } 10^{-1}$

b. $\dfrac{56.1 + 51.1}{6.58} = 1.629 \text{ x } 10^1 = 1.63 \text{ x } 10^1$

c. $(9.1 + 8.6) \text{ x } 26.91 = 4.763 \text{ x } 10^2 = 4.76 \text{ x } 10^2$

d. $0.0065 \text{ x } 3.21 + 0.0911 = 1.119 \text{ x } 10^{-1} = 1.12 \text{ x } 10^{-1}$

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1.110.

a. $\frac{9.345 - 9.005}{9.811} = 0.034\underline{6}5 = 0.0347$

b. $\frac{9.345 + 9.005}{9.811} = 1.87\underline{0}3 = 1.870$

c. $(7.50 + 7.53) \times 3.71 = 55.\underline{7}61 = 55.8$

d. $0.71 \times 0.36 + 17.36 = 17.6\underline{1}56 = 17.62$

1.111.

a. 9.12 cg/mL

b. 66 pm

c. 7.1 μm

d. 56 nm

1.112.

a. 1.86 cg/mL

b. 77 pm

c. 6.5 nm

d. 0.85 μm

1.113.

a. 1.07×10^{-12} s

b. 5.8×10^{-6} m

c. 3.19×10^{-7} m

d. 1.53×10^{-2} s

1.114.

a. 6.6×10^{-3} K

b. 2.75×10^{-10} m

c. 2.21×10^{-2} s

d. 4.5×10^{-5} m

1.115. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (3410°C \times \frac{9°F}{5°C}) + 32°F = 617\underline{0}°F = 6170°F$

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1.116. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (1677°C \times \frac{9°F}{5°C}) + 32°F = 3050.6°F = 3051°F$

1.117. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (825°C \times \frac{9°F}{5°C}) + 32°F = 1517°F = 1.52 \times 10^3°F$

1.118. $t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (50°C \times \frac{9°F}{5°C}) + 32°F = 122°F = 122°F$

1.119. The temperature in kelvins is

$$T_K = (t_C \times \frac{1\ K}{1°C}) + 273.15\ K = (29.8°C \times \frac{1\ K}{1°C}) + 273.15\ K = 302.95\ K = 303.0\ K$$

The temperature in degrees Fahrenheit is

$$t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (29.8°C \times \frac{9°F}{5°C}) + 32°F = 85.64°F = 85.6°F$$

1.120. The temperature in kelvins is

$$T_K = (t_C \times \frac{1\ K}{1°C}) + 273.15\ K = (-38.9°C \times \frac{1\ K}{1°C}) + 273.15\ K = 234.25\ K = 234.3\ K$$

The temperature in degrees Fahrenheit is

$$t_F = (t_C \times \frac{9°F}{5°C}) + 32°F = (-38.9°C \times \frac{9°F}{5°C}) + 32°F = -38.02°F = -38.0°F$$

1.121. The temperature in degrees Celsius is

$$t_C = \frac{5°C}{9°F} \times (t_F - 32°F) = \frac{5°C}{9°F} \times (1666°F - 32°F) = 907.77°C = 907.8°C$$

The temperature in kelvins is

$$T_K = (t_C \times \frac{1\ K}{1°C}) + 273.15\ K = (907.77°C \times \frac{1\ K}{1°C}) + 273.15\ K = 1180.92\ K = 1180.9\ K$$

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1.122. The temperature in degrees Celsius is

$$t_C = \frac{5°C}{9°F} \text{ x } (t_F - 32°F) = \frac{5°C}{9°F} \text{ x } (236°F - 32°F) = 11\underline{3}.3°C = 113°C$$

The temperature in kelvins is

$$T_K = (t_C \text{ x } \frac{1\text{ K}}{1°C}) + 273.15\text{ K} = (11\underline{3}.3°C \text{ x } \frac{1\text{ K}}{1°C}) + 273.15\text{ K} = 386.4\text{ K}$$
$$= 386\text{ K}$$

1.123. $$\text{Density} = \frac{1.74\text{ g}}{1\text{ cm}^3} \text{ x } \frac{1\text{ kg}}{10^3\text{ g}} \text{ x } \left(\frac{1\text{ cm}}{10^{-2}\text{ m}}\right)^3 = 1.74 \text{ x } 10^3 \text{ kg/m}^3$$

1.124. $$\text{Density} = \frac{5.96\text{ g}}{1\text{ cm}^3} \text{ x } \frac{1\text{ kg}}{10^3\text{ g}} \text{ x } \left(\frac{1\text{ cm}}{10^{-2}\text{ m}}\right)^3 = 5.96 \text{ x } 10^3 \text{ kg/m}^3$$

1.125. The volume of the quartz is 65.7 mL − 51.2 mL = 14.5 mL. Then, the density is

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{38.4\text{ g}}{14.5\text{ mL}} = 2.6\underline{4}8\text{ g/mL} = 2.65\text{ g/mL} = 2.65\text{ g/cm}^3$$

1.126. First, determine the volume of water in the flask. The mass of water is obtained as follows. 109.3 g − 70.7 g = 38.6 g. Now, using the density (0.997 g/cm^3),

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{38.6\text{ g}}{0.997\text{ g/ cm}^3} = 38.\underline{7}16\text{ cm}^3 = 38.\underline{7}16\text{ mL}$$

Now, the volume of the ore is 53.2 mL − 38.$\underline{7}$16 mL = 14.$\underline{4}$8 mL, or 14.$\underline{4}$8 cm^3. Therefore, the density of the hematite ore is

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{70.7\text{ g}}{14.\underline{4}8\text{ cm}^3} = 4.8\underline{8}1\text{ g/cm}^3 = 4.88\text{ g/cm}^3$$

1.127. First, determine the density of the liquid sample.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{22.3\text{ g}}{15.0\text{ mL}} = 1.4\underline{8}6\text{ g/mL} = 1.49\text{ g/mL} = 1.49\text{ g/cm}^3$$

This density is closest to that of chloroform (1.489 g/cm^3), so the unknown liquid is chloroform.

1.128. First, determine the density of the calcite sample.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{35.6\text{ g}}{12.9\text{ cm}^3} = 2.7\underline{5}9\text{ g/cm}^3 = 2.76\text{ g/cm}^3$$

Since a substance will float on the liquids with greater densities, calcite will float on tetrabromoethane (2.96 g/cm^3) and methylene iodode (3.33 g/cm^3).

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1.129. First, determine the volume of the cube of platinum.

$$V = (\text{edge})^3 = (4.40\text{ cm})^3 = 85.\underline{1}8\text{ cm}^3$$

Now, use the density to determine the mass of the platinum.

$$\text{Mass} = d \times V = 21.4\text{ g/cm}^3 \times 85.\underline{1}8\text{ cm}^3 = 18\underline{2}2.9\text{ g} = 1.82 \times 10^3\text{ g}$$

1.130. First, determine the volume of the cylinder of silicone.

$$V = \pi r^2 l = \pi \times (4.00\text{ cm})^2 \times 12.40\text{ cm} = 623.\underline{2}9\text{ cm}^3$$

Now, use the density to determine the mass of the silicon.

$$\text{Mass} = d \times V = 2.33\text{ g/cm}^3 \times 623.\underline{2}9\text{ cm}^3 = 14\underline{5}2.2\text{ g} = 1.45 \times 10^3\text{ g}$$

1.131. $$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{35.00\text{ g}}{1.053\text{ g/ mL}} = 33.2\underline{3}8\text{ mL} = 33.24\text{ mL}$$

1.132. First, convert kilograms to grams (1 kg = 10^3 g). Thus, 0.035 kg = 35 g. Then

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{35\text{ g}}{0.902\text{ g/ mL}} = 3\underline{8}.80\text{ mL}$$

Finally, convert the volume to liters (1000 mL = 1 L).

$$\text{Volume} = 3\underline{8}.80\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = 0.03\underline{8}80\text{ L} = 0.039\text{ L}$$

1.133.

a. $$8.45\text{ kg} \times \frac{10^3\text{ g}}{1\text{ kg}} \times \frac{1\text{ μg}}{10^{-6}\text{ g}} = 8.45 \times 10^9\text{ μg}$$

b. $$318\text{ μs} \times \frac{10^{-6}\text{ s}}{1\text{ μs}} \times \frac{1\text{ ms}}{10^{-3}\text{ s}} = 3.18 \times 10^{-1}\text{ ms}$$

c. $$93\text{ km} \times \frac{10^3\text{ m}}{1\text{ km}} \times \frac{1\text{ nm}}{10^{-9}\text{ m}} = 9.3 \times 10^{13}\text{ nm}$$

d. $$37.1\text{ mm} \times \frac{10^{-3}\text{ m}}{1\text{ mm}} \times \frac{1\text{ cm}}{10^{-2}\text{ m}} = 3.71\text{ cm}$$

1.134.

a. $$125\text{ Å} \times \frac{10^{-10}\text{ m}}{1\text{ Å}} \times \frac{1\text{ μm}}{10^{-6}\text{ m}} = 1.25 \times 10^{-2}\text{ μm}$$

b. $$32.4\text{ kg} \times \frac{10^3\text{ g}}{1\text{ kg}} \times \frac{1\text{ mg}}{10^{-3}\text{ g}} = 3.24 \times 10^7\text{ mg}$$

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c. $16.8\ \text{cm} \times \frac{10^{-2}\ \text{m}}{1\ \text{cm}} \times \frac{1\ \text{mm}}{10^{-3}\ \text{m}} = 168\ \text{mm}$

d. $2.2\ \text{ns} \times \frac{10^{-9}\ \text{s}}{1\ \text{ns}} \times \frac{1\ \mu\text{s}}{10^{-6}\ \text{s}} = 2.2 \times 10^{-3}\ \mu\text{s}$

1.135.

a. $5.91\ \text{kg} \times \frac{10^{3}\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mg}}{10^{-3}\ \text{g}} = 5.91 \times 10^{6}\ \text{mg}$

b. $753\ \text{mg} \times \frac{10^{-3}\ \text{g}}{1\ \text{mg}} \times \frac{1\ \mu\text{g}}{10^{-6}\ \text{g}} = 7.53 \times 10^{5}\ \mu\text{g}$

c. $90.1\ \text{MHz} \times \frac{10^{6}\ \text{Hz}}{1\ \text{MHz}} \times \frac{1\ \text{kHz}}{10^{3}\ \text{Hz}} = 9.01 \times 10^{4}\ \text{kHz}$

d. $498\ \text{mJ} \times \frac{10^{-3}\ \text{J}}{1\ \text{mJ}} \times \frac{1\ \text{kJ}}{10^{3}\ \text{J}} = 4.98 \times 10^{-4}\ \text{kJ}$

1.136.

a. $7.19\ \mu\text{g} \times \frac{10^{-6}\ \text{g}}{1\ \mu\text{g}} \times \frac{1\ \text{mg}}{10^{-3}\ \text{g}} = 7.19 \times 10^{-3}\ \text{mg}$

b. $104\ \text{pm} \times \frac{10^{-12}\ \text{m}}{1\ \text{pm}} \times \frac{1\ \text{Å}}{10^{-10}\ \text{m}} = 1.04\ \text{Å}$

c. $0.010\ \text{mm} \times \frac{10^{-3}\ \text{m}}{1\ \text{mm}} \times \frac{1\ \text{cm}}{10^{-2}\ \text{m}} = 1.0 \times 10^{-3}\ \text{cm}$

d. $0.0605\ \text{kPa} \times \frac{10^{3}\ \text{Pa}}{1\ \text{kPa}} \times \frac{1\ \text{cPa}}{10^{-2}\ \text{Pa}} = 6.05 \times 10^{3}\ \text{cPa}$

1.137. $\text{Volume} = 12{,}230\ \text{km}^3 \times \left(\frac{10^{3}\ \text{m}}{1\ \text{km}}\right)^3 \times \left(\frac{1\ \text{dm}}{10^{-1}\ \text{m}}\right)^3 \times \frac{1\ \text{L}}{1\ \text{dm}^3} = 1.2230 \times 10^{16}\ \text{L}$

1.138. $\text{Volume} = 0.501\ \text{km}^3 \times \left(\frac{10^{3}\ \text{m}}{1\ \text{km}}\right)^3 \times \left(\frac{1\ \text{dm}}{10^{-1}\ \text{m}}\right)^3 \times \frac{1\ \text{L}}{1\ \text{dm}^3} = 5.01 \times 10^{11}\ \text{L}$

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1.139. First, calculate the volume of the room in cubic feet.

$$\text{Volume} = LWH = 10.0 \text{ ft} \times 11.0 \text{ ft} \times 9.0 \text{ ft} = 990 \text{ ft}^3$$

Next, convert the volume to liters.

$$V = 990 \text{ ft}^3 \times \left(\frac{12 \text{ in}}{1 \text{ ft}}\right)^3 \times \left(\frac{2.54 \text{ cm}}{1 \text{ in}}\right)^3 \times \frac{1 \text{ L}}{10^3 \text{ cm}^3} = 2.80 \times 10^4 \text{ L} = 2.8 \times 10^4 \text{ L}$$

1.140. First, calculate the volume of the cylinder in cubic feet.

$$\text{Volume} = \pi r^2 l = \pi \times (15.0 \text{ ft})^2 \times 5.0 \text{ ft} = 3534 \text{ ft}^3$$

Next, convert the volume to liters.

$$V = 3534 \text{ ft}^3 \times \left(\frac{12 \text{ in}}{1 \text{ ft}}\right)^3 \times \left(\frac{2.54 \text{ cm}}{1 \text{ in}}\right)^3 \times \frac{1 \text{ L}}{10^3 \text{ cm}^3} = 1.00 \times 10^5 \text{ L}$$

$$= 1.0 \times 10^5 \text{ L}$$

1.141. $$\text{Mass} = 275 \text{ carats} \times \frac{200 \text{ mg}}{1 \text{ carat}} \times \frac{10^{-3} \text{ g}}{1 \text{ mg}} = 55.00 \text{ g} = 55.0 \text{ g}$$

1.142. $$\text{Mass} = 49.6 \times 10^6 \text{ troy oz} \times \frac{31.10 \text{ g}}{1 \text{ troy oz}} \times \frac{1 \text{ ton}}{10^6 \text{ g}} = 1.542 \times 10^3 \text{ ton}$$

$$= 1.54 \times 10^3 \text{ ton}$$

1.143. The adhesive is not permanent, is easily removable, and does no harm to the object.

1.144. The scientific question Art Fry was trying to answer was: "Is there an adhesive that will not permanently stick things together?"

1.145. Chromatography depends on how fast a substance moves in a stream of gas or liquid, past a stationary phase to which the substance is slightly attracted.

1.146. The moving stream is a gaseous mixture of vaporized substances plus a gas such as helium, the carrier. The gas is passed through a column containing a stationary phase. As the gas passes through the column, the substances are attracted differently to the stationary column packing and thus are separated. The separated gases pass through a detector, and the results are displayed graphically.

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SOLUTIONS TO STRATEGY PROBLEMS

1.147. 5×10^{-2} mg = 0.05 mg. So 4.6 mg − 0.05 mg = 4.55 mg = 4.6 mg

1.148. $V = \dfrac{m}{d} = \dfrac{33.0\text{ g}}{0.797\text{ g/cm}^3} = 41.405 = 41.4\text{ cm}^3$

1.149. $V = V_A + V_B = \dfrac{m_A}{d_A} + 50.0\text{ mL} = \dfrac{175\text{ g}}{3.00\text{ g/mL}} + 50.0\text{ mL} = 58.33\text{ mL} + 50.0\text{ mL}$

$= 108.33 = 108.3\text{ mL}$

1.150.

a. $r = \dfrac{d}{t} = \dfrac{832\text{ mi}}{21\text{ h}} = 39.619\text{ mi/h} = 40.\text{ mi/h}$

b. $\dfrac{832\text{ mi}}{21\text{ h}} \times \dfrac{1.609\text{ km}}{1\text{ mi}} = 63.74 = 64\text{ km/h}$

c. $\dfrac{832\text{ mi}}{29\text{ gal}} \times \dfrac{1.609\text{ km}}{1\text{ mi}} \times \dfrac{1\text{ gal}}{4\text{ qt}} \times \dfrac{1\text{ qt}}{0.9464\text{ L}} = 12.19\text{ km/L} = 12\text{ km/L}$

1.151.

a. Since there is the same number of atoms of the gas in each container, the mass is the same in each container.

b. Since $d = m/V$, for the same mass, when the volume is smaller, the density is greater. Since the volume is less in container A, the density is greater.

c. If the volume of container A was doubled, the density would decrease and become equal to the density in container B.

1.152.

a. $d = \dfrac{m}{V} = \dfrac{39.45\text{ g}}{(3.50\text{ cm})^3} = 0.92011 = 0.920\text{ g/cm}^3$

b. $\dfrac{400.4\text{ mL}}{1} \times \dfrac{1\text{ cm}^3}{1\text{ mL}} \times \dfrac{39.45\text{ g}}{(3.50\text{ cm})^3} = 368.41 = 368\text{ g}$

1.153. $\dfrac{300\text{ million people}}{1} \times \dfrac{1 \times 10^{10}\text{ miles}}{1\text{ person}} \times \dfrac{1.609\text{ km}}{1\text{ mi}} \times \dfrac{1000\text{ m}}{1\text{ km}} \times \dfrac{1\text{ lightyear}}{9.46 \times 10^{15}\text{ m}}$

$= 5.102 \times 10^5 = 5 \times 10^5$ lightyears

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1.154. $\frac{1.16\text{ g}}{1\text{ bucket}} \times \frac{1\text{ bucket}}{4.08\text{ L}} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1\text{ mL}}{1\text{ cm}^3} \times \left(\frac{2.54\text{ cm}}{1\text{ in}}\right)^3 \times \left(\frac{12\text{ in}}{1\text{ ft}}\right)^3$

$\times \frac{2.38 \times 10^3\text{ ft}^3}{1} = 1.9\underline{1}61 \times 10^4\text{ g} = 1.92 \times 10^4\text{ g}$

1.155.

a. Since $d = m/V$, an increased mass for the same volume means a higher density for the solution.

b. There would be less water for the same mass, so the density would be higher than in part a.

c. Since there would be a greater volume of water for the same mass of salt, the density would be lower than in part a.

1.156. The water will have a lower density than the salt solution. It will not conduct electricity. It will have different chemical properties, such as reaction with silver nitrate solution; and different physical properties, such as the boiling point. Also, you could boil away the water from the salt solution and recover the salt.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

1.157. The mass of hydrochloric acid is obtained from the density and the volume.

Mass = density x volume = 1.096 g/mL x 50.0 mL = 54.$\underline{8}$0 g

Next, from the law of conservation of mass,

Mass of marble + mass of acid = mass of solution + mass of carbon dioxide gas

Plugging in gives

10.0 g + 54.$\underline{8}$0 g = 60.4 g + mass of carbon dioxide gas

Mass of carbon dioxide gas = 10.0 g + 54.$\underline{8}$0 g − 60.4 g = 4.$\underline{4}$0 g

Finally, use the density to convert the mass of carbon dioxide gas to volume.

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{4.\underline{4}0\text{ g}}{1.798\text{ g/ L}} = 2.\underline{4}47\text{ L} = 2.4\text{ L}$$

1.158. The mass of sulfuric acid is obtained from the density and the volume.

Mass = density x volume = 1.153 g/mL x 50.0 mL = 57.$\underline{6}$5 g

Next, from the law of conservation of mass,

Mass of ore + mass of acid = mass of solution + mass of hydrogen sulfide gas

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Plugging in gives

$$10.8\text{ g} + 57.\underline{6}5\text{ g} = 65.1\text{ g} + \text{mass of hydrogen sulfide gas}$$

$$\text{Mass of hydrogen sulfide gas} = 10.8\text{ g} + 57.\underline{6}5\text{ g} - 65.1\text{ g} = 3.\underline{3}5\text{ g}$$

Finally, use the density to convert the mass of hydrogen sulfide gas to volume.

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{3.\underline{3}5\text{ g}}{1.393\text{ g/ L}} = 2.\underline{4}0\text{ L} = 2.4\text{ L}$$

1.159. First, calculate the volume of the steel sphere.

$$V = (4/3)\pi r^3 = (4/3)\pi \times (1.58\text{ in})^3 \times \left(\frac{2.54\text{ cm}}{1\text{ in}}\right)^3 = 27\underline{0}.7\text{ cm}^3$$

Next, determine the mass of the sphere using the density.

$$\text{Mass} = \text{density} \times \text{volume} = 7.88\text{ g/cm}^3 \times 27\underline{0}.7\text{ cm}^3 = 21\underline{3}3\text{ g} = 2.13 \times 10^3\text{ g}$$

1.160. First, calculate the volume of the balloon. Note that the radius is one-half the diameter, or 1.50 ft.

$$V = (4/3)\pi r^3 = (4/3)\pi \times (1.50\text{ ft})^3 \times \left(\frac{12\text{ in}}{1\text{ ft}}\right)^3 \times \left(\frac{2.54\text{ cm}}{1\text{ in}}\right)^3 \times \frac{1\text{ L}}{10^3\text{ cm}}$$

$$= 40\underline{0}.3\text{ L}$$

Next, determine the mass of the helium using the density.

$$\text{Mass} = \text{density} \times \text{volume} = 0.166\text{ g/L} \times 40\underline{0}.3\text{ L} = 66.\underline{4}53\text{ g} = 66.5\text{ g}$$

1.161. The area of the ice is $840{,}000\text{ mi}^2 - 132{,}000\text{ mi}^2 = 708{,}000\text{ mi}^2$. Now, determine the volume of this ice.

$$\text{Volume} = \text{area} \times \text{thickness}$$

$$= 708{,}000\text{ mi}^2 \times 5000\text{ ft} \times \left(\frac{5280\text{ ft}}{1\text{ mi}}\right)^2 \times \left(\frac{12\text{ in}}{1\text{ ft}}\right)^3 \times \left(\frac{2.54\text{ cm}}{1\text{ in}}\right)^3$$

$$= 2.794 \times 10^{21}\text{ cm}^3$$

Now use the density to determine the mass of the ice.

$$\text{Mass} = \text{density} \times \text{volume} = 0.917\text{ g/cm}^3 \times 2.794 \times 10^{21}\text{ cm}^3 = 2.\underline{5}6 \times 10^{21}\text{ g}$$

$$= 2.6 \times 10^{21}\text{ g}$$

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1.162. The height of the ice is 7500 ft − 1500 ft = 6000 ft. Now, determine the volume of the ice.

$$\text{Volume} = \text{area} \times \text{thickness}$$

$$= 5{,}500{,}000 \text{ mi}^2 \times 6000 \text{ ft} \times \left(\frac{5280 \text{ ft}}{1 \text{ mi}}\right)^2 \times \left(\frac{12 \text{ in}}{1 \text{ ft}}\right)^3 \times \left(\frac{2.54 \text{ cm}}{1 \text{ in}}\right)^3$$

$$= 2.605 \times 10^{22} \text{ cm}^3$$

Now use the density to determine the mass of the ice.

$$\text{Mass} = \text{density} \times \text{volume} = 0.917 \text{ g/cm}^3 \times 2.605 \times 10^{22} \text{ cm}^3 = 2.3\underline{8} \times 10^{22} \text{ g}$$

$$= 2.4 \times 10^{22} \text{ g}$$

1.163. Let x = mass of ethanol and y = mass of water. Then, use the total mass to write $x + y = 49.6$ g, or $y = 49.6 \text{ g} - x$. Thus, the mass of water is $49.6 \text{ g} - x$. Next,

$$\text{Total volume} = \text{volume of ethanol} + \text{volume of water}$$

Since the volume is equal to the mass divided by density, you can write

$$\text{Total volume} = \frac{\text{mass of ethanol}}{\text{density of ethanol}} + \frac{\text{mass of water}}{\text{density of water}}$$

Substitute in the known and unknown values to get an equation for x.

$$54.2 \text{ cm}^3 = \frac{x}{0.789 \text{ g/cm}^3} + \frac{49.6 \text{ g} - x}{0.998 \text{ g/cm}^3}$$

Multiply both sides of this equation by (0.789)(0.998). Also, multiply both sides by g/cm^3 to simplify the units. This gives the following equation to solve for x.

$$(0.789)(0.998)(54.2) \text{ g} = (0.998)\,x + (0.789)(49.6 \text{ g} - x)$$

$$42.\underline{6}78 \text{ g} = 0.998 \times + 39.\underline{1}34 \text{ g} - 0.789\,x$$

$$0.209\,x = 3.\underline{5}44 \text{ g}$$

$$x = \text{mass of ethanol} = 1\underline{6}.95 \text{ g}$$

The percentage of ethanol (by mass) in the solution can now be calculated.

$$\text{Percent (mass)} = \frac{\text{mass of ethanol}}{\text{mass of solution}} \times 100\% = \frac{1\underline{6}.95 \text{ g}}{49.6 \text{ g}} \times 100\% = 3\underline{4}.1\% = 34\%$$

To determine the proof, you must first find the percentage by volume of ethanol in the solution. The volume of ethanol is obtained using the mass and the density.

$$\text{Volume} = \frac{\text{mass of ethanol}}{\text{density of ethanol}} = \frac{1\underline{6}.95 \text{ g}}{0.789 \text{ g/ cm}^3} = 2\underline{1}.48 \text{ cm}^3$$

The percentage of ethanol (by volume) in the solution can now be calculated.

$$\text{Percent (volume)} = \frac{\text{volume of ethanol}}{\text{volume of solution}} \times 100\% = \frac{2\underline{1}.48 \text{ cm}^3}{54.2 \text{ cm}^3} \times 100\% = 3\underline{9}.63\%$$

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The proof can now be calculated.

$$\text{Proof} = 2 \times \text{Percent (volume)} = 2 \times 39.63 = 79.27 = 79 \text{ proof}$$

1.164. Let x = mass of gold and y = mass of silver. Then, use the total mass to write $x + y = 9.35$ g, or $y = 9.35 \text{ g} - x$. Thus, the mass of silver is $9.35 \text{ g} - x$. Next,

$$\text{Total volume} = \text{volume of gold} + \text{volume of silver}$$

Since the volume is equal to the mass divided by density, you can write

$$\text{Total volume} = \frac{\text{mass of gold}}{\text{density of gold}} + \frac{\text{mass of silver}}{\text{density of silver}}$$

Substitute in the known and unknown values to get an equation for x.

$$0.654 \text{ cm}^3 = \frac{x}{19.3 \text{ g/cm}^3} + \frac{9.35 \text{ g} - x}{10.5 \text{ g/cm}^3}$$

Multiply both sides of this equation by (19.3)(10.5). Also multiply both sides by g/cm^3 to simplify the units. This gives the following equation to solve for x.

$$(19.3)(10.5)(0.654) \text{ g} = (10.5)\,x + (19.3)(9.35 \text{ g} - x)$$

$$132.53 \text{ g} = 10.5\,x + 180.45 \text{ g} - 19.3\,x$$

$$8.8\,x = 47.92 \text{ g}$$

$$x = \text{mass of gold} = 5.445 \text{ g}$$

The percentage of gold (by mass) in the solution can now be calculated.

$$\text{Percent (mass)} = \frac{\text{mass of gold}}{\text{mass of jewlrey}} \times 100\% = \frac{5.445 \text{ g}}{9.35 \text{ g}} \times 100\% = 58.2\% = 58\%$$

The relative amount of gold in the alloy can now be calculated. The fraction of gold in the alloy is 58.2% / 100% = 0.582. Thus,

$$\text{Proportion of gold} = 24 \text{ karats} \times 0.582 = 13.9 \text{ karats} = 14 \text{ karats}$$

1.165. The volume of the mineral can be obtained from the mass difference between the water displaced and the air displaced, and the densities of water and air.

$$\text{Mass difference} = 18.49 \text{ g} - 16.21 \text{ g} = 2.28 \text{ g}$$

$$\text{Volume of mineral} = \frac{\text{mass difference}}{\text{density of water} - \text{density of air}}$$

$$= \frac{2.28 \text{ g}}{0.9982 \text{ g/cm}^3 - 1.205 \times 10^{-3} \text{ g/cm}^3} = 2.286 \text{ cm}^3$$

The mass of the mineral is equal to its mass in air plus the weight of the displaced air. The weight of the displaced air is obtained from the volume of the mineral and the density of air.

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Mass of displaced air = density x volume

$$= 1.205 \text{ g/L} \times 2.2\underline{8}6 \text{ cm}^3 \times \frac{1 \text{ L}}{10^3 \text{ cm}^3} = 2.7\underline{5}5 \times 10^{-3} \text{ g}$$

Mass of mineral = 18.49 g + $2.7\underline{5}5 \times 10^{-3}$ g = 18.4$\underline{9}$27 g

The density of the mineral can now be calculated.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{18.4\underline{9}27 \text{ g}}{2.2\underline{8}6 \text{ cm}^3} = 8.0\underline{8}9 \text{ g/cm}^3 = 8.09 \text{ g/cm}^3$$

1.166. The volume of the mineral can be obtained from the mass of the water displaced and the density of water.

Mass difference = 7.35 g − 5.40 g = 1.95 g

$$\text{Volume of mineral} = \frac{\text{mass difference}}{\text{density of water - density of air}}$$

$$\text{Volume of mineral} = \frac{1.95 \text{ g}}{0.9982 \text{ g/cm}^3 - 1.205 \times 10^{-3} \text{ g/cm}^3} = 1.9\underline{5}5 \text{ cm}^3$$

The mass of the mineral is equal to its mass in air plus the weight of the displaced air. The weight of the displaced air is obtained from the volume of the mineral and the density of air.

Mass of displaced air = density x volume

$$= 1.205 \text{ g/L} \times 1.9\underline{5}5 \text{ cm}^3 \times \frac{1 \text{ L}}{10^3 \text{ cm}^3} = 2.3\underline{5}6 \times 10^{-3} \text{ g}$$

Mass of mineral = 7.35 g + $2.3\underline{5}6 \times 10^{-3}$ g = 7.3$\underline{5}$2 g

The density of the mineral can now be calculated.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{7.352 \text{ g}}{1.955 \text{ cm}^3} = 3.7\underline{6}0 \text{ g/cm}^3 = 3.76 \text{ g/cm}^3$$

1.167. The volume of the object can be obtained from the mass of the ethanol displaced and the density of ethanol.

Mass of ethanol displaced = 15.8 g − 10.5 g = 5.3 g

$$\text{Volume of object} = \frac{\text{mass of ethanol}}{\text{density of ethanol}} = \frac{5.3 \text{ g}}{0.789 \text{ g/ cm}^3} = 6.\underline{7}17 \text{ cm}^3$$

The density of the object can now be calculated.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{15.8 \text{ g}}{6.\underline{7}17 \text{ cm}^3} = 2.\underline{3}52 \text{ g/cm}^3 = 2.4 \text{ g/cm}^3$$

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1.168. The volume of the metal can be obtained from the mass of the mercury displaced and the density of mercury.

$$\text{Mass of mercury displaced} = 255\text{ g} - 101\text{ g} = 154\text{ g}$$

$$\text{Volume of object} = \frac{\text{mass of mercury}}{\text{density of mercury}} = \frac{154\text{ g}}{13.6\text{ g/cm}^3} = 11.\underline{3}23\text{ cm}^3$$

The density of the metal can now be calculated.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{255\text{ g}}{11.\underline{3}23\text{ cm}^3} = 22.\underline{5}1\text{ g/cm}^3 = 22.5\text{ g/cm}^3$$

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CHAPTER 2

Atoms, Molecules, and Ions

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

2.1. The element with atomic number 17 (the number of protons in the nucleus) is chlorine, symbol Cl. The mass number is 17 + 18 = 35. The symbol is $^{35}_{17}\mathrm{Cl}$.

2.2. Multiply each isotopic mass by its fractional abundance; then sum:

34.96885 amu x 0.75771 = 26.496247

36.96590 amu x 0.24229 = 8.956467

35.452714 = 35.453 amu

The atomic mass of chlorine is 35.453 amu.

2.3.

a. Se: Group VIA, Period 4; nonmetal

b. Cs: Group IA, Period 6; metal

c. Fe: Group VIIIB, Period 4; metal

d. Cu: Group IB, Period 4; metal

e. Br: Group VIIA, Period 4; nonmetal

2.4. Take as many cations as there are units of charge on the anion and as many anions as there are units of charge on the cation. Two K^+ ions have a total charge of 2+, and one CrO_4^{2-} ion has a charge of 2–, giving a net charge of zero. The simplest ratio of K^+ to CrO_4^{2-} is 2:1, and the formula is K_2CrO_4.

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2.5.

a. CaO: Calcium, a Group IIA metal, is expected to form only a 2+ ion (Ca^{2+}, the calcium ion). Oxygen (Group VIA) is expected to form an anion of charge equal to the group number minus 8 (O^{2-}, the oxide ion). The name of the compound is calcium oxide.

b. $PbCrO_4$: Lead has more than one monatomic ion. You can find the charge on the Pb ion if you know the formula of the anion. From Table 2.5, the CrO_4 refers to the anion CrO_4^{2-} (the chromate ion). Therefore, the Pb cation must be Pb^{2+} to give electrical neutrality. The name of Pb^{2+} is lead(II) ion, so the name of the compound is lead(II) chromate.

2.6. Thallium(III) nitrate contains the thallium(III) ion, Tl^{3+}, and the nitrate ion, NO_3^-. The formula is $Tl(NO_3)_3$.

2.7.

a. Dichlorine hexoxide

b. Phosphorus trichloride

c. Phosphorus pentachloride

2.8.

a. CS_2

b. SO_3

2.9.

a. Boron trifluoride

b. Hydrogen selenide

2.10. When you remove one H^+ ion from $HBrO_4$, you obtain the BrO_4^- ion. You name the ion from the acid by replacing *-ic* with *-ate*. The anion is called the perbromate ion.

2.11. Sodium carbonate decahydrate

2.12. Sodium thiosulfate is composed of sodium ions (Na^+) and thiosulfate ions ($S_2O_3^{2-}$), so the formula of the anhydrous compound is $Na_2S_2O_3$. Since the material is a pentahydrate, the formula of the compound is $Na_2S_2O_3 \cdot 5H_2O$.

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2.13. Balance O first in parts (a) and (b) because it occurs in only one product. Balance S first in part (c) because it appears in only one product. Balance H first in part (d) because it appears in just one reactant as well as in the product.

a. Write a 2 in front of $POCl_3$ for O; this requires a 2 in front of PCl_3 for final balance:

$$O_2 + 2PCl_3 \rightarrow 2POCl_3$$

b. Write a 6 in front of N_2O to balance O; this requires a 6 in front of N_2 for final balance:

$$P_4 + 6N_2O \rightarrow 6N_2 + P_4O_6$$

c. Write $2As_2S_3$ and $6SO_2$ to achieve an even number of oxygens on the right to balance what will always be an even number of oxygens on the left. The $2As_2S_3$ then requires $2As_2O_3$. Finally, to balance (6 + 12) O's on the right, write $9O_2$.

$$2As_2S_3 + 9O_2 \rightarrow 2As_2O_3 + 6SO_2$$

d. Write a 4 in front of H_3PO_4; this requires a 3 in front of $Ca(H_2PO_4)_2$ for twelve H's.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

■ ANSWERS TO CONCEPT CHECKS

2.1. CO_2 is a compound that is a combination of 1 carbon atom and 2 oxygen atoms. Therefore, the chemical model must contain a chemical combination of 3 atoms stuck together with 2 of the atoms being the same (oxygen). Since each "ball" represents an individual atom, the three models on the left can be eliminated since they don't contain the correct number of atoms. Keeping in mind that balls of the same color represent the same element, only the model on the far right contains two elements with the correct ratio of atoms, 1:2; therefore, it must be CO_2.

2.2. If 7999 out of 8000 alpha particles deflected back at the alpha-particle source, this would imply that the atom was a solid, impenetrable mass. Keep in mind that this is in direct contrast to what was observed in the actual experiments, where the majority of the alpha particles passed through without being deflected.

2.3. Elements are listed together in groups because they have similar chemical and/or physical properties.

2.4.

a. This compound is an ether because it has a functional group of an oxygen atom between two carbon atoms (–O–).

b. This compound is an alcohol because it has an –OH functional group.

c. This compound is a carboxylic acid because it has the –COOH functional group.

d. This compound is a hydrocarbon because it contains only carbon and hydrogen atoms.

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2.5. A bottle containing a compound with the formula Al_2Q_3 would have an anion, Q, with a charge of 2–. The total positive charge in the compound due to the Al^{3+} is 6+ (2 x 3+), so the total negative charge must be 6–; Therefore, each Q ion must have a charge of 2–. Thus, Q would probably be an element from Group VIA on the periodic table.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

2.1. Atomic theory is an explanation of the structure of matter in terms of different combinations of very small particles called atoms. Since compounds are composed of atoms of two or more elements, there is no limit to the number of ways in which the elements can be combined. Each compound has its own unique properties. A chemical reaction consists of the rearrangement of the atoms present in the reacting substances to give new chemical combinations present in the substances formed by the reaction.

2.2. Divide each amount of chlorine, 1.270 g and 1.904 g, by the lower amount, 1.270 g. This gives 1.000 and 1.499, respectively. Convert these to whole numbers by multiplying by 2, giving 2.000 and 2.998. The ratio of these amounts of chlorine is essentially 2:3. This is consistent with the law of multiple proportions because, for a fixed mass of iron (1 gram), the masses of chlorine in the other two compounds are in a ratio of small whole numbers.

2.3. A cathode-ray tube consists of a negative electrode, or cathode, and a positive electrode, or anode, in an evacuated tube. Cathode rays travel from the cathode to the anode when a high voltage is turned on. Some of the rays pass through the hole in the anode to form a beam, which is then bent toward positively charged electric plates in the tube. This implies that a cathode ray consists of a beam of negatively charged particles (or electrons) and that electrons are constituents of all matter.

2.4. Millikan performed a series of experiments in which he obtained the charge on the electron by observing how a charged drop of oil falls in the presence and in the absence of an electric field. An atomizer introduces a fine mist of oil drops into the top chamber (Figure 2.6). Several drops happen to fall through a small hole into the lower chamber, where the experimenter follows the motion of one drop with a microscope. Some of these drops have picked up one or more electrons as a result of friction in the atomizer and have become negatively charged. A negatively charged drop will be attracted upward when the experimenter turns on a current to the electric plates. The drop's upward speed (obtained by timing its rise) is related to its mass-to-charge ratio, from which you can calculate the charge on the electron.

2.5. The nuclear model of the atom is based on experiments of Geiger, Marsden, and Rutherford. Rutherford stated that most of the mass of an atom is concentrated in a positively charged center called the nucleus around which negatively charged electrons move. The nucleus, although it contains most of the mass, occupies only a very small portion of the space of the atom. Most of the alpha particles passed through the metal atoms of the foil undeflected by the lightweight electrons. When an alpha particle does happen to hit a metal-atom nucleus, it is scattered at a wide angle because it is deflected by the massive, positively charged nucleus (Figure 2.8).

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2.6. The atomic nucleus consists of two kinds of particles, protons and neutrons. The mass of each is about the same, on the order of 1.67×10^{-27} kg, and about 1800 times that of the electron. An electron has a much smaller mass, on the order of 9.11×10^{-31} kg. The neutron is electrically neutral, but the proton is positively charged. An electron is negatively charged. The charges on the proton and the electron are equal in magnitude.

2.7. Protons (hydrogen nuclei) were discovered as products of experiments involving the collision of alpha particles with nitrogen atoms that resulted in a proton being knocked out of the nitrogen nucleus. Neutrons were discovered as the radiation product of collisions of alpha particles with beryllium atoms. The resulting radiation was discovered to consist of particles having a mass approximately equal to that of a proton and having no charge (neutral).

2.8. Oxygen consists of three different isotopes, each having 8 protons but a different number of neutrons.

2.9. The percentages of the different isotopes in most naturally occurring elements have remained essentially constant over time and in most cases are independent of the origin of the element. Thus, what Dalton actually calculated were average atomic masses (relative masses). He could not weigh individual atoms, but he could find the average mass of one atom relative to the average mass of another.

2.10. A mass spectrometer measures the mass-to-charge ratio of positively charged atoms (and molecules). It produces a mass spectrum, which shows the relative numbers of atoms (fractional abundances) of various masses (isotopic masses). The mass spectrum gives us all the information needed to calculate the atomic weight.

2.11. The atomic mass of an element is the average atomic mass for the naturally occurring element expressed in atomic mass units. The atomic mass would be different elsewhere in the universe if the percentages of isotopes in the element were different from those on earth.

2.12. The element in Group IVA and Period 5 is tin (atomic number 50).

2.13. A metal is a substance or mixture that has characteristic luster, or shine, and is generally a good conductor of heat and electricity.

2.14. The formula for ethane is C_2H_6.

2.15. A molecular formula gives the exact number of different atoms of an element in a molecule. A structural formula is a chemical formula that shows how the atoms are bonded to one another in a molecule.

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2.16. Organic molecules contain carbon combined with other elements such as hydrogen, oxygen, and nitrogen. An inorganic molecule is composed of elements other than carbon. Some inorganic molecules that contain carbon are carbon monoxide (CO), carbon dioxide (CO_2), carbonates, and cyanides.

2.17. An ionic binary compound: NaCl; a molecular binary compound: H_2O.

2.18.

a. The elements are represented by B, F, and I.

b. The compounds are represented by A, E, and G.

c. The mixtures are represented by C, D, and H.

d. The ionic solid is represented by A.

e. The gas made up of an element and a compound is represented by C.

f. The mixtures of elements are represented by D and H.

g. The solid element is represented by F.

h. The solids are represented by A and F.

i. The liquids are represented by E, H, and I.

2.19. In the Stock system, CuCl is called copper(I) chloride, and $CuCl_2$ is called copper(II) chloride.

One of the advantages of the Stock system is that more than two different ions of the same metal can be named with this system. In the former (older) system, a new suffix other than *-ic* and *-ous* must be established and/or memorized.

2.20. A balanced chemical equation has the numbers of atoms of each element equal on both sides of the arrow. The coefficients are the smallest possible whole numbers.

2.21. The answer is a: 50 p, 69 n, and 48 e^-.

2.22. The answer is d: 65%.

2.23. The answer is c: magnesium hydroxide, $Mg(OH)_2$.

2.24. The answer is b: Li.

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■ ANSWERS TO CONCEPT EXPLORATIONS

2.25. **Part I**

a. $\text{Average mass} = \dfrac{2.00\text{ g} + 2.00\text{ g} + 2.00\text{ g} + 2.00\text{ g}}{4} = 2.00\text{ g}$

Part II

a. $\text{Average mass} = \dfrac{2.00\text{ g} + 1.75\text{ g} + 3.00\text{ g} + 1.25\text{ g}}{4} = 2.00\text{ g}$

b. The average mass of a sphere in the two samples is the same. The average does not represent the individual masses. Also, it does not indicate the variability in the individual masses.

Part III

a. $\dfrac{50\text{ blue spheres}}{1} \times \dfrac{2.00\text{ g}}{1\text{ blue sphere}} = 100.00\text{ g}$

b. If 50 spheres were removed at random, then 50 spheres would remain in the jar. You can use the average mass to calculate the total mass.

$$\frac{50\text{ spheres}}{1} \times \frac{2.00\text{ g}}{1\text{ sphere}} = 100.00\text{ g}$$

c. No, the average mass does not represent the mass of an individual sphere.

d. $\dfrac{80.0\text{ g}}{1} \times \dfrac{1\text{ blue sphere}}{2.00\text{ g}} = 40.0\text{ blue spheres}$

e. $\dfrac{60.0\text{ g}}{1} \times \dfrac{1\text{ sphere}}{2.00\text{ g}} = 30.0\text{ spheres}$

The assumption is that the average mass of a sphere (2.00 g) can be used in the calculation. Also, assume the sample is well mixed.

Part IV

a. For green spheres: $X = \dfrac{3\text{ green}}{3\text{ green} + 1\text{ blue}} = 0.750$

For blue spheres: $X = \dfrac{1\text{ blue}}{3\text{ green} + 1\text{ blue}} = 0.250$

b. $\text{Average mass} = (0.750) \times \dfrac{3.00\text{ g}}{1\text{ green sphere}} + (0.250) \times \dfrac{1.00\text{ g}}{1\text{ blue sphere}} = 2.50\text{ g}$

c. The atomic mass of an element is the weighted average calculated as in part (b) of Part IV above, using fractional abundances and individual masses.

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2.26.

a. Atom A has three protons.

b. The number of protons is the same as the atomic number for that element.

c. Lithium, Li, has atomic number 3.

d. The charge on element A is zero. There are three protons, each +1, and three electrons, each −1. This yields a net charge of zero.

e. The nuclide symbol for A is $^{7}_{3}\mathrm{Li}$.

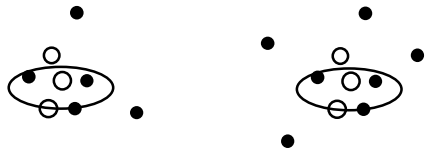
f. Atom B has three protons and thus atomic number 3. It is lithium, with symbol Li.

g. Atom B has three protons and three neutrons. Its mass number is 6. This is different from the mass number of atom A, which is 7.

h. Atom B has three protons and three electrons and thus is neutral.

i. The nuclide symbol for B is $^{6}_{3}\mathrm{Li}$. The atomic number is 3 and the mass number is 6 for both nuclides.

j.



$^{6}_{3}\mathrm{Li}^{+}$ $^{6}_{3}\mathrm{Li}^{-}$

k. Two different lithium isotopes are depicted, lithium-6 and lithium-7.

l. The mass number of an isotope is the total number of protons and neutrons in its nucleus. Its value is an integer. It is related to the mass of the isotope but not related to the atomic mass, which is a weighted average over the fractional abundances and isotopic masses.

■ ANSWERS TO CONCEPTUAL PROBLEMS

2.27. If atoms were balls of positive charge with the electrons evenly distributed throughout, there would be no massive, positive nucleus to deflect the beam of alpha particles when it is shot at the gold foil.

2.28. Once the subscripts of the compounds in the original chemical equation are changed (the molecule N_2 was changed to the atom N), the substances reacting are no longer the same. Your friend may be able to balance the second equation, but it is no longer the same chemical reaction.

2.29. You could group elements by similar physical properties such as density, mass, color, conductivity, etc., or by chemical properties, such as reaction with air, reaction with water, etc.

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2.30. You would name the ions with the formulas XO_4^{2-}, XO_3^{2-}, and XO^{2-} using the name for XO_2^{2-} (excite) as the example to determine the root name of the element X (exc). Thus XO_4^{2-}, with the greatest number of oxygen atoms in the group, would be perexcate; XO_3^{2-} would be excate; and XO^{2-}, with the fewest oxygen atoms in the group, would be hypoexcite.

2.31.

a. In each case, the total positive charge and the total negative charge in the compounds must cancel. Therefore, the compounds with the cations X^+, X^{2+}, and X^{5+}, combined with the SO_4^{2-} anion, are X_2SO_4, XSO_4, and $X_2(SO_4)_5$, respectively.

b. You recognize the fact that whenever a cation can have multiple oxidation states (1+, 2+, and 5+ in this case), the name of the compound must indicate the charge. Therefore, the names of the compounds in part (a) would be exy(I) sulfate, exy(II) sulfate, and exy(V) sulfate, respectively.

2.32.

a. This model contains three atoms of two different elements (H and O). Therefore, the model is of H_2O.

b. This model represents a crystal that contains two different elements in a 1:1 ratio (K^+ and Cl^-). Therefore, the model represents the ionic compound, KCl.

c. This model contains six atoms, four of which are the same (H), and two others (C and O). Therefore, the model is of CH_3OH.

d. This model contains four atoms of two different elements (N and H). Therefore, the model is of NH_3.

2.33. A potassium-39 atom in this case would contain 19 protons and 20 neutrons. If the charge of the proton were twice that of an electron, it would take twice as many electrons as protons, or 38 electrons, to maintain a charge of zero.

2.34.

a. Since the mass of an atom is not due only to the sum of the masses of the protons, neutrons, and electrons, when you change the element in which you are basing the amu, the mass of the amu must change as well.

b. Since the amount of material that makes up a hydrogen atom doesn't change, when the amu gets larger, as in this problem, the hydrogen atom must have a smaller mass in amu.

2.35.

a. $2Li + Cl_2 \rightarrow 2LiCl$

b. $16Na + S_8 \rightarrow 8Na_2S$

c. $2Al + 3Br_2 \rightarrow 2AlBr_3$

d. $3Mg + N_2 \rightarrow Mg_3N_2$

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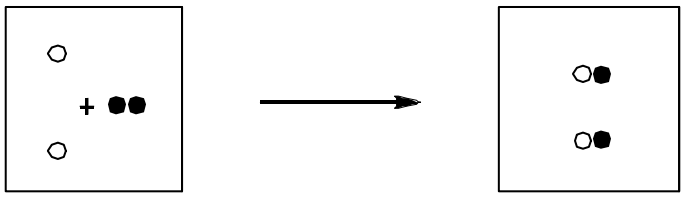
e. $6Ca + P_4 \rightarrow 2Ca_3P_2$

2.36.

a. 

b. $2A + B_2 \rightarrow 2AB$

c. Some possible real elements with formula B_2 are F_2, Cl_2, Br_2, and I_2.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

2.37.

a. Argon

b. Zinc

c. Silver

d. Magnesium

2.38.

a. Calcium

b. Copper

c. Mercury

d. Tin

2.39.

a. K

b. S

c. Fe

d. Mn

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2.40.

a. C

b. Na

c. Ni

d. Pb

2.41. The mass of the electron is found by multiplying the two values:

$$1.602 \times 10^{-19}\ \text{C} \times \frac{5.64 \times 10^{-12}\ \text{kg}}{1\ \text{C}} = 9.035 \times 10^{-31}\ \text{kg} = 9.04 \times 10^{-31}\ \text{kg}$$

2.42. The mass of the fluorine atom is found by multiplying the two values:

$$1.602 \times 10^{-19}\ \text{C} \times \frac{1.97 \times 10^{-7}\ \text{kg}}{1\ \text{C}} = 3.155 \times 10^{-26}\ \text{kg} = 3.16 \times 10^{-26}\ \text{kg}$$

2.43. The isotope of atom A is the atom with 18 protons, atom C; the atom that has the same mass number as atom A (37) is atom D.

2.44. The isotope of atom A is the atom with 32 protons, atom B; the atom that has the same mass number as atom A (71) is atom D.

2.45. Each isotope of chlorine (atomic number 17) has 17 protons. Each neutral atom will also have 17 electrons. The number of neutrons for Cl-35 is 35 – 17 = 18 neutrons. The number of neutrons for Cl-37 is 37 – 17 = 20 neutrons.

2.46. Each isotope of lithium (atomic number 3) has three protons. Each neutral atom will also have three electrons. The number of neutrons for Li-6 is 6 – 3 = 3 neutrons. The number of neutrons for Li-7 is 7 – 3 = 4 neutrons.

2.47. The element with 14 protons in its nucleus is silicon (Si). The mass number = 14 + 14 = 28. The notation for the nucleus is $^{28}_{14}\text{Si}$.

2.48. The element with 11 protons in its nucleus is sodium (Na).
The mass number = 11 + 11 = 22. The notation for the nucleus is $^{22}_{11}Na$.

2.49. Since the atomic ratio of nitrogen to hydrogen is 1:3, divide the mass of N by one-third of the mass of hydrogen to find the relative mass of N.

$$\frac{\text{Atomic mass of N}}{\text{Atomic mass of H}} = \frac{7.933\ \text{g}}{1/3 \times 1.712\ \text{g}} = \frac{13.901\ \text{g N}}{1\ \text{g H}} = \frac{13.90}{1}$$

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2.50. Since the atomic ratio of hydrogen to sulfur is 2:1, divide the mass of S by one-half of the mass of hydrogen to find the relative mass of S.

$$\frac{\text{Atomic mass of S}}{\text{Atomic mass of H}} = \frac{9.330\text{ g}}{1/2 \times 0.587\text{ g}} = \frac{31.78\text{ g S}}{1\text{ g H}} = \frac{31.8}{1}$$

2.51. Multiply each isotopic mass by its fractional abundance, and then sum:

X-63: 62.930 x 0.6909 = 43.4783

X-65: 64.928 x 0.3091 = 20.0692

63.5475 = 63.55 amu

The element is copper, atomic mass 63.546 amu.

2.52. Multiply each isotopic mass by its fractional abundance, and then sum:

49.9472 x 0.002500 = 0.124868

50.9440 x 0.9975 = 50.81664

= 50.94150 = 50.94 amu

The atomic mass of this element is 50.94 amu. The element is vanadium (V).

2.53. Multiply each isotopic mass by its fractional abundance, and then sum:

38.964 x 0.9326 = 36.3378

39.964 x 1.00×10^{-4} = 0.0039964

40.962 x 0.0673 = 2.75674

= 39.09853 = 39.10 amu

The atomic mass of this element is 39.10 amu. The element is potassium (K).

2.54. Multiply each isotopic mass by its fractional abundance, and then sum:

27.977 x 0.9221 = 25.798

28.976 x 0.0470 = 1.362

29.974 x 0.0309 = 0.9262

= 28.086 = 28.09 amu

The atomic mass of this element is 28.09 amu. The element is silicon (Si).

2.55. According to the picture, there are 20 atoms, 5 of which are brown and 15 of which are green. Using the isotopic masses in the problem, the atomic mass of element X is

$$\frac{5}{20}(23.02\text{ amu}) + \frac{15}{20}(25.147\text{ amu}) = 5.755 + 18.8602 = 24.6152 = 24.615\text{ amu}$$

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2.56. According to the picture, there are 24 atoms, 8 of which are brown and 16 of which are green. Using the isotopic masses in the problem, the atomic mass of element X is

$$\frac{8}{24}(47.510 \text{ amu}) + \frac{16}{24}(51.126 \text{ amu}) = 15.836 + 34.084 = 49.920 = 49.921 \text{ amu}$$

2.57.

a. C: Group IVA, Period 2; nonmetal
b. Po: Group VIA, Period 6; metal
c. Cr: Group VIB, Period 4; metal
d. Mg: Group IIA, Period 3; metal
e. B: Group IIIA, Period 2; metalloid

2.58.

a. S: Group VIA, Period 3; nonmetal
b. Fe: Group VIIIB, Period 4; metal
c. Ba: Group IIA, Period 6; metal
d. Cu: Group IB, Period 4; metal
e. Ne: Group VIIIA, Period 2; nonmetal

2.59.

a. Tellurium
b. Aluminum

2.60.

a. Bismuth
b. Magnesium

2.61. Examples are:

a. O (oxygen)
b. Na (sodium)
c. Fe (iron)
d. Ce (cerium)

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2.62. Examples are:

a. Zr (zirconium)

b. Cl (chlorine)

c. B (boron)

d. U (uranium)

2.63. They are different in that the solid sulfur consists of S_8 molecules, whereas the hot vapor consists of S_2 molecules. The S_8 molecules are four times as heavy as the S_2 molecules. Hot sulfur is a mixture of S_8 and S_2 molecules, but at high enough temperatures only S_2 molecules are formed. Both hot sulfur and solid sulfur consist of molecules with only sulfur atoms.

2.64. They are different in that the solid phosphorus consists of P_4 molecules, whereas the hot vapor consists of P_2 molecules. The P_4 molecules are twice as heavy as the P_2 molecules. Hot phosphorus is a mixture of P_4 and P_2 molecules above the boiling point, but at high temperatures only P_2 molecules are formed. Both solid phosphorus and phosphorus vapor consist of molecules with only phosphorus atoms.

2.65. The number of nitrogen atoms in the 1.50-g sample of N_2O is

$$2.05 \times 10^{22}\ N_2O \text{ molecules} \times \frac{2\ N \text{ atoms}}{1\ N_2O \text{ molecule}} = 4.10 \times 10^{22}\ N \text{ atoms}$$

The number of nitrogen atoms in 1.00 g of N_2O is

$$1.00\ g \times \frac{4.10 \times 10^{22}\ N \text{ atoms}}{1.50\ g\ N_2O} = 2.73\underline{3} \times 10^{22}\ N \text{ atoms} = 2.73 \times 10^{22}\ N \text{ atoms}$$

2.66. Since each HNO_3 molecule contains one N atom, in 4.30×10^{22} HNO_3 molecules there are 4.30×10^{22} N atoms. The number of oxygen atoms in 2.81 g of HNO_3 is obtained as follows.

$$2.81\ g \times \frac{4.30 \times 10^{22}\ HNO_3 \text{ molecules}}{4.50\ g\ HNO_3} \times \frac{3\ O \text{ atoms}}{1\ HNO_3 \text{ molecule}}$$

$$= 8.05\underline{5}3 \times 10^{22}\ O \text{ atoms} = 8.06 \times 10^{22}\ O \text{ atoms}$$

2.67. $3.3 \times 10^{21}\ H \text{ atoms} \times \frac{1\ NH_3 \text{ molecule}}{3\ H \text{ atoms}} = 1.1 \times 10^{21}\ NH_3 \text{ molecules}$

2.68. $4.2 \times 10^{23}\ H \text{ atoms} \times \frac{1\ C_2H_5OH \text{ molecule}}{6\ H \text{ atoms}} = 7.0 \times 10^{22}\ C_2H_5OH \text{ molecules}$

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2.69.

a. N_2H_4

b. H_2O_2

c. C_3H_8O

d. PCl_3

2.70.

a. $C_3H_8O_3$

b. Si_2H_6

c. NH_3O

d. SF_4

2.71.

a. PCl_5

b. NO_2

c. $C_3H_6O_2$

2.72.

a. H_2SO_4

b. C_6H_6

c. C_3H_6O

2.73. $\dfrac{1 \text{ Fe atom}}{1 \text{ Fe}(NO_3)_2 \text{ unit}} \times \dfrac{1 \text{ Fe}(NO_3)_2 \text{ unit}}{2 \text{ } NO_3^- \text{ ions}} \times \dfrac{1 \text{ } NO_3^- \text{ ion}}{3 \text{ O atoms}} = \dfrac{1 \text{ Fe atom}}{6 \text{ O atoms}} = \dfrac{1}{6}$

Thus, the ratio of iron atoms to oxygen atoms is one Fe atom to six O atoms.

2.74. $\dfrac{3 \text{ } NH_4^+ \text{ ions}}{1 \text{ } (NH_4)_3PO_4 \text{ unit}} \times \dfrac{4 \text{ H atoms}}{1 \text{ } NH_4^+ \text{ ion}} \times \dfrac{1 \text{ } (NH_4)_3PO_4 \text{ unit}}{4 \text{ O atoms}} = \dfrac{12 \text{ H atoms}}{4 \text{ O atoms}} = \dfrac{3}{1}$

Thus, the ratio of hydrogen atoms to oxygen atoms is three H atoms to one O atom.

2.75.

a. $Fe(CN)_3$

b. K_2SO_4

c. Li_3N

d. Ca_3P_2

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2.76.

a. Co_3N_2

b. $(NH_4)_3PO_4$

c. Na_2CO_3

d. $Fe(OH)_3$

2.77.

a. Na_2SO_4: sodium sulfate (Group IA forms only 1+ cations.)

b. CaS: calcium sulfide (Group IIA forms only 2+ cations.)

c. CuCl: copper(I) chloride (Group IB forms 1+ and 2+ cations.)

d. Cr_2O_3: chromium(III) oxide (Group VIB forms numerous oxidation states.)

2.78.

a. Na_2O: sodium oxide (Group IA forms only 1+ cations.)

b. Mn_2O_3: manganese(III) oxide (Group VIIB forms numerous oxidation states.)

c. NH_4HCO_3: ammonium bicarbonate or ammonium hydrogen carbonate.

d. $Cu(NO_3)_2$: copper(II) nitrate (Group IB forms 1+ and 2+ cations.)

2.79.

a. Lead(II) permanganate: $Pb(MnO_4)_2$ (Permanganate is in Table 2.5.)

b. Barium hydrogen carbonate: $Ba(HCO_3)_2$ (The HCO_3^- ion is in Table 2.5.)

c. Cesium sulfide: Cs_2S (Group 1A ions form 1+ cations.)

d. Iron(II) acetate: $Fe(C_2H_3O_2)_2$ (The acetate ion = 1– [from Table 2.5]; for the sum of charges to be zero, two must be used.)

2.80.

a. Sodium thiosulfate: $Na_2S_2O_3$ (The $S_2O_3^{2-}$ is in Table 2.5.)

b. Copper(I) hydroxide: CuOH (Cu must be 1+ to balance one OH^-.)

c. Calcium hydrogen carbonate: $Ca(HCO_3)_2$ (The HCO_3^- ion is in Table 2.5.)

d. Nickel(II) phosphide: Ni_3P_2 (Two P^{3-} must be used to balance three Ni^{2+}.)

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2.81.

a. Molecular
b. Ionic
c. Molecular
d. Ionic

2.82.

a. Ionic
b. Molecular
c. Molecular
d. Ionic

2.83.

a. Dinitrogen monoxide
b. Tetraphosphorus dec(a)oxide
c. Arsenic trichloride
d. Dichlorine hept(a)oxide

2.84.

a. Dinitrogen difluoride
b. Carbon tetrachloride
c. Dinitrogen pent(a)oxide
d. Tetr(a)arsenic hex(a)oxide

2.85.

a. NBr_3
b. XeO_4
c. OF_2
d. Cl_2O_5

2.86.

a. ClF_3
b. NO_2
c. N_2F_4
d. PF_5

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2.87.

a. Selenium trioxide
b. Disulfur dichloride
c. Carbon monoxide

2.88.

a. Nitrogen trifluoride
b. Diphosphorus tetrahydride
c. Oxygen difluoride

2.89.

a. Bromic acid: $HBrO_3$
b. Hyponitrous acid: $H_2N_2O_2$
c. Disulfurous acid: $H_2S_2O_5$
d. Arsenic acid: H_3AsO_4

2.90.

a. Selenous acid: H_2SeO_3
b. Sulfurous acid: H_2SO_3
c. Hypoiodous acid: HIO
d. Nitrous acid: HNO_2

2.91. $Na_2SO_4 \cdot 10H_2O$ is sodium sulfate decahydrate.

2.92. $NiSO_4 \cdot 6H_2O$ is nickel(II) sulfate hexahydrate.

2.93. Iron(II) sulfate heptahydrate is $FeSO_4 \cdot 7H_2O$.

2.94. Cobalt(II) chloride hexahydrate is $CoCl_2 \cdot 6H_2O$.

2.95. $Pb(NO_3)_2 \times \frac{6 \text{ O atoms}}{1 \text{ } Pb(NO_3)_2 \text{ unit}} + K_2CO_3 \times \frac{3 \text{ O atoms}}{1 \text{ } K_2CO_3 \text{ unit}} = 9 \text{ O atoms}$

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2.96. $2\ \text{PbO} \times \dfrac{1\ \text{O atom}}{1\ \text{PbO unit}} + 2\ \text{SO}_2 \times \dfrac{2\ \text{O atoms}}{1\ \text{SO}_2\ \text{unit}} = 6\ \text{O atoms}$

The equation is not balanced as written.

2.97.

a. Balance: $Sn + NaOH \rightarrow Na_2SnO_2 + H_2$

If Na is balanced first by writing a 2 in front of NaOH, the entire equation is balanced.

$$Sn + 2NaOH \rightarrow Na_2SnO_2 + H_2$$

b. Balance: $Al + Fe_3O_4 \rightarrow Al_2O_3 + Fe$

First balance O (it appears once on each side) by writing a 3 in front of Fe_3O_4 and a 4 in front of Al_2O_3:

$$Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + Fe$$

Now balance Al against the 8 Al's on the right and Fe against the 9 Fe's on the left:

$$8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$$

c. Balance: $CH_3OH + O_2 \rightarrow CO_2 + H_2O$

First balance H (it appears once on each side) by writing a 2 in front of H_2O:

$$CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$$

To avoid fractional coefficients for O, multiply the equation by 2:

$$2CH_3OH + 2O_2 \rightarrow 2CO_2 + 4H_2O$$

Finally, balance O by changing $2O_2$ to "$3O_2$"; this balances the entire equation:

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$$

d. Balance: $P_4O_{10} + H_2O \rightarrow H_3PO_4$

First balance P (it appears once on each side) by writing a 4 in front of H_3PO_4:

$$P_4O_{10} + H_2O \rightarrow 4H_3PO_4$$

Finally, balance H by writing a 6 in front of H_2O; this balances the entire equation:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

e. Balance: $PCl_5 + H_2O \rightarrow H_3PO_4 + HCl$

First balance Cl (it appears once on each side) by writing a 5 in front of HCl:

$$PCl_5 + H_2O \rightarrow H_3PO_4 + 5HCl$$

Finally, balance H by writing a 4 in front of H_2O; this balances the entire equation:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

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2.98.

a. Balance: $Cl_2O_7 + H_2O \rightarrow HClO_4$

Balance Cl (appears only once on each side) by writing a 2 in front of $HClO_4$; this balances the entire equation:

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$

b. Balance: $MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$

First balance O (appears only once on each side) by writing a 2 in front of H_2O:

$$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

Finally, balance H and Cl by writing a 4 in front of HCl to balance the entire equation:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

c. Balance: $Na_2S_2O_3 + I_2 \rightarrow NaI + Na_2S_4O_6$

First balance S by writing a 2 in front of $Na_2S_2O_3$:

$$2Na_2S_2O_3 + I_2 \rightarrow NaI + Na_2S_4O_6$$

Finally, balance Na by writing a 2 in front of NaI; this balances the entire equation:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

d. Balance: $Al_4C_3 + H_2O \rightarrow Al(OH)_3 + CH_4$

First balance Al with a 4 in front of $Al(OH)_3$, and balance C with a 3 in front of CH_4:

$$Al_4C_3 + H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

Finally, balance H and O with a 12 in front of H_2O; this balances the entire equation:

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

e. Balance: $NO_2 + H_2O \rightarrow HNO_3 + NO$

First balance H with a 2 in front of HNO_3:

$$NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Finally, balance N with a 3 in front of NO_2; this balances the entire equation:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

2.99. Balance: $Ca_3(PO_4)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_3PO_4(aq)$

Balance Ca first with a 3 in front of $CaSO_4$:

$$Ca_3(PO_4)_2(s) + H_2SO_4(aq) \rightarrow 3CaSO_4(s) + H_3PO_4(aq)$$

Next, balance the P with a 2 in front of H_3PO_4:

$$Ca_3(PO_4)_2(s) + H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$$

Finally, balance the S with a 3 in front of H_2SO_4; this balances the equation:

$$Ca_3(PO_4)_2(s) + 3H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$$

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2.100. Balance: $Na(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$

Balance H first with a 2 in front of H_2O and NaOH:

$$Na + 2H_2O \rightarrow 2NaOH + H_2$$

Then, balance Na with a 2 in front of Na; this balances the equation:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

2.101. Balance: $NH_4Cl(aq) + Ba(OH)_2(aq) \rightarrow NH_3(g) + BaCl_2(aq) + H_2O(l)$

Balance O first with a 2 in front of H_2O:

$$NH_4Cl + Ba(OH)_2 \rightarrow NH_3 + BaCl_2 + 2H_2O$$

Balance H with a 2 in front of NH_4Cl and a 2 in front of NH_3; this balances the equation:

$$2NH_4Cl(aq) + Ba(OH)_2(aq) \xrightarrow{\Delta} 2NH_3(g) + BaCl_2(aq) + 2H_2O(l)$$

2.102. Balance: $PbS(s) + PbSO_4(s) \rightarrow Pb(l) + SO_2(g)$

Balance S first with a 2 in front of SO_2:

$$PbS + PbSO_4 \rightarrow Pb + 2SO_2$$

Balance Pb with a 2 in front of Pb; this balances the equation:

$$PbS(s) + PbSO_4(s) \xrightarrow{\Delta} 2Pb(l) + 2SO_2(g)$$

■ SOLUTIONS TO GENERAL PROBLEMS

2.103. Calculate the ratio of oxygen for 1 g (fixed amount) of nitrogen in both compounds:

$$\text{A: } \frac{2.755 \text{ g O}}{1.206 \text{ g N}} = \frac{2.2844 \text{ g O}}{1 \text{ g N}} \qquad \text{B: } \frac{4.714 \text{ g O}}{1.651 \text{ g N}} = \frac{2.8552 \text{ g O}}{1 \text{ g N}}$$

Next, find the ratio of oxygen per gram of nitrogen for the two compounds.

$$\frac{\text{g O in B/1 g N}}{\text{g O in A/1 g N}} = \frac{2.8552 \text{ g O}}{2.2844 \text{ g O}} = \frac{1.2498 \text{ g O}}{1\text{g O}}$$

B contains 1.25 times as many O atoms as A does (there are five O's in B for every four O's in A).

2.104. Calculate the ratio of oxygen for 1 g (fixed amount) of sulfur in both compounds:

$$\text{A: } \frac{1.811 \text{ g O}}{1.210 \text{ g S}} = \frac{1.4966 \text{ g O}}{1 \text{ g S}} \qquad \text{B: } \frac{1.779 \text{ g O}}{1.783 \text{ g S}} = \frac{0.99775 \text{ g O}}{1 \text{ g S}}$$

Next, find the ratio of oxygen per gram of sulfur for the two compounds.

$$\frac{\text{g O in A/1 g S}}{\text{g O in B/1 g S}} = \frac{1.4966 \text{ g O}}{0.99775 \text{ g O}} = \frac{1.4999 \text{ g O}}{1\text{g O}}$$

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A contains 1.50 times as many O atoms as B does (there are three O's in A for every two O's in B).

2.105. The smallest difference is between -1.12×10^{-18} C and 9.60×10^{-19} C and is equal to -1.6×10^{-19} C. If this charge is equivalent to one electron, the number of excess electrons on a drop may be found by dividing the negative charge by the charge of one electron.

Drop 1: $$\frac{-3.20 \times 10^{-19}\ \text{C}}{-1.6 \times 10^{-19}\ \text{C}} = 2.\underline{0} \cong 2 \text{ electrons}$$

Drop 2: $$\frac{-6.40 \times 10^{-19}\ \text{C}}{-1.6 \times 10^{-19}\ \text{C}} = 4.\underline{0} \cong 4 \text{ electrons}$$

Drop 3: $$\frac{-9.60 \times 10^{-19}\ \text{C}}{-1.6 \times 10^{-19}\ \text{C}} = 6.\underline{0} \cong 6 \text{ electrons}$$

Drop 4: $$\frac{-1.12 \times 10^{-18}\ \text{C}}{-1.6 \times 10^{-19}\ \text{C}} = 7.\underline{0} \cong 7 \text{ electrons}$$

2.106. The smallest difference in charge for the oil drop is -1.85×10^{-19}; assume this is the fundamental unit of negative charge. Use this to divide into each drop's charge:

Drop 1: $$\frac{-5.55 \times 10^{-19}\ \text{C}}{-1.85 \times 10^{-19}\ \text{C}} = 3.\underline{0} \cong 3 \text{ electrons}$$

Drop 2: $$\frac{-9.25 \times 10^{-19}\ \text{C}}{-1.85 \times 10^{-19}\ \text{C}} = 5.\underline{0} \cong 5 \text{ electrons}$$

Drop 3: $$\frac{-1.11 \times 10^{-18}\ \text{C}}{-1.85 \times 10^{-19}\ \text{C}} = 6.\underline{0} \cong 6 \text{ electrons}$$

Drop 4: $$\frac{-1.48 \times 10^{-18}\ \text{C}}{-1.85 \times 10^{-19}\ \text{C}} = 8.\underline{0} \cong 8 \text{ electrons}$$

2.107. For the Eu atom to be neutral, the number of electrons must equal the number of protons, so a neutral europium atom has 63 electrons. The +3 charge on the Eu^{3+} indicates there are three more protons than electrons, so the number of electrons is $63 - 3 = 60$.

2.108. For the Cs atom to be neutral, the number of electrons must equal the number of protons, so a neutral cesium atom has 55 electrons. The +1 charge on the Cs^{+} indicates there is one more proton than electrons, so the number of electrons is $55 - 1 = 54$.

2.109. The number of protons = mass number – number of neutrons $= 81 - 46 = 35$. The element with $Z = 35$ is bromine (Br).

The ionic charge = number of protons – number of electrons $= 35 - 36 = -1$.

Symbol: $^{81}_{35}Br^{-}$.

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2.110. The number of protons = mass number – number of neutrons = 80 – 55 = 25. The element with $Z = 25$ is manganese (Mn).

The ionic charge = number of protons – number of electrons = 25 – 23 = +2.

Symbol: $^{80}_{25}Mn^{2+}$.

2.111. The sum of the fractional abundances must equal 1. Let y equal the fractional abundance of ^{63}Cu. Then the fractional abundance of ^{65}Cu equals $(1 - y)$. We write one equation in one unknown:

$$\text{Atomic mass} = 63.546 = 62.9298y + 64.9278(1 - y)$$

$$63.546 = 64.9278 - 1.9980y$$

$$y = \frac{64.9278 - 63.546}{1.9980} = 0.691\underline{5}9$$

The fractional abundance of $^{63}Cu = 0.691\underline{5}9 = 0.6916$.

The fractional abundance of $^{65}Cu = 1 - 0.69159 = 0.308\underline{4}1 = 0.3084$.

2.112. As in the previous problem, the sum of the fractional abundances must equal 1. Thus, the abundance of one isotope can be expressed in terms of the other. Let y equal the fractional abundance of Ag-107. Then the fractional abundance of Ag-109 equals $(1 - y)$. We can write one equation in one unknown:

$$\text{Atomic mass} = 107.87 = 106.91y + 108.90(1 - y)$$

$$107.87 = 108.90 - 1.99y$$

$$y = \frac{108.90 - 107.87}{1.99} = 0.51\underline{7}58$$

The fractional abundance of Ag-107 = 0.51758 = 0.518.

The fractional abundance of Ag-109 = 1 – 0.51758 = 0.48241 = 0.482.

2.113.

a. Bromine, Br

b. Hydrogen, H

c. Niobium, Nb

d. Fluorine, F

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2.114.

a. Bromine, Br
b. Mercury, Hg
c. Gallium, Ga
d. Rubidium, Rb

2.115.

a. Chromium(III) ion
b. Lead(IV) ion
c. Copper(I) ion
d. Copper(II) ion

2.116.

a. Manganese(II) ion
b. Nickel(II) ion
c. Cobalt(II) ion
d. Cobalt(III) ion

2.117. All possible ionic compounds: Na_2SO_4, NaCl, $NiSO_4$, and $NiCl_2$.

2.118. All possible ionic compounds: CaO, $Ca(NO_3)_2$, Cr_2O_3, and $Cr(NO_3)_3$.

2.119.

a. Tin(II) phosphate
b. Ammonium nitrite
c. Magnesium hydroxide
d. Chromium(II) sulfate

2.120.

a. Copper(II) nitrite
b. Ammonium phosphide
c. Sodium sulfate
d. Mercury(II) chloride

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2.121.

a. Hg_2S [Mercury(I) exists as the polyatomic Hg_2^{2+} ion (Table 2.5).]

b. $Co_2(SO_3)_3$

c. $(NH_4)_2Cr_2O_7$

d. AlN

2.122.

a. H_2O_2

b. $AlPO_4$

c. Pb_3P_4

d. BF_3

2.123.

a. Arsenic tribromide

b. Hydrogen selenide (dihydrogen selenide)

c. Diphosphorus pent(a)oxide

d. Silicon dioxide

2.124.

a. Chlorine tetrafluoride

b. Carbon disulfide

c. Nitrogen trifluoride

d. Sulfur hexafluoride

2.125.

a. Balance the C and H first:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$$

Avoid a fractional coefficient for O on the left by doubling all coefficients except O_2's, and then balance the O's:

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

b. Balance the P first:

$$P_4O_6 + H_2O \rightarrow 4H_3PO_3$$

Then balance the O (or H), which also gives the H (or O) balance:

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

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c. Balancing the O first is the simplest approach. (Starting with K and Cl and then proceeding to O will cause the initial coefficient for $KClO_3$ to be changed in balancing O last.)

$$4KClO_3 \rightarrow KCl + 3KClO_4$$

d. Balance the N first:

$$(NH_4)_2SO_4 + NaOH \rightarrow 2NH_3 + H_2O + Na_2SO_4$$

Then balance the Na, followed by O; this also balances the H:

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

e. Balance the N first:

$$2NBr_3 + NaOH \rightarrow N_2 + NaBr + HOBr$$

Note that NaOH and HOBr each have one O and that NaOH and NaBr each have one Na; thus the coefficients of all three must be equal; from $2NBr_3$, this coefficient must be $6Br/2 = 3$:

$$2NBr_3 + 3NaOH \rightarrow N_2 + 3NaBr + 3HOBr$$

2.126.

a. Balance the Na first:

$$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + H_2O$$

Then balance the O; this also balances the H:

$$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$$

b. Balance the Cl with a 4 in front of the HCl; then balance the O's with a 2 in front of H_2O:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

c. Balance the O first with an 8 in front of CO; then balance the C with an 8 in front of C:

$$Ca_3(PO_4)_2 + 8C \rightarrow Ca_3P_2 + 8CO$$

d. Balance the O by multiplying O_2 by 3 and doubling both products to give a total of six O's on both sides of the equation:

$$H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

Then balance H and S with a 2 in front of H_2S:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

e. Since the reaction has two N's on the left and one N on the right, try a tentative N-balancing by writing a 2 in front of NO_2:

$$N_2O_5 \rightarrow 2NO_2 + O_2$$

Now there are five O's on the left and six O's on the right. Begin to balance the O's with a 6 in front of N_2O_5; this gives

$$6N_2O_5 \rightarrow 2NO_2 + O_2$$

Because changing NO_2 will change the oxygen balance, first balance the N's using $12NO_2$:

$$6N_2O_5 \rightarrow 12NO_2 + O_2$$

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Now there are only (24 + 2) O's on the right, so balance the O's by writing $3O_2$:

$$6N_2O_5 \rightarrow 12NO_2 + 3O_2$$

This can be reduced to

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

2.127. Let: x = number of protons. Then $1.21x$ is the number of neutrons. Since the mass number is 62, you get

$$62 = x + 1.21x = 2.21x$$

Thus, $x = 28.054$, or 28. The element is nickel (Ni). Since the ion has a +2 charge, there are 26 electrons.

2.128. Let: x = number of protons. Then $1.30x$ is the number of neutrons. Since the mass number is 85, you get

$$85 = x + 1.30x = 2.30x$$

Thus, $x = 36.95$, or 37. The element is rubidium (Rb). Since the ion has a +1 charge, there are 36 electrons.

2.129. The average atomic mass would be

Natural carbon:	12.011 x 1/2	=	6.005500
Carbon-13:	13.00335 x 1/2	=	6.501675
	Average	=	12.507175

The average atomic mass of the sample is 12.507 amu.

2.130. The average atomic mass would be

Natural chlorine:	35.4527 x 1/2	=	17.726350
Chlorine-35:	34.96885 x 1/2	=	17.4844250
	Average	=	35.210775

The average atomic mass of the sample is 35.2108 amu.

2.131. The island of stability is a region of the periodic table where a relatively stable superheavy nuclide is at the peak of stability and is surrounded by foothills consisting of less stable nuclides. It is centered around the most stable nuclide, which is predicted to have an atomic number of 114 and a mass number of 298.

2.132. $^{70}_{30}\text{Zn} + {}^{208}_{82}\text{Pb} \rightarrow {}^{277}_{112}\text{Uub} + {}^{1}_{0}\text{n}$

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■ SOLUTIONS TO STRATEGY PROBLEMS

2.133. SO_3, sulfur trioxide

NO_2, nitrogen dioxide

PO_4^{3-}, phosphate ion

N_2, nitrogen

$Mg(OH)_2$, magnesium hydroxide

2.134. The unknown metal, M, is a cation with a +3 charge. An example is aluminum.

2.135. The name of the product is aluminum sulfide. The reaction is

$$16Al(s) + 3S_8(s) \rightarrow 8Al_2S_3(s)$$

2.136. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$

2.137. $(0.7721)(37.24 \text{ amu}) + (1 - 0.7721)(x) = 37.45 \text{ amu}$

$$x = \frac{37.45 - (0.7721)(37.24)}{(1 - 0.7721)} = 38.\underline{1}61 \text{ amu} = 38.2 \text{ amu}$$

2.138. Sulfur has atomic number 16, so S^{2+} has 16 minus 2 or 14 electrons, which is the number of neutrons in the unknown ion. The number of protons is 27 minus 14 = 13, which is the atomic number, so the element is aluminum. The number of electrons is 13 – 3 = 10.

2.139. 6.5×10^{20} formula units $CaCl_2 \times \frac{3 \text{ ions}}{1 \text{ formula unit}} = 1.95 \times 10^{21}$ ions

2.140. $MgCO_3$, magnesium carbonate

Mg_3P_2, magnesium phosphide

$Pb(CO_3)_2$, lead(IV) carbonate

Pb_3P_4, lead(IV) phosphide

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2.141. SO_3, sulfur trioxide

HNO_2, nitrous acid

Mg_3N_2, magnesium nitride

HBr, hydrogen bromide

$Cu_3(PO_4)_2$, copper(II) phosphate

$CuSO_4 \cdot 5H_2O$, copper(II) sulfate pentahydrate

2.142. $Pb(IO_3)_2$, lead(II) iodate

KIO_4, potassium periodate

$Zn(IO)_2$, zinc hypoiodite

$Al(IO_2)_3$, aluminum iodite

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

2.143. The spheres occupy a diameter of 2 x 1.86 Å = 3.72 Å. The line of sodium atoms would stretch a length of

$$\text{Length} = \frac{3.72\ \text{Å}}{1\ \text{Na atom}} \times 2.619 \times 10^{22}\ \text{Na atoms} = 9.7\underline{4}2 \times 10^{22}\ \text{Å}$$

Now, convert this to miles.

$$9.7\underline{4}2 \times 10^{22}\ \text{Å} \times \frac{10^{-10}\ \text{m}}{1\ \text{Å}} \times \frac{1\ \text{mile}}{1.609 \times 10^{3}\ \text{m}} = 6.0\underline{5}5 \times 10^{9}\ \text{miles}$$

$$= 6.06 \times 10^{9}\ \text{miles}$$

2.144. The spheres occupy a diameter of 2 x 0.99 Å = 1.98 Å. The line of chlorine atoms would stretch a length of

$$\text{Length} = \frac{1.98\ \text{Å}}{1\ \text{Cl atom}} \times 1.699 \times 10^{22}\ \text{Cl atoms} = 3.3\underline{6}4 \times 10^{22}\ \text{Å}$$

Now, convert this to miles.

$$3.3\underline{6}4 \times 10^{22}\ \text{Å} \times \frac{10^{-10}\ \text{m}}{1\ \text{Å}} \times \frac{1\ \text{mile}}{1.609 \times 10^{3}\ \text{m}} = 2.0\underline{9}0 \times 10^{9}\ \text{miles}$$

$$= 2.09 \times 10^{9}\ \text{miles}$$

2.145. $NiSO_4 \cdot 7H_2O(s) \rightarrow NiSO_4 \cdot 6H_2O(s) + H_2O(g)$

[8.753] = [8.192 g + (8.753 – 8.192 = 0.561 g)]

The 8.192 g of $NiSO_4 \cdot 6H_2O$ must contain 6 x 0.561 = 3.366 g H_2O.

Mass of anhydrous $NiSO_4$ = 8.192 g $NiSO_4 \cdot 6H_2O$ – 3.366 g $6H_2O$ = 4.826 g

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2.146. $CoSO_4 \cdot 7H_2O(s) \rightarrow CoSO_4 \cdot H_2O(s) + 6H_2O(g)$

[3.548 g] = [2.184 g + (3.548 – 2.184 = 1.364 g)]

Mass of one H_2O per 3.548 g of $CoSO_4 \cdot 7H_2O$ = 1.364 g ÷ 6 = 0.22733 g

Mass of anhydrous $CoSO_4$ = 2.184 g $CoSO_4 \cdot H_2O$ – 0.22733 g H_2O = 1.95$\underline{6}$6 g = 1.957 g

2.147. Mass of O = 0.6015 L x $\frac{1.330 \text{ g O}}{1 \text{ L}}$ = 0.799$\underline{9}$95 g

15.9994 amu O x $\frac{3.177 \text{ g X}}{0.799\underline{9}95 \text{ g O}}$ = 63.5$\underline{3}$8 amu X = 63.54 amu

The atomic mass of X is 63.54 amu; X is copper.

2.148. Mass of Cl = 0.4810 L x $\frac{2.948 \text{ g Cl}}{1 \text{ L}}$ = 1.41$\underline{7}$99 g Cl

35.453 amu Cl x $\frac{4.315 \text{ g X}}{1.41\underline{7}99 \text{ g Cl}}$ = 107.$\underline{8}$8 amu X = 107.9 amu

The atomic mass of X is 107.9 amu; X is silver.

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CHAPTER 3

Calculations with Chemical Formulas and Equations

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

3.1.

a. NO_2

1 x AM of N	=		14.0067 amu
2 x AM of O	=	2 x 15.9994	= 31.9988 amu
MM of NO_2	=	46.0055	= 46.0 amu (3 s.f.)

b. $C_6H_{12}O_6$

6 x AM of C	=	6 x 12.011	= 72.066 amu
12 x AM of H	=	12 x 1.0079	= 12.0948 amu
6 x AM of O	=	6 x 15.9994	= 95.9964 amu
MM of $C_6H_{12}O_6$ =			180.1572 amu
= 180. amu (3 s.f.)			

c. NaOH

1 x AM of Na	=	22.98977 amu
1 x AM of O	=	15.9994 amu
1 x AM of H	=	1.0079 amu
MM of NaOH =		39.9971 amu
= 40.0 amu (3 s.f.)		

d. $Mg(OH)_2$

1 x AM of Mg	=		24.305 amu
2 x AM of O	=	2 x 15.9994	= 31.9988 amu
2 x AM of H	=	2 x 1.0079	= 2.0158 amu
MM of $Mg(OH)_2$ =			58.3196 amu
= 58.3 amu (3 s.f.)			

3.2.

a. The molecular model represents a molecule made up of one S and three O. The chemical formula is SO_3. Calculating the formula mass by using the same approach as in Example 3.1 in the text yields 80.07 amu.

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b. The molecular model represents one S, four O, and two H. The chemical formula is then H_2SO_4. The formula mass is 98.09 amu.

3.3.

a. The atomic mass of Ca = 40.08 amu; thus, the molar mass = 40.08 g/mol, and 1 mol Ca = 6.022×10^{23} Ca atoms.

$$\text{Mass of one Ca} = \frac{40.08 \text{ g}}{1 \text{ mol Ca}} = \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 6.655\underline{6} \times 10^{-23}$$

$$= 6.656 \times 10^{-23} \text{ g/atom}$$

b. The molecular mass of C_2H_5OH, or C_2H_6O, = (2 x 12.01) + (6 x 1.008) + 16.00 = 46.0$\underline{6}$8. Its molar mass = 46.07 g/mol, and 1 mol = 6.022×10^{23} molecules of C_2H_6O.

$$\text{Mass of one } C_2H_6O = \frac{46.07 \text{ g}}{1 \text{ mol } C_2H_6O} = \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}}$$

$$= 7.65\underline{0}3 \times 10^{-23} = 7.650 \times 10^{-23} \text{ g/molecule}$$

3.4. The molar mass of H_2O_2 is 34.02 g/mol. Therefore,

$$0.909 \text{ mol } H_2O_2 \times \frac{34.02 \text{ g } H_2O_2}{1 \text{ mol } H_2O_2} = 30.\underline{9}2 = 30.9 \text{ g } H_2O_2$$

3.5. The molar mass of HNO_3 is 63.01 g/mol. Therefore,

$$28.5 \text{ g } HNO_3 \times \frac{1 \text{ mol } HNO_3}{63.01 \text{ g } HNO_3} = 0.45\underline{2}3 = 0.452 \text{ mol } HNO_3$$

3.6. Convert the mass of HCN from milligrams to grams. Then convert grams of HCN to moles of HCN. Finally, convert moles of HCN to the number of HCN molecules.

$$56 \text{ mg HCN} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol HCN}}{27.02 \text{ g HCN}} \times \frac{6.022 \times 10^{23} \text{ HCN molecules}}{1 \text{ mol HCN}}$$

$$= 1.\underline{2}48 \times 10^{21} = 1.2 \times 10^{21} \text{ HCN molecules}$$

3.7. The molecular mass of NH_4NO_3 = 80.05; thus, its molar mass = 80.05 g/mol. Hence

$$\text{Percent N} = \frac{28.02 \text{ g}}{80.05 \text{ g}} \times 100\% = 35.\underline{0}0 = 35.0\%$$

$$\text{Percent H} = \frac{4.032 \text{ g}}{80.05 \text{ g}} \times 100\% = 5.0\underline{3}6 = 5.04\%$$

$$\text{Percent O} = \frac{48.00 \text{ g}}{80.05 \text{ g}} \times 100\% = 59.\underline{9}6 = 60.0\%$$

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3.8. From the previous exercise, NH_4NO_3 is 35.0% N (fraction N = 0.350), so the mass of N in 48.5 g of NH_4NO_3 is

$$48.5 \text{ g } NH_4NO_3 \times (0.350 \text{ g N}/1 \text{ g } NH_4NO_3) = 16.\underline{9}75 = 17.0 \text{ g N}$$

3.9. First, convert the mass of CO_2 to moles of CO_2. Next, convert this to moles of C (1 mol CO_2 is equivalent to 1 mol C). Finally, convert to mass of carbon, changing milligrams to grams first:

$$5.80 \times 10^{-3} \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g}} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 1\ 5\underline{8}3 \times 10^{-3} \text{g C}$$

Do the same series of calculations for water, noting that 1 mol H_2O contains 2 mol H.

$$1.58 \times 10^{-3} \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g}} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 1.7\underline{6}7 \times 10^{-4} \text{g H}$$

The mass percentages of C and H can be calculated using the masses from the previous calculations:

$$\text{Percent C} = \frac{1.583 \text{ mg}}{3.87 \text{ mg}} \times 100\% = 40.\underline{9}0 = 40.9\% \text{ C}$$

$$\text{Percent H} = \frac{0.1767 \text{ mg}}{3.87 \text{ mg}} \times 100\% = 4.5\underline{6}58 = 4.57\% \text{ H}$$

The mass percentage of O can be determined by subtracting the sum of the above percentages from 100%:

$$\text{Percent O} = 100.000\% - (40.90 + 4.5658) = 54.\underline{5}342 = 54.5\% \text{ O}$$

3.10. Convert the masses to moles that are proportional to the subscripts in the empirical formula:

$$33.4 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 1.0\underline{4}14 \text{ mol S}$$

$$(83.5 - 33.4) \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.1\underline{3}12 \text{ mol O}$$

Next, obtain the smallest integers from the moles by dividing each by the smallest number of moles:

$$\text{For O: } \frac{3.1312}{1.0414} = 3.01 \qquad \text{For S: } \frac{1.0414}{1.0414} = 1.00$$

The empirical formula is SO_3.

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3.11. For a 100.0-g sample of benzoic acid, 68.8 g are C, 5.0 g are H, and 26.2 g are O. Using the molar masses, convert these masses to moles:

$$68.8 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 5.729 \text{ mol C}$$

$$5.0 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.96 \text{ mol H}$$

$$26.2 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.638 \text{ mol O}$$

These numbers are in the same ratio as the subscripts in the empirical formula. They must be changed to integers. First, divide each one by the smallest number of moles:

$$\text{For C: } \frac{5.729}{1.638} = 3.497 \qquad \text{For H: } \frac{4.96}{1.638} = 3.03 \qquad \text{For O: } \frac{1.638}{1.638} = 1.000$$

Rounding off, we obtain $C_{3.5}H_{3.0}O_{1.0}$. Multiplying the numbers by 2 gives whole numbers, for an empirical formula of $C_7H_6O_2$.

3.12. For a 100.0-g sample of acetaldehyde, 54.5 g are C, 9.2 g are H, and 36.3 g are O. Using the molar masses, convert these masses to moles:

$$54.5 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.537 \text{ mol C}$$

$$9.2 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 9.12 \text{ mol H}$$

$$36.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.268 \text{ mol O}$$

These numbers are in the same ratio as the subscripts in the empirical formula. They must be changed to integers. First, divide each one by the smallest number of moles:

$$\text{For C: } \frac{4.537}{2.268} = 2.000 \qquad \text{For H: } \frac{9.12}{2.268} = 4.02 \qquad \text{For O: } \frac{2.268}{2.268} = 1.000$$

Rounding off, we obtain C_2H_4O, the empirical formula, which is also the molecular formula.

3.13. $H_2 + Cl_2 \rightarrow 2HCl$

1 molec. (mol) H_2 + 1 molec. (mol) Cl_2 → 2 molec. (mol) HCl (molec., mole interp.)

2.016 g H_2 + 70.9 g Cl_2 → 2 x 36.5 g HCl (mass interp.)

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3.14. Equation: $Na + H_2O \rightarrow 1/2H_2 + NaOH$, or $2Na + 2H_2O \rightarrow H_2 + 2NaOH$. From this equation, one mole of Na corresponds to one-half mole of H_2, or two moles of Na corresponds to one mole of H_2. Therefore,

$$7.81 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Na}}{1 \text{ mol } H_2} \times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}} = 17\underline{8}.1 = 178 \text{ g Na}$$

3.15. Balanced equation: $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

Convert grams of ZnS to moles of ZnS. Then determine the relationship between ZnS and O_2 (2ZnS is equivalent to $3O_2$). Finally, convert to mass of O_2.

$$5.00 \times 10^3 \text{g ZnS} \times \frac{1 \text{ mol ZnS}}{97.46 \text{ g ZnS}} \times \frac{3 \text{ mol } O_2}{2 \text{ mol ZnS}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$= 2.4\underline{6}3 = 2.46 \text{ kg } O_2$$

3.16. Balanced equation: $2HgO \rightarrow 2Hg + O_2$

Convert the mass of O_2 to moles of O_2. Using the fact that one mole of O_2 is equivalent to two moles of Hg, determine the number of moles of Hg, and convert to mass of Hg.

$$6.47 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{2 \text{ mol Hg}}{1 \text{ mol } O_2} \times \frac{200.59 \text{ g Hg}}{1 \text{ mol Hg}} = 81.\underline{1}1 = 81.1 \text{ g Hg}$$

3.17. First, determine the limiting reactant by calculating the moles of $AlCl_3$ that would be obtained if Al and HCl were totally consumed:

$$0.15 \text{ mol Al} \times \frac{2 \text{ mol } AlCl_3}{2 \text{ mol Al}} = 0.1\underline{5}0 \text{ mol } AlCl_3$$

$$0.35 \text{ mol HCl} \times \frac{2 \text{ mol } AlCl_3}{6 \text{ mol HCl}} = 0.1\underline{1}66 \text{ mol } AlCl_3$$

Because the HCl produces the smaller amount of $AlCl_3$, the reaction will stop when HCl is totally consumed but before all the Al is consumed. The limiting reactant is therefore HCl. The amount of $AlCl_3$ produced must be 0.1$\underline{1}$66, or 0.12 mol.

3.18. First, determine the limiting reactant by calculating the moles of ZnS produced by totally consuming Zn and S_8:

$$7.36 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{8 \text{ mol ZnS}}{8 \text{ mol Zn}} = 0.11\underline{2}56 \text{ mol ZnS}$$

$$6.45 \text{ g } S_8 \times \frac{1 \text{ mol } S_8}{256.56 \text{ g } S_8} \times \frac{8 \text{ mol ZnS}}{1 \text{ mol } S_8} = 0.20\underline{1}1 \text{ mol ZnS}$$

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The reaction will stop when Zn is totally consumed; S_8 is in excess, and not all of it is converted to ZnS. The limiting reactant is therefore Zn. Now convert the moles of ZnS obtained from the Zn to grams of ZnS:

$$0.11256 \text{ mol ZnS} \times \frac{97.46 \text{ g ZnS}}{1 \text{ mol ZnS}} = 10.\underline{9}7 = 11.0 \text{ g ZnS}$$

3.19. First, write the balanced equation:

$$CH_3OH + CO \rightarrow HC_2H_3O_2$$

Convert grams of each reactant to moles of acetic acid:

$$15.0 \text{ g } CH_3OH \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} \times \frac{1 \text{ mol } HC_2H_3O_2}{1 \text{ mol } CH_3OH} = 0.46\underline{8}1 \text{ mol } HC_2H_3O_2$$

$$10.0 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} \times \frac{1 \text{ mol } HC_2H_3O_2}{1 \text{ mol CO}} = 0.35\underline{7}0 \text{ mol } HC_2H_3O_2$$

Thus, CO is the limiting reactant, and 0.03570 mol $HC_2H_3O_2$ is obtained. The mass of product is

$$0.3570 \text{ mol } HC_2H_3O_2 \times \frac{60.05 \text{ g } HC_2H_3O_2}{1 \text{ mol } HC_2H_3O_2} = 21.\underline{4}4 \text{ g } HC_2H_3O_2$$

The percentage yield is

$$\frac{19.1 \text{ g actual yield}}{21.44 \text{ g theoretical yield}} \times 100\% = 89.\underline{0}8 = 89.1\%$$

■ ANSWERS TO CONCEPT CHECKS

3.1.

a. Each tricycle has one seat, so you have a total of 1.5 mol of seats.

b. Each tricycle has three tires, so you have 1.5 mol x 3 = 4.5 mol of tires.

c. Each $Mg(OH)_2$ has two OH^- ions, so there are 1.5 mol x 2 = 3.0 mol OH^- ions.

3.2.

a. When conducting this type of experiment, you are assuming that all of the carbon and hydrogen show up in the CO_2 and H_2O, respectively. In this experiment, where all of the carbon and hydrogen do not show up, when you analyze the CO_2 for carbon and H_2O for hydrogen, you find that the masses in the products are less than those in the carbon and hydrogen you started with.

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b. Since you collected less carbon and hydrogen than were present in the original sample, the calculated mass percentage will be less than the expected (real) value. For example, say you have a 10.0-g sample that contains 7.5 g of carbon. You run the experiment on the 10.0-g sample and collect only 5.0 g of carbon. The calculated percent carbon based on your experimental results would be 50% instead of the correct amount of 75%.

3.3.

a. $C_2H_8O_2$ is not an empirical formula because each of the subscripts can be divided by 2 to obtain a possible empirical formula of CH_4O. (The empirical formula is not the smallest integer ratio of subscripts.)

b. $C_{1.5}H_4$ is not a correct empirical formula because one of the subscripts is not an integer. Multiply each of the subscripts by 2 to obtain the possible empirical formula C_3H_8. (Since the subscript of carbon is the decimal number 1.5, the empirical formula is not the smallest integer ratio of subscripts.)

c. Yes, the empirical formula and the molecular formula can be the same, as is the case in this problem, where the formula is written with the smallest integer subscripts.

3.4.

a. Correct. Coefficients in balanced equations can represent amounts in atoms and molecules.

b. Incorrect. The coefficients in a balanced chemical equation do not represent amounts in grams. One gram of carbon and one gram of oxygen represent different molar amounts.

c. Incorrect. The coefficients in a balanced chemical equation do not represent amounts in grams.

d. Correct. You might initially think this is an incorrect representation; however, 12 g of C, 32 g of O_2, and 44 g of CO_2 all represent one mole of the substance, so the relationship of the chemical equation is obeyed.

e. Correct. The coefficients in balanced equations can represent amounts in moles.

f. Incorrect. The amount of O_2 present is not enough to react completely with one mole of carbon. Only one-half of the carbon would react, and one-half mole of CO_2 would form.

g. Incorrect. In this representation, oxygen is being shown as individual atoms of O, not as molecules of O_2, so the drawings are not correctly depicting the chemical reaction.

h. Correct. The molecular models correctly depict a balanced chemical reaction since the same number of atoms of each element appears on both sides of the equation.

3.5.

a. $X_2(g) + 2Y(g) \rightarrow 2XY(g)$

b. Since the product consists of a combination of X and Y in a 1:1 ratio, it must consist of two atoms hooked together. If you count the total number of X atoms (split apart the X_2 molecules) and Y atoms present prior to the reaction, you find that there are four X atoms and three Y atoms. From these starting quantities, you are limited to three XY molecules and left with an unreacted X. Option #1 represents this situation and is therefore the correct answer.

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c. Since Y(*g*) was completely used up during the course of the reaction, it is the limiting reactant.

ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

3.1. The molecular mass is the sum of the atomic masses of all the atoms in a molecule of the substance whereas the formula mass is the sum of the atomic masses of all the atoms in one formula unit of the compound, whether the compound is molecular or not. A given substance could have both a molecular mass and a formula mass if it existed as discrete molecules.

3.2. To obtain the formula mass of a substance, sum up the atomic masses of all atoms in the formula of the compound.

3.3. A mole of N_2 contains Avogadro's number (6.02×10^{23}) of N_2 molecules and $2 \times 6.02 \times 10^{23}$ N atoms. One mole of $Fe_2(SO_4)_3$ contains three moles of SO_4^{2-} ions, and it contains twelve moles of O atoms.

3.4. A sample of the compound of known mass is burned, and CO_2 and H_2O are obtained as products. Next, you relate the masses of CO_2 and H_2O to the masses of carbon and hydrogen. Then you calculate the mass percentages of C and H. You find the mass percentage of O by subtracting the mass percentages of C and H from 100.

3.5. The empirical formula is obtained from the percentage composition by assuming for the purposes of the calculation a sample of 100 g of the substance. Then the mass of each element in the sample equals the numerical value of the percentage. Convert the masses of the elements to moles of the elements using the atomic mass of each element. Divide the moles of each by the smallest number to obtain the smallest ratio of each atom. If necessary, find a whole-number factor to multiply these results by to obtain integers for the subscripts in the empirical formula.

3.6. The empirical formula is the formula of a substance written with the smallest integer (whole-number) subscripts. Each of the subscripts in the formula $C_6H_{12}O_2$ can be divided by 2, so the empirical formula of the compound is C_3H_6O.

3.7. The number of empirical formula units in a compound, *n*, equals the molecular mass divided by the empirical formula mass.

$$n = \frac{34.0 \text{ amu}}{17.0 \text{ amu}} = 2.00$$

The molecular formula of hydrogen peroxide is therefore $(HO)_2$, or H_2O_2.

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3.8. The coefficients in a chemical equation can be interpreted directly in terms of molecules or moles. For the mass interpretation, you will need the molar masses of CH_4, O_2, CO_2, and H_2O, which are 16.0, 32.0, 44.0, and 18.0 g/mol, respectively. A summary of the three interpretations is given below the balanced equation:

CH_4	+	$2O_2$	$\rightarrow$	CO_2	+	$2H_2O$
1 molecule	+	2 molecules	$\rightarrow$	1 molecule	+	2 molecules
1 mole	+	2 moles	$\rightarrow$	1 mole	+	2 moles
16.0 g	+	2 x 32.0 g	$\rightarrow$	44.0 g	+	2 x 18.0 g

3.9. A chemical equation yields the mole ratio of a reactant to a second reactant or product. Once the mass of a reactant is converted to moles, this can be multiplied by the appropriate mole ratio to give the moles of a second reactant or product. Multiplying this number of moles by the appropriate molar mass gives mass. Thus, the masses of two different substances are related by a chemical equation.

3.10. The limiting reactant is the reactant that is entirely consumed when the reaction is complete. Because the reaction stops when the limiting reactant is used up, the moles of product are always determined by the starting number of moles of the limiting reactant.

3.11. Two examples are given in the book. The first involves making cheese sandwiches. Each sandwich requires two slices of bread and one slice of cheese. The limiting reactant is the cheese because some bread is left unused. The second example is assembling automobiles. Each auto requires one steering wheel, four tires, and other components. The limiting reactant is the tires, since they will run out first.

3.12. Since the theoretical yield represents the maximum amount of product that can be obtained by a reaction from given amounts of reactants under any conditions, in an actual experiment you can never obtain more than this amount.

3.13. The answer is a, 3.27 g of NH_3.

3.14. The answer is b, 1 g of formaldehyde.

3.15. The answer is d, 4.85×10^{24} atoms.

3.16. The answer is a, $C_3H_4O_3$.

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■ ANSWERS TO CONCEPT EXPLORATIONS

3.17. **Part 1**

a. $0.2\ \text{kg} \times \frac{500\ \text{nails}}{1\ \text{kg}} = \underline{1}00\ \text{nails} = 1 \times 10^{2}\ \text{nails}$

b. $10\ \text{dozen} \times \frac{12\ \text{nails}}{1\ \text{dozen}} \times \frac{1\ \text{kg}}{500\ \text{nails}} = 0.240\ \text{kg}$

c. $1\ \text{nail} \times \frac{1\ \text{kg}}{500\ \text{nails}} = 0.00200\ \text{kg} = 2.00\ \text{g}$

d. $2.0\ \text{mol} \times \frac{6.02 \times 10^{23}\ \text{nails}}{1\ \text{mol}} \times \frac{1\ \text{kg}}{500\ \text{nails}} = 2.\underline{4}08 \times 10^{21} = 2.4 \times 10^{21}\ \text{kg}$

Part 2

a. $0.2\ \text{kg} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol}}{4.003\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} = \underline{3}.00 \times 10^{25} = 3 \times 10^{25}\ \text{atoms}$

b. $10\ \text{dozen} \times \frac{12\ \text{atoms}}{1\ \text{dozen}} \times \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{atoms}} \times \frac{4.003\ \text{g}}{1\ \text{mol}} = 7.9\underline{7}9 \times 10^{-22} = 7.98 \times 10^{-22}\ \text{g}$

c. $1\ \text{atom} \times \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{atoms}} \times \frac{4.003\ \text{g}}{1\ \text{mol}} = 6.6\underline{4}6 \times 10^{-24} = 6.65 \times 10^{-24}\ \text{g}$

d. $2.0\ \text{mol} \times \frac{4.003\ \text{g}}{1\ \text{mol}} = 8.\underline{0}06 = 8.0\ \text{g}$

Part 3

a. A nail and a helium atom have very different masses. You would not expect an equal mass of each, 1.0 kg, to have an equal number of binkles.

b. A binkle is a fixed number of objects, 3×10^{12}. You would expect 3.5 binkles of nails and 3.5 binkles of helium atoms to have equal counts. A nail has a larger mass than a helium atom, so a binkle of nails would have more mass.

c. A helium atom has a smaller mass than a lithium atom, so 3.5 g of helium contains more atoms than 3.5 g of lithium atoms.

3.18. **Part 1**

a. There are two hydrogen atoms and one oxygen atom in each molecule of H_2O.

b. There are two moles of hydrogen atoms and one mole of oxygen atoms in each mole of H_2O.

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c. $\text{Mass H} = 1.0 \text{ mol } H_2O \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \times \frac{1.008 \text{ g}}{1 \text{ mol H}} = 2.\underline{0}16 = 2.0 \text{ g H}$

$\text{Mass O} = 1.0 \text{ mol } H_2O \times \frac{1 \text{ mol O}}{1 \text{ mol } H_2O} \times \frac{16.00 \text{ g}}{1 \text{ mol O}} = 1\underline{6}.00 = 16 \text{ g O}$

d. The mass of 1.0 mol H_2O is $2.016 + 16.00 = 1\underline{8}.016 = 18$ g/mol.

Part 2

a. $\text{Molar mass } XCl_2 = \frac{100.0 \text{ g}}{0.25 \text{ mol}} = 4\underline{0}0 = 4.0 \times 10^2 \text{ g/mol}$

$\text{Molar mass } YCl_2 = \frac{125.0 \text{ g}}{0.50 \text{ mol}} = 2\underline{5}0 = 2.5 \times 10^2 \text{ g/mol}$

b. Since there are two chloride ions in each compound, 1.0 mol XCl_2 and 1.0 mol YCl_2 contain the same number of chloride ions.

c. Element X is heavier than element Y. Therefore, for 1.0 mol XCl_2 and 1.0 mol YCl_2, the mass of element X is more than the mass of Y.

d. The mass of chloride ion is the same for both. In 1.0 mole,

$$1.0 \text{ mol} \times \frac{2 \text{ mol } Cl^- \text{ ions}}{1 \text{ mol } XCl_2} \times \frac{35.45 \text{ g}}{1 \text{ mol Cl}} = 7\underline{0}.90 = 71 \text{ g}$$

e. $\text{Molar mass X} = 4\underline{0}0.0 - 70.90 = 3\underline{2}9.1 = 3.3 \times 10^2 \text{ g/mol}$

$\text{Molar mass Y} = 2\underline{5}0.0 - 70.90 = 1\underline{7}9.1 = 1.8 \times 10^2 \text{ g/mol}$

f. $200.0 \text{ g} \times \frac{1 \text{ mol } XCl_2}{400 \text{ g}} \times \frac{1 \text{ mol X ions}}{1 \text{ mol } XCl_2} = 0.5\underline{0}0 = 0.50 \text{ mol X ions}$

$200.0 \text{ g} \times \frac{1 \text{ mol } XCl_2}{400 \text{ g}} \times \frac{2 \text{ mol } Cl^- \text{ ions}}{1 \text{ mol } XCl_2} = 1.\underline{0}0 = 1.0 \text{ mol } Cl^- \text{ ions}$

g. $250.0 \text{ g} \times \frac{1 \text{ mol } YCl_2}{250 \text{ g}} \times \frac{1 \text{ mol Y ions}}{1 \text{ mol } YCl_2} \times \frac{179.10 \text{ g}}{1 \text{ mol Y}} = 1\underline{7}9.10 = 1.8 \times 10^2 \text{g Y ions}$

h. $\text{Molar mass } YBr_3 = 1\underline{7}9.10 + 3 \times 79.90 = 4\underline{1}8.8 = 4.2 \times 10^2 \text{ g/mol}$

Part 3

If the sample of $AlCl_3$ contains 12 chloride ions, it must also contain 4 aluminum ions. This makes a total of 4 $AlCl_3$ units.

a. $4 \text{ } AlCl_3 \text{ units} \times \frac{1 \text{ mol } AlCl_3}{6.02 \times 10^{23} \text{ units}} \times \frac{133.33 \text{ g}}{1 \text{ mol } AlCl_3} = 8.8\underline{5}9 \times 10^{-22} = 8.86 \times 10^{-22} \text{ g}$

b. $4 \text{ } AlCl_3 \text{ units} \times \frac{1 \text{ mol } AlCl_3}{6.02 \times 10^{23} \text{ units}} = 6.6\underline{4}4 \times 10^{-24} = 6.64 \times 10^{-24} \text{ mol}$

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■ ANSWERS TO CONCEPTUAL PROBLEMS

3.19.

a. $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$

b. Since there is no H_2 present in the container, it was entirely consumed during the reaction, which makes it the limiting reactant.

c. According to the chemical reaction, three molecules of H_2 are required for every molecule of N_2. Since there are two molecules of unreacted N_2, you would need six additional molecules of H_2 to complete the reaction.

3.20.

a. The limiting reactant in cooking with a gas grill would be the propane. This makes sense because propane is the material you must purchase in order to cook your food.

b. Since the chemical reaction requires only propane and oxygen, if the grill will not light with ample propane present, the limiting reactant must be the oxygen.

c. Once again, here is a case where you have adequate propane, so you can conclude that a yellow flame indicates that not enough oxygen is present to combust all of the propane. If there is not enough O_2 available for complete combustion, a reasonable assumption is that some of the products will have fewer oxygen atoms than CO_2. Therefore, a mixture of products would be obtained in this case, including carbon monoxide (CO) and soot (carbon particles).

3.21.

a. This answer is unreasonable because 1.0×10^{-3} g is too small a mass for 0.33 mol of an element. For example, 0.33 mol of hydrogen, the lightest element, would have a mass of 0.33 g.

b. This answer is unreasonable because 1.80×10^{-10} g is too large for one water molecule. (The mass of one water molecule is 2.99×10^{-23} g.)

c. This answer is reasonable because 3.01×10^{23} is one-half of Avogadro's number.

d. This answer is unreasonable because the units for molar mass should be g/mol, so this quantity is 1000 times too large.

3.22.

a. In order to have a complete reaction, a ratio of 2 moles of hydrogen to every mole of oxygen is required. In this case, there is not enough oxygen in the air outside of the bubble for the complete reaction of hydrogen.

b. In this case, you have a ratio of 1 mole of H_2 to 1 mole of O_2. According to the balanced chemical reaction, every mole of O_2 can react with 2 moles of H_2. In this case, when 0.5 mole of O_2 has reacted, all of the H_2 (1 mole) will be consumed, leaving behind 0.5 mole of unreacted O_2.

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c. In this case, you have a ratio of 2 moles of H_2 to 1 mole of O_2, which is the correct stoichiometric amount, so all of the hydrogen and all of the oxygen react completely.

d. In order for reaction to occur, both oxygen and hydrogen must be present. Oxygen does not combust, and there is no hydrogen present to burn, so no reaction occurs.

3.23.

a. The limiting reactant would be the charcoal because the air would supply as much oxygen as is needed.

b. The limiting reactant would be the magnesium because the beaker would contain much more water than is needed for the reaction (approximately 18 mL of water is 1 mole).

c. The limiting reactant would be the H_2 because the air could supply as much nitrogen as is needed.

3.24.

a. Since the balanced chemical equation for the reaction is $2H_2 + O_2 \rightarrow 2H_2O$ in order to form the water, you need 2 molecules of hydrogen for every 1 molecule of oxygen. Given the quantities of reactants present in the container and applying the 2:1 ratio, you can produce a maximum of twelve molecules of water.

b. The drawing of the container after the reaction should contain 12 H_2O molecules and 2 O_2 molecules.

3.25.

a. The problem is that Avogadro's number was inadvertently used for the molar mass of calcium, which should be 40.08 g/mol. The correct calculation is

$$27.0 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} = 0.67\underline{3}6 = 0.674 \text{ mol Ca}$$

b. The problem here is an incorrect mole ratio. There are 2 mol K^+ ions per 1 mol K_2SO_4. The correct calculation is

$$2.5 \text{ mol } K_2SO_4 \times \frac{2 \text{ mol } K^+ \text{ ions}}{1 \text{ mol } K_2SO_4} \times \frac{6.022 \times 10^{23} \text{ } K^+ \text{ ions}}{1 \text{ mol } K^+ \text{ ions}}$$

$$= 3.\underline{0}1 \times 10^{24} = 3.0 \times 10^{24} \text{ } K^+ \text{ ions}$$

c. The problem here is an incorrect mole ratio. The result should be

$$0.50 \text{ mol Na} \times \frac{2 \text{ mol } H_2O}{2 \text{ mol Na}} = 0.50 \text{ mol } H_2O$$

3.26.

a. The missing concept is the mole ratio. His reasoning would be correct only if the reactants reacted in a one-to-one mole ratio. Here, the ratio is 5 mol O_2/2 mol C_2H_2. This means that, for every 2 moles of C_2H_2, 5 moles of O_2 are required. Since there are only 4 moles here, there is insufficient O_2, and it is the limiting reactant.

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b. The missing concept again is the mole ratio. Since in this problem the reactants react in a one-to-one mole ratio, the reactant with the fewest moles is the limiting reactant, and the lucky guess works.

SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

3.27.

a. FM of CH_3OH = AM of C + 4(AM of H) + AM of O

= 12.01 amu + (4 x 1.008 amu) + 16.00 amu
= 32.0$\underline{4}$2 = 32.0 amu (3 s.f.)

b. FM of NO_3 = AM of N + 3(AM of O)

= 14.01 amu + (3 x 16.00 amu) = 62.01 = 62.0 amu (3 s.f.)

c. FM of K_2CO_3 = 2(AM of K) + AM of C + 3(AM of O)

= (2 x 39.10 amu) + 12.01 amu + (3 x 16.00 amu)
= 138.2$\underline{1}$0 = 138 amu (3 s.f.)

d. FM of $Ni_3(PO_4)_2$ = 3(AM of Ni) + 2(AM of P) + 8(AM of O)

= (3 x 58.70 amu) + (2 x 30.97 amu) + (8 x 16.00 amu)
= 366.0$\underline{4}$0 = 366 amu (3 s.f.)

3.28.

a. FM of H_2SO_4 = 2(AM of H) + AM of S + 4(AM of O)

= (2 x 1.008 amu) + 32.07 amu + (4 x 16.00 amu)
= 98.0$\underline{8}$6 = 98.1 amu (3 s.f.)

b. FM of PCl_5 = AM of P + 5(AM of Cl)

= 30.97 amu + (5 x 35.45 amu)
= 208.2$\underline{2}$0 = 208 amu (3 s.f.)

c. FM of K_2SO_3 = 2(AM of K) + AM of S + 3(AM of O)

= (2 x 39.10 amu) + 32.07 amu + (3 x 16.00 amu)
= 158.2$\underline{7}$0 = 158 amu (3 s.f.)

d. FM of $Ca(OH)_2$ = AM of Ca + 2(AM of H) + 2(AM of O)

= 40.08 amu + (2 x 1.008 amu) + (2 x 16.00 amu)
= 74.0$\underline{9}$6 = 74.1 amu (3 s.f.)

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3.29.

a. SO_2 1 x AM of S = 32.07 amu

2 x AM of O = 2 x 16.00 = 32.00 amu

MM of NO_2 = 64.07 amu = 64.1 amu (3 s.f.)

b. PCl_3 1 x AM of P = 30.97 amu

3 x AM of Cl = 3 x 35.45 = 106.35 amu

MM of PCl_3 = 137.32 amu = 137 amu (3 s.f.)

3.30.

a. HNO_2 1 x AM of H = 1.008 amu

1 x AM of N = 14.01 amu

2 x AM of O =2 x 16.00 = 32.00 amu

MM of HNO_2 = 47.018 amu = 47.0 amu (3 s.f.)

b. CO 1 x AM of C = 12.01 amu

1 x AM of O = 16.00 amu

MM of CO = 28.01 amu = 28.0 amu (3 s.f.)

3.31. First, find the formula mass of NH_4NO_3 by adding the respective atomic masses. Then convert it to the molar mass:

FM of NH_4NO_3 = 2(AM of N) + 4(AM of H) + 3(AM of O)

= (2 x 14.01 amu) + (4 x 1.008 amu) + (3 x 16.00 amu)

= 80.052 amu

The molar mass of NH_4NO_3 is 80.05 g/mol.

3.32. First, find the formula mass of H_3PO_4 by adding the respective atomic masses. Then convert it to the molar mass:

FM of H_3PO_4 = 3(AM of H) + AM of P + 4(AM of O)

= (3 x 1.008) + 30.97 + (4 x 16.00)

= 97.994 amu

The molar mass of H_3PO_4 is 97.99 g/mol.

3.33.

a. The atomic mass of Na equals 22.99 amu; thus, the molar mass equals 22.99 g/mol. Because 1 mol of Na atoms equals 6.022×10^{23} Na atoms, we calculate

$$\text{Mass of one Na atom} = \frac{22.99 \text{ g/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 3.8177 \times 10^{-23}$$

$$= 3.818 \times 10^{-23} \text{ g/atom}$$

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b. The atomic mass of N equals 14.01 amu; thus, the molar mass equals 14.01 g/mol. Because 1 mol of N atoms equals 6.022×10^{23} N atoms, we calculate

$$\text{Mass of one N atom} = \frac{14.01 \text{ g/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 2.32\underline{6}4 \times 10^{-23}$$

$$= 2.326 \times 10^{-23} \text{ g/atom}$$

c. The formula mass of CH_3Cl = [12.01 + (3 x 1.008) + 35.45] = 50.48 amu; thus, the molar mass equals 50.48 g/mol. Because 1 mol of CH_3Cl molecules equals 6.022×10^{23} CH_3Cl molecules, we calculate

$$\text{Mass of one } CH_3Cl \text{ molecule} = \frac{50.48 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}} = 8.38\underline{2}6 \times 10^{-23}$$

$$= 8.383 \times 10^{-23} \text{ g/molecule}$$

d. The formula mass of $Hg(NO_3)_2$ = 200.59 + (2 x 14.01) + (6 x 16.00)] = 324.61 amu; thus, the molar mass equals 324.61 g/mol. Because 1 formula mass of $Hg(NO_3)_2$ equals 6.022×10^{23} $Hg(NO_3)_2$ formula units, we calculate

$$\text{Mass of one } Hg(NO_3)_2 = \frac{324.61 \text{ g/mol}}{6.022 \times 10^{23} \text{ units/mol}} = 5.39\underline{0}4 \times 10^{-22}$$

$$= 5.390 \times 10^{-22} \text{ g/unit}$$

3.34.

a. $$\text{Mass of one Ar atom} = \frac{39.95 \text{ g/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 6.6\underline{3}4 \times 10^{-23} = 6.63 \times 10^{-23} \text{ g/atom}$$

b. $$\text{Mass of one Te atom} = \frac{127.60 \text{ g/mol}}{6.022 \times 10^{23} \text{ atom/mol}} = 2.11\underline{8}8 \times 10^{-22} = 2.119 \times 10^{-22} \text{ g/atom}$$

c. $$\text{Mass of one } PBr_3 \text{ molecule} = \frac{270.67 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}} = 4.49\underline{4}7 \times 10^{-22}$$

$$= 4.495 \times 10^{-22} \text{ g/molecule}$$

d. $$\text{Mass of one } Fe(OH)_3 \text{ unit} = \frac{106.87 \text{ g/mol}}{6.022 \times 10^{23} \text{ unit/mol}} = 1.77\underline{4}7 \times 10^{-22}$$

$$= 1.775 \times 10^{-22} \text{ g/unit}$$

3.35. First, find the formula mass (in amu) using the periodic table (inside front cover):

$$\text{FM of } (CH_3CH_2)_2O = (4 \times 12.01 \text{ amu}) + (10 \times 1.008 \text{ amu}) + 16.00 \text{ amu} = 74.12 \text{ amu}$$

$$\text{Mass of one } (CH_3CH_2)_2O \text{ molecule} = \frac{74.12 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}}$$

$$= 1.23\underline{0}8 \times 10^{-22} = 1.231 \times 10^{-22} \text{ g/molecule}$$

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3.36. First, find the formula mass (in amu) using the periodic table (inside front cover):

$$\text{FM of glycerol} = (3 \times 12.01 \text{ amu}) + (8 \times 1.008 \text{ amu}) + (3 \times 16.00 \text{ amu})$$
$$= 92.09 \text{ amu}$$

$$\text{Mass of one glycerol molecule} = \frac{92.09 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}}$$
$$= 1.529 \times 10^{-22} = 1.53 \times 10^{-22} \text{ g/molecule}$$

3.37. From the table of atomic masses, we obtain the following molar masses for parts a through d: Na = 22.99 g/mol; S = 32.07 g/mol; C = 12.01 g/mol; H = 1.008 g/mol; Cl = 35.45 g/mol; and N = 14.01 g/mol.

a. $0.15 \text{ mol Na} \times \frac{22.99 \text{ g}}{1 \text{ mol Na}} = 3.448 = 3.4 \text{ g Na}$

b. $0.594 \text{ mol S} \times \frac{32.07 \text{ g S}}{1 \text{ mol S}} = 19.04 = 19.0 \text{ g S}$

c. Using molar mass = 84.93 g/mol for CH_2Cl_2, we obtain

$$2.78 \text{ mol } CH_2Cl_2 \times \frac{84.93 \text{ g } CH_2Cl_2}{1 \text{ mol } CH_2Cl_2} = 236.1 = 236 \text{ g } CH_2Cl_2$$

d. Using molar mass = 68.14 g/mol for $(NH_4)_2S$, we obtain

$$38 \text{ mol } (NH_4)_2S \times \frac{68.14 \text{ g } (NH_4)_2S}{1 \text{ mol } (NH_4)_2S} = 2.58 \times 10^3 = 2.6 \times 10^3 \text{ g } (NH_4)_2S$$

3.38. From the table of atomic masses, we obtain the following molar masses for parts a through d: C = 12.01 g/mol; O = 16.00 g/mol; K = 39.10 g/mol; Cr = 52.00 g/mol; Fe = 55.85 g/mol; and F = 19.00 g/mol.

a. $0.205 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} = 11.44 = 11.4 \text{ g Fe}$

b. $0.79 \text{ mol F} \times \frac{19.00 \text{ g F}}{1 \text{ mol F}} = 15.01 = 15 \text{ g F}$

c. Using molar mass = 44.01 g/mol for CO_2, we obtain

$$5.8 \text{ mol } CO_2 \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 255.2 = 2.6 \times 10^2 \text{ g } CO_2$$

d. Using molar mass 194.20 g/mol for K_2CrO_4, we obtain

$$48.1 \text{ mol } K_2CrO_4 \times \frac{194.20 \text{ g } K_2CrO_4}{1 \text{ mol } K_2CrO_4} = 9341.02 = 9.34 \times 10^3 \text{ g } K_2CrO_4$$

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3.39. First, find the molar mass of H_3BO_3: (3 x 1.008 amu) + 10.81 amu + (3 x 16.00 amu) = 61.83. Therefore, the molar mass of H_3BO_3 = 61.83 g/mol. The mass of H_3BO_3 is calculated as follows:

$$0.543 \text{ mol } H_3BO_3 \times \frac{61.83 \text{ g } H_3BO_3}{1 \text{ mol } H_3BO_3} = 33.\underline{5}7 = 33.6 \text{ g } H_3BO_3$$

3.40. First, find the molar mass of CS_2: 12.01 amu + (2 x 32.07 amu) = 76.15 amu. Therefore, the molar mass of CS_2 = 76.15 g/mol. The mass of CS_2 is calculated as follows:

$$0.0205 \text{ mol } CS_2 \times \frac{76.15 \text{ g } CS_2}{1 \text{ mol } CS_2} = 1.5\underline{6}10 = 1.56 \text{ g } CS_2$$

3.41. From the table of atomic masses, we obtain the following rounded molar masses for parts a through d: C = 12.01 g/mol; Cl = 35.45 g/mol; H = 1.008 g/mol; Al = 26.98 g/mol; and O = 16.00 g/mol.

a. $$2.86 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.23\underline{8}1 = 0.238 \text{ mol C}$$

b. $$7.05 \text{ g } Cl_2 \times \frac{1 \text{ mol } Cl_2}{70.90 \text{ g } Cl_2} = 0.099\underline{4}3 = 0.0994 \text{ mol } Cl_2$$

c. The molar mass of C_4H_{10} = (4 x 12.01) + (10 x 1.008) = 58.12 g C_4H_{10}/mol C_4H_{10}. The mass of C_4H_{10} is calculated as follows:

$$76 \text{ g } C_4H_{10} \times \frac{1 \text{ mol } C_4H_{10}}{58.12 \text{ g } C_4H_{10}} = 1.\underline{3}07 = 1.3 \text{ mol } C_4H_{10}$$

d. The molar mass of $Al_2(CO_3)_3$ = (2 x 26.98) + (3 x 12.01) + (9 x 16.00 g) =233.99 g/mol $Al_2(CO_3)_3$. The mass of $Al_2(CO_3)_3$ is calculated as follows:

$$26.2 \text{ g } Al_2(CO_3)_3 \times \frac{1 \text{ mol } Al_2(CO_3)_3}{233.99 \text{ g } Al_2(CO_3)_3} = 0.11\underline{1}9 = 0.112 \text{ mol } Al_2(CO_3)_3$$

3.42. From the table of atomic masses, we obtain the following rounded molar masses for parts a through d: As = 74.92 g/mol; S = 32.07 g/mol; N = 14.01 g/mol; H = 1.008 g/mol; Al = 26.98 g/mol; and O = 16.00 g/mol.

a. $$2.57 \text{ g As} \times \frac{1 \text{ mol As}}{74.92 \text{ g As}} = 0.034\underline{3}0 = 0.0343 \text{ mol As}$$

b. $$7.83 \text{ g } S_8 \times \frac{1 \text{ mol } S_8}{256.56 \text{ g } S_8} = 0.030\underline{5}1 = 0.0305 \text{ mol } S_8$$

c. The molar mass of N_2H_4 = (2 x 14.01) + (4 x 1.008) = 32.052 g N_2H_4/mol N_2H_4. The moles of N_2H_4 is calculated as follows:

$$36.5 \text{ g} \times \frac{1 \text{ mol } N_2H_4}{32.052 \text{ g } N_2H_4} = 1.1\underline{3}87 = 1.14 \text{ mol } N_2H_4$$

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d. The molar mass of $Al_2(SO_4)_3$ = (2 x 26.98) + (3 x 32.07) + (12 x 16.00) = 342.17 g $Al_2(SO_4)_3$/mol $Al_2(SO_4)_3$. The mass of $Al_2(SO_4)_3$ is calculated as follows:

$$227 \text{ g } Al_2(SO_4)_3 \times \frac{1 \text{ mol } Al_2(SO_4)_3}{342.17 \text{ g } Al_2(SO_4)_3} = 0.66\underline{3}4 = 0.663 \text{ mol } Al_2(SO_4)_3$$

3.43. Calculate the formula mass of calcium sulfate: 40.08 amu + 32.07 amu + (4 x 16.00 amu) = 136.15 amu. Therefore, the molar mass of $CaSO_4$ is 136.15 g/mol. Use this to convert the mass of $CaSO_4$ to moles:

$$0.791 \text{ g } CaSO_4 \times \frac{1 \text{ mol } CaSO_4}{136.15 \text{ g } CaSO_4} = 5.8\underline{0}9 \times 10^{-3} = 5.81 \times 10^{-3} \text{ mol } CaSO_4$$

Calculate the molecular mass of water: (2 x 1.008 amu) + 16.00 amu = 18.02 amu. Therefore, the molar mass of H_2O equals 18.02 g/mol. Use this to convert the rest of the sample to moles of water:

$$0.209 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 1.1\underline{5}9 \times 10^{-2} = 1.16 \times 10^{-2} \text{ mol } H_2O$$

Because 0.01159 mol is about twice 0.005811 mol, both numbers of moles are consistent with the formula, $CaSO_4 \bullet 2H_2O$.

3.44. Calculate the formula mass of copper(II) sulfate: 63.55 amu + 32.07 amu + (4 x 16.00 amu) = 159.62 amu. Thus, the molar mass of $CuSO_4$ is 159.62 g/mol. From the previous problem, the molar mass of H_2O is 18.02 g/mol. Use this to convert the rest of the sample to moles of water:

$$0.558 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.030\underline{9}6 \text{ mol } H_2O$$

Calculate the moles of $CuSO_4$ in order to be able to compare relative molar amounts of $CuSO_4$ and H_2O. Then, divide the moles of H_2O by the moles of $CuSO_4$:

$$0.989 \text{ g } CuSO_4 \times \frac{1 \text{ mol } CuSO_4}{159.62 \text{ g } CuSO_4} = 0.006\underline{1}96 \text{ mol } CuSO_4$$

$$0.03096 \text{ mol } H_2O \div 0.006196 \text{ mol } CuSO_4 = 4.99/1, \text{ or about } 5:1$$

(consistent with $CuSO_4 \bullet 5H_2O$)

3.45. The following rounded atomic masses are used: Li = 6.94 g/mol; Br = 79.90 g/mol; N = 14.01 g/mol; H = 1.008 g/mol; Pb = 207.2 g/mol; Cr = 52.00 g/mol; O = 16.00 g/mol; and S = 32.07 g/mol. Also, Avogadro's number is 6.022×10^{23} atoms, so

a. $$\text{No. Li atoms} = 8.21 \text{ g Li} \times \frac{6.022 \times 10^{23} \text{ atoms}}{6.941 \text{ g Li}} = 7.1\underline{2}2 \times 10^{23} = 7.12 \times 10^{23} \text{ atoms}$$

b. $$\text{No. Br atoms} = 32.0 \text{ g } Br_2 \times \frac{2 \times 6.022 \times 10^{23} \text{ atoms}}{(2 \times 79.90) \text{ g } Br_2} = 2.4\underline{1}2 \times 10^{23}$$

$$= 2.41 \times 10^{23} \text{ atoms}$$

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c. No. NH_3 molecules = 45 g NH_3 x $\frac{6.022 \times 10^{23} \text{ molecules}}{17.03 \text{ g } NH_3}$ = $1.\underline{5}9 \times 10^{24}$

= 1.6×10^{24} molecules

d. No. $PbCrO_4$ units = 201 g $PbCrO_4$ x $\frac{6.022 \times 10^{23} \text{ units}}{323.2 \text{ g } PbCrO_4}$ = $3.7\underline{4}5 \times 10^{23}$ = 3.75×10^{23} units

e. No. SO_4^{2-} ions = 14.3 g $Cr_2(SO_4)_3$ x $\frac{3 \times 6.022 \times 10^{23} \text{ ions}}{392.21 \text{ g } Cr_2(SO_4)_3}$ = $6.5\underline{8}7 \times 10^{22}$

= 6.59×10^{22} ions

3.46. These rounded atomic masses are used: Al = 26.98 g/mol; I = 126.90 g/mol; N = 14.01 g/mol; O = 16.00 g/mol; Na = 22.99 g/mol; Cl = 35.45 g/mol; Ca = 40.08 g/mol; and P = 30.97 g/mol. Also, Avogadro's number is 6.022×10^{23} atoms, so

a. No. Al atoms = 25.7 g Al x $\frac{6.022 \times 10^{23} \text{ atoms}}{26.98 \text{ g Al}}$ = $5.7\underline{3}6 \times 10^{23}$ = 5.74×10^{23} atoms

b. No. I atoms = 8.71 g I_2 x $\frac{2 \times 6.022 \times 10^{23} \text{ atoms}}{2 \times 126.90 \text{ g } I_2}$ = $4.1\underline{3}3 \times 10^{22}$ = 4.13×10^{22} atoms

c. No. N_2O_5 molecules = 14.9 g N_2O_5 x $\frac{6.022 \times 10^{23} \text{ molecules}}{108.02 \text{ g } N_2O_5}$ = $8.3\underline{0}6 \times 10^{22}$

= 8.31×10^{22} molecules

d. No. $NaClO_4$ units = 3.31 g $NaClO_4$ x $\frac{6.022 \times 10^{23} \text{ units}}{122.44 \text{ g } NaClO_4}$ = $1.6\underline{2}8 \times 10^{22}$

= 1.63×10^{22} units

e. No. Ca^{2+} ions = 4.71 g $Ca_3(PO_4)_2$ x $\frac{3 \times 6.022 \times 10^{23} \text{ ions}}{310.18 \text{ g } Ca_3(PO_4)_2}$ = $2.7\underline{4}3 \times 10^{22}$

= 2.74×10^{22} ions

3.47. Calculate the molecular mass of CCl_4: 12.01 amu + (4 x 35.45 amu) = 153.81 amu. Use this and Avogadro's number to express it as 153.81 g/N_A in order to calculate the number of molecules:

7.58 mg CCl_4 x $\frac{1 \text{ g}}{1000 \text{ mg}}$ x $\frac{6.022 \times 10^{23} \text{ molecules}}{153.81 \text{ g } CCl_4}$ = $2.9\underline{6}8 \times 10^{19}$

= 2.97×10^{19} molecules

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3.48. Calculate the molecular mass of ClF_3: 35.45 amu + (3 x 19.00 amu) = 92.45 amu. Use this and Avogadro's number to express it as 92.45 g/N_A in order to calculate the number of molecules:

$$5.88 \text{ mg } ClF_3 \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{92.45 \text{ g } ClF_3} = 3.830 \times 10^{19}$$

$$= 3.83 \times 10^{19} \text{ molecules}$$

3.49. $$\text{Mass percentage carbon} = \frac{\text{mass of C in sample}}{\text{mass of sample}} \times 100\%$$

$$\text{Percent carbon} = \frac{1.584 \text{ g}}{1.836 \text{ g}} \times 100\% = 86.274 = 86.27\%$$

3.50. $$\text{Mass percentage alcohol} = \frac{\text{mass of alcohol in solution}}{\text{mass of sample}} \times 100\%$$

$$\text{Percent alcohol} = \frac{4.01 \text{ g}}{6.01 \text{ g}} \times 100\% = 66.72 = 66.7\%$$

3.51. $$\text{Mass percentage phosphorus} = \frac{\text{mass of P in sample}}{\text{mass of sample}} \times 100\%$$

$$\text{Percent P} = \frac{1.72 \text{ mg}}{8.53 \text{ mg}} \times 100\% = 20.16 = 20.2\%$$

3.52. $$\text{Mass percentage sulfur} = \frac{\text{mass of S in sample}}{\text{mass of sample}} \times 100\%$$

$$\text{Percent sulfur} = \frac{1.64 \text{ mg}}{3.17 \text{ mg}} \times 100\% = 51.73 = 51.7\%$$

3.53. Start with the definition for percentage nitrogen, and rearrange this equation to find the mass of N in the fertilizer.

$$\text{Mass percentage nitrogen} = \frac{\text{mass of N in fertilizer}}{\text{mass of fertilizer}} \times 100\%$$

$$\text{Mass N} = \frac{\text{mass \% N}}{100\%} \times \text{mass of fertilizer} = \frac{14.0\%}{100\%} \times 4.15 \text{ kg} = 0.5810 = 0.581 \text{ kg N}$$

3.54. Start by finding the mass of 2.50 L of seawater using the density of 1.025 g/cm^3.

$$\text{Mass seawater} = 2.50 \text{ L} \times \frac{10^3 \text{ cm}^3}{1 \text{ L}} \times \frac{1.025 \text{ g}}{1 \text{ cm}^3} = 2.5625 \times 10^3 \text{ g}$$

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Continue with the definition for percentage of bromine in the seawater, and rearrange this equation to find the mass of Br in the seawater.

$$\text{Mass percentage Br} = \frac{\text{mass of Br in seawater}}{\text{mass of seawater}} \times 100\%$$

$$\text{Mass Br} = \frac{\text{mass \% Br}}{100\%} \times \text{mass seawater} = \frac{0.0065\%}{100\%} \times 2.5625 \times 10^3 \text{ g}$$

$$= 0.1\underline{6}6 = 0.17 \text{ g Br}$$

3.55. Convert moles to mass using the molar masses from the respective atomic masses. Then calculate the mass percentages from the respective masses.

$$0.0898 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 2.4\underline{2}2 \text{ g Al}$$

$$0.0381 \text{ mol Mg} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = 0.92\underline{6}2 \text{ g Mg}$$

$$\text{Percent Al} = \frac{\text{mass of Al}}{\text{mass of alloy}} = \frac{2.422 \text{ g Al}}{3.349 \text{ g alloy}} \times 100\% = 72.\underline{3}4 = 72.3\% \text{ Al}$$

$$\text{Percent Mg} = \frac{\text{mass of Mg}}{\text{mass of alloy}} = \frac{0.9262 \text{ g Mg}}{3.349 \text{ g alloy}} \times 100\% = 27.\underline{6}55 = 27.7\% \text{ Mg}$$

3.56. Convert moles to mass using the molar masses from the respective atomic masses of 20.18 g/mol for Ne and 83.80 g/mol for Kr. Then calculate the mass percentages from the respective masses.

$$0.0856 \text{ mol Ne} \times \frac{20.18 \text{ g Ne}}{1 \text{ mol Ne}} = 1.7\underline{2}7 \text{ g Ne}$$

$$0.0254 \text{ mol Kr} \times \frac{83.80 \text{ g Kr}}{1 \text{ mol Kr}} = 2.1\underline{2}9 \text{ g Kr}$$

$$\text{Percent Ne} = \frac{\text{mass of Ne}}{\text{mass of mix}} = \frac{1.727 \text{ g Ne}}{3.856 \text{ g mix}} \times 100\% = 44.\underline{7}9 = 44.8\% \text{ Ne}$$

$$\text{Percent Kr} = \frac{\text{mass of Kr}}{\text{mass of mix}} = \frac{2.129 \text{ g Kr}}{3.856 \text{ g mix}} \times 100\% = 55.\underline{2}1 = 55.2\% \text{ Kr}$$

3.57. In each part, the numerator consists of the mass of the element in one mole of the compound; the denominator is the mass of one mole of the compound. Use the atomic weights of C = 12.01 g/mol; O = 16.00 g/mol; Na = 22.99 g/mol; H = 1.008 g/mol; P = 30.97 g/mol; Co = 58.93 g/mol; and N = 14.01 g/mol.

a. $$\text{Percent C} = \frac{\text{mass of C}}{\text{mass of CO}} = \frac{12.01 \text{ g C}}{28.01 \text{ g CO}} \times 100\% = 42.878 = 42.9\%$$

$$\text{Percent O} = 100.000\% - 42.878\%\text{C} = 57.122 = 57.1\%$$

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b. $$\text{Percent C} = \frac{\text{mass of C}}{\text{mass of } CO_2} = \frac{12.01 \text{ g C}}{44.01 \text{ g } CO_2} \times 100\% = 27.289 = 27.3\%$$

$$\text{Percent O} = 100.000\% - 27.289\% \text{ C} = 72.711 = 72.7\%$$

c. $$\text{Percent Na} = \frac{\text{mass of Na}}{\text{mass of } NaH_2PO_4} = \frac{22.99 \text{ g Na}}{119.98 \text{ g } NaH_2PO_4} \times 100\% = 19.161 = 19.2\%$$

$$\text{Percent H} = \frac{\text{mass of H}}{\text{mass of } NaH_2PO_4} = \frac{2.016 \text{ g H}}{119.98 \text{ g } NaH_2PO_4} \times 100\% = 1.6802 = 1.68\%$$

$$\text{Percent P} = \frac{\text{mass of P}}{\text{mass of } NaH_2PO_4} = \frac{30.97 \text{ g P}}{119.98 \text{ g } NaH_2PO_4} \times 100\% = 25.812 = 25.8\%$$

$$\text{Percent O} = 100.000\% - (19.161 + 1.6802 + 25.812)\% = 53.346 = 53.3\%$$

d. $$\text{Percent Co} = \frac{\text{mass of Co}}{\text{mass of } Co(NO_3)_2} = \frac{58.93 \text{ g Co}}{182.95 \text{ g } Co(NO_3)_2} \times 100\% = 32.211 = 32.2\%$$

$$\text{Percent N} = \frac{\text{mass of N}}{\text{mass of } Co(NO_3)_2} = \frac{2 \times 14.01 \text{ g N}}{182.95 \text{ g } Co(NO_3)_2} \times 100\% = 15.316 = 15.3\%$$

$$\text{Percent O} = 100.000\% - (32.211 + 15.316)\% = 52.473 = 52.5\%$$

3.58. In each part, the numerator consists of the mass of the element in one mole of the compound; the denominator is the mass of one mole of the compound. Answers are rounded to three significant figures.

a. $$\text{Percent N} = \frac{\text{mass of N}}{\text{mass of } NO_2} = \frac{14.01 \text{ g N}}{46.01 \text{ g } NO_2} \times 100\% = 30.449 = 30.4\%$$

$$\text{Percent O} = 100.000\% - 30.449\% \text{ N} = 69.551 = 69.6\%$$

b. $$\text{Percent H} = \frac{\text{mass of H}}{\text{mass of } H_2O_2} = \frac{2.016 \text{ g H}}{34.02 \text{ g } H_2O_2} \times 100\% = 5.9259 = 5.93\%$$

$$\text{Percent O} = 100.000\% - 5.2959\% \text{ H} = 94.07 = 94.1\%$$

c. $$\text{Percent K} = \frac{\text{mass of K}}{\text{mass of } KClO_4} = \frac{39.10 \text{ g K}}{138.55 \text{ g } KClO_4} \times 100\% = 28.221 = 28.2\%$$

$$\text{Percent Cl} = \frac{\text{mass of Cl}}{\text{mass of } KClO_4} = \frac{35.45 \text{ g Cl}}{138.55 \text{ g } KClO_4} \times 100\% = 25.586 = 25.6\%$$

$$\text{Percent O} = 100.000\% - (28.221 + 25.586)\% = 46.193 = 46.2\%$$

d. $$\text{Percent Mg} = \frac{\text{mass of Mg}}{\text{mass of } Mg(NO_2)_2} = \frac{24.31 \text{ g Mg}}{116.33 \text{ g } Mg(NO_2)_2} = 20.897 = 20.9\%$$

$$\text{Percent N} = \frac{\text{mass of N}}{\text{mass of } Mg(NO_2)_2} = \frac{2 \times 14.01 \text{ g N}}{116.33 \text{ g } Mg(NO_2)_2} = 24.086 = 24.1\%$$

$$\text{Percent O} = 100.000\% - (20.897 + 24.086)\% = 55.017 = 55.0\%$$

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3.59. The molecular model of toluene contains seven carbon atoms and eight hydrogen atoms, so the molecular formula of toluene is C_7H_8. The molar mass of toluene is 92.134 g/mol. The mass percentages are

$$\text{Percent C} = \frac{\text{mass of C}}{\text{mass of } C_7H_8} = \frac{7 \times 12.01\ \text{g}}{92.134\ \text{g}} \times 100\% = 91.247 = 91.2\%$$

$$\text{Percent H} = 100\% - 91.247 = 8.753 = 8.75\%$$

3.60. The molecular model of 2-propanol contains three carbon atoms, eight hydrogen atoms, and one oxygen atom, so the molecular formula of 2-propanol is C_3H_8O. The molar mass of 2-propanol is 60.094 g/mol. The mass percentages are

$$\text{Percent C} = \frac{\text{mass of C}}{\text{mass of } C_3H_8O} = \frac{3 \times 12.01\ \text{g}}{60.094\ \text{g}} \times 100\% = 59.956 = 60.0\%$$

$$\text{Percent H} = \frac{\text{mass of H}}{\text{mass of } C_3H_8O} = \frac{8 \times 1.008\ \text{g}}{60.094\ \text{g}} \times 100\% = 13.418 = 13.4\%$$

$$\text{Percent O} = 100\% - (59.956 + 13.418) = 26.626 = 26.6\%$$

3.61. Find the moles of C in each amount in one-step operations. Calculate the moles of each compound using the molar mass; then multiply by the number of moles of C per mole of compound:

$$\text{Mol C (glucose)} = 6.01\ \text{g} \times \frac{1\ \text{mol}}{180.2\ \text{g}} \times \frac{6\ \text{mol C}}{1\ \text{mol glucose}} = 0.20\underline{0}\ \text{mol}$$

$$\text{Mol C (ethanol)} = 5.85\ \text{g} \times \frac{1\ \text{mol}}{46.07\ \text{g}} \times \frac{2\ \text{mol C}}{1\ \text{mol ethanol}} = 0.25\underline{4}\ \text{mol (more C)}$$

3.62. Find the moles of S in each amount in one-step operations. Calculate the moles of each compound using the molar mass; then multiply by the number of moles of S per mole of compound.

$$\text{Mol S } (CaSO_4) = 40.8\ \text{g} \times \frac{1\ \text{mol } CaSO_4}{136.15\ \text{g}} \times \frac{1\ \text{mol S}}{1\ \text{mol } CaSO_4} = 0.29\underline{9}7\ \text{mol (more S)}$$

$$\text{Mol S } (Na_2SO_3) = 35.2\ \text{g} \times \frac{1\ \text{mol } Na_2SO_3}{126.05\ \text{g}} \times \frac{1\ \text{mol S}}{1\ \text{mol } Na_2SO_3} = 0.27\underline{9}3\ \text{mol}$$

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3.63. First, calculate the mass of C in the glycol by multiplying the mass of CO_2 by the molar mass of C and the reciprocal of the molar mass of CO_2. Next, calculate the mass of H in the glycol by multiplying the mass of H_2O by the molar mass of 2H and the reciprocal of the molar mass of H_2O. Then use the masses to calculate the mass percentages. Calculate O by difference.

$$9.06 \text{ mg } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 2.472 \text{ mg C}$$

$$5.58 \text{ mg } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ H}}{1 \text{ } H_2O} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.6243 \text{ mg H}$$

Mass O = 6.38 mg − (2.472 + 0.6243) = 3.284 mg O

Percent C = (2.472 mg C/6.38 mg glycol) x 100% = 38.74 = 38.7%

Percent H = (0.6243 mg H/6.38 mg glycol) x 100% = 9.785 = 9.79%

Percent O = (3.284 mg O/6.38 mg glycol) x 100% = 51.47 = 51.5%

3.64. First, calculate the mass of C in the phenol by multiplying the mass of CO_2 by the molar mass of C and the reciprocal of the molar mass of CO_2. Next, calculate the mass of H in the phenol by multiplying the mass of H_2O by the molar mass of 2H and the reciprocal of the molar mass of H_2O. Then use the masses to calculate the mass percentages. Calculate O by difference.

$$14.67 \text{ mg } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 4.0033 \text{ mg C}$$

$$3.01 \text{ mg } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } CO_2} \times \frac{2 \text{ H}}{1 \text{ } H_2O} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.3368 \text{ mg H}$$

Mass O = 5.23 mg − (4.0033 + 0.3368) = 0.8899 mg O

Percent C = (4.0033 mg/5.23 mg) x 100% = 76.54 = 76.5%

Percent H = (0.3368 mg/5.23 mg) x 100% = 6.439 = 6.44%

Percent O = (0.8899 mg/5.23 mg) x 100% = 17.0 = 17%

3.65. Start by calculating the moles of Os and O; then divide each by the smaller number of moles to obtain integers for the empirical formula.

$$\text{Mol Os} = 2.16 \text{ g Os} \times \frac{1 \text{ mol Os}}{190.2 \text{ g Os}} = 0.01136 \text{ mol (smaller number)}$$

$$\text{Mol O} = (2.89 - 2.16) \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0456 \text{ mol}$$

Integer for Os = 0.01136 ÷ 0.01136 = 1.000

Integer for O = 0.0456 ÷ 0.01136 = 4.01

Within experimental error, the empirical formula is OsO_4.

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3.66. Start by calculating the moles of W and O; then divide each by the smaller number of moles to obtain integers for the empirical formula.

$$\text{Mol W} = 4.23 \text{ g W} \times \frac{1 \text{ mol W}}{183.85 \text{ g W}} = 0.02301 \text{ mol (smaller number)}$$

$$\text{Mol O} = (5.34 - 4.23) \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.06938 \text{ mol}$$

Integer for W = 0.02301 ÷ 0.02301 = 1.000

Integer for O = 0.06938 ÷ 0.02301 = 3.015

Because 3.015 = 3.0 within experimental error, the empirical formula is WO_3

3.67. Assume a sample of 100.0 g of potassium manganate. By multiplying this by the percentage composition, we obtain 39.6 g of K, 27.9 g of Mn, and 32.5 g of O. Convert each of these masses to moles by dividing by molar mass.

$$\text{Mol K} = 39.6 \text{ g K} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} = 1.013 \text{ mol}$$

$$\text{Mol Mn} = 29.7 \text{ g Mn} \times \frac{1 \text{ mol Mn}}{54.94 \text{ g Mn}} = 0.5078 \text{ mol (smallest number)}$$

$$\text{Mol O} = 32.5 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.031 \text{ mol}$$

Now, divide each number of moles by the smallest number to obtain the smallest set of integers for the empirical formula.

Integer for K = 1.013 ÷ 0.5078 = 1.998, or 2

Integer for Mn = 0.5078 ÷ 0.5078 = 1.000, or 1

Integer for O = 2.031 ÷ 0.5078 = 3.999, or 4

The empirical formula is thus K_2MnO_4.

3.68. Assume a sample of 100.0 g of hydroquinone. By multiplying this by the percentage composition, we obtain 65.4 g of C, 5.5 g of H, and 29.1 g of O. Convert each of these masses to moles by dividing by the molar mass.

$$\text{Mol C} = 65.4 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 5.445 \text{ mol}$$

$$\text{Mol H} = 5.5 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 5.46 \text{ mol}$$

$$\text{Mol O} = 29.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.819 \text{ mol (smallest number)}$$

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Now, divide each number of moles by the smallest number to obtain the smallest set of integers for the empirical formula.

Integer for C = 5.445 ÷ 1.819 = 2.99, or 3

Integer for H = 5.46 ÷ 1.819 = 3.0, or 3

Integer for O = 1.819 ÷ 1.819 = 1.00, or 1

The empirical formula is thus C_3H_3O.

3.69. Assume a sample of 100.0 g of acrylic acid. By multiplying this by the percentage composition, we obtain 50.0 g C, 5.6 g H, and 44.4 g O. Convert each of these masses to moles by dividing by the molar mass.

$$\text{Mol C} = 50.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.163 \text{ mol}$$

$$\text{Mol H} = 5.6 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 5.56 \text{ mol}$$

$$\text{Mol O} = 44.0 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.775 \text{ mol (smallest number)}$$

Now, divide each number of moles by the smallest number to obtain the smallest number of moles and the tentative integers for the empirical formula.

Tentative integer for C = 4.163 ÷ 2.775 = 1.50, or 1.5

Tentative integer for H = 5.56 ÷ 2.775 = 2.00, or 2

Tentative integer for O = 2.775 ÷ 2.775 = 1.00, or 1

Because 1.5 is not a whole number, multiply each tentative integer by 2 to obtain the final integer for the empirical formula:

C: 2 x 1.5 = 3

H: 2 x 2 = 4

O: 2 x 1 = 2

The empirical formula is thus $C_3H_4O_2$.

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3.70. Assume a sample of 100.0 g of malonic acid. By multiplying this by the percentage composition, we obtain 34.6 g C, 3.9 g H, and 61.5 g O. Convert each of these masses to moles by dividing by the molar mass.

$$\text{Mol C} = 34.6 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.881 \text{ mol (smallest number)}$$

$$\text{Mol H} = 3.9 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 3.87 \text{ mol}$$

$$\text{Mol O} = 61.5 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.844 \text{ mol}$$

Now, divide each number of moles by the smallest number to obtain the smallest number of moles and the tentative integers for the empirical formula.

Tentative integer for C = 2.881 ÷ 2.881 = 1.00, or 1

Tentative integer for H = 3.87 ÷ 2.881 = 1.34, or 4/3

Tentative integer for O = 3.884 ÷ 2.881 = 1.334, or 4/3

Because 4/3 is not a whole number, multiply each tentative integer by 3 to give the final integer for the empirical formula:

C: 3 x 1 = 3

H: 3 x 4/3 = 4

O: 3 x 4/3 = 4

The empirical formula is thus $C_3H_4O_4$.

3.71.

a. Assume for the calculation that you have 100.0 g; of this quantity, 92.25 g is C and 7.75 g is H. Now, convert these masses to moles:

$$92.25 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.6809 \text{ mol C}$$

$$7.75 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 7.688 \text{ mol H}$$

Usually, you divide all the mole numbers by the smaller one, but in this case the mole numbers are equal, so the ratio of the number of C atoms to the number of H atoms is 1:1. Thus, the empirical formula for both compounds is CH.

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b. Obtain *n*, the number of empirical formula units in the molecule, by dividing the molecular mass of 52.03 amu and 78.05 amu by the empirical formula mass of 13.018 amu:

$$\text{For 52.03: } n = \frac{52.03 \text{ amu}}{13.018 \text{ amu}} = 3.996\underline{8}, \text{ or } 4$$

$$\text{For 78.05: } n = \frac{78.05 \text{ amu}}{13.018 \text{ amu}} = 5.995\underline{5}, \text{ or } 6$$

The molecular formulas are as follows: for 52.03, $(CH)_4$ or C_4H_4; for 78.05, $(CH)_6$ or C_6H_6.

3.72.

a. Assume for the calculation that you have 100.0 g; of this quantity, 85.62 g is C and 14.38 g is H. Now convert these masses to moles:

$$85.62 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.12\underline{9}05 \text{ mol C}$$

$$14.38 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 14.\underline{2}6 \text{ mol H}$$

Divide both mole numbers by the smaller one:

$$\text{For C: } \frac{7.129 \text{ mol}}{7.129 \text{ mol}} = 1.0\underline{0}$$

$$\text{For H: } \frac{14.26 \text{ mol}}{7.129 \text{ mol}} = 2.00\underline{0}2$$

The empirical formula is obviously CH_2.

b. Obtain *n*, the number of empirical formula units in the molecule, by dividing the molecular masses of 28.03 amu and 56.06 amu by the empirical formula weight of 14.026 amu:

$$\text{For 28.03: } n = \frac{28.03 \text{ amu}}{14.026 \text{ amu}} = 1.998\underline{4}, \text{ or } 2$$

$$\text{For 56.06: } n = \frac{56.06 \text{ amu}}{14.026 \text{ amu}} = 3.996\underline{8}, \text{ or } 4$$

The molecular formulas are as follows: for 28.03, $(CH_2)_2$ or C_2H_4; for 56.06, $(CH_2)_4$ or C_4H_8.

3.73. The formula mass corresponding to the empirical formula C_2H_6N may be found by adding the respective atomic masses.

$$\text{Formula mass} = (2 \times 12.01 \text{ amu}) + (6 \times 1.008 \text{ amu}) + 14.01 \text{ amu}$$

$$= 44.08 \text{ amu}$$

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Dividing the molecular mass by the formula mass gives the number of times the C_2H_6N unit occurs in the molecule. Because the molecular mass is an average of 88.5 ([90 + 87] ÷ 2), this quotient is

88.5 amu ÷ 44.1 amu = 2.006, or 2

Therefore, the molecular formula is $(C_2H_6N)_2$, or $C_4H_{12}N_2$.

3.74. The formula mass corresponding to the empirical formula BH_3 may be found by adding the respective atomic masses.

Formula mass = 10.81 amu + (3 x 1.008 amu) = 13.83 amu

Dividing the molecular mass by the formula mass gives the number of times the BH_3 unit occurs in the molecule. Because the molecular mass is 28 amu, this quotient is

28 amu ÷ 13.83 amu = 2.02

Therefore, the molecular formula is $(BH_3)_2$, or B_2H_6.

3.75. Assume a sample of 100.0 g of oxalic acid. By multiplying this by the percentage composition, we obtain 26.7 g C, 2.2 g H, and 71.1 g O. Convert each of these masses to moles by dividing by the molar mass.

$$\text{Mol C} = 26.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.223 \text{ mol}$$

$$\text{Mol H} = 2.2 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 2.18 \text{ mol (smallest number)}$$

$$\text{Mol O} = 71.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 4.443 \text{ mol}$$

Now, divide each number of moles by the smallest number to obtain the smallest set of integers for the empirical formula.

Integer for C = 2.223 ÷ 2.18 = 1.02, or 1

Integer for H = 2.18 ÷ 2.18 = 1.00, or 1

Integer for O = 4.443 ÷ 2.18 = 2.038, or 2

The empirical formula is thus CHO_2. The formula mass corresponding to this formula may be found by adding the respective atomic masses:

Formula mass = 12.01 amu + 1.008 amu + (2 x 16.00 amu) = 45.02 amu

Dividing the molecular mass by the formula mass gives the number of times the CHO_2 unit occurs in the molecule. Because the molecular mass is 90 amu, this quotient is

90 amu ÷ 45.02 amu = 2.00, or 2

The molecular formula is thus $(CHO_2)_2$, or $C_2H_2O_4$.

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3.76. Assume a sample of 100.0 g of adipic acid. By multiplying this by the percentage composition, we obtain 49.3 g C, 6.9 g H, and 43.8 g O. Convert each of these masses to moles by dividing by the molar mass.

$$\text{Mol C} = 49.3 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.1\underline{0}5 \text{ mol}$$

$$\text{Mol H} = 6.9 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 6.\underline{8}5 \text{ mol}$$

$$\text{Mol O} = 43.8 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.7\underline{3}8 \text{ mol (smallest number)}$$

Now, divide each number of moles by the smallest number to obtain the smallest set of integers for the empirical formula.

Tentative integer for C = 4.105 ÷ 2.738 = 1.4$\underline{9}$9, or 1.5

Tentative integer for H = 6.85 ÷ 2.738 = 2.$\underline{5}$0, or 2.5

Tentative integer for O = 2.738 ÷ 2.738 = 1.0$\underline{0}$0, or 1

Because 1.5 and 2.5 are not whole numbers, multiply each tentative integer by 2 to give the final integers for the empirical formula:

C: 2 x 1.5 = 3

H: 2 x 2.5 = 5

O: 2 x 1 = 2

The empirical formula is thus $C_3H_5O_2$. The formula mass corresponding to this formula may be found by adding the respective atomic masses:

Formula mass = (3 x 12.01 amu) + (5 x 1.008 amu) + (2 x 16.00 amu) = 73.1 amu

Dividing the molecular mass by the formula mass gives the number of times the CHO_2 unit occurs in the molecule. Because the molecular mass is 146 amu, this quotient is

146 amu ÷ 73.1 amu = 2.$\underline{0}$0, or 2

The molecular formula is thus $(C_3H_5O_2)_2$, or $C_6H_{10}O_4$.

3.77.

C_2H_4	+	$3O_2$	$\rightarrow$	$2CO_2$	+	$2H_2O$
1 molecule C_2H_4	+	3 molecules O_2	$\rightarrow$	2 molecules CO_2	+	2 molecules H_2O
1 mole C_2H_4	+	3 moles O_2	$\rightarrow$	2 moles CO_2	+	2 moles H_2O
28.052 g C_2H_4	+	3 x 32.00 g O_2	$\rightarrow$	2 x 44.01 g CO_2	+	2 x 18.016 g H_2O

3.78.

$2H_2S$	+	$3O_2$	$\rightarrow$	$2SO_2$	+	$2H_2O$
2 molecules H_2S	+	3 molecules O_2	$\rightarrow$	2 molecules SO_2	+	2 molecules H_2O
2 moles H_2S	+	3 moles O_2	$\rightarrow$	2 moles SO_2	+	2 moles H_2O
2 x 34.09 g H_2S	+	3 x 32.00 g O_2	$\rightarrow$	2 x 64.07 g CO_2	+	2 x 18.016 g H_2O

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3.79. By inspecting the balanced equation, obtain a conversion factor of eight mol CO_2 to two mol C_4H_{10}. Multiply the given amount of 0.30 mole of C_4H_{10} by the conversion factor to obtain the moles of CO_2.

$$0.30 \text{ mol } C_4H_{10} \times \frac{8 \text{ mol } CO_2}{2 \text{ mol } C_4H_{10}} = 1.\underline{2}0 = 1.2 \text{ mol } CO_2$$

3.80. By inspecting the balanced equation, obtain a conversion factor of three mol H_2O to one mol C_2H_5OH. Multiply the given amount of 0.69 mol of C_2H_5OH by the conversion factor to obtain the moles of H_2O.

$$0.69 \text{ mol } C_2H_5OH \times \frac{3 \text{ mol } H_2O}{1 \text{ mol } C_2H_5OH} = 2.\underline{0}7 = 2.1 \text{ mol } H_2O$$

3.81. By inspecting the balanced equation, obtain a conversion factor of three mol O_2 to two mol Fe_2O_3. Multiply the given amount of 3.91 mol Fe_2O_3 by the conversion factor to obtain moles of O_2.

$$3.91 \text{ mol } Fe_2O_3 \times \frac{3 \text{ mol } O_2}{2 \text{ mol } Fe_2O_3} = 5.8\underline{6}5 = 5.87 \text{ mol } O_2$$

3.82. By inspecting the balanced equation, obtain a conversion factor of three mol $NiCl_2$ to one mol $Ni_3(PO_4)_2$. Multiply the given amount of 0.517 mol $Ni_3(PO_4)_2$ by the conversion factor to obtain moles of $NiCl_2$.

$$0.517 \text{ mol } Ni_3(PO_4)_2 \times \frac{3 \text{ mol } NiCl_2}{1 \text{ mol } Ni_3(PO_4)_2} = 1.5\underline{5}1 = 1.55 \text{ mol } NiCl_2$$

3.83. $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Three moles of NO_2 are equivalent to two moles of HNO_3 (from equation).

One mole of NO_2 is equivalent to 46.01 g NO_2 (from molecular mass of NO_2).

One mole of HNO_3 is equivalent to 63.02 g HNO_3 (from molecular mass of HNO_3).

$$7.50 \text{ g } HNO_3 \times \frac{1 \text{ mol } HNO_3}{63.02 \text{ g } HNO_3} \times \frac{3 \text{ mol } NO_2}{2 \text{ mol } HNO_3} \times \frac{46.01 \text{ g } NO_2}{1 \text{ mol } NO_2} = 8.2\underline{1}3$$

$$= 8.21 \text{ g } NO_2$$

3.84. $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 6CaSiO_3 + 10CO$

Two moles of $Ca_3(PO_4)_2$ are equivalent to one mole of P_4 (from equation).

One mol of P_4 is equivalent to 123.9 g P_4 (from molecular mass of P_4).

One mol of $Ca_3(PO_4)_2$ is equivalent to 310.2 g $Ca_3(PO_4)_2$ [from molecular mass of $Ca_3(PO_4)_2$].

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$$15.0 \text{ g } P_4 \times \frac{1 \text{ mol } P_4}{123.88 \text{ g } P_4} \times \frac{2 \text{ mol } Ca_3(PO_4)_2}{1 \text{ mol } P_4} \times \frac{310.18 \text{ g } Ca_3(PO_4)_2}{1 \text{ mol } Ca_3(PO_4)_2}$$

$$= 75.\underline{1}1 = 75.1 \text{ g } Ca_3(PO_4)_2$$

3.85. $WO_3 + 3H_2 \rightarrow W + 3H_2O$

One mole of W is equivalent to three moles of H_2 (from equation).

One mole of H_2 is equivalent to 2.016 g H_2 (from molecular mass of H_2).

One mole of W is equivalent to 183.8 g W (from atomic mass of W).

4.81 kg of H_2 is equivalent to 4.81×10^3 g of H_2.

$$4.81 \times 10^3 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{1 \text{ mol W}}{3 \text{ mol } H_2} \times \frac{183.85 \text{ g W}}{1 \text{ mol W}}$$

$$= 1.4\underline{6}2 \times 10^5 = 1.46 \times 10^5 \text{ g W}$$

3.86. $4C_3H_6 + 6NO \rightarrow 4C_3H_3N + 6H_2O + N_2$

Four moles of C_3H_6 are equivalent to four moles of C_3H_3N (from equation).

One mole of C_3H_6 is equivalent to 42.08 g C_3H_6 (from molecular mass of C_3H_6).

One mole of C_3H_3N is equivalent to 53.06 g C_3H_3N (from molecular mass of C_3H_3N).

452 kg of C_3H_6 are equivalent to 4.52×10^5 g C_3H_6.

$$4.52 \times 10^5 \text{ g } C_3H_6 \times \frac{1 \text{ mol } C_3H_6}{42.08 \text{ g } C_3H_6} \times \frac{4 \text{ mol } C_3H_3N}{4 \text{ mol } C_3H_6} \times \frac{53.06 \text{ g } C_3H_3N}{1 \text{ mol } C_3H_3N}$$

$$= 5.6\underline{9}9 \times 10^5 = 5.70 \times 10^5 \text{ g } C_3H_3N$$

3.87. Write the equation, and set up the calculation below the equation (after calculating the two molecular masses):

$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$

$$62.7 \text{ g } Cl_2 \times \frac{1 \text{ mol } Cl_2}{70.90 \text{ g } Cl_2} \times \frac{1 \text{ mol } CS_2}{3 \text{ mol } Cl_2} \times \frac{76.15 \text{ g } CS_2}{1 \text{ mol } CS_2} \quad 22.\underline{4}48 = 22.4 \text{ g } CS_2$$

3.88. From the molecular models, the balanced chemical equation is

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

The molar mass of NH_3 is 17.03 g/mol, and for O_2, it is 32.00 g/mol. This gives

$$6.1 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} \times \frac{5 \text{ mol } O_2}{4 \text{ mol } NH_3} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 1\underline{4}.32 = 14 \text{ g } O_2$$

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3.89. Write the equation, and set up the calculation below the equation (after calculating the two molecular masses):

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

$$1.315 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{4 \text{ mol } NO_2}{1 \text{ mol } O_2} \times \frac{46.01 \text{ g } NO_2}{1 \text{ mol } NO_2} = 7.562\underline{8} = 7.563 \text{ g } NO_2$$

3.90. Write the equation, and set up the calculation below the equation (after calculating the two formula masses):

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$6.01 \text{ g } Cu(NO_3)_2 \times \frac{1 \text{ mol } Cu(NO_3)_2}{187.56 \text{ g } Cu(NO_3)_2} \times \frac{2 \text{ mol NO}}{3 \text{ mol } Cu(NO_3)_2} \times \frac{30.01 \text{ g NO}}{1 \text{ mol NO}}$$

$$= 0.641\underline{0} = 0.641 \text{ g NO}$$

3.91. First determine whether KO_2 or H_2O is the limiting reactant by calculating the moles of O_2 that each would form if it were the limiting reactant. Identify the limiting reactant by the smaller number of moles of O_2 formed.

$$0.15 \text{ mol } H_2O \times \frac{3 \text{ mol } O_2}{2 \text{ mol } H_2O} = 0.22\underline{5} \text{ mol } O_2$$

$$0.25 \text{ mol } KO_2 \times \frac{3 \text{ mol } O_2}{4 \text{ mol } KO_2} = 0.18\underline{7} \text{ mol } O_2 \text{ } (KO_2 \text{ is the limiting reactant.})$$

Moles of O_2 produced = 0.19 mol

3.92. First, determine whether NaOH or Cl_2 is the limiting reactant by calculating the moles of NaClO that each would form if it were the limiting reactant. Identify the limiting reactant by the smaller number of moles of NaClO formed.

$$1.23 \text{ mol NaOH} \times \frac{1 \text{ mol NaClO}}{2 \text{ mol NaOH}} = 0.615 \text{ mol NaClO (smaller number)}$$

$$1.47 \text{ mol } Cl_2 \times \frac{1 \text{ mol NaClO}}{1 \text{ mol } Cl_2} = 1.47 \text{ mol NaClO}$$

NaOH is the limiting reactant, and 0.615 mol of NaClO will form.

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3.93. First determine whether CO or H_2 is the limiting reactant by calculating the moles of CH_3OH that each would form if it were the limiting reactant. Identify the limiting reactant by the smaller number of moles of CH_3OH formed. Use the molar mass of CH_3OH to calculate the mass of CH_3OH formed. Then calculate the mass of the unconsumed reactant.

$$CO + 2H_2 \rightarrow CH_3OH$$

$$10.2 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{1 \text{ mol } CH_3OH}{2 \text{ mol } H_2} = 2.529 \text{ mol } CH_3OH$$

$$35.4 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} \times \frac{1 \text{ mol } CH_3OH}{1 \text{ mol CO}} = 1.263 \text{ mol } CH_3OH$$

CO is the limiting reactant.

$$\text{Mass } CH_3OH \text{ formed} = 1.263 \text{ mol } CH_3OH \times \frac{32.042 \text{ g } CH_3OH}{1 \text{ mol } CH_3OH}$$

$$= 40.47 = 40.5 \text{g } CH_3OH$$

Hydrogen is left unconsumed at the end of the reaction. The mass of H_2 that reacts can be calculated from the moles of product obtained:

$$1.263 \text{ mol } CH_3OH \times \frac{2 \text{ mol } H_2}{1 \text{ mol } CH_3OH} \times \frac{2.016 \text{ g } H_2}{1 \text{ mol } H_2} = 5.092 \text{ g } H_2$$

$$\text{Unreacted } H_2 = 10.2 \text{ g total } H_2 - 5.092 \text{ g reacted } H_2 = 5.108 = 5.1 \text{ g } H_2$$

3.94. First, determine whether CS_2 or O_2 is the limiting reactant by calculating the moles of SO_2 that each would form if it were the limiting reactant. Identify the limiting reactant by the smaller number of moles of SO_2 formed. Use the molar mass of SO_2 to calculate the mass of SO_2 formed. Then calculate the mass of the unconsumed reactant.

$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$$

$$30.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{2 \text{ mol } SO_2}{3 \text{ mol } O_2} = 0.6250 \text{ mol } SO_2$$

$$35.0 \text{ g } CS_2 \times \frac{1 \text{ mol } CS_2}{76.15 \text{ g } CS_2} \times \frac{2 \text{ mol } SO_2}{1 \text{ mol } CS_2} = 0.9192 \text{ mol } SO_2$$

O_2 is the limiting reactant.

$$\text{Mass } SO_2 \text{ formed} = 0.6250 \text{ mol } SO_2 \times \frac{64.07 \text{ g } SO_2}{1 \text{ mol } SO_2} = 40.04 = 40.0 \text{ g}$$

CS_2 is left unconsumed at the end of the reaction. The mass of CS_2 that reacts can be calculated from the moles of product obtained:

$$0.6250 \text{ mol } SO_2 \times \frac{1 \text{ mol } CS_2}{2 \text{ mol } SO_2} \times \frac{76.15 \text{ g } CS_2}{1 \text{ mol } CS_2} = 23.79 \text{ g } CS_2$$

$$\text{Unreacted } CS_2 = 35.0 \text{ g total } CS_2 - 23.79 \text{ g reacted } CS_2 = 11.20 = 11.2 \text{ g } CS_2$$

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3.95. First, determine which of the three reactants is the limiting reactant by calculating the moles of $TiCl_4$ that each would form if it were the limiting reactant. Identify the limiting reactant by the smallest number of moles of $TiCl_4$ formed. Use the molar mass of $TiCl_4$ to calculate the mass of $TiCl_4$ formed.

$$3TiO_2 + 4C + 6Cl_2 \rightarrow 3TiCl_4 + 2CO_2 + 2CO$$

$$4.15 \text{ g } TiO_2 \times \frac{1 \text{ mol } TiO_2}{79.88 \text{ g } TiO_2} \times \frac{3 \text{ mol } TiCl_4}{3 \text{ mol } TiO_2} = 0.05195 \text{ mol } TiCl_4$$

$$5.67 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{3 \text{ mol } TiCl_4}{4 \text{ mol C}} = 0.35407 \text{ mol } TiCl_4$$

$$6.78 \text{ g } Cl_2 \times \frac{1 \text{ mol } Cl_2}{70.90 \text{ g } Cl_2} \times \frac{3 \text{ mol } TiCl_4}{6 \text{ mol } Cl_2} = 0.04781 \text{ mol } TiCl_4$$

Cl_2 is the limiting reactant.

$$\text{Mass } TiCl_4 \text{ formed} = 0.04781 \text{ mol } TiCl_4 \times \frac{189.68 \text{ g } TiCl_4}{1 \text{ mol } TiCl_4} = 9.068 = 9.07 \text{ g } TiCl_4$$

3.96. First, determine which of the three reactants is the limiting reactant by calculating the moles of HCN that each would form if it were the limiting reactant. Identify the limiting reactant by the smallest number of moles of HCN formed. Use the molar mass of HCN to calculate the mass of HCN formed.

$$2NH_3 + 3O_2 + 2CH_4 \rightarrow 2HCN + 6H_2O$$

$$11.5 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} \times \frac{2 \text{ mol HCN}}{2 \text{ mol } NH_3} = 0.675 \text{ mol HCN}$$

$$10.5 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} \times \frac{2 \text{ mol HCN}}{2 \text{ mol } CH_4} = 0.654 \text{ mol HCN}$$

$$12.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{2 \text{ mol HCN}}{3 \text{ mol } O_2} = 0.2500 \text{ mol HCN}$$

O_2 is the limiting reactant.

$$\text{Mass HCN formed} = 0.2500 \text{ mol HCN} \times \frac{27.03 \text{ g HCN}}{1 \text{ mol HCN}} = 6.757 = 6.76 \text{ g HCN}$$

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3.97. First, determine which of the two reactants is the limiting reactant by calculating the moles of aspirin that each would form if it were the limiting reactant. Identify the limiting reactant by the smallest number of moles of aspirin formed. Use the molar mass of aspirin to calculate the theoretical yield in grams of aspirin. Then calculate the percentage yield.

$$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$$

$$4.00 \text{ g } C_4H_6O_3 \times \frac{1 \text{ mol } C_4H_6O_3}{102.09 \text{ g } C_4H_6O_3} \times \frac{1 \text{ mol } C_9H_8O_4}{1 \text{ mol } C_4H_6O_3} = 0.039\underline{1}8 \text{ mol } C_9H_8O_4$$

$$2.00 \text{ g } C_7H_6O_3 \times \frac{1 \text{ mol } C_7H_6O_3}{138.12 \text{ g } C_7H_6O_3} \times \frac{1 \text{ mol } C_9H_8O_4}{1 \text{ mol } C_7H_6O_3} = 0.014\underline{4}8 \text{ mol } C_9H_8O_4$$

Thus, $C_7H_6O_3$ is the limiting reactant. The theoretical yield of $C_9H_8O_4$ is

$$0.014\underline{4}8 \text{ mol } C_9H_8O_4 \times \frac{180.15 \text{ g } C_9H_8O_4}{1 \text{ mol } C_9H_8O_4} = 2.6\underline{0}9 \text{ g } C_9H_8O_4$$

The percentage yield is

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{1.86 \text{ g}}{2.609 \text{ g}} \times 100\% = 71.\underline{2}9 = 71.3\%$$

3.98. First, determine which of the two reactants is the limiting reactant by calculating the moles of methyl salicylate that each would form if it were the limiting reactant. Identify the limiting reactant by the smallest number of moles of methyl salicylate formed. Use the molar mass of methyl salicylate to calculate the theoretical yield in grams of methyl salicylate. Then calculate the percentage yield.

$$C_7H_6O_3 + CH_3OH \rightarrow C_8H_8O_3 + H_2O$$

$$11.20 \text{ g } CH_3OH \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} \times \frac{1 \text{ mol } C_8H_8O_3}{1 \text{ mol } CH_3OH} = 0.34\underline{9}6 \text{ mol } C_8H_8O_3$$

$$1.50 \text{ g } C_7H_6O_3 \times \frac{1 \text{ mol } C_7H_6O_3}{138.12 \text{ g } C_7H_6O_3} \times \frac{1 \text{ mol } C_8H_8O_3}{1 \text{ mol } C_7H_6O_3} = 0.010\underline{8}6 \text{ mol } C_8H_8O_3$$

Thus, $C_7H_6O_3$ is the limiting reactant. The theoretical yield of $C_8H_8O_3$ is

$$0.010\underline{8}6 \text{ mol } C_8H_8O_3 \times \frac{152.14 \text{ g } C_8H_8O_3}{1 \text{ mol } C_8H_8O_3} = 1.6\underline{5}2 \text{ g } C_8H_8O_3$$

The percentage yield is

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{1.27 \text{ g}}{1.652 \text{ g}} \times 100\% = 76.\underline{8}7 = 76.9\%$$

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SOLUTIONS TO GENERAL PROBLEMS

3.99. For 1 mol of caffeine, there are eight mol of C, ten mol of H, four mol of N, and two mol of O. Convert these amounts to masses by multiplying them by their respective molar masses:

8 mol C x 12.01 g C/1 mol C	=	96.08 g C
10 mol H x 1.008 g H/1 mol H	=	10.08 g H
4 mol N x 14.01 g N/1 mol N	=	56.04 g N
2 mol O x 16.00 g O/1 mol O	=	32.00 g O
1 mol of caffeine (total)	=	194.20 g (molar mass)

Each mass percentage is calculated by dividing the mass of the element by the molar mass of caffeine and multiplying by 100 percent: Mass percentage = (mass element ÷ mass caffeine) x 100%.

Mass percentage C = (96.08 g ÷ 194.20 g) x 100% = 49.5% (3 s.f.)

Mass percentage H = (10.08 g ÷ 194.20 g) x 100% = 5.19% (3 s.f.)

Mass percentage N = (56.04 g ÷ 194.20 g) x 100% = 28.9% (3 s.f.)

Mass percentage O = (32.00 g ÷ 194.20 g) x 100% = 16.5% (3 s.f.)

3.100. For each mole of morphine, there are 17 mol C, 19 mol H, 1 mol N, and 3 mol O. Convert these amounts to masses by multiplying by the respective molar masses:

17 mol C x 12.01 g C/1 mol C	=	204.17 g C
19 mol H x 1.008 g H/1 mol H	=	19.15 g H
1 mol N x 14.01 g N/1 mol N	=	14.01 g N
3 mol O x 16.00 g O/1 mol O	=	48.00 g O
1 mol of morphine (total)	=	285.33 g (molar mass)

Each mass percentage is calculated by dividing the mass of the element by the molar mass of morphine and multiplying by 100%: Mass percentage = (mass element ÷ mass morphine) x 100%.

Mass percentage C = (204.17 g ÷ 285.33 g) x 100% = 71.6% (3 s.f.)

Mass percentage H = (19.15 g ÷ 285.33 g) x 100% = 6.71% (3 s.f.)

Mass percentage N = (14.01 g ÷ 285.33 g) x 100% = 4.91% (3 s.f.)

Mass percentage O = (48.00 g ÷ 285.33 g) x 100% = 16.8% (3 s.f.)

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3.101. Assume a sample of 100.0 g of dichlorobenzene. By multiplying this by the percentage composition, we obtain 49.1 g C, 2.7 g of H, and 48.2 g of Cl. Convert each mass to moles by dividing by the molar mass:

$$49.1 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.088 \text{ mol C}$$

$$2.7 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 2.68 \text{ mol H}$$

$$48.2 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 1.360 \text{ mol Cl}$$

Divide each number of moles by the smallest number to obtain the smallest set of integers for the empirical formula.

Integer for C = 4.088 mol ÷ 1.360 mol = 3.00, or 3

Integer for H = 2.68 mol ÷ 1.360 mol = 1.97, or 2

Integer for Cl = 1.360 mol ÷ 1.360 mol = 1.00, or 1

The empirical formula is thus C_3H_2Cl. Find the formula mass by adding the atomic masses:

Formula mass = (3 x 12.01 amu) + (2 x 1.008 amu) + 35.45 amu

= 73.496 = 73.50 amu

Divide the molecular mass by the formula mass to find the number of times the C_3H_2Cl unit occurs in the molecule. Because the molecular mass is 147 amu, this quotient is

147 amu ÷ 73.50 amu = 2.00, or 2

The molecular formula is $(C_3H_2Cl)_2$, or $C_6H_4Cl_2$.

3.102. Assume a sample of 100.0 g of sorbic acid. By multiplying this by the percentage composition, we obtain 64.3 g C, 7.2 g H, and 28.5 g O. Convert each mass to moles by dividing by the molar mass.

$$64.3 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 5.353 \text{ mol C}$$

$$7.2 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 7.14 \text{ mol H}$$

$$28.5 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.781 \text{ mol O}$$

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Divide each number of moles by the smallest number to obtain the smallest set of integers for the empirical formula.

Integer for C = 5.353 mol ÷ 1.781 mol = 3.01, or 3

Integer for H = 7.14 mol ÷ 1.781 mol = 4.0, or 4

Integer for O = 1.781 mol ÷ 1.781 mol = 1.00, or 1

The empirical formula is thus C_3H_4O.

Find the formula mass by adding the atomic masses:

Formula mass = (3 x 12.01 amu) + (4 x 1.008 amu) + 16.00 amu

= 56.062 = 56.06 amu

Divide the molecular mass by the formula mass to find the number of times the C_3H_4O unit occurs in the molecule. Because the molecular mass was given as 112 amu, this quotient is

112 amu ÷ 56.06 amu = 2.00, or 2

The molecular formula is $(C_3H_4O)_2$, or $C_6H_8O_2$.

3.103. Find the percentage composition of C and S from the analysis:

$$0.01665 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 0.004544 \text{ g C}$$

Percent C = (0.004544 g C ÷ 0.00796 g comp.) x 100% = 57.09%

$$0.01196 \text{ g } BaSO_4 \times \frac{1 \text{ mol } BaSO_4}{233.39 \text{ g } BaSO_4} \times \frac{1 \text{ mol S}}{1 \text{ mol } BaSO_4} \times \frac{32.07 \text{ g S}}{1 \text{ mol S}} = 0.001643 \text{ g S}$$

Percent S = (0.001643 g S ÷ 0.00431 g comp.) x 100% = 38.12%

Percent H = 100.00% − (57.09 + 38.12)% = 4.79%

We now obtain the empirical formula by calculating moles from the grams corresponding to each mass percentage of element:

$$57.09 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.754 \text{ mol C}$$

$$38.12 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 1.189 \text{ mol S}$$

$$4.79 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.752 \text{ mol H}$$

Dividing the moles of the elements by the smallest number (1.189), we obtain for C: 3.997, or 4; for S: 1.000, or 1; and for H: 3.996, or 4. Thus, the empirical formula is C_4H_4S (formula mass = 84). Because the formula mass was given as 84 amu, the molecular formula is also C_4H_4S.

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3.104. Find the percentage composition of H and N from the analysis:

$$0.00663 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.0007417 \text{ g H}$$

1.46 mg N_2 from the analysis is equivalent to 0.00146 g N.

Percent H = (0.0007417 g H ÷ 0.00971 g comp.) x 100% = 7.64%

Percent N = (0.00146 g N ÷ 0.00971 g comp.) x 100% = 15.0%

Percent C = 100.00% − (7.64 + 15.0)% = 77.4%

Calculate the moles from grams to obtain the empirical formula:

$$77.4 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 6.44 \text{ mol C}$$

$$7.64 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 7.58 \text{ mol H}$$

$$15.0 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.07 \text{ mol N}$$

Dividing the moles of elements by the smallest number (1.07) gives for C: 6.02, or 6; for H: 7.08, or 7; and for N: 1.00, or 1. The empirical formula is thus C_6H_7N (formula mass = 93 amu). Because the molecular mass was given as 93 amu, the molecular formula is also C_6H_7N.

3.105. For g $CaCO_3$, use this equation: $CaCO_3 + H_2C_2O_4 \rightarrow CaC_2O_4 + H_2O + CO_2$.

$$0.472 \text{ g } CaC_2O_4 \times \frac{1 \text{ mol } CaC_2O_4}{128.10 \text{ g } CaC_2O_4} \times \frac{1 \text{ mol } CaCO_3}{1 \text{ mol } CaC_2O_4} \times \frac{100.09 \text{ g } CaCO_3}{1 \text{ mol } CaCO_3}$$

$$= 0.3688 \text{ g } CaCO_3$$

$$\text{Mass percentage } CaCO_3 = \frac{\text{mass } CaCO_3}{\text{mass limestone}} \times 100\% = \frac{0.3688 \text{ g}}{0.438 \text{ g}} \times 100\%$$

$$= 84.19 = 84.2\%$$

3.106. For the mass of TiO_2, use this equation: $TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$.

$$35.4 \text{ g } TiCl_4 \times \frac{1 \text{ mol } TiCl_4}{189.68 \text{ g } TiCl_4} \times \frac{1 \text{ mol } TiO_2}{1 \text{ mol } TiCl_4} \times \frac{79.88 \text{ g } TiO_2}{1 \text{ mol } TiO_2} = 14.91 \text{ g } TiO_2$$

$$\text{Mass percentage } TiO_2 = \frac{\text{mass } TiO_2}{\text{mass rutile}} \times 100\% = \frac{14.91 \text{ g}}{17.4 \text{ g}} \times 100\% = 85.68 = 85.7\%$$

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3.107. Calculate the theoretical yield using this equation: $2C_2H_4 + O_2 \rightarrow 2C_2H_4O$.

$$10.6\text{ g } C_2H_4 \times \frac{1\text{ mol } C_2H_4}{28.05\text{ g } C_2H_4} \times \frac{2\text{ mol } C_2H_4O}{2\text{ mol } C_2H_4} \times \frac{44.05\text{ g } C_2H_4O}{1\text{ mol } C_2H_4O} = 16.\underline{6}5\text{ g } C_2H_4O$$

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{9.91\text{ g}}{16.65\text{ g}} \times 100\% = 59.\underline{5}3 = 59.5\%$$

3.108. Calculate the theoretical yield using this equation:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

$$22.4\text{ g } C_6H_6 \times \frac{1\text{ mol } C_6H_6}{78.11\text{ g } C_6H_6} \times \frac{1\text{ mol } C_6H_5NO_2}{1\text{ mol } C_6H_6} \times \frac{123.11\text{ g } C_6H_5NO_2}{1\text{ mol } C_6H_5NO_2}$$

$$= 35.\underline{3}0\text{ g } C_6H_5NO_2$$

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{31.6\text{ g}}{35.\underline{3}0\text{ g}} \times 100\% = 89.\underline{5}1 = 89.5\%$$

3.109. To find Zn, use these equations:

$$2C + O_2 \rightarrow 2CO \text{ and } ZnO + CO \rightarrow Zn + CO_2$$

Two moles of C produces 2 mol CO; because 1 mol ZnO reacts with 1 mol CO, 2 mol ZnO will react with 2 mol CO. Thus, 2 mol C is equivalent to 2 mol ZnO, or 1 mol C is equivalent to 1 mol ZnO.

Using this to calculate mass of C from mass of ZnO, we have

$$75.0\text{ g ZnO} \times \frac{1\text{ mol ZnO}}{81.39\text{ g ZnO}} \times \frac{1\text{ mol C}}{1\text{ mol ZnO}} \times \frac{12.01\text{ g C}}{1\text{ mol C}} = 11.\underline{0}7\text{ g C}$$

Thus, all of the ZnO is used up in reacting with just 11.07 g of C, making ZnO the limiting reactant. Use the mass of ZnO to calculate the mass of Zn formed:

$$75.0\text{ g ZnO} \times \frac{1\text{ mol ZnO}}{81.39\text{ g ZnO}} \times \frac{1\text{ mol Zn}}{1\text{ mol ZnO}} \times \frac{65.39\text{ g Zn}}{1\text{ mol Zn}} = 60.\underline{2}56 = 60.3\text{ g Zn}$$

3.110. To find CH_4, use these equations:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2NO + 2CH_4 \rightarrow 2HCN + 2H_2O + H_2$$

Four moles of NH_3 produces 4 mol NO; because 2 mol CH_4 reacts with 2 mol NO, 4 mol CH_4 will react with 4 mol NO. Thus, 4 mol NH_3 is equivalent to 4 mol CH_4. Using this to calculate the mass of CH_4 from the mass of NH_3, we have

$$24.2\text{ g } NH_3 \times \frac{1\text{ mol } NH_3}{17.03\text{ g } NH_3} \times \frac{4\text{ mol } CH_4}{4\text{ mol } NH_3} \times \frac{16.04\text{ g } CH_4}{1\text{ mol } CH_4} = 22.\underline{8}\text{ g } CH_4$$

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Thus, all of the NH_3 is used up in reacting with just 22.8 g of CH_4, making NH_3 the limiting reactant. Use the mass of NH_3 to calculate the mass of HCN formed:

$$24.2 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} \times \frac{4 \text{ mol HCN}}{4 \text{ mol } NH_3} \times \frac{27.03 \text{ g HCN}}{1 \text{ mol HCN}} = 38.\underline{4}1 = 38.4 \text{ g HCN}$$

3.111. For $CaO + 3C \rightarrow CaC_2 + CO$, find the limiting reactant in terms of moles of CaC_2 obtainable:

$$\text{Mol } CaC_2 = 2.60 \times 10^3 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{1 \text{ mol } CaC_2}{3 \text{ mol C}} = 72.\underline{1}6 \text{ mol}$$

$$\text{Mol } CaC_2 = 2.60 \times 10^3 \text{ g CaO} \times \frac{1 \text{ mol CaO}}{56.08 \text{ g CaO}} \times \frac{1 \text{ mol } CaC_2}{1 \text{ mol CaO}} = 46.\underline{3}62 \text{ mol}$$

Because CaO is the limiting reactant, calculate the mass of CaC_2 from it:

$$\text{Mass } CaC_2 = 46.\underline{3}62 \text{ mol } CaC_2 \times \frac{64.10 \text{ g } CaC_2}{1 \text{ mol } CaC_2} = 2.9\underline{7}1 \times 10^3 = 2.97 \times 10^3 \text{ g } CaC_2$$

3.112. For $CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$, find the limiting reactant in terms of moles of HF obtainable:

$$\text{Mol HF} = 11.9 \text{ g } CaF_2 \times \frac{1 \text{ mol } CaF_2}{78.08 \text{ g } CaF_2} \times \frac{2 \text{ mol HF}}{1 \text{ mol } CaF_2} = 0.30\underline{4}8 \text{ mol}$$

$$\text{Mol HF} = 10.3 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } H_2SO_4} \times \frac{2 \text{ mol HF}}{1 \text{ mol } H_2SO_4} = 0.21\underline{0}0 \text{ mol}$$

Because H_2SO_4 is the limiting reactant, calculate the mass of HF from it:

$$\text{Mass HF} = 0.2100 \text{ mol HF} \times \frac{20.01 \text{ g HF}}{1 \text{ mol HF}} = 4.2\underline{0}2 = 4.20 \text{ g HF}$$

3.113. From the equation $2Na + H_2O \rightarrow 2NaOH + H_2$, convert mass of H_2 to mass of Na, and then use the mass to calculate the percentage:

$$0.108 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Na}}{1 \text{ mol } H_2} \times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}} = 2.4\underline{6}3 \text{ g Na}$$

$$\text{Percent Na} = \frac{\text{mass Na}}{\text{mass amalgam}} \times 100\% = \frac{2.463 \text{ g}}{15.23 \text{ g}} \times 100\% = 16.\underline{1}7 = 16.2\%$$

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3.114. From the equation $CaCO_3 \rightarrow CaO + CO_2$, convert the mass of CO_2 to mass of $CaCO_3$, and then use the mass to calculate the percentage:

$$0.00395 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol } CaCO_3}{1 \text{ mol } CO_2} \times \frac{100.09 \text{ g } CaCO_3}{1 \text{ mol } CaCO_3}$$

$$= 0.008983 \text{ g } CaCO_3$$

$$\text{Percent } CaCO_3 = \frac{\text{mass } CaCO_3}{\text{mass sandstone}} \times 100\% = \frac{0.008983 \text{ g}}{0.0187 \text{ g}} \times 100\%$$

$$= 48.039 = 48.0\%$$

Because the sandstone contains only SiO_2 and $CaCO_3$, the difference between 100 percent and the percentage of $CaCO_3$ is the percentage of SiO_2:

$$\text{Percent } SiO_2(\text{silica}) = 100.00\% - 48.039\% = 51.96 = 52.0\%$$

3.115. The mass spectrometer measures the masses of positive ions produced from a very small sample and displays the data as a mass spectrum. This mass spectrum can be used to identify a substance or to obtain the molecular formula of a compound. The mass spectrum contains a wealth of information about molecular structure.

3.116. The mass spectrum of a molecule is much more complicated for several reasons. First, the molecular ions produced often break into fragments, giving several different kinds of positive ions. Second, many of the atoms in any ion can occur with different isotopic masses, so each ion often has many peaks.

■ SOLUTIONS TO STRATEGY PROBLEMS

3.117.

a. $$48 \text{ } O_2 \text{ molecules} \times \frac{2 \text{ } H_2 \text{ molec}}{1 \text{ } O_2 \text{ molec}} = 96 \text{ } H_2 \text{ molecules}$$

b. $$5 \text{ mol } H_2O \times \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O} = 2.5 \text{ mol } O_2$$

$$5 \text{ mol } H_2O \times \frac{2 \text{ mol } H_2}{2 \text{ mol } H_2O} = 5.0 \text{ mol } H_2$$

c. $$37.5 \text{ g } O_2 \times \frac{4.0 \text{ g } H_2}{32 \text{ g } O_2} = 4.68 = 4.7 \text{ g } H_2$$

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d. The mass of water formed is 4.0 g + 32 g = 3<u>6</u>.0 g

$$30.0 \text{ g } H_2O \times \frac{32 \text{ g } O_2}{36 \text{ g } H_2O} = 2\underline{6}.6 = 27 \text{ g } O_2$$

$$30.0 \text{ g } H_2O \times \frac{4.0 \text{ g } H_2}{36 \text{ g } H_2O} = 3.\underline{3}3 = 3.3 \text{ g } H_2$$

3.118. The balanced equation is $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$.

a. $$41 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{1 \text{ mol } Fe_2O_3}{2 \text{ mol Al}} = 0.7\underline{5}98 = 0.76 \text{ mol } Fe_2O_3$$

b. First, determine the limiting reactant.

$$99.1 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{2 \text{ mol Fe}}{2 \text{ mol Al}} = 3.6\underline{7}3 = 3.67 \text{ mol Fe}$$

$$3.14 \text{ mol } Fe_2O_3 \times \frac{2 \text{ mol Fe}}{1 \text{ mol } Fe_2O_3} = 6.2\underline{8} \text{ mol Fe}$$

Since the limiting reactant is Al, 3.67 mol Fe will form.

c. $$7.0 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} \times \frac{2 \text{ mol Al}}{2 \text{ mol Fe}} \times \frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{ mol}} = 7.\underline{5}4 \times 10^{22}$$

$$= 7.5 \times 10^{22} \text{ atoms}$$

3.119.

a. First, determine the limiting reactant.

$$25 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.086 \text{ g}} \times \frac{1 \text{ mol } K_2SO_4}{1 \text{ mol } H_2SO_4} \times \frac{174.27 \text{ g}}{1 \text{ mol } K_2SO_4} = 4\underline{4}.4 = 44 \text{ g}$$

$$7.7 \text{ g KOH} \times \frac{1 \text{ mol KOH}}{56.108 \text{ g}} \times \frac{1 \text{ mol } K_2SO_4}{2 \text{ mol KOH}} \times \frac{174.27 \text{ g}}{1 \text{ mol } K_2SO_4} = 1\underline{1}.95 = 12 \text{ g}$$

KOH is the limiting reactant, and 12 g K_2SO_4 is produced.

b. KOH is the limiting reactant. The mass of H_2SO_4 that reacts is

$$7.7 \text{ g KOH} \times \frac{1 \text{ mol KOH}}{56.108 \text{ g}} \times \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol KOH}} \times \frac{98.086 \text{ g}}{1 \text{ mol } H_2SO_4} = 6.\underline{7}3 \text{ g reacted}$$

The mass remaining after reaction is 25 g − 6.73 g = 1<u>8</u>.27 = 18 g.

c. The theoretical yield was determined in part a to be 1<u>1</u>.9 g. For an actual yield of 47.2%, the amount of K_2SO_4 formed is

$$11.95 \text{ g} \times 0.472 = 5.\underline{6}44 = 5.6 \text{ g}$$

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3.120.

a. First, determine the mass of C, H, and O in the compound.

$$\text{Mass C} = 0.561 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g}} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 0.15\underline{3}1 \text{ g}$$

$$\text{Mass H} = 0.306 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.018 \text{ g}} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.034\underline{2}3 \text{ g}$$

$$\text{Mass O} = 0.255 \text{ g} - 0.1531 \text{ g} - 0.03423 \text{ g} = 0.06\underline{7}6 \text{ g}$$

Next, determine the empirical formula.

$$\text{mol C} = 0.1531 \text{ g} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.012\underline{7}5 \text{ mol C}$$

$$\text{mol H} = 0.03423 \text{ g} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.033\underline{9}6 \text{ mol H}$$

$$\text{mol O} = 0.0676 \text{ g} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.004\underline{2}3 \text{ mol O}$$

Because the smallest number of moles is 0.00423 mol O, divide each molar quantity by this factor.

$$\frac{0.01275 \text{ mol C}}{0.00423 \text{ mol O}} = 3.0; \quad \frac{0.03396 \text{ mol H}}{0.00423 \text{ mol O}} = 8.0; \quad \frac{0.00423 \text{ mol O}}{0.00423 \text{ mol O}} = 1$$

Therefore, the empirical formula is C_3H_8O.

b. The empirical formula mass is 60.094 g/formula unit. Thus, the multiplication factor is

$$n = \frac{180 \text{ g/mol}}{60.094 \text{ g/unit}} = 2.99 = 3$$

The molecular formula of the compound is $C_9H_{24}O_3$.

3.121. The balance chemical equation is $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. The theoretical yield of NO is

$$8.5 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.034 \text{ g } NH_3} \times \frac{4 \text{ mol NO}}{4 \text{ mol } NH_3} \times \frac{30.01 \text{ g NO}}{1 \text{ mol NO}} = 1\underline{4}.97 \text{ g NO}$$

The percentage yield is

$$\text{Percentage Yield} = \frac{12.0 \text{ g}}{14.97 \text{ g}} \times 100\% = 8\underline{0}.1\% = 80.\%$$

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3.122. The fraction of Pb in Pb_3N_2 is

$$X = \frac{621.6 \text{ g Pb}}{649.62 \text{ g } Pb_3N_2} = 0.95687$$

The mass of lead in the paint is

$$\text{Mass Pb} = 27.5 \text{ g } Pb_3N_2 \times 0.95687 = 26.31 = 26.3 \text{ g Pb}$$

3.123. The fraction of O in Na_2SO_3 is

$$X_1 = \frac{48.00 \text{ g O}}{126.03 \text{ g } Na_2SO_3} = 0.38086$$

The fraction of O in $MgSO_4$ is

$$X_2 = \frac{64.00 \text{ g O}}{120.38 \text{ g } MgSO_4} = 0.53165$$

The total mass of oxygen present is

$$\text{Mass O} = (0.38086 \times 12.1 \text{ g}) + (0.53165 \times 15.5 \text{ g})$$
$$= 4.608 \text{ g} + 8.240 \text{ g} = 12.848 = 12.85 \text{ g}$$

3.124. First, calculate the mass of KO_2 actually used in the reaction.

$$195 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{4 \text{ mol } KO_2}{3 \text{ mol } O_2} \times \frac{71.10 \text{ g } KO_2}{1 \text{ mol } KO_2} = 577.68 \text{ g } KO_2 \text{ used}$$

Therefore, the KO_2 was not completely consumed in the reaction. The mass of KO_2 left over is $750 \text{ g} - 577.68 \text{ g} = 172.3 = 172 \text{ g}$.

The mass of additional oxygen that could be produced is

$$172.3 \text{ g } KO_2 \times \frac{1 \text{ mol } KO_2}{71.10 \text{ g } KO_2} \times \frac{3 \text{ mol } O_2}{4 \text{ mol } KO_2} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 58.16 = 58.2 \text{ g } O_2$$

3.125. $$175 \text{ tablets} \times \frac{68.4 \times 10^{-3} \text{ g}}{1 \text{ tablet}} \times \frac{1 \text{ mol } CaCO_3}{100.09 \text{ g } CaCO_3} = 0.1196 = 0.120 \text{ mol } CaCO_3$$

3.126. First, calculate the molar mass of the compound. Note that 6.61×10^5 mg = 661 g.

$$\text{Molar mass} = \frac{661 \text{ g}}{2.21 \text{ mol}} = 299.09 \text{ g/mol}$$

Lead has two main ionic forms, Pb^{2+} and Pb^{4+}. Either way, there is only one lead atom per formula unit. Thus the mass of nitrite per formula unit is

$$299.09 \text{ g/mol} - 207.2 \text{ g Pb/mol} = 91.89 \text{ g nitrite per formula unit.}$$

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The percent composition of nitrite is

$$\%NO_2^- = \frac{91.89 \text{ g } NO_2^-/\text{mol}}{299 \text{ g/mol}} \text{ x } 100\% = 30.73 = 31\%$$

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

3.127. Let y equal the mass of CuO in the mixture. Then 0.500 g − y equals the mass of Cu_2O in the mixture. Multiplying the appropriate conversion factors for Cu times the mass of each oxide will give one equation in one unknown for the mass of 0.425 g Cu:

$$0.425 = y\left[\frac{63.55 \text{ g Cu}}{79.55 \text{ g CuO}}\right] + (0.500 - y)\left[\frac{127.10 \text{ g Cu}}{143.10 \text{ g } Cu_2O}\right]$$

Simplifying the equation by dividing the conversion factors and combining terms gives

$$0.425 = 0.79887\, y + 0.888190\, (0.500 - y)$$

$$0.08932\, y = 0.019095$$

$$y = 0.2139 = 0.21 \text{ g} = \text{mass of CuO}$$

3.128. Let y equal the mass of Fe_2O_3 in the mixture. Then 0.500 g − y equals the mass of FeO in the mixture. The mass of Fe in the mixture is 0.720 x 0.500 g = 0.360 g. Multiplying the appropriate conversion factors for Fe times the mass of each oxide will give one equation in one unknown for the mass of 0.360 g Fe in the mixture:

$$0.360 = y\left[\frac{111.70 \text{ g Fe}}{159.70 \text{ g } Fe_2O_3}\right] + (0.500 - y)\left[\frac{55.85 \text{ g Fe}}{71.85 \text{ g FeO}}\right]$$

Simplifying the equation by dividing the conversion factors and combining terms gives

$$0.360 = 0.6994\, y + 0.7773\, (0.500 - y)$$

$$0.07790\, y = 0.02865$$

$$y = 0.3677 = 0.368 \text{ g} = \text{mass of } Fe_2O_3$$

3.129. If one heme molecule contains one iron atom, then the number of moles of heme in 35.2 mg of heme must be the same as the number of moles of iron in 3.19 mg of iron. Start by calculating the moles of Fe (equals moles of heme):

$$3.19 \text{ x } 10^{-3} \text{ g Fe x } \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 5.712 \text{ x } 10^{-5} \text{ mol Fe or heme}$$

$$\text{Molar mass of heme} = \frac{35.2 \text{ x } 10^{-3} \text{ g}}{5.712 \text{ x } 10^{-5} \text{ mol}} = 616.2 = 616 \text{ g/mol}$$

The molecular mass of heme is 616 amu.

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3.130. Convert the mass of $BaSO_4$ to mass of S to find the percentage of sulfur:

$$0.00546 \text{ g } BaSO_4 \times \frac{1 \text{ mol } BaSO_4}{233.40 \text{ g } BaSO_4} \times \frac{1 \text{ mol S}}{1 \text{ mol } BaSO_4} \times \frac{32.07 \text{ g S}}{1 \text{ mol S}}$$

$$= 0.7502 \times 10^{-3} \text{ g S}$$

$$\text{Mass percentage S} = \frac{0.7502 \times 10^{-3} \text{ g S}}{8.19 \times 10^{-3} \text{ g pen. V}} \times 100\% = 9.1\underline{6}0 = 9.16\%$$

Convert the mass of S to moles; then, recognizing that moles of S equals moles of pen. V, use that number of moles to calculate the molar mass:

$$0.7502 \times 10^{-3} \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 2.3\underline{3}9 \times 10^{-5} \text{ mol S}$$

$$\text{Molar mass pen. V} = \frac{8.19 \times 10^{-3} \text{ g}}{2.339 \times 10^{-5} \text{ mol}} = 35\underline{0}.1 = 350. \text{ g/mol}$$

The molecular mass of penicillin V is 350 amu.

3.131. Use the data to find the molar mass of the metal and anion. Start with X_2.

Mass X_2 in MX = 4.52 g − 3.41 g = 1.11 g

Molar mass X_2 = 1.11 g ÷ 0.0158 mol = 70.2<u>5</u> g/mol

Molar mass X = 70.25 ÷ 2 = 35.<u>1</u>4 = 35.1 g/mol

Thus X is Cl, chlorine.

Moles of M in 4.52 g MX = 0.0158 × 2 = 0.0316 mol

Molar mass of M = 3.41 g ÷ 0.0316 mol = 10<u>7</u>.9 = 108 g/mol

Thus M is Ag, silver.

3.132. Use the data to find the molar mass of the metal and the anion. Start with M^{2+}.

Mol M^{2+} in MX_2 = 0.158 mol ÷ 2 = 0.0790 mol

Molar mass of M^{2+} = 1.92 g ÷ 0.0790 mol = 24.<u>3</u>0 = 24.3 g/mol

Thus M^{2+} is Mg^{2+}.

Now, find the mass of MX_2, and then find the molar mass of X:

(1 − 0.868) mass MX_2 = 1.92 g, or mass MX_2 = 14.<u>5</u>45 g

Mass of X in MX_2 = 14.<u>5</u>45 g − 1.92 g = 12.<u>6</u>25 g

Moles of X in MX_2 = 0.158 mol

Molar mass of X = 12.<u>6</u>25 g ÷ 0.158 mol = 79.<u>9</u>05 = 79.9 g/mol

Thus X is Br (molar mass 79.90).

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3.133. After finding the volume of the alloy, convert it to mass Fe using density and percent Fe. Then use Avogadro's number and the atomic mass for the number of atoms.

$$\text{Volume} = 10.0\text{ cm} \times 20.0\text{ cm} \times 15.0\text{ cm} = 3.00 \times 10^3\text{ cm}^3$$

$$\text{Mass Fe} = 3.00 \times 10^3\text{ cm}^3 \times \frac{8.17\text{ g alloy}}{1\text{ cm}^3} \times \frac{54.7\text{ g Fe}}{100.0\text{ g alloy}} = 1.3\underline{4}07 \times 10^4\text{ g}$$

$$\text{No. of Fe atoms} = 1.3\underline{4}07 \times 10^{-4}\text{ g Fe} \times \frac{1\text{ mol Fe}}{55.85\text{ g Fe}} \times \frac{6.022 \times 10^{23}\text{ Fe atoms}}{1\text{ mol Fe}}$$

$$= 1.4\underline{4}56 \times 10^{26} = 1.45 \times 10^{26}\text{ Fe atoms}$$

3.134. After finding the volume of the cylinder, convert it to mass Co using density and percent Co. Then use Avogadro's number and the atomic mass for the number of atoms.

$$\text{Volume} = 3.1416 \times (2.50\text{ cm})^2 \times 10\text{ cm} = 196.35\text{ cm}^3$$

$$\text{Mass Co} = 196.35\text{ cm}^3 \times \frac{8.20\text{ g alloy}}{1\text{ cm}^3} \times \frac{12.0\text{ g Co}}{100.0\text{ g alloy}} = 1.9\underline{3}2 \times 10^2\text{ g}$$

$$\text{No. of Co atoms} = 1.9\underline{3}2 \times 10^2\text{ g Co} \times \frac{1\text{ mol Co}}{58.93\text{ g Co}} \times \frac{6.022 \times 10^{23}\text{ Co atoms}}{1\text{ mol Co}}$$

$$= 1.9\underline{7}4 \times 10^{24} = 1.97 \times 10^{24}\text{ Co atoms}$$

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CHAPTER 4

Chemical Reactions

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

4.1.

a. According to Table 4.1, all compounds that contain sodium, Na^+, are soluble. Thus, NaBr is soluble in water.

b. According to Table 4.1, most compounds that contain hydroxides, OH^-, are insoluble in water. However, $Ba(OH)_2$ is listed as one of the exceptions to this rule, so it is soluble in water.

c. Calcium carbonate is $CaCO_3$. According to Table 4.1, most compounds that contain carbonate, CO_3^{2-}, are insoluble. $CaCO_3$ is not one of the exceptions, so it is insoluble in water.

4.2.

a. The problem states that HNO_3 is a strong electrolyte, but $Mg(OH)_2$ is a solid, so retain its formula. On the product side, $Mg(NO_3)_2$ is a soluble ionic compound, but water is a nonelectrolyte, so retain its formula. The resulting complete ionic equation is

$$2H^+(aq) + 2NO_3^-(aq) + Mg(OH)_2(s) \rightarrow 2H_2O(l) + Mg^{2+}(aq) + 2NO_3^-(aq)$$

The corresponding net ionic equation is

$$2H^+(aq) + Mg(OH)_2(s) \rightarrow 2H_2O(l) + Mg^{2+}(aq)$$

b. Both reactants are soluble ionic compounds, and on the product side, $NaNO_3$ is also a soluble ionic compound. $PbSO_4$ is a solid, so retain its formula. The resulting complete ionic equation is

$$Pb^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$$

The corresponding net ionic equation is

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

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4.3. The formulas of the compounds are NaI and $Pb(C_2H_3O_2)_2$. Exchanging anions, you get sodium acetate, $NaC_2H_3O_2$, and lead(II) iodide, PbI_2. The equation for the exchange reaction is

$$NaI + Pb(C_2H_3O_2)_2 \rightarrow NaC_2H_3O_2 + PbI_2$$

From Table 4.1, you see that NaI is soluble, $Pb(C_2H_3O_2)_2$ is soluble, $NaC_2H_3O_2$ is soluble, and PbI_2 is insoluble. Thus, lead(II) iodide precipitates. The balanced molecular equation with phase labels is

$$Pb(C_2H_3O_2)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaC_2H_3O_2(aq)$$

To get the net ionic equation, you write the soluble ionic compounds as ions and cancel the spectator ions, ($C_2H_3O_2^-$ and Na^+). The final result is

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

4.4.

a. H_3PO_4 is not listed as a strong acid in Table 4.3, so it is a weak acid.

b. Hypochlorous acid, HClO, is not one of the strong acids listed in Table 4.3, so we assume that HClO is a weak acid.

c. As noted in Table 4.3, $HClO_4$ is a strong acid.

d. As noted in Table 4.3, $Sr(OH)_2$ is a strong base.

4.5. The salt consists of the cation from the base (Li^+) and the anion from the acid (CN^-); its formula is LiCN. You will need to add H_2O as a product to complete and balance the molecular equation:

$$HCN(aq) + LiOH(aq) \rightarrow LiCN(aq) + H_2O(l)$$

Note that LiOH (a strong base) and LiCN (a soluble ionic substance) are strong electrolytes; HCN is a weak electrolyte (it is not one of the strong acids in Table 4.3). After eliminating the spectator ions (Li^+ and CN^-), the net ionic equation is

$$HCN(aq) + OH^-(aq) \rightarrow H_2O(l) + CN^-(aq)$$

4.6. The first step in the neutralization is described by the following molecular equation:

$$H_2SO_4(aq) + KOH(aq) \rightarrow KHSO_4(aq) + H_2O(l)$$

The corresponding net ionic equation is

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The reaction of the acid salt $KHSO_4$ is given by the following molecular equation:

$$KHSO_4(aq) + KOH(aq) \rightarrow K_2SO_4(aq) + H_2O(l)$$

The corresponding net ionic equation is

$$HSO_4^-(aq) + OH^-(aq) \rightarrow H_2O(l) + SO_4^{2-}(aq)$$

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4.7. First, write the molecular equation for the exchange reaction, noting that the products of the reaction would be soluble $Ca(NO_3)_2$ and H_2CO_3. The carbonic acid decomposes to water and carbon dioxide gas. The molecular equation for the process is

$$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

The corresponding net ionic equation is

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$$

4.8.

a. For potassium dichromate, $K_2Cr_2O_7$,

2 x (oxidation number of K) + 2 x (oxidation number of Cr) + 7 x (oxidation number of O) = 0

For oxygen, the oxidation number is −2 (rule 3), and for potassium ion, the oxidation number is +1 (rule 2)

[2 x (+1)] + 2 x (oxidation number of Cr) + [7 x (−2)] = 0

Therefore,

2 x oxidation number of Cr = − [2 x (+1)] − [7 x (−2)] = +12

or, oxidation number of Cr = +6.

b. For the permanganate ion, MnO_4^-,

(Oxidation number of Mn) + 4 x (oxidation number of O) = −1

For oxygen, the oxidation number is −2 (rule 3).

(oxidation number of Mn) + [4 x (−2)] = −1

Therefore,

Oxidation number of Mn = −1 − [4 x (−2)] = +7

4.9. Identify the oxidation states of the elements.

$$\overset{0}{Ca} + \overset{0}{Cl_2} \rightarrow \overset{+2\ -1}{CaCl_2}$$

Break the reaction into two half-reactions, making sure that both mass and charge are balanced.

$$Ca \rightarrow Ca^{2+} + 2e^-$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Since each half-reaction has two electrons, it is not necessary to multiply the reactions by any factors to cancel them out. Adding the two half-reactions together and canceling out the electrons, you get

$$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$$

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4.10. Convert mass of NaCl (molar mass, 58.44 g) to moles of NaCl. Then divide moles of solute by liters of solution. Note that 25.0 mL = 0.0250 L.

$$0.0678 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 1.1\underline{6}0 \times 10^{-3} \text{ mol NaCl}$$

$$\text{Molarity} = \frac{1.160 \times 10^{-3} \text{ mol NaCl}}{0.0250 \text{ L soln}} = 0.046\underline{4}1 = 0.0464\ M$$

4.11. Convert grams of NaCl (molar mass, 58.44 g) to moles NaCl and then to volume of NaCl solution.

$$0.0958 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{1 \text{ L solution}}{0.163 \text{ mol NaCl}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 10.\underline{0}6 = 10.1 \text{ mL NaCl}$$

4.12. One (1) liter of solution is equivalent to 0.15 mol NaCl. The amount of NaCl in 50.0 mL of solution is

$$50.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.15 \text{ mol NaCl}}{1 \text{ L soln}} = 0.007\underline{5}0 \text{ mol NaCl}$$

Convert to grams using the molar mass of NaCl (58.44 g/mol).

$$0.00750 \text{ mol NaCl} \times \frac{58.4 \text{ g NaCl}}{1 \text{ mol NaCl}} = 0.4\underline{3}8 = 0.44 \text{ g NaCl}$$

4.13. Use the rearranged version of the dilution formula from the text to calculate the initial volume of 1.5 *M* sulfuric acid required:

$$V_i = \frac{M_f V_f}{M_i} = \frac{0.18\ M \times 100.0 \text{ mL}}{1.5\ M} = 1\underline{2}.0 = 12 \text{ mL}$$

4.14. There are two different reactions taking place in forming the CaC_2O_4 (molar mass 128.10 g/mol) precipitate. These are

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

$$CaCl_2(aq) + Na_2C_2O_4(aq) \rightarrow CaC_2O_4(s) + 2NaCl(aq)$$

The overall stoichiometry of the reactions is one mol $CaCO_3$/one mol CaC_2O_4. Also note that each $CaCO_3$ contains one Ca atom, so this gives an overall conversion factor of one mol Ca/one mol CaC_2O_4.

The mass of Ca can now be calculated.

$$0.1402 \text{ g } CaC_2O_4 \times \frac{1 \text{ mol } CaC_2O_4}{128.10 \text{ g } CaC_2O_4} \times \frac{1 \text{ mol Ca}}{1 \text{ mol } CaC_2O_4} \times \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}}$$

$$= 0.043866 \text{ g Ca}$$

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Now, calculate the percentage of calcium in the 128.3 mg (0.1283 g) limestone:

$$\frac{0.043866 \text{ g Ca}}{0.1283 \text{ g limestone}} \times 100\% = 34.190 = 34.19\%$$

4.15. Convert the volume of Na_3PO_4 to moles using the molarity of Na_3PO_4. Note that 45.7 mL = 0.0457 L.

$$0.0457 \text{ L } Na_3PO_4 \times \frac{0.265 \text{ mol } Na_3PO_4}{1 \text{ L}} = 0.012111 \text{ mol } Na_3PO_4$$

Finally, calculate the amount of $NiSO_4$ required to react with this amount of Na_3PO_4:

$$0.012111 \text{ mol } Na_3PO_4 \times \frac{3 \text{ mol } NiSO_4}{2 \text{ mol } Na_3PO_4} \times \frac{1 \text{ L } NiSO_4}{0.375 \text{ mol } NiSO_4} = 0.048444 \text{ L (48.4 mL)}$$

4.16. Convert the volume of NaOH solution (0.0391 L) to moles NaOH (from the molarity of NaOH). Then convert moles NaOH to moles $HC_2H_3O_2$ (from the chemical equation). Finally, convert moles of $HC_2H_3O_2$ (molar mass 60.05 g/mol) to grams $HC_2H_3O_2$.

$$0.0391 \text{ L NaOH} \times \frac{0.108 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol } HC_2H_3O_2}{1 \text{ mol NaOH}} \times \frac{60.05 \text{ g } HC_2H_3O_2}{1 \text{ mol } HC_2H_3O_2}$$

$$= 0.25359 \text{ g}$$

The mass percentage of acetic acid in the vinegar can now be calculated.

$$\text{Percentage mass} = \frac{0.25359 \text{ g } HC_2H_3O_2}{5.00 \text{ g vinegar}} \times 100\% = 5.071 = 5.07\%$$

■ ANSWERS TO CONCEPT CHECKS

4.1. The left beaker contains two types of individual atoms (ions) and no solid; therefore, it must represent the soluble, LiI. Because LiI is a soluble ionic compound, it is an electrolyte. The beaker on the right represents a molecular compound that is soluble but not dissociated in solution. Therefore, it must be the CH_3OH. Because the CH_3OH is not dissociated in solution, and no ions are present, it is a nonelectrolyte.

4.2.

a. In order to solve this part of the problem, keep in mind that this is an exchange (metathesis) reaction. Since you are given the products in the picture, you need to work backward to determine the reactants. Starting with the solid $SrSO_4(s)$, you know that the SO_4^{2-} anion started the reaction with a different cation (not Sr^{2+}). Since Na^+ is the only option, you can conclude that one of the reactants must be Na_2SO_4. Based on solubility rules, you know that Na_2SO_4 is soluble, so you represent it as $Na_2SO_4(aq)$. The remaining cation and anion indicate that the other reactant is the soluble $Sr(C_2H_3O_2)_2$. Observing the soluble and insoluble species in the picture, you can conclude that the molecular equation is

$$Na_2SO_4(aq) + Sr(C_2H_3O_2)_2(aq) \rightarrow SrSO_4(s) + 2NaC_2H_3O_2(aq)$$

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b. Writing the strong electrolytes in the form of ions and the solid with its molecular formula, the complete ionic equation for the reaction is

$$2Na^+(aq) + SO_4^{2-}(aq) + Sr^{2+}(aq) + 2C_2H_3O_2^-(aq) \rightarrow SrSO_4(s) + 2Na^+(aq) + 2C_2H_3O_2^-(aq)$$

c. After canceling the spectator ions, the net ionic equation for the reaction is

$$Sr^{2+}(aq) + SO_4^{2-}(aq) \rightarrow SrSO_4(s)$$

4.3.

a. MOH must be a base since OH^- is being produced in solution. It must be a strong base because the reaction indicates that MOH is completely soluble (strong electrolyte). In order to maintain charge balance in the formula, the element M must be a 1+ cation, probably a metal from Group IA of the periodic table. Examples of bases that fall into this category include NaOH and KOH.

b. This must be an acid since H^+ is being produced in solution. It is a weak acid because the double arrow is used, indicating only a partial ionization in solution. From the chemical reaction, A^- represents an anion with a 1− charge. Acetic acid, $HC_2H_3O_2$, is a weak acid of this type.

c. This must be an acid since H^+ is being produced in solution. $H_2A(aq)$ is a weak acid because the equation indicates only partial ionization in solution. A^{2-} represents an anion with a 2− charge. Carbonic acid, H_2CO_3, is a weak acid of this type.

d. Examples of M include Na^+, K^+, and Li^+. Examples of A for reaction b include F^-, $C_2H_3O_2^-$, and CN^-. Examples of A for reaction c. include S^{2-}, CO_3^{2-}, and $C_4H_4O_6^{2-}$.

4.4.

a. In order to answer this question, you need to compare the number of atoms of X per unit of volume. In order to compare volumes, use the lines on the sides of the beakers. Beaker A has concentration of five atoms per two volume units, 5/2 or 2.5/1. Beaker B has a concentration of ten atoms per one volume unit, 10/1. Beaker C has a concentration of ten atoms per two volume units, 10/2 or 5/1. Beaker D has a concentration of five atoms per volume unit, 5/1. Comparing the concentrations reveals that the ranking from lowest to highest concentration is Beaker A < Beaker C = Beaker D < Beaker B.

b. To make the concentrations of X equal in each beaker, they all have to be made to match the beaker with the lowest concentration. This is Beaker A, which has five atoms of X in one-half a beaker of solution. To make the concentrations equal, do the following: double the volume of Beakers C and D, and quadruple the volume of Beaker B by adding the solvent. Overall, Beakers A and B will contain a full beaker of solution, and Beakers C and D will contain a half-beaker of solution.

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4.5.

a. Since flask C required three times the amount of titrant (NaOH) as of acid A, you have learned that acid C has three times as many acidic protons as acid A. Since flask B required two times the amount of titrant as of acid A, you have also learned that acid B has two times as many acidic protons as acid A.

b. If you assume that acid A contains a monoprotic acid, then you know the number of moles of A in the flask. After performing the titration, you know that the moles of NaOH must equal the moles of acid in flask A. You take the number of moles of NaOH and divide it by the volume of NaOH added during the titration to determine the concentration of the NaOH solution.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

4.1. Some electrolyte solutions are strongly conducting because they are almost completely ionized, and others are weakly conducting because they are weakly ionized. The former solutions will have many more ions to conduct electricity than will the latter solutions if both are present at the same concentrations.

4.2. A strong electrolyte is an electrolyte that exists in solution almost entirely as ions. An example is NaCl. When NaCl dissolves in water, it dissolves almost completely to give Na^+ and Cl^- ions. A weak electrolyte is an electrolyte that dissolves in water to give a relatively small percentage of ions. An example is NH_3. When NH_3 dissolves in water, it reacts very little with the water, so the level of NH_3 is relatively high, and the level of the NH_4^+ and OH^- ions is relatively low.

4.3. Soluble means the ability of a substance to dissolve in water. A compound is insoluble if it does not dissolve appreciably in water. An example of a soluble ionic compound is sodium chloride, NaCl, and an example of an insoluble ionic compound is calcium carbonate, $CaCO_3$.

4.4. The advantage of using a molecular equation to represent an ionic equation is that it states explicitly what chemical species have been added and what chemical species are obtained as products. It also makes stoichiometric calculations easy to perform. The disadvantages are (1) the molecular equation does not represent the fact that the reaction actually involves ions, and (2) the molecular equation does not indicate which species exist as ions and which exist as molecular solids or molecular gases.

4.5. A spectator ion is an ion that does not take part in the reaction. In the following ionic reaction, the Na^+ and Cl^- are spectator ions:

$$Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

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4.6. A net ionic equation is an ionic equation from which spectator ions have been canceled. The value of such an equation is that it shows the reaction that actually occurs at the ionic level. An example is the ionic equation representing the reaction of calcium chloride ($CaCl_2$) with potassium carbonate(K_2CO_3).

$$CaCl_2(aq) + K_2CO_3(aq) \rightarrow CaCO_3(s) + 2\,KCl(aq):$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \qquad \text{(net ionic equation)}$$

4.7. The three major types of chemical reactions are precipitation reactions, acid–base reactions, and oxidation–reduction reactions. Oxidation–reduction reactions can be further classified as combination reactions, decomposition reactions, displacement reactions, and combustion reactions. Brief descriptions and examples of each are given below.

A precipitation reaction is a reaction that involves the formation of an insoluble solid compound. An example is $2KCl\,(aq) + Pb(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + PbI_2(s)$.

An acid–base reaction, or neutralization reaction, results in an ionic compound and possibly water. An example is $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$.

A combination reaction is a reaction in which two substances combine to form a third substance. An example is $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$.

A decomposition reaction is a reaction in which a single compound reacts to give two or more substances. An example is $2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$.

A displacement reaction, or single replacement reaction, is a reaction in which an element reacts with a compound displacing an element from it. An example is $Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$.

A combustion reaction is a reaction of a substance with oxygen, usually with rapid release of heat to produce a flame. The products include one or more oxides. An example is $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$.

4.8. To prepare crystalline AgCl and $NaNO_3$, first make solutions of $AgNO_3$ and NaCl by weighing equivalent molar amounts of both solid compounds. Then mix the two solutions together, forming a precipitate of silver chloride and a solution of soluble sodium nitrate. Filter off the silver chloride, and wash it with water to remove the sodium nitrate solution. Then allow it to dry to obtain pure crystalline silver chloride. Finally, take the filtrate containing the sodium nitrate and evaporate it, leaving pure crystalline sodium nitrate.

4.9. An example of a neutralization reaction is

$$\underset{\text{acid}}{HBr} + \underset{\text{base}}{KOH} \rightarrow \underset{\text{salt}}{KBr} + H_2O(l)$$

4.10. An example of a polyprotic acid is carbonic acid, H_2CO_3. The successive neutralization is given by the following molecular equations:

$$H_2CO_3(aq) + NaOH(aq) \rightarrow NaHCO_3(aq) + H_2O(l)$$

$$NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$$

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4.11. Since an oxidation–reduction reaction is an electron transfer reaction, one substance must lose the electrons and be oxidized while another substance must gain electrons and be reduced.

4.12. A displacement reaction is an oxidation–reduction reaction in which a free element reacts with a compound, displacing an element from it.

$$Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$$

Ag^+ is the oxidizing agent, and Cu is the reducing agent.

4.13. The number of moles present does not change when the solution is diluted.

4.14. The reaction is

$$HCl + NaOH \rightarrow NaCl + H_2O$$

After titration, the volume of hydrochloric acid is converted to moles of HCl using the molarity. Since the stoichiometry of the reaction is 1 mol HCl to 1 mol NaOH, these quantities are equal.

Moles HCl = moles NaOH = molarity x volume

You could then multiply by the molar mass of NaOH to obtain the amount in the mixture.

4.15. The answer is e, $HF(aq) + OH^-(aq) \rightarrow F^-(aq) + H_2O(l)$.

4.16. The answer is c, magnesium hydroxide(*s*).

4.17. The answer is d, $MgCl_2$.

4.18. The answer is d, HNO_2.

■ ANSWERS TO CONCEPT EXPLORATIONS

4.19. **Part 1**

a. $NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$

b. $C_{12}H_{22}O_{11}(s) \xrightarrow{H_2O} C_{12}H_{22}O_{11}(aq)$

c. NH_3 forms ions by reacting with water. But it reacts very little with water, and only a small percentage of ions are formed. Thus, it is a weak electrolyte. Sucrose dissolves in water but does not form any ions. Thus, it is a nonelectrolyte.

d. $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

e. NH_3 and HCl both react with water to form ions. Therefore, both compounds are electrolytes.

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f. HCl reacts completely with water to form ions, so it is a strong electrolyte. NH_3 reacts very little with water, so it is a weak electrolyte.

g. The ionic compounds are KCl, $MgBr_2$, $Ca(OH)_2$, and PbS. The molecular compounds are NH_3, CO_2, HCl, and $HC_2H_3O_2$.

h. KCl and $MgBr_2$ are both soluble by Rule 3, that most chlorides, bromides, and iodides are soluble. Neither compound is listed as an exception. $Ca(OH)_2$ is soluble by Rule 8, that most hydroxides are insoluble, but $Ca(OH)_2$ is listed as an exception. PbS is insoluble by Rule 7. It is not listed as an exception.

i. If you placed a soluble ionic compound in water it would mix with the water and form ions. After a while, the solid would no longer be evident and only ions would be in the solution. If you placed an insoluble ionic compound in water, it would mix with the water and dissolve only partially to form ions. After a while, the undissolved solid would settle to the bottom of the beaker. No, these substances do not react with water when they are added to water.

j. $KCl(s) \xrightarrow{H_2O} K^+(aq) + Cl^-(aq)$

$MgBr_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2Br^-(aq)$

$Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$

k. All three soluble ionic compounds are strong electrolytes because they dissolve in water completely to form ions.

l. $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

$HI(aq) + H_2O(l) \rightarrow H_3O^+(aq) + I^-(aq)$

m. NaCl and HI have different behavior in aqueous solution. NaCl dissolves in water completely to form ions. HI reacts with water completely to form ions. The reactions are

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$

$$HI(aq) + H_2O(l) \rightarrow H_3O^+(aq) + I^-(aq)$$

Part 2

a. Since AX is a strong electrolyte, it would ionize completely. The solution would be made up primarily of ions, with no AX molecules present. Since AY is a weak electrolyte, it would ionize only partially. The solution would consist primarily of AY molecules with relatively few ions present. Therefore, AY(*aq*) is much larger than AX(*aq*).

b. Since AX is a strong electrolyte, it would ionize completely. There would be a large amount of $X^-(aq)$ present. Since AY is a weak electrolyte, it would ionize only partially. There would be a very small amount of $Y^-(aq)$ present. Therefore, $X^-(aq)$ is much larger than $Y^-(aq)$.

4.20. **Part 1**

a. $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

$MgCl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$

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b. The picture on the left has eight larger spheres and four smaller spheres. The picture on the right has four larger spheres and four smaller spheres. Since Cl^- ions are the largest of the ions present, they are represented by the larger spheres. Therefore, there is a 2-to-1 ratio of Cl^- ions to cations in the picture on the left and a 1–to–1 ratio of Cl^- ions to cations in the picture on the right. This means that $MgCl_2$ is shown in the picture on the left, and NaCl is shone in the picture on the right.

c. 1.0 L of 1.0 M of each compound contains 1.0 mol.

d. For NaCl there is a 1–to–1 mole ratio of chloride ions to NaCl. Therefore 1.0 mol of NaCl, contains 1.0 mol of Cl^- ions. For $MgCl_2$, there is a 2–to–1 mole ratio of chloride ions to $MgCl_2$. Therefore 1.0 mol of $MgCl_2$ contains 2.0 mol of Cl^- ions.

e. Since the volumes of the solutions are 1.0 L, the molarity and the moles are numerically the same. Thus, for the NaCl solution the concentration of Cl^- is 1.0 *M*, and in the $MgCl_2$ beaker the concentration of Cl^- is 2.0 *M*.

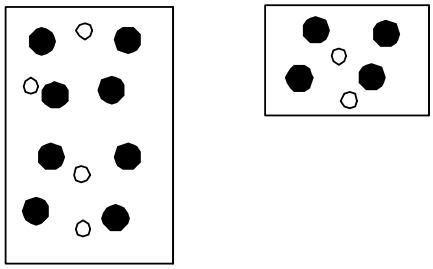
f. Since the mole ratio of chloride ion to original compound is different for each compound, different concentrations of chloride ions result from equal amounts of the original compounds.

Part 2

a. Since the solution is homogeneous, the concentrations are the same throughout the solution. Both the part remaining and the part removed still have the same concentration as before, so $MgCl_2(aq)$ is 1.0 *M* and $Cl^-(aq)$ is 2.0 *M*.

b. Since half of the solution was removed, half of the moles were also removed. Thus, there is 0.50 mol $MgCl_2$ and 1.0 mol Cl^-.

c. The solution is homogeneous and the concentration is uniform throughout the solution. One-half the volume contains one-half the amount of substance. Thus, one-half the amount of substance in one-half the volume is equivalent to the same concentration as before.



Part 3

a. Since $M_1V_1 = M_2V_2$, doubling the volume reduces the concentration by an equal factor. Thus the concentration of NaCl(*aq*) would be 0.50 *M*.

b. Since no solution was removed, there is still the same number of moles of NaCl as before, 1.0 mol.

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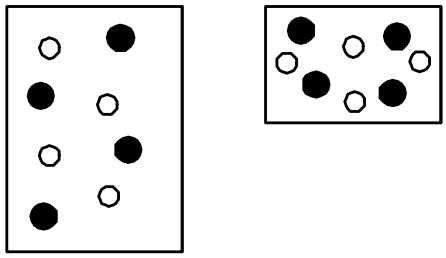
c. The number of moles does not change because nothing was removed from the solution. The concentration does change because the volume of the solution changed upon addition of more water. Having the same number of moles in a larger volume is equivalent to a smaller concentration.



■ ANSWERS TO CONCEPTUAL PROBLEMS

4.21.

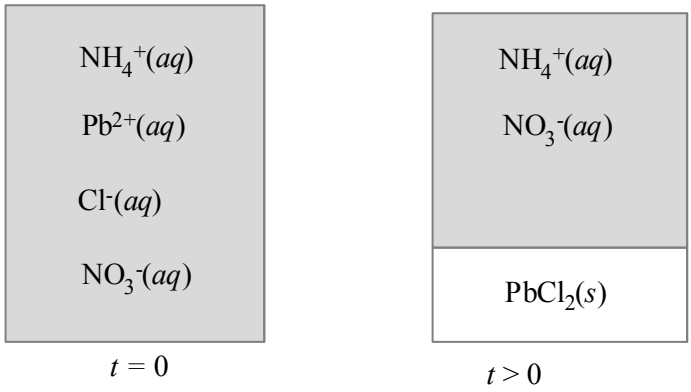
a. Any soluble salt that will form a precipitate when reacted with Ag^+ ions in solution will work, for example: $CaCl_2$, Na_2S, $(NH_4)_2CO_3$.

b. No, no precipitate will form.

c. You would underestimate the amount of silver present in the solution.

4.22.

a.



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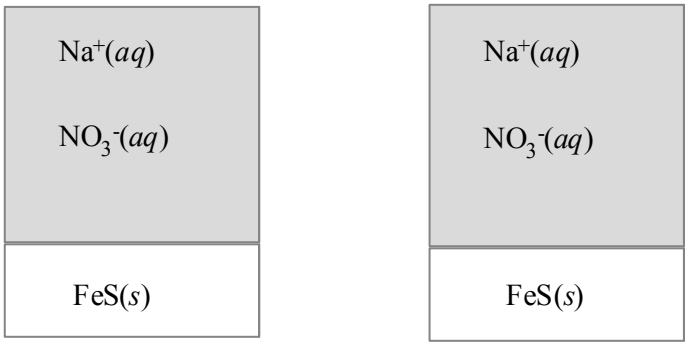
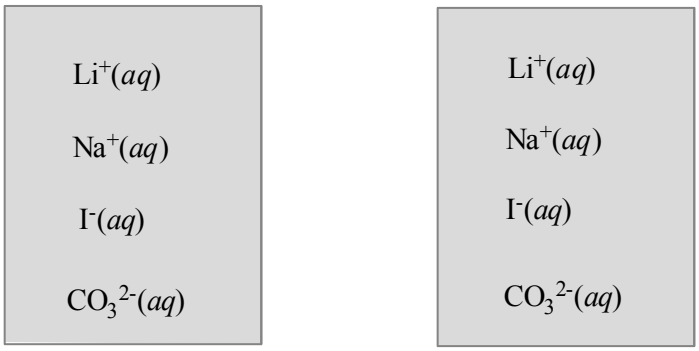
b.



$t = 0$ $t > 0$

c.



$t = 0$ $t > 0$

4.23.

a. $3Ca(C_2H_3O_2)_2(aq) + 2(NH_4)_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6NH_4C_2H_3O_2(aq)$

b. $3Ca^{2+}(aq) + 6C_2H_3O_2^-(aq) + 6NH_4^+(aq) + 2PO_4^{3-}(aq)$
$\rightarrow Ca_3(PO_4)_2(s) + 6NH_4^+(aq) + 6C_2H_3O_2^-(aq)$

c. $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$

4.24.

a. Sample 1, Sample 2, Sample 3

b. They all will require the same volume of 0.1 *M* NaOH.

4.25. Probably not, since the ionic compound that is a nonelectrolyte is not soluble.

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4.26. A good starting point is to identify the solution that contains the base. Since bases produce OH^- in aqueous solution, we would expect to see OH^- present in the BZ solution. The center beaker depicts OH^- in the solution, so it must be the base. By default, the remaining two beakers must contain acid. This is confirmed by the presence of H_3O^+ in both the left and right beakers. Keeping in mind that weak acids only partially dissociate, for the weak acid HA, we would expect to observe HA, H_3O^+, and A^- in the solution. In the case of the strong acid, HX, that completely dissociates, we would expect to observe only H_3O^+ and X^- in the solution. The beaker on the right has only H_3O^+ and one other species in solution, so it must be the strong acid HX. Examining the beaker on the left reveals that there are three species present, which indicates that it must be the weak acid.

4.27.

a. Since both solutions are made with compounds that contain chloride ions, the total chloride ion concentration is highest.

b. First, determine the concentrations of the compounds after mixing them together. Use the dilution relationship, $M_1V_1 = M_2V_2$. Since equal volumes of equal molar solutions are mixed, the resulting concentrations are 0.50 *M* KBr and 0.50 *M* K_3PO_4.There is one Br^- ion per KBr, so the concentration of Br^- is 0.50 *M*. There is also one PO_4^{3-} ion per K_3PO_4, so its concentration is also 0.50 *M*. Potassium ion can be determined as follows:

$$0.50\ M\ \text{KBr} \times \frac{1\ \text{mol}\ K^+}{1\ \text{mol KBr}} + 0.50\ M\ K_3PO_4 \times \frac{3\ \text{mol}\ K^+}{1\ \text{mol}\ K_3PO_4} = 2.0\ \text{M}\ K^+$$

4.28. Since equal moles of the compounds are used, the highest Cl^- concentration is for the compound(*s*) with the largest subscript on Cl in the formula. Thus the order, from highest to lowest, is $AlCl_3 > KCl = NaCl = HCl > PbCl_2 = NH_3 = KOH = HCN$.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

4.29.

a. Insoluble

b. Soluble

c. Soluble

d. Soluble

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4.30.

a. Insoluble
b. Soluble
c. Soluble
d. Soluble

4.31.

a. Insoluble
b. Soluble; The ions present would be NH_4^+ and SO_4^{2-}.
c. Insoluble
d. Soluble; The ions present would be Na^+ and CO_3^{2-}.

4.32.

a. Soluble; The ions present would be Li^+ and SO_4^{2-}.
b. Insoluble
c. Insoluble
d. Soluble; The ions present would be Ca^{2+} and NO_3^-.

4.33.

a. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
b. $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
c. $S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g)$
d. $OH^-(aq) + NH_4^+(aq) \rightarrow NH_3(g) + H_2O(l)$

4.34.

a. $H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$
b. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
c. $Pb^{2+}(aq) + 2Br^-(aq) \rightarrow PbBr_2(s)$
d. $MgCO_3(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$

4.35. Molecular equation: $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

Net ionic equation: $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

4.36. Molecular equation: $K_2CO_3(aq) + 2HBr(aq) \rightarrow CO_2(g) + H_2O(l) + 2KBr(aq)$

Net ionic equation: $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$

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4.37.

a. $FeSO_4(aq) + NaCl(aq) \rightarrow NR$

b. $Na_2CO_3(aq) + MgBr_2(aq) \rightarrow MgCO_3(s) + 2NaBr(aq)$

$CO_3^{2-}(aq) + Mg^{2+}(aq) \rightarrow MgCO_3(s)$

c. $MgSO_4(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$

$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$

d. $NiCl_2(aq) + NaBr(aq) \rightarrow NR$

4.38.

a. $AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$

$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

b. $Ba(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KNO_3(aq)$

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

c. $Mg(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow NR$

d. $CaCl_2(aq) + Al(NO_3)_3(aq) \rightarrow NR$

4.39.

a. $Ba(NO_3)_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + 2LiNO_3(aq)$

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

b. $Ca(NO_3)_2(aq) + NaBr(aq) \rightarrow NR$

c. $Al_2(SO_4)_3(aq) + 6NaOH(aq) \rightarrow 2Al(OH)_3(s) + 3Na_2SO_4(aq)$

$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$

d. $3CaBr_2(aq) + 2Na_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6NaBr(aq)$

$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$

4.40.

a. $ZnCl_2(aq) + Na_2S(aq) \rightarrow ZnS(s) + 2NaCl(aq)$

$Zn^{2+}(aq) + S^{2-}(aq) \rightarrow ZnS(s)$

b. $CaCl_2(aq) + Na_2S(aq) \rightarrow CaS(s) + 2NaCl(aq)$

$Ca^{2+}(aq) + S^{2-}(aq) \rightarrow CaS(s)$

c. $MgSO_4(aq) + KBr(aq) \rightarrow NR$

d. $MgSO_4(aq) + K_2CO_3(aq) \rightarrow MgCO_3(s) + K_2SO_4(aq)$

$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$

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4.41.

a. Weak acid

b. Strong base

c. Strong acid

d. Weak acid

4.42.

a. Weak base

b. Weak acid

c. Strong base

d. Strong acid

4.43.

a. $NaOH(aq) + HNO_3(aq) \rightarrow H_2O(l) + NaNO_3(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

b. $2HCl(aq) + Ba(OH)_2(aq) \rightarrow 2H_2O(l) + BaCl_2(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

c. $2HC_2H_3O_2(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(C_2H_3O_2)_2(aq)$

$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_2H_3O_2^-(aq)$

d. $NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$

$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

4.44.

a. $Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$

$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$

b. $2HBr(aq) + Sr(OH)_2(aq) \rightarrow 2H_2O(l) + SrBr_2(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

c. $Ba(OH)_2(aq) + 2HC_2H_3O_2(aq) \rightarrow Ba(C_2H_3O_2)_2(aq) + 2H_2O(l)$

$OH^-(aq) + HC_2H_3O_2(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$

d. $HNO_3(aq) + KOH(aq) \rightarrow H_2O(l) + KNO_3(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

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4.45.

a. $2HBr(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + CaBr_2(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

b. $3HNO_3(aq) + Al(OH)_3(s) \rightarrow 3H_2O(l) + Al(NO_3)_3(aq)$

$3H^+(aq) + Al(OH)_3(s) \rightarrow 3H_2O(l) + Al^{3+}(aq)$

c. $2HCN(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(CN)_2(aq)$

$HCN(aq) + OH^-(aq) \rightarrow H_2O(l) + CN^-(aq)$

d. $HCN(aq) + LiOH(aq) \rightarrow H_2O(l) + LiCN(aq)$

$HCN(aq) + OH^-(aq) \rightarrow H_2O(l) + CN^-(aq)$

4.46.

a. $HClO_4(aq) + LiOH(aq) \rightarrow H_2O(l) + LiClO_4(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

b. $2HNO_2(aq) + Ba(OH)_2(aq) \rightarrow 2H_2O(l) + Ba(NO_2)_2(aq)$

$HNO_2(aq) + OH^-(aq) \rightarrow H_2O(l) + NO_2^-(aq)$

c. $HNO_2(aq) + NaOH(aq) \rightarrow H_2O(l) + NaNO_2(aq)$

$HNO_2(aq) + OH^-(aq) \rightarrow H_2O(l) + NO_2^-(aq)$

d. $2HCN(aq) + Sr(OH)_2(aq) \rightarrow 2H_2O(l) + Sr(CN)_2(aq)$

$HCN(aq) + OH^-(aq) \rightarrow H_2O(l) + CN^-(aq)$

4.47.

a. $2KOH(aq) + H_3PO_4(aq) \rightarrow K_2HPO_4(aq) + 2H_2O(l)$

$2OH^-(aq) + H_3PO_4(aq) \rightarrow HPO_4^{2-}(aq) + 2H_2O(l)$

b. $3H_2SO_4(aq) + 2Al(OH)_3(s) \rightarrow 6H_2O(l) + Al_2(SO_4)_3(aq)$

$3H^+(aq) + Al(OH)_3(s) \rightarrow 3H_2O(l) + Al^{3+}(aq)$

c. $2HC_2H_3O_2(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(C_2H_3O_2)_2(aq)$

$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_2H_3O_2^-(aq)$

d. $H_2SO_3(aq) + NaOH(aq) \rightarrow H_2O(l) + NaHSO_3(aq)$

$H_2SO_3(aq) + OH^-(aq) \rightarrow HSO_3^-(aq) + H_2O(l)$

4.48.

a. $Ca(OH)_2(aq) + 2H_2SO_4(aq) \rightarrow 2H_2O(l) + Ca(HSO_4)_2(aq)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

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b. $2H_3PO_4(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(H_2PO_4)_2(aq)$

$H_3PO_4(aq) + OH^-(aq) \rightarrow H_2O(l) + H_2PO_4^-(aq)$

c. $NaOH(aq) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$

$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$

d. $Sr(OH)_2(aq) + 2H_2CO_3(aq) \rightarrow Sr(HCO_3)_2(aq) + 2H_2O(l)$

$OH^-(aq) + H_2CO_3(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

4.49. Molecular equations: $2H_2SO_3(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(HSO_3)_2(aq)$

$Ca(HSO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + 2CaSO_3(s)$

Ionic equations: $H_2SO_3(aq) + OH^-(aq) \rightarrow H_2O(l) + HSO_3^-(aq)$

$Ca^{2+}(aq) + HSO_3^-(aq) + OH^-(aq) \rightarrow CaSO_3(s) + H_2O(l)$

4.50. Molecular equations: $2H_3PO_4(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca(H_2PO_4)_2(aq)$

$Ca(H_2PO_4)_2(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + 2CaHPO_4(aq)$

$2CaHPO_4(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + Ca_3(PO_4)_2(s)$

Ionic equations: $H_3PO_4(aq) + OH^-(aq) \rightarrow H_2O(l) + H_2PO_4^-(aq)$

$H_2PO_4^-(aq) + OH^-(aq) \rightarrow H_2O(l) + HPO_4^{2-}(aq)$

$2HPO_4^{2-}(aq) + 2OH^-(aq) + 3Ca^{2+}(aq) \rightarrow 2H_2O(l) + Ca_3(PO_4)_2(s)$

4.51.

a. Molecular equation: $CaS(s) + 2HBr(aq) \rightarrow CaBr_2(aq) + H_2S(g)$

Ionic equation: $CaS(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2S(g)$

b. Molecular equation: $MgCO_3(s) + 2HNO_3(aq) \rightarrow CO_2(g) + H_2O(l) + Mg(NO_3)_2(aq)$

Ionic equation: $MgCO_3(s) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l) + Mg^{2+}(aq)$

c. Molecular equation: $K_2SO_3(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + SO_2(g) + H_2O(l)$

Ionic equation: $SO_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l)$

4.52.

a. Molecular equation: $BaCO_3(s) + 2HNO_3(aq) \rightarrow CO_2(g) + H_2O(l) + Ba(NO_3)_2(aq)$

Ionic equation: $BaCO_3(s) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l) + Ba^{2+}(aq)$

b. Molecular equation: $K_2S(aq) + 2HCl(aq) \rightarrow H_2S(g) + 2KCl(aq)$

Ionic equation: $S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g)$

c. Molecular equation: $CaSO_3(s) + 2HI(aq) \rightarrow SO_2(g) + H_2O(l) + CaI_2(aq)$

Ionic equation: $CaSO_3(s) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l) + Ca^{2+}(aq)$

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4.53. Molecular equation: $FeS(s) + 2HCl(aq) \rightarrow H_2S(g) + FeCl_2(aq)$

Ionic equation: $FeS(s) + 2H^+(aq) \rightarrow H_2S(g) + Fe^{2+}(aq)$

4.54. Molecular equation: $BaCO_3(s) + 2HBr(aq) \rightarrow BaBr_2(aq) + CO_2(g) + H_2O(l)$

Ionic equation: $BaCO_3(s) + 2H^+(aq) \rightarrow Ba^{2+}(aq) + CO_2(g) + H_2O(l)$

4.55.

a. Because all three O's = a total of −6, both Ga's = +6; thus, the oxidation number of Ga = +3.

b. Because both O's = a total of −4, the oxidation number of Nb = +4.

c. Because the four O's = a total of −8 and K = +1, the oxidation number of Br = +7.

d. Because the four O's = a total of −8 and the 2 K's = +2, the oxidation number of Mn = +6.

4.56.

a. Because the three O's = a total of −6, the oxidation number of Cr = +6.

b. Because the two Cl's = a total of −2, both Hg's = +2; thus, the oxidation number of Hg = +1.

c. Because the three O's = a total of −6 and the 3 H's = a total of +3, the oxidation number of Ga = +3.

d. Because the four O's = a total of −8 and the 3 Na's = a total of +3, the oxidation number of P = +5.

4.57.

a. Because the charge of −1 = $[x_N$ + 2 (from 2 H's)], x_N must equal −3.

b. Because the charge of −1 = $[x_I$ − 6 (from 3 O's)], x_I must equal +5.

c. Because the charge of −1 = $[x_{Al}$ − 8 (4 O's) + 4 (4 H's)], x_{Al} must equal +3.

d. Because the charge of 0 = $[x_{Cl}$ − 8 (4 O's) + 1 (1 H's)], x_{Cl} must equal +7.

4.58.

a. Because the charge of −1 = $[x_N$ − 4 (from 2 O's)], x_N must equal +3.

b. Because the charge of −2 = $[x_{Cr}$ − 8 (from 4 O's)], x_{Cr} must equal +6.

c. Because the charge of −2 = $[x_{Zn}$ − 8 (4 O's) + 4 (4 H's)], x_{Zn} must equal +2.

d. Because the charge of −1 = $[x_{As}$ − 6 (3 O's) + 2 (2 H's)], x_{As} must equal +3.

4.59.

a. From the list of common polyatomic anions in Table 2.5, the formula of the ClO_3 anion must be ClO_3^-. Thus, the formula of Mn is Mn^{2+} (see also Table 4.5). Since the oxidation state of O is −2 and the net ionic charge is −1, the oxidation state of chlorine is determined by $x_{Cl} - 6 = -1$, so x_{Cl} must equal +5.

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b. From the list of common polyatomic anions in Table 2.5, the formula of the CrO_4 anion must be CrO_4^{2-}. Thus, the formula of Fe is Fe^{3+}. Since the oxidation state of O is −2 and the net ionic charge is −2, the oxidation state of Cr is determined by $x_{Cr} - 8 = -2$, so x_{Cr} must equal +6.

c. From the list of common polyatomic anions in Table 2.5, the formula of the Cr_2O_7 anion must be $Cr_2O_7^{2-}$. Thus, the formula of Hg is Hg^{2+}. Since the oxidation state of O is −2 and the net ionic charge is −2, the oxidation state of Cr determined by $2x_{Cr} - 14 = -2$, so x_{Cr} must equal +6.

d. From the list of common polyatomic anions in Table 2.5, the formula of the PO_4 anion must be PO_4^{3-}. Thus, the formula of Co is Co^{2+}. Since the oxidation state of O is −2 and the net ionic charge is −3, the oxidation state of P is determined by $x_P - 8 = -3$, so x_P must equal +5.

4.60.

a. From the formula of ClO_3^- in the list of common polyatomic anions in Table 2.5, the formula of the BrO_3 anion must be BrO_3^-. Thus, the oxidation state of Hg is +1, and its formula must be Hg_2^{2+} (from Table 4.5). Since the oxidation state of O is −2 and the net ionic charge is −1, the oxidation state of Br is determined by $x_{Br} - 6 = -1$, so x_{Br} must equal +5.

b. From the list of common polyatomic anions in Table 2.5, the formula of the SO_4 anion must be SO_4^{2-}. Thus, the oxidation state of Cr is +3. Since the oxidation state of O is −2 and the net ionic charge is −2, the oxidation state of S is determined by $x_S - 8 = -2$, so x_S must equal +6.

c. From the formula of SO_4^{2-} in the list of common polyatomic anions in Table 2.5, the formula of the SeO_4 anion must be SeO_4^{2-}. Thus, the oxidation state of Co is +2. Since the oxidation state of O is −2 and the net ionic charge is −2, the oxidation state of Se is determined by $x_{Se} - 8 = -2$, so x_{Se} must be +6.

d. The formula of the hydroxide anion is OH^-. Thus, the oxidation state of Pb is +2. As usual, the oxidation state of H is +1 and the oxidation state of O is −2.

4.61.

a. Phosphorus changes from an oxidation number of zero in P_4 to +5 in P_4O_{10}, losing electrons and acting as a reducing agent. Oxygen changes from an oxidation number of zero in O_2 to −2 in P_4O_{10}, gaining electrons and acting as an oxidizing agent.

b. Cobalt changes from an oxidation number of zero in Co(*s*) to +2 in $CoCl_2$, losing electrons and acting as a reducing agent. Chlorine changes from an oxidation number of zero in Cl_2 to −1 in $CoCl_2$, gaining electrons and acting as an oxidizing agent.

4.62.

a. Carbon changes from an oxidation number of zero in C to +2 in CO, losing electrons and acting as a reducing agent. Zinc changes from an oxidation number of +2 in ZnO to zero in Zn, gaining electrons and acting as an oxidizing agent.

b. Iron changes from an oxidation number of zero in Fe(*s*) to +2 in FeS, losing electrons and acting as a reducing agent. Sulfur changes from an oxidation number of 0 in S_8 to −2 in FeS, gaining electrons and acting as an oxidizing agent.

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4.63.

a. Al changes from oxidation number zero to +3; Al is the reducing agent.

F changes from oxidation number zero to −1; F_2 is the oxidizing agent.

b. Hg changes from oxidation state +2 to 0; Hg^{2+} is the oxidizing agent.

N changes from oxidation state +3 to +5; NO_2^- is the reducing agent.

4.64.

a. C changes from oxidation number +2 to +4; the CO is the reducing agent.

Fe changes from oxidation number +3 to 0; the Fe_2O_3 is the oxidizing agent.

b. S changes from oxidation number −2 to +6; the PbS is the reducing agent.

O changes from oxidation number −1 to −2; the H_2O_2 is the oxidizing agent.

4.65.

a. First, identify the species being oxidized and reduced, and assign the appropriate oxidation states. Since $CuCl_2$ and $AlCl_3$ are both soluble ionic compounds, Cl^- is a spectator ion and can be removed from the equation. The resulting net ionic equation is

$$\overset{+2}{Cu^{2+}}(aq) + \overset{0}{Al}(s) \rightarrow \overset{+3}{Al^{3+}}(aq) + \overset{0}{Cu}(s)$$

Next, write the half-reactions in an unbalanced form.

$Al \rightarrow Al^{3+}$ (oxidation)

$Cu^{2+} \rightarrow Cu$ (reduction)

Next, balance the charge in each equation by adding electrons to the more positive side to create balanced half-reactions.

$Al \rightarrow Al^{3+} + 3e^-$ (oxidation half-reaction)

$Cu^{2+} + 2e^- \rightarrow Cu$ (reduction half-reaction)

Multiply each half-reaction by a factor that will cancel out the electrons.

$2 \times (Al \rightarrow Al^{3+} + 3e^-)$

$3 \times (Cu^{2+} + 2e^- \rightarrow Cu)$

$3Cu^{2+} + 2Al + \cancel{6e^-} \rightarrow 2Al^{3+} + 3Cu + \cancel{6e^-}$

Therefore, the balanced oxidation-reduction reaction is

$3Cu^{2+} + 2Al \rightarrow 2Al^{3+} + 3Cu$

Finally, add six Cl^- ions to each side, and add phase labels. The resulting balanced equation is

$3CuCl_2(aq) + 2Al(s) \rightarrow 2AlCl_3(aq) + 3Cu(s)$

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b. First, identify the species being oxidized and reduced, and assign the appropriate oxidation states.

$$\overset{+3}{Cr^{3+}}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cr}(s) + \overset{+2}{Zn^{2+}}(aq)$$

Next, write the half-reactions in an unbalanced form.

$Zn \rightarrow Zn^{2+}$ (oxidation)

$Cr^{3+} \rightarrow Cr$ (reduction)

Next, balance the charge in each equation by adding electrons to the more positive side to create balanced half-reactions.

$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation half-reaction)

$Cr^{3+} + 3e^- \rightarrow Cr$ (reduction half-reaction)

Multiply each half-reaction by a factor that will cancel out the electrons.

$3 \times (Zn \rightarrow Zn^{2+} + 2e^-)$

$2 \times (Cr^{3+} + 3e^- \rightarrow Cr)$

$$2Cr^{3+} + 3Zn + \cancel{6e^-} \rightarrow 2Cr + 3Zn^{2+} + \cancel{6e^-}$$

Therefore, the balanced oxidation-reduction reaction, including phase labels, is

$$2Cr^{3+}(aq) + 3Zn(s) \rightarrow 2Cr(s) + 3Zn^{2+}(aq)$$

4.66.

a. First, identify the species being oxidized and reduced, and assign the appropriate oxidation states. Since FeI_3 and MgI_2 are both soluble ionic compounds, I^- is a spectator ion and can be removed from the equation. The resulting net ionic equation is

$$\overset{+3}{Fe^{3+}}(aq) + \overset{0}{Mg}(s) \rightarrow \overset{0}{Fe}(s) + \overset{+2}{Mg^{2+}}(aq)$$

Next, write the half-reactions in an unbalanced form.

$Mg \rightarrow Mg^{2+}$ (oxidation)

$Fe^{3+} \rightarrow Fe$ (reduction)

Next, balance the charge in each equation by adding electrons to the more positive side to create balanced half-reactions.

$Mg \rightarrow Mg^{2+} + 2e^-$ (oxidation half-reaction)

$Fe^{3+} + 3e^- \rightarrow Fe$ (reduction half-reaction)

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Multiply each half-reaction by a factor that will cancel out the electrons.

$$3 \times (Mg \rightarrow Mg^{2+} + 2e^-)$$
$$2 \times (Fe^{3+} + 3e^- \rightarrow Fe)$$

$$2Fe^{3+} + 3Mg + \cancel{6e^-} \rightarrow 2Fe + 3Mg^{2+} + \cancel{6e^-}$$

Therefore, the balanced oxidation-reduction reaction is

$$2Fe^{3+} + 3Mg \rightarrow 2Fe + 3Mg^{2+}$$

Finally, add six I^- ions to each side, and add phase labels. The resulting balanced equation is

$$2FeI_3(aq) + 3Mg(s) \rightarrow 2Fe(s) + 3MgI_2(aq)$$

b. First, identify the species being oxidized and reduced, and assign the appropriate oxidation states.

$$\overset{0}{H_2(g)} + \overset{+1}{Ag^+(aq)} \rightarrow \overset{0}{Ag(s)} + \overset{+1}{H^+(aq)}$$

Next, write the half-reactions in an unbalanced form, making sure that mass is balanced.

$H_2 \rightarrow 2H^+$ (oxidation)

$Ag^+ \rightarrow Ag$ (reduction)

Next, balance the charge in each equation by adding electrons to the more positive side to create balanced half-reactions.

$H_2 \rightarrow 2H^+ + 2e^-$ (oxidation half-reaction)

$Ag^+ + e^- \rightarrow Ag$ (reduction half-reaction)

Multiply each half-reaction by a factor that will cancel out the electrons.

$$1 \times (H_2 \rightarrow 2H^+ + 2e^-)$$
$$2 \times (Ag^+ + e^- \rightarrow Ag)$$

$$H_2 + 2Ag^+ + \cancel{2e^-} \rightarrow 2Ag + 2H^+ + \cancel{2e^-}$$

Therefore, the balanced oxidation-reduction reaction, including phase labels, is

$$H_2(g) + 2Ag^+(aq) \rightarrow 2Ag(s) + 2H^+(aq)$$

4.67. $$\text{Molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \frac{0.0512 \text{ mol}}{0.0250 \text{ L}} = 2.048 = 2.05\ M$$

4.68. $$\text{Molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \frac{0.0285 \text{ mol}}{0.0500 \text{ L}} = 0.5700 = 0.570\ M$$

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4.69. Find the number of moles of solute ($KMnO_4$) using the molar mass of 158.03 g $KMnO_4$ per 1 mol $KMnO_4$:

$$0.798 \text{ g } KMnO_4 \times \frac{1 \text{ mol } KMnO_4}{158.03 \text{ g } KMnO_4} = 5.0\underline{4}97 \times 10^{-3} \text{ mol } KMnO_4$$

$$\text{Molarity} = \frac{\text{moles solute}}{\text{liters of solution}} = \frac{5.0497 \times 10^{-3} \text{ mol}}{0.0500 \text{ L}} = 0.10\underline{0}99 = 0.101 \, M$$

4.70. Find the number of moles of solute ($H_2C_2O_4$) using the molar mass of 90.04 g $H_2C_2O_4$ per 1 mol $H_2C_2O_4$:

$$1.192 \text{ g } H_2C_2O_4 \times \frac{1 \text{ mol } H_2C_2O_4}{90.04 \text{ g } H_2C_2O_4} = 0.013\underline{2}38 \text{ mol } H_2C_2O_4$$

$$\text{Molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \frac{0.013238 \text{ mol}}{0.1000 \text{ L}} = 0.132\underline{3}8 = 0.1324 \, M$$

4.71. $$0.150 \text{ mol } CuSO_4 \times \frac{1 \text{ L solution}}{0.120 \text{ mol } CuSO_4} = 1.2\underline{5}0 = 1.25 \text{ L solution}$$

4.72. $$0.102 \text{ mol } HClO_4 \times \frac{1 \text{ L solution}}{0.126 \text{ mol } HClO_4} = 0.80\underline{9}52 = 0.810 \text{ L} = 8.10 \times 10^2 \text{ mL}$$

4.73. $$0.0353 \text{ g KOH} \times \frac{1 \text{ mol KOH}}{56.10 \text{ g KOH}} \times \frac{1 \text{ L solution}}{0.0176 \text{ mol KOH}} = 0.035\underline{7}51 \text{ L} = 35.8 \text{ mL}$$

4.74. $$0.949 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } H_2SO_4} \times \frac{1 \text{ L soln}}{0.215 \text{ mol } H_2SO_4} = 0.044\underline{9}99 \text{ L} \quad (45.0 \text{ mL soln})$$

4.75. From the molarity, one L of heme solution is equivalent to 0.0019 mol of heme solute. Before starting the calculation, note that 150 mL of solution is equivalent to 150×10^{-3} L of solution:

$$150 \times 10^{-3} \text{ L soln} \times \frac{0.0019 \text{ mol heme}}{1 \text{ L solution}} = 2.\underline{8}50 \times 10^{-4} = 2.9 \times 10^{-4} \text{ mol heme}$$

4.76. From the molarity, one L of insulin solution is equivalent to 0.0048 mol of insulin solute. Before starting the calculation, note that 28 mL of solution is equivalent to 28×10^{-3} L of solution:

$$28 \times 10^{-3} \text{ L soln} \times \frac{0.0048 \text{ mol insulin}}{1 \text{ L soln}} = 1.\underline{3}44 \times 10^{-4} = 1.3 \times 10^{-4} \text{ mol insulin}$$

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4.77. Multiply the volume of solution by molarity to convert it to moles; then convert to mass of solute by multiplying by the molar mass:

$$100.0 \times 10^{-3} \text{ L soln} \times \frac{0.025 \text{ mol } Na_2Cr_2O_7}{1 \text{ L solution}} \times \frac{262.0 \text{ g } Na_2Cr_2O_7}{1 \text{ mol } Na_2Cr_2O_7}$$

$$= 0.6\underline{5}50 = 0.66 \text{ g } Na_2Cr_2O_7$$

4.78. Multiply the desired volume of solution by the molarity to convert it to moles; then convert to mass of solute by multiplying by the molar mass:

$$0.250 \text{ L soln} \times \frac{0.20 \text{ mol } Na_2SO_4}{1 \text{ L solution}} \times \frac{142.05 \text{ g } Na_2SO_4}{1 \text{ mol } Na_2SO_4} = 7.\underline{1}0 = 7.1 \text{ g } Na_2SO_4$$

Weigh out 7.1 g of pure Na_2SO_4, and place it in a 250-mL volumetric flask. Add enough water to fill the flask to the mark on the neck.

4.79. Use the rearranged version of the dilution formula to calculate the initial volume of 15.8 *M* HNO_3 required:

$$V_i = \frac{M_f V_f}{M_i} = \frac{0.12\ M \times 1000 \text{ mL}}{15.8\ M} = 7.\underline{5}9 = 7.6 \text{ mL}$$

4.80. Use the rearranged version of the dilution formula to calculate the initial volume of 12.4 *M* HCl required:

$$V_i = \frac{M_f V_f}{M_i} = \frac{0.50\ M \times 1500 \text{ mL}}{12.4\ M} = 6\underline{0}.4 = 60. \text{ mL}$$

4.81. The initial concentration of KCl (molar mass, 74.55 g/mol) is

$$3.50 \text{ g KCl} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{1}{0.0100 \text{ L}} = 4.6\underline{9}4\ M$$

Using the dilution factor, $M_1V_1 = M_2V_2$, with V_2 = 10.0 mL + 60.0 mL = 70.0 mL, after the solutions are mixed, the concentration of KCl is

$$M_2 = \frac{M_1V_1}{V_2} = \frac{4.694\ M \times 10.0 \text{ mL}}{70.0 \text{ mL}} = 0.6706\underline{9}\ M \text{ KCl}$$

For $CaCl_2$, the concentration is

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.500\ M \times 10.0 \text{ mL}}{70.0 \text{ mL}} = 0.428\underline{5}7\ M\ CaCl_2$$

Therefore, the concentrations of the ions are 0.671 *M* K^+ and 0.429 *M* Ca^{2+}. For Cl^-, it is 0.67069 *M* + 2 x 0.42857 *M* = 1.5278 *M* = 1.528 *M*

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4.82. Using the dilution factor, $M_1V_1 = M_2V_2$, with V_2 = 50.0 mL + 25.0 mL = 75.0 mL, after the solutions are mixed, the concentration of $NaClO_3$ is

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.20\ M \text{ x } 50.0\ \text{mL}}{75.0\ \text{mL}} = 0.1\underline{3}33\ M\ NaClO_3$$

For Na_2SO_4, the concentration is

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.20\ M \text{ x } 25.0\ \text{mL}}{75.0\ \text{mL}} = 0.06\underline{6}66\ M\ Na_2SO_4$$

Therefore, the concentrations of the ions are 0.13 M ClO_3^- and 0.067 M SO_4^{2-}. For Na^+, it is 0.1$\underline{3}$33 M + 2 x 0.06$\underline{6}$66 M = 0.2$\underline{6}$66 = 0.27 M.

4.83. Use the appropriate conversion factors to convert the mass of $BaSO_4$ to the mass of Ba^{2+} ions:

$$0.513\ \text{g}\ BaSO_4 \text{ x } \frac{1\ \text{mol}\ BaSO_4}{233.40\ \text{g}\ BaSO_4} \text{ x } \frac{1\ \text{mol}\ Ba^{2+}}{1\ \text{mol}\ BaSO_4} \text{ x } \frac{137.33\ \text{g}\ Ba^{2+}}{1\ \text{mol}\ Ba^{2+}}$$

$$= 0.30\underline{1}84\ \text{g}\ Ba^{2+}$$

Then calculate the percentage of barium in the 458 mg (0.458 g) compound:

$$\frac{0.30184\ \text{g}\ Ba^{2+}}{0.458\ \text{g}} \text{ x } 100\% = 65.\underline{9}039 = 65.9\%\ Ba^{2+}$$

4.84. Use the appropriate conversion factors to convert the mass of AgI to the mass of I^- ions:

$$2.185\ \text{g AgI} \text{ x } \frac{1\ \text{mol AgI}}{234.77\ \text{g AgI}} \text{ x } \frac{1\ \text{mol}\ I^-}{1\ \text{mol AgI}} \text{ x } \frac{126.90\ \text{g}\ I^-}{1\ \text{mol}\ I^-} = 1.18\underline{1}05\ \text{g}\ I^-$$

Then calculate the percentage of iodine in the 1.545 g compound:

$$\frac{1.18105\ \text{g}\ I^-}{1.545\ \text{g}} \text{ x } 100\% = 76.4\underline{4}3 = 76.44\%\ I^-$$

4.85.

a. The mass of chloride ion in the AgCl from the copper chloride compound is

$$86.00\ \text{mg AgCl} \text{ x } \frac{35.45\ \text{mg}\ Cl^-}{143.32\ \text{mg AgCl}} = 21.2\underline{7}1\ \text{mg}\ Cl^-$$

The percentage of chlorine in the 59.40 mg sample is

$$\frac{21.2\underline{7}1\ \text{mg}\ Cl^-}{59.40\ \text{mg sample}} \text{ x } 100\% = 35.8\underline{0}9 = 35.81\%\ Cl^-$$

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b. Of the various approaches, it is as easy to calculate the theoretical percentage of Cl^- in both CuCl and $CuCl_2$ as it is to use another approach:

$$\text{CuCl: } \frac{35.45 \text{ mg Cl}^-}{99.00 \text{ mg CuCl}} \times 100\% = 35.808\%$$

$$\text{CuCl}_2\text{: } \frac{70.90 \text{ mg Cl}^-}{134.45 \text{ mg CuCl}_2} \times 100\% = 52.733\%$$

The compound is obviously CuCl.

4.86.

a. The mass of chloride ion in the AgCl from the gold chloride compound is

$$100.3 \text{ mg AgC1} \times \frac{35.45 \text{ mg Cl}^-}{143.32 \text{ mg AgCl}} = 24.809 \text{ mg Cl}^-$$

The percentage of chloride in the 162.7 mg sample is

$$\frac{24.809 \text{ mg Cl}^-}{162.7 \text{ mg sample}} \times 100\% = 15.248 = 15.25\% \text{ Cl}^-$$

b. Of the various approaches, it is as easy to calculate the theoretical percentage of Cl^- in both AuCl and $AuCl_3$ as it is to use another approach:

$$\text{AuCl: } \frac{35.45 \text{ mg Cl}^-}{232.4 \text{ mg AuCl}} \times 100\% = 15.253\%$$

$$\text{AuCl}_3\text{: } \frac{106.35 \text{ mg Cl}^-}{303.32 \text{ mg AuCl}_3} \times 100\% = 35.0620\%$$

The compound is obviously AuCl.

4.87. First, calculate the moles of chlorine in the compound:

$$0.3048 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol AgCl}} = 0.0021267 \text{ mol Cl}^-$$

Then, calculate the g Fe^{x+} from the g Cl^-:

$$\text{g Fe}^{x+} = 0.01348 \text{ g comp} - \left(0.0021267 \text{ mol Cl}^- \times \frac{35.45 \text{ g Cl}^-}{1 \text{ mol Cl}^-} \right) = 0.059408 \text{ g Fe}^{x+}$$

Now, calculate the moles of Fe^{x+} using the molar mass:

$$0.059408 \text{ g Fe}^{x+} \times \frac{1 \text{ mol Fe}^{x+}}{55.85 \text{ g Fe}^{x+}} = 0.0010637 \text{ mol Fe}^{x+}$$

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Finally, divide the mole numbers by the smallest mole number:

$$\text{For Cl: } \frac{0.002127 \text{ mol } Cl^-}{0.0010637 \text{ mol}} = 2.00; \text{ for } Fe^{x+}: \frac{0.0010637 \text{ mol } Fe^{x+}}{0.0010637 \text{ mol}} = 1.00$$

Thus, the formula is $FeCl_2$.

4.88. First, calculate the moles of Ba^{2+} in the compound:

$$2.012 \text{ g } BaCrO_4 \times \frac{1 \text{ mol } BaCrO_4}{253.33 \text{ g } BaCrO_4} \times \frac{1 \text{ mol } Ba^{2+}}{1 \text{ mol } BaCrO_4} = 0.0079422 \text{ mol } Ba^{2+}$$

Next, calculate the g O from the g Ba^{2+}:

$$\text{g O} = 1.345 \text{ g comp} - \left(0.0079422 \text{ mol } Ba^{2+} \times \frac{137.33 \text{ g } Ba^{2+}}{1 \text{ mol } Ba^{2+}} \right) = 0.25430 \text{ mol O}$$

Now, calculate the moles of O using the molar mass:

$$0.25430 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.015894 \text{ mol O}$$

Finally, divide the mole numbers by the smallest mole number:

$$\text{For O: } \frac{0.015894 \text{ mol O}}{0.0079422 \text{ mol}} = 2.00; \text{ for } Ba^{2+}: \frac{0.0079422 \text{ mol } Ba^{2+}}{0.0079422 \text{ mol}} = 1.00$$

Thus, the formula is BaO_2 (barium peroxide).

4.89. Using molarity, convert the volume of Na_2CO_3 to moles of Na_2CO_3; then use the equation to convert to moles of HNO_3 and finally to volume:

$$2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + H_2O + CO_2$$

$$44.8 \times 10^{-3} \text{ L } Na_2CO_3 \times \frac{0.150 \text{ mol } Na_2CO_3}{1 \text{ L soln}} \times \frac{2 \text{ mol } HNO_3}{1 \text{ mol } Na_2CO_3} \times \frac{1 \text{ L } HNO_3}{0.250 \text{ mol } HNO_3}$$

$$= 0.05376 \text{ L} = 0.0538 \text{ L} = 53.8 \text{ mL}$$

4.90. As in the previous problem, use molarity to convert to volume; then use the equation to convert to moles of the other reactant and finally to volume:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$

$$49.8 \times 10^{-3} \text{ L } Ca(OH)_2 \times \frac{0.150 \text{ mol } Ca(OH)_2}{1 \text{ L soln}} \times \frac{1 \text{ mol } Na_2CO_3}{1 \text{ mol } Ca(OH)_2} \times \frac{1 \text{ L } Na_2CO_3}{0.350 \text{ mol } Na_2CO_3}$$

$$= 0.02134 \text{ L (21.3 mL) } Na_2CO_3$$

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4.91. The reaction is $H_2SO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + 2H_2O + CO_2$.

$$8.20 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.01 \text{ g } NaHCO_3} \times \frac{1 \text{ mol } H_2SO_4}{2 \text{ mol } NaHCO_3} \times \frac{1 \text{ L soln}}{0.150 \text{ mol } H_2SO_4}$$

$$= 0.3253 \text{ L (325 mL) soln}$$

4.92. The reaction is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 4H_2O$$

$$3.36 \text{ g } FeSO_4 \times \frac{1 \text{ mol } FeSO_4}{151.92 \text{ g } FeSO_4} \times \frac{2 \text{ mol } KMnO_4}{10 \text{ mol } FeSO_4} \times \frac{1 \text{ L soln}}{0.250 \text{ mol } KMnO_4}$$

$$= 0.01769 \text{ L (17.7 mL) soln}$$

4.93. First, find the mass of H_2O_2 required to react with $KMnO_4$.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5O_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$51.7 \times 10^{-3} \text{ L } KMnO_4 \times \frac{0.145 \text{ mol } KMnO_4}{1 \text{ L soln}} \times \frac{5 \text{ mol } H_2O_2}{2 \text{ mol } KMnO_4} \times \frac{34.02 \text{ g } H_2O_2}{1 \text{ mol } H_2O_2}$$

$$= 0.6375 \text{ g } H_2O_2$$

Percent H_2O_2 = (mass H_2O_2 ÷ mass sample) x 100%

= (0.6375 g ÷ 20.0 g) x 100% = 3.187 = 3.19%

4.94. First, find the mass of Fe^{2+} required to react with the $K_2Cr_2O_7$.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$

$$43.7 \times 10^{-3} \text{ L } K_2Cr_2O_7 \times \frac{0.150 \text{ mol } K_2Cr_2O_7}{1 \text{ L soln}} \times \frac{6 \text{ mol } FeSO_4}{1 \text{ mol } K_2Cr_2O_7}$$

$$\times \frac{1 \text{ mol } Fe^{2+}}{1 \text{ mol } FeSO_4} \times \frac{55.85 \text{ g } Fe^{2+}}{1 \text{ mol } Fe^{2+}} = 2.196 \text{ g } Fe^{2+}$$

2.196 g Fe^{2+} in reaction = 2.196 g Fe^{2+} in ore, so

Percent Fe = (mass Fe^{2+} ÷ mass ore) x 100% = (2.196 g ÷ 3.33 g) x 100%

= 65.96 = 66.0%

■ SOLUTIONS TO GENERAL PROBLEMS

4.95. For the reaction of magnesium metal and hydrobromic acid, the equations are as follows.

Molecular equation: $Mg(s) + 2HBr(aq) \rightarrow H_2(g) + MgBr_2(aq)$

Ionic equation: $Mg(s) + 2H^+(aq) \rightarrow H_2(g) + Mg^{2+}(aq)$

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4.96. For the reaction of aluminum metal and perchloric acid, the equations are as follows.

Molecular equation: $2Al(s) + 6HClO_4(aq) \rightarrow 3H_2(g) + 2Al(ClO_4)_3(aq)$

Ionic equation: $2Al(s) + 6H^+(aq) \rightarrow 3H_2(g) + 2Al^{3+}(aq)$

4.97. For the reaction of nickel(II) sulfate and lithium hydroxide, the equations are as follows.

Molecular equation: $NiSO_4(aq) + 2LiOH(aq) \rightarrow Ni(OH)_2(s) + Li_2SO_4(aq)$

Ionic equation: $Ni^{2+}(aq) + 2OH^-(aq) \rightarrow Ni(OH)_2(s)$

4.98. For the reaction of potassium sulfate and barium bromide, the equations are as follows.

Molecular equation: $BaBr_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KBr(aq)$

Ionic equation: $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

4.99.

a. Molecular equation: $LiOH(aq) + HCN(aq) \rightarrow LiCN(aq) + H_2O(l)$

Ionic equation: $OH^-(aq) + HCN(aq) \rightarrow CN^-(aq) + H_2O(l)$

b. Molecular equation: $Li_2CO_3(aq) + 2HNO_3(aq) \rightarrow 2LiNO_3(aq) + CO_2(g) + H_2O(l)$

Ionic equation: $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$

c. Molecular equation: $LiCl(aq) + AgNO_3(aq) \rightarrow LiNO_3(aq) + AgCl(s)$

Ionic equation: $Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

d. Molecular equation: $MgSO_4(aq) + LiCl(aq) \rightarrow$ NR

(Li_2SO_4 and $MgCl_2$ are soluble.)

4.100.

a. Molecular equation: $Al(OH)_3(s) + 3HNO_3(aq) \rightarrow Al(NO_3)_3(aq) + 3H_2O(l)$

Ionic equation: $Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$

b. Molecular equation: $NaBr(aq) + HClO_4(aq) \rightarrow$ NR

(HBr and $NaClO_4$ are soluble.)

c. Molecular equation: $CaCl_2(aq) + NaNO_3(aq) \rightarrow$ NR

($Ca(NO_3)_2$ and NaCl are soluble.)

d. Molecular equation: $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Ionic equation: $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

4.101.

a. Molecular equation: $Sr(OH)_2(aq) + 2HC_2H_3O_2(aq) \rightarrow Sr(C_2H_3O_2)_2(aq) + 2H_2O(l)$

Ionic equation: $HC_2H_3O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$

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b. Molecular equation: $NH_4I(aq) + CsCl(aq) \rightarrow NR$

(NH_4Cl and CsI are soluble.)

c. Molecular equation: $NaNO_3(aq) + CsCl(aq) \rightarrow NR$

($NaCl$ and $CsNO_3$ are soluble.)

d. Molecular equation: $NH_4I(aq) + AgNO_3(aq) \rightarrow NH_4NO_3(aq) + AgI(s)$

Ionic equation: $I^-(aq) + Ag^+(aq) \rightarrow AgI(s)$

4.102.

a. Molecular equation: $2HClO_4(aq) + BaCO_3(s) \rightarrow$

$Ba(ClO_4)_2(aq) + H_2CO_3(aq)\ [CO_2(g) + H_2O(l)]$

Ionic equation: $2H^+(aq) + BaCO_3(s) \rightarrow Ba^{2+}(aq) + CO_2(g) + H_2O(l)$

b. Molecular equation: $H_2CO_3(aq) + Sr(OH)_2(aq) \rightarrow 2H_2O(l) + SrCO_3(s)$

Ionic equation: $H_2CO_3(aq) + Sr^{2+}(aq) + 2OH^-(aq) \rightarrow 2H_2O(l) + SrCO_3(s)$

c. Molecular equation: $2K_3PO_4(aq) + 3MgCl_2(aq) \rightarrow 6KCl(aq) + Mg_3(PO_4)_2(s)$

Ionic equation: $2PO_4^{3-}(aq) + 3Mg^{2+}(aq) \rightarrow Mg_3(PO_4)_2(s)$

d. Molecular equation: $FeSO_4(aq) + MgCl_2(aq) \rightarrow NR$

($FeCl_2$ and $MgSO_4$ are soluble.)

4.103. For each preparation, the compound to be prepared is given first, followed by the compound from which it is to be prepared. Then the method of preparation is given, followed by the molecular equation for the preparation reaction. Steps such as evaporation are not given in the molecular equation.

a. To prepare $CuCl_2$ from $CuSO_4$, add a solution of $BaCl_2$ to a solution of the $CuSO_4$, precipitating $BaSO_4$. The $BaSO_4$ can be filtered off, leaving aqueous $CuCl_2$, which can be obtained in solid form by evaporation. Molecular equation:

$CuSO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + CuCl_2(aq)$

b. To prepare $Ca(C_2H_3O_2)_2$ from $CaCO_3$, add a solution of acetic acid, $HC_2H_3O_2$, to the solid $CaCO_3$, forming CO_2, H_2O, and aqueous $Ca(C_2H_3O_2)_2$. The aqueous $Ca(C_2H_3O_2)_2$ can be converted to the solid form by evaporation, which also removes the CO_2 and H_2O products. Molecular equation:

$CaCO_3(s) + 2HC_2H_3O_2(aq) \rightarrow Ca(C_2H_3O_2)_2(aq) + CO_2(g) + H_2O(l)$

c. To prepare $NaNO_3$ from Na_2SO_3, add a solution of nitric acid, HNO_3, to the solid Na_2SO_3, forming SO_2, H_2O, and aqueous $NaNO_3$. The aqueous $NaNO_3$ can be converted to the solid by evaporation, which also removes the SO_2 and H_2O products. Molecular equation:

$Na_2SO_3(s) + 2HNO_3(aq) \rightarrow 2NaNO_3(aq) + SO_2(g) + H_2O(l)$

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d. To prepare $MgCl_2$ from $Mg(OH)_2$, add a solution of hydrochloric acid (HCl) to the solid $Mg(OH)_2$, forming H_2O and aqueous $MgCl_2$. The aqueous $MgCl_2$ can be converted to the solid form by evaporation. Molecular equation:

$$Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$$

4.104. For each preparation, the compound to be prepared is given first, followed by the compound from which it is to be prepared. Then, the method of preparation is given, followed by the molecular equation for the preparation reaction. Steps such as evaporation are not given in the molecular equation.

a. To prepare $MgCl_2$ from $MgCO_3$, add a solution of hydrochloric acid (HCl) to the solid $MgCO_3$, forming CO_2, H_2O, and aqueous $MgCl_2$. The aqueous $MgCl_2$ can be converted to the solid form by evaporation. Molecular equation:

$$MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + CO_2(g) + H_2O(l)$$

b. To prepare $NaNO_3$ from NaCl, add a solution of $AgNO_3$ to a solution of the NaCl, precipitating AgCl. The AgCl can be filtered off, leaving aqueous $NaNO_3$, which can be obtained in solid form by evaporation. Molecular equation:

$$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

c. To prepare $Al(OH)_3$ from $Al(NO_3)_3$, add a solution of NaOH to a solution of $Al(NO_3)_3$, precipitating $Al(OH)_3$. The $Al(OH)_3$ can be filtered off and dried to remove any water adhering to it. Molecular equation:

$$Al(NO_3)_3(aq) + 3NaOH(aq) \rightarrow Al(OH)_3(s) + 3NaNO_3(aq)$$

d. To prepare HCl from H_2SO_4, add a solution of $BaCl_2$ to the solution of H_2SO_4, precipitating $BaSO_4$. The $BaSO_4$ can be filtered off, leaving the desired solution of aqueous HCl. Molecular equation:

$$H_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$$

4.105.

a. Decomposition

b. Decomposition

c. Combination

d. Displacement

4.106.

a. Combination

b. Displacement

c. Decomposition

d. Combination

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4.107.

a. $Pb(NO_3)_2 + H_2SO_4$ [$\rightarrow PbSO_4(s) + HNO_3(aq)$]

$Pb(NO_3)_2 + MgSO_4$ [$\rightarrow PbSO_4(s) + Mg(NO_3)_2(aq)$]

$Pb(NO_3)_2 + Ba(OH)_2$ [$\rightarrow Pb(OH)_2(s) + Ba(NO_3)_2(aq)$]

b. $Ba(OH)_2 + MgSO_4$ [$\rightarrow BaSO_4(s) + Mg(OH)_2(s)$]

c. $Ba(OH)_2 + H_2SO_4$ [$\rightarrow BaSO_4(s) + H_2O(l)$]

4.108.

a. $AgNO_3 + H_3PO_4$ [$\rightarrow Ag_3PO_4(s) + HNO_3(aq)$]

$AgNO_3 + Sr(OH)_2$ [$\rightarrow AgOH(s) + Sr(NO_3)_2(aq)$]

$CuSO_4 + H_3PO_4$ [$\rightarrow Cu_3(PO_4)_2(s) + H_2SO_4(aq)$]

b. $Sr(OH)_2 + CuSO_4$ [$\rightarrow SrSO_4(s) + Cu(OH)_2(s)$]

c. $Sr(OH)_2 + H_3PO_4$ [$\rightarrow Sr_3(PO_4)_2(s) + H_2O(l)$]

4.109. Divide the mass of $CaCl_2$ by its molar mass and volume to find molarity:

$$4.50 \text{ g } CaCl_2 \times \frac{1 \text{ mol } CaCl_2}{110.98 \text{ g } CaCl_2} \times \frac{1}{1.000 \text{ L soln}} = 0.040\underline{5}4 = 0.0405 \, M \, CaCl_2$$

The $CaCl_2$ dissolves to form Ca^{2+} and $2Cl^-$ ions. Therefore, the molarities of the ions are 0.0405 *M* Ca^{2+} and 2 x 0.04054, or 0.0811, *M* Cl^- ions.

4.110. Divide the mass of $Fe_2(SO_4)_3$ by its molar mass and volume to find molarity:

$$3.45 \text{ g } Fe_2(SO_4)_3 \times \frac{1 \text{ mol } Fe_2(SO_4)_3}{399.91 \text{ g } Fe_2(SO_4)_3} \times \frac{1}{1.000 \text{ L soln}} = 0.008\underline{6}27$$

$$= 0.00863 \, M \, Fe_2(SO_4)_3$$

The $Fe_2(SO_4)_3$ dissolves to form $2Fe^{3+}$ and $3SO_4^{2-}$ ions. Therefore, the molarities of the ions are 2 x 0.00863, or 0.0173, *M* Fe^{3+} and 3 x 0.00863, or 0.0259, *M* SO_4^{2-}.

4.111. Divide the mass of $K_2Cr_2O_7$ by its molar mass and volume to find molarity. Then calculate the volume needed to prepare 1.00 L of a 0.100 *M* solution.

$$89.3 \text{ g } K_2Cr_2O_7 \times \frac{1 \text{ mol } K_2Cr_2O_7}{294.20 \text{ g } K_2Cr_2O_7} = 0.30\underline{3}5 \text{ mol } K_2Cr_2O_7$$

$$\text{Molarity} = \frac{0.3035 \text{ mol } K_2Cr_2O_7}{1.00 \text{ L}} = 0.30\underline{3}5 \, M$$

$$V_i = \frac{M_f \times V_f}{M_i} = \frac{0.100 \, M \times 1.00 \text{ L}}{0.3035 \, M} = 0.32\underline{9}4 \text{ L (329 mL)}$$

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4.112. Divide the mass by the molar mass and then by volume to find molarity. Then, calculate the volume needed to prepare 1.00 L of 0.1150 *M*.

$$71.2 \text{ g } H_2C_2O_4 \text{ x } \frac{1 \text{ mol } H_2C_2O_4}{90.04 \text{ g } H_2C_2O_4} = 0.790\underline{7} \text{ mol } H_2C_2O_4$$

$$\text{Molarity} = \frac{0.7907 \text{ mol } H_2C_2O_4}{1.00 \text{ L}} = 0.790\underline{7} = 0.791 \, M$$

$$V_i = \frac{M_f \text{ x } V_f}{M_i} = \frac{0.150 \, M \text{ x } 1.00 \text{ L}}{0.7907 \, M} = 0.189\underline{6} \text{ L (190. mL)}$$

Place 190. mL of the 0.791 *M* solution in a 1 L volumetric flask, and dilute to 1.00 L.

4.113. Assume a volume of 1.000 L (1000 cm^3) for the 6.00% NaBr solution, and convert to moles and then to molarity.

$$1000 \text{ cm}^3 \text{ x } \frac{1.046 \text{ g soln}}{1 \text{ cm}^3} \text{ x } \frac{6.00 \text{ g NaBr}}{100 \text{ g soln}} \text{ x } \frac{1 \text{ mol NaBr}}{102.89 \text{ g NaBr}} = 0.609\underline{9} \text{ mol}$$

$$\text{Molarity NaBr} = \frac{0.6099 \text{ mol NaBr}}{1.000 \text{ L}} = 0.609\underline{9} = 0.610 \, M$$

4.114. Assume a volume of 1.000 L (1000 mL) for the 4.00% NH_3 solution, and convert to moles and then to molarity.

$$1000 \text{ mL} \text{ x } \frac{0.979 \text{ g soln}}{1 \text{ mL}} \text{ x } \frac{4.00 \text{ g } NH_3}{100 \text{ g soln}} \text{ x } \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} = 2.29\underline{9} \text{ mol } NH_3$$

$$\text{Molarity } NH_3 = \frac{2.299 \text{ mol } NH_3}{1.000 \text{ L}} = 2.29\underline{9} = 2.30 \, M$$

4.115. First, calculate the moles of $BaCl_2$:

$$1.128 \text{ g } BaSO_4 \text{ x } \frac{1 \text{ mol } BaSO_4}{233.40 \text{ g } BaSO_4} \text{ x } \frac{1 \text{ mol } BaCl_2}{1 \text{ mol } BaSO_4} = 0.0048329 \text{ mol } BaCl_2$$

Then calculate the molarity from the moles and volume (0.0500 L):

$$\text{Molarity} = \frac{0.0048329 \text{ mol } BaCl_2}{0.0500 \text{ L}} = 0.096\underline{6}58 = 0.0967 \, M$$

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4.116. First, calculate the moles of $CaCl_2$:

$$1.437 \text{ g } CaC_2O_4 \text{ x } \frac{1 \text{ mol } CaC_2O_4}{128.10 \text{ g } CaC_2O_4} \text{ x } \frac{1 \text{ mol } CaCl_2}{1 \text{ mol } CaC_2O_4} = 0.0112\underline{1}77 \text{ mol } CaCl_2$$

Then calculate the molarity from the moles and volume (0.0500 L):

$$\text{Molarity} = \frac{0.0112177 \text{ mol } CaCl_2}{0.0500 \text{ L}} = 0.22\underline{4}35 = 0.224 \, M$$

4.117. First, calculate the grams of thallium(I) sulfate:

$$0.2122 \text{ g TlI} \text{ x } \frac{1 \text{ mol TlI}}{331.28 \text{ g TlI}} \text{ x } \frac{1 \text{ mol } Tl_2SO_4}{2 \text{ mol TlI}} \text{ x } \frac{504.83 \text{ g } Tl_2SO_4}{1 \text{ mol } Tl_2SO_4} = 0.161\underline{6}8 \text{ g } Tl_2SO_4$$

Then calculate the percent Tl_2SO_4 in the rat poison:

$$\text{Percent } Ti_2SO_4 = \frac{0.16168 \text{ g}}{0.7590 \text{ g}} \text{ x } 100\% = 21.3\underline{0}1 = 21.30\%$$

4.118. First, calculate the grams of $CaCO_3$:

$$0.629 \text{ g } CaC_2O_4 \text{ x } \frac{1 \text{ mol } CaC_2O_4}{128.10 \text{ g } CaC_2O_4} \text{ x } \frac{1 \text{ mol } CaCO_3}{1 \text{ mol } CaC_2O_4} \text{ x } \frac{100.1 \text{ g } CaCO_3}{1 \text{ mol } CaCO_3}$$

$$= 0.49\underline{1}51 \text{ g } CaCO_3$$

Then calculate the percent $CaCO_3$ in the antacid:

$$\text{Percent } CaCO_3 = \frac{0.49151 \text{ g}}{0.680 \text{ g}} \text{ x } 100\% = 72.\underline{2}8 = 72.3\%$$

4.119. The mass of copper(II) ion and the mass of sulfate ion in the 98.77-mg sample are

$$0.09877 \text{ g x } 0.3250 = 0.0321\underline{0}0 \text{ g } Cu^{2+} \text{ ion}$$

$$0.11666 \text{ g } BaSO_4 \text{ x } \frac{96.07 \text{ g } SO_4^{2-}}{233.40 \text{ g } BaSO_4} = 0.0480\underline{1}9 = 0.04802 \text{ g } SO_4^{2-}$$

$$\text{Mass of water left} = 0.09877 \text{ g} - (0.03210 \text{ g } Cu^{2+} + 0.04802 \text{ g } SO_4^{2-}) = 0.01865 \text{ g } H_2O$$

$$\text{Moles of water left} = 0.01865 \text{ g} \div 18.02 \text{ g/mol} = 1.035 \text{ x } 10^{-3} \text{ mol}$$

$$\text{Moles of } Cu^{2+} = 0.03210 \text{ g} \div 63.55 \text{ g/mol} = 5.05\underline{1}1 \text{ x } 10^{-4} \text{ mol}$$

$$\text{Ratio of water to } Cu^{2+}, \text{ or } CuSO_4 = 1.035 \text{ x } 10^{-3} \div 5.0511 \text{ x } 10^{-4} = 2.05, \text{ or } 2$$

The formula is thus $CuSO_4 \bullet 2H_2O$.

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4.120. The mass of copper(II) ion and the mass of sulfate ion in the 85.42-mg sample are

$$0.08542 \text{ g} \times 0.2976 = 0.025421 \text{ g } Cu^{2+} \text{ ion}$$

$$0.09333 \text{ g } BaSO_4 \times \frac{96.07 \text{ g } SO_4^{2-}}{233.40 \text{ g } BaSO_4} = 0.038416 = 0.03842 \text{ g } SO_4^{2-}$$

$$\text{Mass of water left} = 0.08542 \text{ g} - (0.025421 \text{ g } Cu^{2+} + 0.038416 \text{ g } SO_4^{2-})$$
$$= 0.021583 \text{ g } H_2O$$

$$\text{Moles of water left} = 0.021583 \div 18.02 \text{ g/mol} = 1.1977 \times 10^{-3} \text{ mol}$$

$$\text{Moles of } Cu^{2+} = 0.025421 \text{ g} \div 63.55 \text{ g/mol} = 4.0002 \times 10^{-4} \text{ mol}$$

$$\text{Ratio of water to } Cu^{2+}, \text{ or } CuSO_4 = 1.1977 \times 10^{-3} \div 4.000 \times 10^{-4} = 2.99, \text{ or } 3$$

The formula is $CuSO_4 \cdot 3H_2O$.

4.121. For these calculations, the relative numbers of moles of gold and chlorine must be determined. These can be found from the masses of the two elements in the sample:

$$\text{Total mass} = \text{mass of Au} + \text{mass of Cl} = 328 \text{ mg}$$

The mass of chlorine in the precipitated AgCl is equal to the mass of chlorine in the compound of gold and chlorine. The mass of Cl in the 0.464 g of AgCl is

$$0.464 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol Cl}}{1 \text{ mol AgCl}} \times \frac{35.45 \text{ g Cl}}{1 \text{ mol Cl}}$$

$$= 0.11476 \text{ g Cl} \quad (114.76 \text{ mg Cl})$$

$$\text{Mass percentage Cl} = \frac{\text{mass Cl}}{\text{mass comp}} \times 100\% = \frac{114.76 \text{ mg}}{328 \text{ mg}} \times 100\% = 35.0\% \text{ Cl}$$

To find the empirical formula, convert each mass to moles:

$$\text{Mass percentage Au} = 328 \text{ mg} - 114.76 \text{ mg Cl} = 213.23 \text{ mg Au}$$

$$0.11476 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.003238 \text{ mol Cl}$$

$$0.21323 \text{ g Au} \times \frac{1 \text{ mol Au}}{196.97 \text{ g Au}} = 0.001082 \text{ mol Au}$$

Divide both numbers of moles by the smaller number (0.001082) to find the integers.

$$\text{Integer for Cl: } 0.003238 \text{ mol} \div 0.001082 \text{ mol} = 2.99, \text{ or } 3$$

$$\text{Integer for Au: } 0.001082 \text{ mol} \div 0.001082 \text{ mol} = 1.00, \text{ or } 1$$

The empirical formula is $AuCl_3$.

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4.122. To find the mass percentages of Cl and Sc, find the mass of the chlorine in the precipitated AgCl, which is equal to the mass of the chlorine in the compound of scandium and chlorine. The mass of Cl in the 167.4 mg (0.1674 g) of AgCl is

$$0.1674 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol Cl}}{1 \text{ mol AgCl}} \times \frac{35.45 \text{ g Cl}}{1 \text{ mol Cl}} = 0.04141 \text{ g Cl}$$

The mass of Sc equals the difference between the sample mass and the mass of Cl:

$$\text{Mass Sc} = 0.0589 \text{ g} - 0.04141 \text{ g} = 0.01749 \text{ g Sc}$$

The mass percentage of each element is found by dividing the mass of the element by the mass of the compound and multiplying by 100%: Mass percentage = (mass elem. ÷ mass comp.) x 100%.

$$\text{Mass percentage Cl} = (0.04141 \text{ g} \div 0.0589 \text{ g}) \times 100\% = 70.305 = 70.3\%$$

$$\text{Mass percentage Sc} = (0.01749 \text{ g} \div 0.0589 \text{ g}) \times 100\% = 29.69 = 29.7\%$$

To find the empirical formula, convert each mass to moles:

$$0.04141 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.0011680 \text{ mol Cl}$$

$$0.01749 \text{ g Sc} \times \frac{1 \text{ mol Sc}}{44.96 \text{ g Sc}} = 0.0003890 \text{ mol Sc}$$

Divide both numbers of moles by the smaller number (0.0003890) to find the integers:

$$\text{Integer for Cl} = 0.0011680 \text{ mol} \div 0.0003890 \text{ mol} = 3.00, \text{ or } 3$$

$$\text{Integer for Sc} = 0.0003890 \text{ mol} \div 0.0003890 \text{ mol} = 1.00, \text{ or } 1$$

The empirical formula is $ScCl_3$.

4.123. From the equations $NH_3 + HCl \rightarrow NH_4Cl$ and $NaOH + HCl \rightarrow NaCl + H_2O$, we write

$$\text{Mol } NH_3 = \text{mol HCl}(NH_3)$$

$$\text{Mol NaOH} = \text{mol HCl(NaOH)}$$

We can calculate the mol NaOH and the sum [mol $HCl(NH_3)$ + mol HCl(NaOH)] from the titration data. Because the sum equals mol NH_3 plus mol NaOH, we can calculate the unknown mol NH_3 from the difference: Mol NH_3 = sum − mol NaOH.

$$\text{Mol HCl (NaOH)} + \text{mol HCl } (NH_3) = 0.0463 \text{ L} \times \frac{0.213 \text{ mol HCl}}{1.000 \text{ L}}$$

$$= 0.009862 \text{ mol HCl}$$

$$\text{Mol NaOH} = 0.0443 \text{ L} \times \frac{0.128 \text{ mol NaOH}}{1.000 \text{ L}} = 0.005670 \text{ mol NaOH}$$

$$\text{Mol HCl}(NH_3) = 0.009862 \text{ mol} - 0.005670 \text{ mol} = 0.004192 \text{ mol}$$

$$\text{Mol } NH_3 = \text{mol HCl}(NH_3) = 0.004192 \text{ mol } NH_3$$

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Because all the N in the $(NH_4)_2SO_4$ was liberated as and titrated as NH_3, the amount of N in the fertilizer is equal to the amount of N in the NH_3. Thus, the moles of NH_3 can be used to calculate the mass percentage of N in the fertilizer:

$$0.004192 \text{ mol } NH_3 \times \frac{1 \text{ mol N}}{1 \text{ mol } NH_3} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} = 0.05873 \text{ g N}$$

$$\text{Mass percentage N} = \frac{\text{mass N}}{\text{mass fert.}} \times 100\% = \frac{0.05873 \text{ g N}}{0.608 \text{ g}} \times 100\% = 9.659 = 9.66\%$$

4.124. From $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ and $HCl + NaOH \rightarrow NaCl + H_2O$, we write

$$\text{Mol } NaHCO_3 = \text{mol HCl}(NaHCO_3)$$

$$\text{Mol NaOH} = \text{mol HCl(NaOH)}$$

We can calculate the mol NaOH and the sum [mol $HCl(NaHCO_3)$ + mol HCl(NaOH)] from the titration data. Because the sum equals mol $NaHCO_3$ plus mol NaOH, we can calculate the unknown mol $NaHCO_3$ from the difference: Mol $NaHCO_3$ = sum − mol NaOH.

$$\text{Mol HCl (NaOH)} + \text{mol HCl } (NaHCO_3) = 0.0500 \text{ L} \times \frac{0.190 \text{ mol HCl}}{1.000 \text{ L}}$$

$$= 0.009500 \text{ mol HCl}$$

$$\text{Mol NaOH} = 0.0471 \text{ L} \times \frac{0.128 \text{ mol NaOH}}{1.000 \text{ L}} = 0.006029 \text{ mol NaOH}$$

$$\text{Mol HCl}(NaHCO_3) = 0.009500 \text{ mol} - 0.006029 \text{ mol} = 0.003471 \text{ mol}$$

$$\text{Mol } NaHCO_3 = \text{mol HCl}(NaHCO_3) = 0.003471 \text{ mol}$$

Because all the $NaHCO_3$ in the tablet was titrated as $NaHCO_3$, the moles of $NaHCO_3$ can be used to calculate the mass percentage of $NaHCO_3$ in the tablet:

$$0.003471 \text{ mol } NaHCO_3 \times \frac{84.01 \text{ g } NaHCO_3}{1 \text{ mol } NaHCO_3} = 0.2916 \text{ g } NaHCO_3$$

$$\text{Mass percentage } NaHCO_3 = \frac{\text{mass } NaHCO_3}{\text{mass tab.}} \times 100\% = \frac{0.2916 \text{ g N}}{0.500 \text{ g}} \times 100\%$$

$$= 58.32 = 58.3\%$$

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■ SOLUTIONS TO STRATEGY PROBLEMS

4.125. The final volume to which the solution must be diluted is

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(3.47\ \text{M})\ (100\ \text{mL})}{1.78\ M} = 19\underline{4}.94\ \text{mL}$$

The amount of water that must be added is 19$\underline{4}$.94 mL − 100 mL = 9$\underline{4}$.94 mL. Since the density of water is 1.00 g/mL, this is equivalent to 9$\underline{4}$.94 g of water, so the amount of ice is

$$94.94\ \text{g water} \times \frac{3\ \text{g ice}}{1\ \text{g water}} = 28\underline{4}.83 = 285\ \text{g ice}$$

4.126. The balanced molecular equation is

$$2AgNO_3(aq) + Na_2CO_3(aq) \rightarrow Ag_2CO_3(s) + 2NaNO_3(aq)$$

Calculate the mass of silver nitrate required to react with the sodium carbonate solution.

$$30.6 \times 10^{-3}\ \text{L} \times 0.511\ M \times \frac{2\ \text{mol}\ AgNO_3}{1\ \text{mol}\ Na_2CO_3} \times \frac{169.88\ \text{g}}{1\ \text{mol}\ AgNO_3} = 5.3\underline{1}26\ \text{g}$$

The mass of $AgNO_3$ remaining is 8.30 g – 5.3126 g = 2.9$\underline{8}$7 g. The volume of the solution is 45.1 mL + 30.6 mL = 75.7 mL (75.7 x 10^{-3} L). The molarity of the silver ion can now be determined.

$$\frac{2.987\ \text{g}\ AgNO_3}{75.7 \times 10^{-3}\ \text{L}} \times \frac{1\ \text{mol}\ AgNO_3}{169.88\ \text{g}} = 0.23\underline{2}2 = 0.232\ M$$

4.127. $$0.248\ M \times 38.2 \times 10^{-3}\ \text{L} \times \frac{2\ \text{mol}\ Al^{3+}}{1\ \text{mol}\ Al_2(SO_4)_3} \times \frac{26.98\ \text{g}}{1\ \text{mol}\ Al^{3+}} = 0.51\underline{1}19 = 0.511\ \text{g}$$

4.128. The ratio of nitrate ion to aluminum nitrate ($Al(NO_3)_3$) is 3 to 1. The molarity of the nitrate ion after dilution is

$$M_2 = \frac{M_1V_1}{V_2} = \frac{(0.256\ \text{M})\ (31.6\ \text{mL})}{63.7\ \text{mL}} \times \frac{3\ \text{mol}\ NO_3^-}{1\ \text{mol}\ Al_2(NO_3)_3} = 0.38\underline{0}9 = 0.381\ M$$

4.129. $$3.33 \times 10^{23}\ \text{ions} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{ions}} \times \frac{1\ \text{mol}\ Zn(C_2H_3O_2)_2}{2\ \text{mol}\ C_2H_3O_2^-} \times \frac{183.478\ \text{g}}{1\ \text{mol}}$$

$$= 50.\underline{7}2 = 50.7\ \text{g}\ Zn(C_2H_3O_2)_2$$

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4.130. The balanced molecular equation is

$$H_3AsO_4(aq) + 3NaOH(aq) \rightarrow Na_3AsO_4(aq) + 3H_2O(l)$$

The molarity of the arsenic acid is

$$M_2 = \frac{(0.6441\ M)\ (53.07\ \text{mL})}{26.14\ \text{mL}} \times \frac{1\ \text{mol}\ H_3AsO_4}{3\ \text{mol NaOH}} = 0.43588 = 0.4359\ M$$

4.131. The reactions are

$$6 \times (K \rightarrow K^+ + e^-)$$

$$\underline{1 \times (N_2 + 6e^- \rightarrow 2N^{3-})}$$

$$6K(s) + N_2(g) + \cancel{6e^-} \rightarrow 2K_3N(s) + \cancel{6e^-}$$

Thus six electrons are canceled.

4.132.

a. oxidation–reduction reaction

b. precipitation reaction

c. neutralization reaction

d. precipitation reaction

4.133. Since the solution is homogeneous, the concentration of the solution in the beaker is the same as the original solution, 0.196 *M*. The concentration of the solution in the large flask is also the same.

4.134. Calculate the mol of chloride ion for each compound in solution. $PbCl_2$ is insoluble, as such it will produce no chloride ions in solution.

$$1.0\ \text{g KCl} \times \frac{1\ \text{mol KCl}}{74.55\ \text{g}} \times \frac{1\ \text{mol Cl}^-}{1\ \text{mol KCl}} = 0.01341\ \text{mol Cl}^-$$

$$1.0\ \text{g}\ CaCl_2 \times \frac{1\ \text{mol}\ CaCl_2}{110.98\ \text{g}} \times \frac{2\ \text{mol Cl}^-}{1\ \text{mol}\ CaCl_2} = 0.01802\ \text{mol Cl}^-$$

Therefore, the $CaCl_2$ mixture would have the highest concentration of Cl^- ion.

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SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

4.135. For this reaction, the formulas are listed first, followed by the molecular and net ionic equations, the names of the products, and the molecular equation for another reaction giving the same precipitate.

Lead(II) nitrate is $Pb(NO_3)_2$, and cesium sulfate is Cs_2SO_4.

Molecular equation: $Pb(NO_3)_2(aq) + Cs_2SO_4(aq) \rightarrow PbSO_4(s) + 2CsNO_3(aq)$

Net ionic equation: $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

$PbSO_4$ is lead(II) sulfate, and $CsNO_3$ is cesium nitrate.

Molecular equation: $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

4.136. For this reaction, the formulas are listed first, followed by the molecular and net ionic equations, the names of the products, and the molecular equation for another reaction giving the same precipitate.

Silver nitrate is $AgNO_3$, and strontium chloride is $SrCl_2$.

Molecular equation: $2AgNO_3(aq) + SrCl_2(aq) \rightarrow 2AgCl(s) + Sr(NO_3)_2(aq)$

Net ionic equation: $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

AgCl is silver(I) chloride, and $Sr(NO_3)_2$ is strontium nitrate.

Molecular equation: $AgClO_4(aq) + NaCl(aq) \rightarrow AgCl(s) + NaClO_4(aq)$

4.137. Net ionic equation: $2Br^{-}(aq) + Cl_2(g) \rightarrow 2Cl^{-}(aq) + Br_2(l)$

Molecular equation: $CaBr_2(aq) + Cl_2(g) \rightarrow CaCl_2(aq) + Br_2(l)$

Mass $Br_2 = 40.0\text{ g} + 14.2\text{ g} - 22.2\text{ g} = 32.0\text{ g}$

Combining the three known masses gives the unknown mass of Br_2. Now, use a ratio of the known masses of $CaBr_2$ to Br_2 to convert pounds of Br_2 to grams of $CaBr_2$:

$$10.0\text{ lb } Br_2 \times \frac{40.0\text{ g } CaBr_2}{32.0\text{ g } Br_2} \times \frac{453.6\text{ g}}{1\text{ lb}} = 5670 = 5.67 \times 10^3\text{ g } CaBr_2$$

4.138. Net ionic equation: $Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$

Molecular equation: $BaS(aq) + Na_2CO_3(aq) \rightarrow Na_2S(aq) + BaCO_3(s)$

Mass$BaCO_3 = 33.9\text{ g} + 21.2\text{ g} - 15.6\text{ g} = 39.5\text{ g}$

Combining the three known masses gives the unknown mass of $BaCO_3$. Now, use a ratio of the known masses of BaS to $BaCO_3$ to ultimately obtain grams of BaS:

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$$5.00 \text{ ton } BaCO_3 \times \frac{33.9 \text{ g BaS}}{39.5 \text{ g } BaCO_3} = 4.2\underline{9}1 \text{ ton BaS}$$

$$4.291 \text{ ton BaS} \times \frac{2000 \text{ lb}}{1 \text{ ton}} \times \frac{453.6 \text{ g}}{1 \text{ lb}} = 3.8\underline{9}2 \times 10^6 = 3.89 \times 10^6 \text{ g BaS}$$

4.139. Molecular equation: $Hg(NO_3)_2 + H_2S(g) \rightarrow HgS(s) + 2HNO_3(aq)$

Net ionic equation: $Hg^{2+} + H_2S(g) \rightarrow HgS(s) + 2H^+(aq)$

The acid formed is nitric acid, a strong acid. The other product is mercury(II) sulfide.

Mass HNO_3 = (81.15 g + 8.52 g) − 58.16 g = 31.5$\underline{1}$ g

Mass of solution = 550.$\underline{0}$ g H_2O + 31.5$\underline{1}$ g HNO_3 = 581.$\underline{5}$1 = 581.5 g

4.140. Molecular equation: $Hg(NO_3)_2 + H_2S \rightarrow HgS(s) + 2HNO_3(aq)$

Net ionic equation: $Hg^{2+} + H_2S \rightarrow HgS(s) + 2H^+(aq)$

The acid formed is nitric acid, a strong acid. The other product is mercury(II) sulfide.

Mass HNO_3 = (65.65 g + 4.26 g) − 54.16 g = 15.7$\underline{5}$ g

Mass of solution = 395.0 g H_2O + 15.75 g HNO_3 = 410.$\underline{7}$5 = 410.8 g

4.141. Let the number of Fe^{3+} ions equal y; then the number of Fe^{2+} ions equals $(7 - y)$. Since Fe_7S_8 is neutral, the number of positive charges must equal the number of negative charges. If the signs are omitted, then

Total charge on both Fe^{2+} and Fe^{3+} = total charge on all eight sulfide ions

$3y + 2(7 - y) = 8 \times 2$

$y + 14 = 16$

$y = 2$

Thus, the ratio of Fe^{2+} to Fe^{3+} is 5/2.

4.142. To define the problem in terms of percentages, use 100 X_2O_3 oxides. Then the number of X^{3+} ions equals 100, and the sum of the X^{2+} and X^{5+} ions also equals 100. Let the number of X^{2+} ions equal y; then the number of X^{5+} ions equals $(100 - y)$. Since X_2O_3 is neutral, the number of positive charges must be equal to the number of negative charges. If the signs are omitted, then;

Total charge on X^{2+}, X^{3+}, and X^{5+} = total charge of all 300 oxide ions

$2y + (100 \times 3) + 5(100 - y) = 300 \times 2$

$-3y + 800 = 600$

$y = (200 \div 3) = 66.67$

The percentage of X^{2+} in the 100 X_2O_3 's is $(66.67 \div 200) \times 100 = 33.3\%$.

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4.143. Use the density, formula mass,, and percentage to convert to molarity. Then combine the 0.200 mol with mol/L to obtain the volume in liters.

$$\frac{0.807 \text{ g soln}}{1 \text{ mL}} \times \frac{0.940 \text{ g ethanol}}{1.00 \text{ g soln}} \times \frac{1 \text{ mol ethanol}}{46.07 \text{ g ethanol}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= \frac{16.\underline{4}65 \text{ mol ethanol}}{1 \text{ L ethanol}}$$

$$\text{L ethanol} = 0.200 \text{ mol ethanol} \times \frac{1 \text{ L ethanol}}{16.465 \text{ mol ethanol}} = 0.012\underline{1}46 = 0.0121 \text{ L}$$

4.144. Use the density, formula mass, and percentage to convert to molarity. Then combine the 0.350 mol with mol/L to obtain the volume in liters.

$$\frac{1.072 \text{ g soln}}{1 \text{ mL}} \times \frac{0.560 \text{ g glycol}}{1.00 \text{ g soln}} \times \frac{1 \text{ mol glycol}}{62.07 \text{ g glycol}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \frac{9.6\underline{7}2 \text{ mol glycol}}{1 \text{ L glycol}}$$

$$\text{L glycol} = 0.350 \text{ mol glycol} \times \frac{1 \text{ L glycol}}{9.6\underline{7}2 \text{ mol glycol}} = 0.036\underline{1}8 = 0.0362 \text{ L}$$

4.145. Convert the 2.183 g of AgI to mol AgI, which is chemically equivalent to mol KI. Use that to calculate the molarity of the KI.

$$2.183 \text{ g AgI} \times \frac{1 \text{ mol AgI}}{234.77 \text{ g AgI}} = 9.29\underline{8}4 \times 10^{-3} \text{ mol AgI (equivalent to mol KI)}$$

$$\text{Molarity} = \frac{9.2984 \times 10^{-3} \text{ mol KI}}{0.0100 \text{ L}} = 0.92\underline{9}8 = 0.930 \, M$$

4.146. Convert the 5.719 g of $BaSO_4$ to moles of $BaSO_4$, which is chemically equivalent to moles of Na_2SO_4. Use that to calculate the molarity of the Na_2SO_4.

$$5.719 \text{ g } BaSO_4 \times \frac{1 \text{ mol } BaSO_4}{233.40 \text{ g } BaSO_4} = 0.024\underline{5}02 \text{ mol } BaSO_4 \text{ (eq. to mol } Na_2SO_4)$$

$$\text{Molarity} = \frac{0.024502 \text{ mol } Na_2SO_4}{0.0250 \text{ L}} = 0.98\underline{0}1 = 0.980 \, M$$

4.147. Convert the 6.026 g of $BaSO_4$ to moles of $BaSO_4$; then, from the equation, deduce that 3 mol of $BaSO_4$ is equivalent to 1 mol of $M_2(SO_4)_3$ and is equivalent to 2 mol of M. Use that with 1.200 g of the metal M to calculate the atomic mass of M.

$$6.026 \text{ g } BaSO_4 \times \frac{1 \text{ mol } BaSO_4}{233.40 \text{ g } BaSO_4} \times \frac{2 \text{ mol M}}{3 \text{ mol } BaSO_4} = 0.017\underline{2}12 \text{ mol M}$$

$$\text{Atomic mass of M in g/mol} = \frac{1.200 \text{ g M}}{0.017212 \text{ mol M}} = 69.7\underline{1}9 \text{ g/mol (gallium)}$$

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4.148. Convert the 7.964 g of AgCl to moles of AgCl; then, from the equation, deduce that 2 mol of AgCl is equivalent to 1 mol of MCl_2 and is equivalent to 1 mol of M. Use that with 2.434 g of the metal M to calculate the atomic mass of M.

$$7.964 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol M}}{2 \text{ mol AgCl}} = 0.027784 \text{ mol M}$$

$$\text{Atomic mass M} = \frac{2.434 \text{ g M}}{0.027784 \text{ mol M}} = 87.604 = 87.60 \text{ g/mol (strontium)}$$

4.149. Use the density, formula mass, percentage, and volume to convert to moles of H_3PO_4. Then, from the equation $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$, deduce that 4 mol H_3PO_4 is equivalent to 1 mol of P_4O_{10}, and use that to convert to moles of P_4O_{10}.

$$1500 \text{ mL} \times \frac{1.025 \text{ g soln}}{1 \text{ mL}} \times \frac{0.0500 \text{ g } H_3PO_4}{1 \text{ g soln}} \times \frac{1 \text{ mol } H_3PO_4}{98.00 \text{ g } H_3PO_4} = 0.7844 \text{ mol } H_3PO_4$$

$$0.7844 \text{ mol } H_3PO_4 \times \frac{1 \text{ mol } P_4O_{10}}{4 \text{ mol } H_3PO_4} = 0.1961 \text{ mol } P_4O_{10}$$

$$\text{Mass } P_4O_{10} = 0.1961 \text{ mol } P_4O_{10} \times \frac{283.92 \text{ g } P_4O_{10}}{1 \text{ mol } P_4O_{10}} = 55.677 = 55.7 \text{ g } P_4O_{10}$$

4.150. Use the density, formula mass, percentage, and volume to convert to moles of $FeCl_3$, which is chemically equivalent to moles of Fe, from the equation $2Fe + 3Cl_2(g) \rightarrow 2FeCl_3$.

$$\frac{1.067 \text{ g soln}}{1 \text{ mL}} \times \frac{0.0900 \text{ g } FeCl_3}{1 \text{ g soln}} \times \frac{1 \text{ mol } FeCl_3}{162.20 \text{ g } FeCl_3} \times 3000 \text{ mL} = 1.7761 \text{ mol } FeCl_3$$

$$1.7761 \text{ mol } FeCl_3 = 1.7761 \text{ mol Fe}$$

$$\text{Mass Fe} = 1.7761 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} = 99.19 = 99.2 \text{ g Fe}$$

4.151. Convert the 0.1068 g of hydrogen to moles of H_2; then deduce from the equation that 3 moles of H_2 is equivalent to 2 mol of Al. Use the moles of Al to calculate mass of Al and the percentage Al.

$$0.1068 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Al}}{3 \text{ mol } H_2} = 0.0353174 \text{ mol Al}$$

$$\text{Percentage Al} = \frac{0.0353174 \text{ mol Al} \times \dfrac{26.98 \text{ g Al}}{1 \text{ mol Al}}}{1.118 \text{ g alloy}} \times 100\% = 85.229 = 85.23\%$$

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4.152. Convert the 0.1152 g of H_2 to moles of H_2; then deduce from the equation that 3 mol of H_2 is equivalent to 2 mol of Fe. Use the moles of Fe to calculate mass of Fe and the percentage Fe.

$$0.1152 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Fe}}{3 \text{ mol } H_2} = 0.038095 \text{ mol Fe}$$

$$\text{Percentage Fe} = \frac{0.038095 \text{ mol Fe} \times \dfrac{55.85 \text{ g Fe}}{1 \text{ mol Fe}}}{2.358 \text{ g alloy}} \times 100\% = 90.229 = 90.23\%$$

4.153. Use the formula mass of $Al_2(SO_4)_3$ to convert to moles of $Al_2(SO_4)_3$. Then deduce from the equation that 1 mol of $Al_2(SO_4)_3$ is equivalent to 3 mol of H_2SO_4, and calculate the moles of H_2SO_4 needed. Combine density, percentage, and formula mass to obtain molarity of H_2SO_4. Then combine molarity and moles to obtain volume.

$$37.4 \text{ g } Al_2(SO_4)_3 \times \frac{1 \text{ mol } Al_2(SO_4)_3}{342.17 \text{ g } Al_2(SO_4)_3} \times \frac{3 \text{ mol } H_2SO_4}{1 \text{ mol } Al_2(SO_4)_3} = 0.3279 \text{ mol } H_2SO_4$$

$$\frac{1.104 \text{ g soln}}{1 \text{ mL}} \times \frac{15.0 \text{ g } H_2SO_4}{100 \text{ g soln}} \times \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } H_2SO_4} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.688 \text{ mol } H_2SO_4 \text{ /L}$$

$$0.3279 \text{ mol } H_2SO_4 \times \frac{1 \text{ L } H_2SO_4}{1.688 \text{ mol } H_2SO_4} = 0.1942 = 0.194 \text{ L (194 mL)}$$

4.154. Use the formula mass of Na_3PO_4 to convert to moles of Na_3PO_4. Then deduce from the equation that 1 mol of Na_3PO_4 is equivalent to 3 mol of NaOH, and calculate the moles of NaOH needed. Combine density, percentage, and formula mass to obtain molarity of NaOH. Then combine molarity and moles to obtain the volume.

$$26.2 \text{ g } Na_3PO_4 \times \frac{1 \text{ mol } Na_3PO_4}{163.94 \text{ g } Na_3PO_4} \times \frac{3 \text{ mol NaOH}}{1 \text{ mol } Na_3PO_4} = 0.4794 \text{ mol NaOH}$$

$$\frac{1.133 \text{ g soln}}{1 \text{ mL}} \times \frac{0.120 \text{ g NaOH}}{1 \text{ g soln}} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.399 \text{ mol NaOH}$$

$$0.4794 \text{ mol NaOH} \times \frac{1 \text{ L NaOH}}{3.399 \text{ mol NaOH}} = 0.14104 \text{ L (141 mL)}$$

4.155. The equations for the neutralization are $2HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2H_2O$ and $3HCl + Al(OH)_3 \rightarrow AlCl_3 + 3H_2O$. Calculate the moles of HCl, and set it equal to the total moles of hydroxide ion, OH^-.

$$0.0485 \text{ L HCl} \times \frac{0.187 \text{ mol HCl}}{1 \text{ L HCl}} = 0.0090695 \text{ mol HCl}$$

$$0.0090695 \text{ mol HCl} = 2 \text{ [mol } Mg(OH)_2\text{]} + 3 \text{ [mol } Al(OH)_3\text{]}$$

Rearrange the last equation, and solve for the moles of $Al(OH)_3$.

$$\text{(Eq 1)} \quad \text{mol } Al(OH)_3 = 0.0030231 \text{ mol HCl} - 2/3 \text{ [mol } Mg(OH)_2\text{]}$$

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The total mass of chloride salts is equal to the sum of the masses of $MgCl_2$ (molar mass = 95.21 g/mol) and $AlCl_3$ (molar mass = 133.33 g/mol).

$$[95.21 \text{ g/mol} \times \text{mol } MgCl_2] + [133.33 \text{ g/mol} \times \text{mol } AlCl_3] = 0.4200 \text{ g}$$

Since the moles of $Mg(OH)_2$ equals the moles of $MgCl_2$, and the moles of $Al(OH)_3$ equals the moles of $AlCl_3$, you can substitute these quantities into the last equation and get

$$[95.21 \text{ g/mol} \times \text{mol } Mg(OH)_2] + [133.33 \text{ g/mol} \times \text{mol } Al(OH)_3] = 0.4200 \text{ g}$$

Substitute Equation 1 into this equation for the moles of $Al(OH)_3$:

$$[95.21 \text{ g/mol} \times \text{mol } Mg(OH)_2] + [133.33 \text{ g/mol} \times (0.0030231 \text{ mol} - 2/3 \text{ mol } Mg(OH)_2)] = 0.4200 \text{ g}$$

Rearrange the equation, and solve for the moles of $Mg(OH)_2$.

$$6.323 \text{ mol } Mg(OH)_2 + 0.403070 = 0.4200$$

$$\text{mol } Mg(OH)_2 = 0.01693 \div 6.323 = 0.0026728 \text{ mol}$$

Calculate the mass of $Mg(OH)_2$ in the antacid tablet (molar mass = 58.33 g/mol).

$$0.0026728 \text{ mol } Mg(OH)_2 \times \frac{58.33 \text{ g } Mg(OH)_2}{1 \text{ mol } Mg(OH)_2} = 0.15590 \text{ g } Mg(OH)_2$$

Use Eq 1 to find the moles and mass of $Al(OH)_3$ (molar mass 78.00 g/mol) in a similar fashion.

$$\text{mol } Al(OH)_3 = 0.0030231 - 2/3[0.0026728 \text{ mol } Mg(OH)_2] = 0.0012412 \text{ mol}$$

$$0.0012412 \text{ mol } Al(OH)_3 \times \frac{78.00 \text{ g } Al(OH)_3}{1 \text{ mol } Al(OH)_3} = 0.096681 \text{ g } Al(OH)_3$$

The mass percentage $Mg(OH)_2$ in the antacid is

$$\text{Mass percentage of } Mg(OH)_2 = [0.15590 \text{ g} \div (0.15590 + 0.096681) \text{ g}] \times 100\%$$
$$= 61.72 = 61.7\%$$

4.156. The equations for the neutralization are $2HCl + MgCO_3 \rightarrow MgCl_2 + H_2O + CO_2$ and $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$. Calculate the moles of HCl, and set it equal to the total moles of carbonate ion, CO_3^{2-}.

$$0.04133 \text{ L HCl} \times \frac{0.08750 \text{ mol HCl}}{1 \text{ L HCl}} = 0.0036164 \text{ mol HCl}$$

$$0.0036164 \text{ mol HCl} = 2 [\text{mol } CaCO_3] + 2 [\text{mol } MgCO_3]$$

Rearrange this equation, and solve for the moles of $MgCO_3$.

$$\text{(Eq 1)} \quad \text{mol } MgCO_3 = 0.0018082 \text{ mol HCl} - \text{mol } CaCO_3$$

The total mass of chloride salts equals the sum of the masses of $MgCl_2$ (molar mass = 95.21 g/mol) and $CaCl_2$ (molar mass = 110.98 g/mol).

$$[110.98 \text{ g/mol} \times \text{mol } CaCl_2] + [95.21 \text{ g/mol x mol } MgCl_2] = 0.1900 \text{ g}$$

Since the moles of $CaCO_3$ equals the moles of $CaCl_2$, and moles of $MgCO_3$ equal the moles of $MgCl_2$, you can substitute these quantities into the last equation and get

$$[110.98 \text{ g/mol} \times \text{mol } CaCO_3] + [95.21 \text{ g/mol x mol } MgCO_3] = 0.1900 \text{ g}$$

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Substitute Eq 1 into this equation for the moles of $MgCO_3$:

$$[110.98 \text{ g/mol} \times \text{mol } CaCO_3] + [95.21 \text{ g/mol} \times (0.0018082 \text{ mol} - \text{mol } CaCO_3)]$$
$$= 0.1900 \text{ g}$$

Rearrange the equation and solve for the moles of $MgCO_3$.

$$15.77 \text{ mol } CaCO_3 + 0.172159 = 0.1900$$

$$\text{mol } CaCO_3 = 0.017\underline{8}41 \div 15.77 = 0.0011\underline{3}13 \text{ mol}$$

Calculate the mass of $CaCO_3$ (molar mass = 100.09 g/mol) in the antacid tablet.

$$0.0011313 \text{ mol } CaCO_3 \times \frac{100.09 \text{ g } CaCO_3}{1 \text{ mol } CaCO_3} = 0.11\underline{3}234 \text{ g } CaCO_3$$

Use Eq 1, and find the moles and mass of $MgCO_3$ (molar mass = 84.32 g/mol) in a similar fashion.

$$\text{mol } MgCO_3 = 0.0018082 \text{ mol} - 0.0011313 \text{ mol } CaCO_3 = 0.0006769 \text{ mol}$$

$$0.0006769 \text{ mol } MgCO_3 \times \frac{84.32 \text{ g } MgCO_3}{1 \text{ mol } MgCO_3} = 0.057076 \text{ g } MgCO_3$$

The mass percentage $CaCO_3$ in the antacid is

$$\text{Mass percentage of } CaCO_3 = [0.113234 \text{ g} \div (0.113234 + 0.057076) \text{ g}] \times 100\%$$
$$= 66.\underline{4}87 = 66.5\%$$

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CHAPTER 5

The Gaseous State

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

5.1. First, convert to atm (57 kPa = 57 x 10^3 Pa).

$$57 \times 10^3 \text{ Pa} \times \frac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} = 0.5\underline{6}2 = 0.56 \text{ atm}$$

Next, convert to mmHg.

$$57 \times 10^3 \text{ Pa} \times \frac{760 \text{ mmHg}}{1.01325 \times 10^5 \text{ Pa}} = 4\underline{2}7.5 = 4.3 \times 10^2 \text{ mmHg}$$

5.2. Application of Boyle's law gives

$$V_f = V_i \times \frac{P_i}{P_f} = 20.0 \text{ L} \times \frac{1.00 \text{ atm}}{0.830 \text{ atm}} = 24.\underline{0}96 = 24.1 \text{ L}$$

5.3. First, convert the temperatures to the Kelvin scale.

$T_i = (19 + 273) = 292$ K

$T_f = (25 + 273) = 298$ K

Following is the data table.

$V_i = 4.38$ dm^3	$P_i = 101$ kPa	$T_i = 292$ K
$V_f = ?$	$P_f = 101$ kPa	$T_f = 298$ K

Apply Charles's law to obtain

$$V_f = V_i \times \frac{T_f}{T_i} = 4.38 \text{ dm}^3 \times \frac{298 \text{ K}}{292 \text{ K}} = 4.4\underline{7}0 = 4.47 \text{ dm}^3$$

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5.4. First, convert the temperatures to kelvins.

$T_i = (24 + 273) = 297$ K

$T_f = (35 + 273) = 308$ K

Following is the data table.

$V_i = 5.41$ dm^3 $P_i = 101.5$ kPa $T_i = 297$ K

$V_f = ?$ $P_f = 102.8$ kPa $T_f = 308$ K

Apply both Boyle's law and Charles's law combined to get

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i} = 5.41 \text{ dm}^3 \times \frac{101.5 \text{ kPa}}{102.8 \text{ kPa}} \times \frac{308 \text{ K}}{297 \text{ K}} = 5.5\underline{3}9 = 5.54 \text{ dm}^3$$

5.5. Use the ideal gas law, $PV = nRT$, and solve for n:

$$n = \frac{PV}{RT} = \left(\frac{V}{RT}\right)P$$

Note that everything in parentheses is constant. Therefore, you can write

n = constant x P

Or, expressing this as a proportion,

$n \propto P$

5.6. First, convert the mass of O_2 to moles of O_2 (molar mass 32.00 g/mol) and convert temperature to kelvins.

$T = 23 + 273 = 296$ K

$$3.03 \text{ kg } O_2 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 94.\underline{6}88 \text{ mol } O_2$$

Summarize the data in a table.

Variable	Value
P	?
V	50.0 L
T	296 K
n	94.$\underline{6}$88 mol

Solve the ideal gas equation for P, and substitute the data to get

$$P = \frac{nRT}{V} = \frac{(94.6\underline{8}8)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(296 \text{ K})}{50.0 \text{ L}} = 46.\underline{0}0 = 46.0 \text{ atm}$$

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5.7. The data given are

Variable	Value
P	$752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.98\underline{9}47 \text{ atm}$
V	1 L (exact number)
T	$(21 + 273) = 294 \text{ K}$
n	?

Using the ideal gas law, solve for n, the moles of helium.

$$n = \frac{PV}{RT} = \frac{(0.98\underline{9}47 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(294 \text{ K})} = 0.041\underline{0}1 \text{ mol}$$

Now convert mol He to grams.

$$0.041\underline{0}1 \text{ mol He} \times \frac{4.00 \text{ g He}}{1 \text{ mol He}} = 0.16\underline{4}04 \text{ g He}$$

Therefore, the density of He at 21°C and 752 mmHg is 0.164 g/L.

The difference in mass between one liter of air and one liter of helium is

$$\text{Mass air} - \text{mass He} = 1.188 \text{ g} - 0.16\underline{4}04 \text{ g} = 1.02\underline{3}96 = 1.024 \text{ g difference}$$

5.8. Tabulate the values of the variables.

Variable	Value
P	0.862 atm
V	1 L (exact number)
T	$(25 + 273) = 298 \text{ K}$
n	?

From the ideal gas law, $PV = nRT$, you obtain

$$n = \frac{PV}{RT} = \frac{(0.862 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.035\underline{2}5 \text{ mol}$$

Dividing the mass of the vapor by moles gives you the mass per mole (the molar mass).

$$\text{Molar mass} = \frac{\text{grams vapor}}{\text{moles vapor}} = \frac{2.26 \text{ g}}{0.03525 \text{ mol}} = 64.\underline{1}14 \text{ g/mol}$$

Therefore, the molecular mass is 64.1 amu.

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5.9. First, determine the number of moles of Cl_2 from the mass of HCl (molar mass36.46 g/mol) and from the stoichiometry of the chemical equation:

$$9.41 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} \times \frac{5 \text{ mol } Cl_2}{16 \text{ mol HCl}} = 0.080\underline{6}53 \text{ mol } Cl_2$$

Tabulate the values of the variables:

Variable	Value
P	$787 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 1.0355 \text{ atm}$
T	$(40 + 273) \text{ K} = 313 \text{ K}$
n	$0.080\underline{6}53 \text{ mol}$
V	?

Rearrange the ideal gas law to obtain V:

$$V = \frac{nRT}{P} = \frac{(0.080653 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(313 \text{ K})}{1.0355 \text{ atm}} = 2.00\underline{1} = 2.00 \text{ L}$$

5.10. Each gas obeys the ideal gas law. In each case, convert grams to moles and substitute into the ideal gas law to determine the partial pressure of each.

$$1.031 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.032\underline{2}188 \text{ mol } O_2$$

$$P = \frac{nRT}{V} = \frac{(0.0322188)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(291 \text{ K})}{10.0 \text{ L}} = 0.076\underline{9}36 \text{ atm}$$

$$0.572 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} = 0.012\underline{9}97 \text{ mol } CO_2$$

$$P = \frac{nRT}{V} = \frac{(0.012997)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(291 \text{ K})}{10.0 \text{ L}} = 0.031\underline{0}36 \text{ atm}$$

The total pressure is equal to the sum of the partial pressures:

$$P = P_{O_2} + P_{CO_2} = 0.076\underline{9}36 + 0.031\underline{0}36 = 0.107\underline{9}7 = 0.1080 \text{ atm}$$

The mole fraction of oxygen in the mixture is

$$\text{Mole fraction } O_2 = \frac{P_{O_2}}{P} = \frac{0.076\underline{9}4 \text{ atm}}{0.108\underline{0}2 \text{ atm}} = 0.712\underline{2} = 0.712$$

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5.11. Determine the number of moles of O_2 from the mass of $KClO_3$ and from the stoichiometry of the chemical reaction.

$$1.300 \text{ g } KClO_3 \text{ x } \frac{1 \text{ mol } KClO_3}{122.5 \text{ g } KClO_3} \text{ x } \frac{3 \text{ mol } O_2}{2 \text{ mol } KClO_3} = 0.0159\underline{1}84 \text{ mol } O_2$$

The vapor pressure of water at 23°C is 21.1 mmHg (Table 5.6). Find the partial pressure of O_2 using Dalton's law:

$$P = P_{O_2} + P_{H_2O}$$

$$P_{O_2} = P - P_{H_2O} = (745 - 21.1) \text{ mmHg} = 72\underline{3}.9 \text{ mmHg}$$

Solve for the volume using the ideal gas law.

Variable	Value
P	$723.9 \text{ mmHg x } \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.95\underline{2}5 \text{ atm}$
V	?
T	$(23 + 273) = 296 \text{ K}$
n	0.0159184

From the ideal gas law, $PV = nRT$, you have

$$V = \frac{nRT}{P} = \frac{(0.0159184 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(296 \text{ K})}{0.9525 \text{ atm}} = 0.40\underline{5}9 = 0.406 \text{ L}$$

5.12. The absolute temperature is (22 + 273) = 295 K. In SI units, the molar mass of carbon tetrachloride, CCl_4, is $153.8 \text{ x } 10^{-3}$ kg/mol. Therefore,

$$u = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \text{ x } 8.31 \text{ kg} \cdot \text{m}^2/(\text{s}^2 \cdot \text{K} \cdot \text{mol}) \text{ x } 295 \text{ K}}{153.8 \text{ x } 10^{-3} \text{ kg/mol}}\right)^{1/2} = 21\underline{8}.7 = 219 \text{ m/s}$$

5.13. Determine the rms molecular speed for N_2 at 455°C (728 K):

$$u = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \text{ x } 8.31 \text{ kg} \cdot \text{m}^2/(\text{s}^2 \cdot \text{K} \cdot \text{mol}) \text{ x } 728 \text{ K}}{28.02 \text{ x } 10^{-3} \text{ kg/mol}}\right)^{1/2} = 80\underline{4}.81 \text{ m/s}$$

After writing this equation with the same speed for H_2, square both sides and solve for T. The molar mass of H_2 in SI units is $2.016 \text{ x } 10^{-3}$ kg/mol. Therefore,

$$T = \frac{u^2M}{3R} = \frac{(804.81)^2(2.016 \text{ x } 10^{-3} \text{ kg/mol})}{(3)(8.31 \text{ kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{K} \cdot \text{mol})} = 52.\underline{3}79 = 52.4 \text{ K}$$

Because the average kinetic energy of a molecule is proportional to only T, the temperature at which an H_2 molecule has the same average kinetic energy as an N_2 molecule at 455°C is exactly the same temperature, 455°C.

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5.14. The two rates of effusion are inversely proportional to the square roots of their molar masses, so you can write

$$\frac{\text{Rate of effusion of } O_2}{\text{Rate of effusion of He}} = \sqrt{\frac{M_m(\text{He})}{M_m(O_2)}}$$

where M_m(He) is the molar mass of He (4.00 g/mol) and $M_m(O_2)$ is the molar mass of O_2 (32.00 g/mol). Substituting these values into the formula gives

$$\frac{\text{Rate of effusion of } O_2}{\text{Rate of effusion of He}} = \sqrt{\frac{4.00 \text{ g/mol}}{32.00 \text{ g/mol}}} = 0.35\underline{3}55$$

Rearranging gives

$$\text{Rate of effusion of } O_2 = 0.35\underline{3}55 \text{ x rate of effusion of He.}$$

Now, the problem states that the rate of effusion can be given in terms of volume of gas effused per second, so

$$\frac{\text{Volume of } O_2}{\text{Time for } O_2} = 0.35\underline{3}55 \text{ x } \frac{\text{Volume of He}}{\text{Time for He}}$$

Substituting in the values gives

$$\frac{10.0 \text{ mL}}{\text{Time for } O_2} = 0.35\underline{3}55 \text{ x } \frac{10.0 \text{ mL}}{3.52 \text{ s}}$$

Rearranging gives

$$\text{Time for } O_2 = \frac{3.52 \text{ s}}{0.35\underline{3}55} = 9.9\underline{5}6 = 9.96 \text{ s}$$

5.15. The problem states that the rate of effusion is inversely proportional to the time it takes for a gas to effuse, so you can write

$$\frac{\text{Rate of effusion of } H_2}{\text{Rate of effusion of gas}} = \frac{\text{time for gas}}{\text{time for } H_2} = \sqrt{\frac{M_m(\text{gas})}{M_m(H_2)}} = 4.67$$

Rearranging and solving for $M_m(H_2)$ gives

$$M_m(\text{gas}) = (4.67)^2 \text{ x } M_m(H_2) = (4.67)^2 \text{ x } 2.016 \text{ g/mol} = 43.\underline{9}6 = 44.0 \text{ g/mol}$$

Thus, the molecular mass of the gas is 44.0 amu.

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5.16. From Table 5.7, $a = 5.570\ L^2 \cdot atm/mol^2$ and $b = 0.06499$ L/mol. Substitute these values into the van der Waals equation, along with $R = 0.08206$ L•atm/K•mol, $T = 273.2$ K, $n = 1.000$ mol, and $V = 22.41$ L.

$$P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$P = \frac{(1.00\ \text{mol})(0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(273.2\ \text{K})}{22.41\ \text{L} - (1.00\ \text{mol})(0.06499\ \text{L/mol})} - \frac{(1.00\ \text{mol})^2 (5.570\ \text{L}^2 \cdot \text{atm/mol}^2)}{(22.41\ \text{L})^2}$$

$$= 1.00\underline{3}3 - 0.011\underline{0}91 = 0.99\underline{2}21 = 0.992\ \text{atm}$$

Using the ideal gas law, $P = 1.00\underline{0}4$ atm (larger).

■ ANSWERS TO CONCEPT CHECKS

5.1. The general relationship between pressure (P) and the height (h) of a liquid column in a barometer is $P = gdh$, where g is the constant acceleration of gravity and d is the density. Examination of the relationship indicates that, for a given pressure, as the density of the liquid in the barometer decreases, the height of the liquid must increase. In order to make this relationship more apparent, you can rearrange the equation to

$$gh = \frac{P}{d}$$

Because you are conducting the experiment at constant pressure and gravity is a constant, this mathematical relationship demonstrates that the height of the liquid in the barometer is inversely proportional to the density of the liquid in the barometer.

$$\left(h \propto \frac{1}{d}\right)$$

This inverse relationship means that as the height of the liquid decreases, the density of the liquid must increase. Since the density of mercury is greater than the density of water, the barometer with the water will have the higher column.

5.2.

a. In the first step, when the temperature decreases, the pressure will also decrease. This is because, according to the combined gas law, the pressure is directly proportional to the temperature ($P \propto T$). In the second step, when the volume increases, the pressure will decrease, since, according to Boyle's law, pressure and volume are inversely related ($P \propto 1/V$). Both changes result in the pressure decreasing, so the final pressure will be less than the starting pressure.

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b. In the first step, when the temperature increases, the pressure will also increase. This is because, according to the combined gas law, pressure is directly proportional to the temperature ($P \propto T$). In the second step, when the volume decreases, the pressure will increase, since, according to the ideal gas law, pressure and volume are inversely related ($P \propto 1/V$). Both changes result in the pressure increasing, so the final pressure will be greater than the starting pressure.

5.3.

a. According to Avogadro's law, equal volumes of any two (or more) gases at the same temperature and pressure contain the same number of molecules (or atoms in this case). Therefore, all three flasks contain the same number of atoms.

b. Since density is mass divided by volume, and all three flasks have the same volume (3.0 L), the gas with the largest molar mass, xenon (Xe), will have the greatest density.

c. According to the ideal gas law, $PV = nRT$, pressure is directly proportional to the temperature. Since the helium flask is being heated, it will have the highest pressure.

d. Since the three flasks started with the same number of atoms, and hence the same number of moles, they would all still have the same number of moles no matter how the temperatures of the flasks were changed.

5.4.

a. In a mixture of gases, each gas exerts the pressure it would exert if it were the only gas in the flask. The pressure of H_2 is the same whether it is in the flask by itself or with the Ar. Therefore, the pressure of H_2 does not change.

b. According to the ideal gas law, $PV = nRT$, pressure (P) is directly proportional to the number of moles (n). Since the number of moles of H_2 and the number of moles of Ar are equal, their pressures are also equal.

c. The total pressure is equal to the sum of the pressures of the H_2 gas and the Ar gas in the container. The total pressure will also be equal to twice the pressure of the H_2 gas when it was in the flask by itself. It is also equal to twice the pressure that the Ar gas would exert if it were in the flask by itself.

5.5.

a. The rate of effusion is inversely proportional to the square root of the molecular mass of the gas at constant temperature and pressure. Thus, He (molecular mass 4.00 amu) will diffuse faster than Ar (molecular weight 39.95 amu) and reach the end of the tube first.

b. The speed of an atom is directly proportional to the absolute temperature. If you raise the temperature of the Ar, you can make it reach the end of the tube at the same time as the He.

5.6.

a. If the real gas molecules occupy a relatively small volume, then the volume of the gas is essentially equal to the volume of the container, the same as for an ideal gas. However, if there were large intermolecular attractions, the pressure would be less than for an ideal gas. Therefore, the pressure would be greater for the ideal gas.

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b. If the real gas molecules occupy a relatively large volume, then the volume available for the gas is less than for an ideal gas, and the pressure will be greater. If there are negligible intermolecular attractions, then the pressure is essentially the same as for an ideal gas. Overall, the pressure would be less for the ideal gas.

c. Since the effect of molecular volume and intermolecular attractions on the pressure of a real gas are opposite, you cannot determine how the pressure of the two gases compare.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

5.1. Pressure is the force exerted per unit area of surface. Force is further defined as mass multiplied by acceleration. The SI unit of mass is kg, of acceleration is m/s^2, and of area is m^2. Therefore, the SI unit of pressure (Pascal) is given by

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{\text{mass x acceleration}}{\text{area}} = \frac{\text{kg x m/s}^2}{\text{m}^2} = \frac{\text{kg}}{\text{m} \bullet \text{s}^2} = \text{Pa}$$

5.2. A manometer is a device that measures the pressure of a gas in a vessel. The gas pressure in the flask is proportional to the difference in height between the liquid levels in the manometer (Figure 5.4).

5.3. The general relationship between the pressure (P) and the height (h) of the liquid in a manometer is $P = gdh$. Therefore, the variables that determine the height of the liquid in a manometer are the density (d) of the liquid and the pressure of the gas being measured. The acceleration of gravity (g) is a constant, 9.81 m/s^2.

5.4. From Boyle's law, PV = constant. Because this is true for conditions P_i and V_i as well as conditions P_f and V_f, we can write

$$P_f V_f = P_i V_i = \text{constant}$$

Dividing both sides of this equation by P_f gives

$$V_f = V_i \text{ x } \frac{P_i}{P_f}$$

5.5. A linear relationship between variables such as x and y is given by the mathematical relation

$$y = a + bx$$

The variable y is directly proportional to x only if $a = 0$.

5.6. First, find the equivalent of absolute zero on the Fahrenheit scale. Converting −273.15°C to degrees Fahrenheit, you obtain −459.67°F. Since the volume of a gas varies linearly with the temperature, you get the following linear relationship:

$$V = a + bt_F$$

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where t_F is the temperature on the Fahrenheit scale. Since the volume of a gas is zero at absolute zero, you get

$$0 = a + b(-459.67), \text{ or } a = 459.67b$$

The equation can now be rewritten as

$$V = 459.67b + bt_F = b(459.67 + t_F) = bT_F$$

where T_F is the temperature in the new absolute scale based on the Fahrenheit scale. The relationship is

$$T_F = t_F + 459.67$$

5.7. From Charles's law, V = constant x T. Because this is true for conditions T_i and V_i as well as conditions T_f and V_f, we can write

$$\frac{V_f}{T_f} = \frac{V_i}{T_i} = \text{constant}$$

Multiplying both sides of the equation by T_f gives

$$V_f = V_i \text{ x } \frac{T_f}{T_i}$$

5.8. Avogadro's law states that equal volumes of any two gases at the same temperature and pressure contain the same number of molecules. The law of combining volumes states that the volumes of reactant gases at a given pressure and temperature are in ratios of small whole numbers. The combining-volume law may be explained from Avogadro's law using the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ as follows. In this equation, the molecules are in a ratio of small whole numbers, 1 to 3 to 2. In Avogadro's law, these numbers represent volumes. But since equal volumes contain the same number of molecules, the ratios for volumes are the same as the ratios for molecules.

5.9. The standard conditions are 0°C and 1 atm pressure (STP).

5.10. The molar gas volume, V_m, is the volume of one mole of gas at any given temperature and pressure. At standard conditions (STP), the molar gas volume equals 22.4 L.

5.11. Boyle's law ($V \propto 1/P$) and Charles's law ($V \propto T$) can be combined and expressed in a single statement: the volume occupied by a given amount of gas is proportional to the absolute temperature divided by the pressure. In equation form, this is

$$V = \text{constant x } \frac{T}{P}$$

The constant is independent of temperature and pressure but does depend on the amount of gas. For one mole, the constant will have a specific value, denoted as R. The molar volume, V_m, is

$$V_m = R \text{ x } \frac{T}{P}$$

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Because V_m has the same value for all gases, we can write this equation for n moles of gas if we multiply both sides by n. This yields the equation

$$nV_m = \frac{nRT}{P}$$

Because V_m is the volume per mole, nV_m is the total volume V. Substituting gives

$$V = \frac{nRT}{P} \quad \text{or} \qquad PV = nRT$$

5.12. The variables in the ideal gas law are P, V, n, and T. The SI units of these variables are pascals (P), cubic meters (V), moles (n), and kelvins (T).

5.13. Use the value of R from Table 5.5 and the conversion factor 1 atm = 760 mmHg. This gives

$$0.082058 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 62.364\underline{0} = 62.364 \frac{\text{L} \bullet \text{mmHg}}{\text{K} \bullet \text{mol}}$$

5.14. Six empirical gas laws can be obtained. They can be stated as follows:

$P \times V = \text{constant}$ (T and n constant)

$\frac{P}{T} = \text{constant}$ (V and n constant)

$\frac{P}{n} = \text{constant}$ (T and V constant)

$\frac{V}{T} = \text{constant}$ (P and n constant)

$\frac{V}{n} = \text{constant}$ (P and T constant)

$n \times T = \text{constant}$ (P and V constant)

5.15. The postulates and supporting evidence are the following:

(1) Gases are composed of molecules whose sizes are negligible compared with the distance between them.

(2) Molecules move randomly in straight lines in all directions and at various speeds.

(3) The forces of attraction or repulsion between two molecules (intermolecular forces) in a gas are very weak or negligible, except when they collide.

(4) When molecules collide with one another, the collisions are elastic.

(5) The average kinetic energy of a molecule is proportional to the absolute temperature.

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One example of evidence that supports the kinetic theory of gases is Boyle's law. Constant temperature means that the average molecular force from collision remains constant. If you increase the volume, you decrease the number of collisions per unit wall area, thus lowering the pressure in accordance with Boyle's law. Another example is Charles's law. If you raise the temperature, you increase the average molecular force from a collision with the wall, thus increasing the pressure. For the pressure to remain constant, it is necessary for the volume to increase so that the frequency of collisions with the wall decreases. Thus, when you raise the temperature of a gas while keeping the pressure constant, the volume increases in accordance with Charles's law.

5.16. Boyle's law requires the temperature to be constant. Postulate 5 of the kinetic theory holds that the average kinetic energy of a molecule is constant at constant temperature. Therefore, the average molecular force from collisions is constant. If we increase the volume of a gas, this decreases the number of molecules per unit volume and so decreases the frequency of collisions per unit wall area, causing the pressure to decrease in accordance with Boyle's law.

5.17. According to kinetic theory, the pressure of a gas results from the bombardment of container walls by molecules.

5.18. The rms speed of a molecule equals $(3RT/M_m)^{1/2}$. Therefore, it varies directly with the square root of the absolute temperature. The rms speed does not depend on the molar volume.

5.19. A gas appears to diffuse more slowly because it never travels very far in one direction before it collides with another molecule and moves in another direction. Thus, it must travel a very long, crooked path as the result of collisions.

5.20. Effusion is the process in which a gas flows through a small hole in a container. It results from the gas molecules encountering the hole by chance, rather than by colliding with the walls of the container. The faster the molecules move, the more likely they are to encounter the hole. Thus, the rate of effusion depends on the average molecular speed, which depends inversely on molecular mass.

5.21. The behavior of a gas begins to deviate significantly from that predicted by the ideal gas law at high pressures and at relatively low temperatures.

5.22. The constant *a* is the proportionality constant in the van der Waals equation related to intermolecular forces The term *nb* represents the volume occupied by *n* moles of molecules.

5.23. The answer is a; "the greater the volume occupied by a given amount of gas, the higher the intermolecular force" is not part of the kinetic-molecular theory.

5.24. The answer is c, the container volume didn't change.

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5.25. The answer is b, to occupy the entire 22.4 L volume of the box.

5.26. The answer is d; it is *not* true that the Ar atoms hit the walls of the flask with the greatest force of the three gases.

■ ANSWERS TO CONCEPT EXPLORATIONS

5.27.

a. For the same volume and temperature, pressure is proportional to the number of molecules in the sample. Since container B contains twice as many particles, the pressure in container B is double the pressure in container A.

b. Since all the containers have the same volume and temperature, the pressure in containers C, D, and E are all the same. Since container F contains twice as many particles, the pressure is double the pressure in the other containers.

c. Since pressure is inversely proportional to volume, and since the number of particles is the same for both containers, the pressure in container H is one-half the pressure in container G.

d. There would be twice the number of particles in double the volume, so overall, the pressures in containers G and H are now equal.

e. Pressure is directly proportional to temperature and inversely proportional to volume. Here, the temperature is doubled, effectively doubling the pressure. But the volume is also doubled, effectively reducing the pressure by one-half. Overall, the pressures in containers J and L are the same.

5.28.

a. The gas atom is creating pressure by colliding with the walls of the container. The collisions exert a force on the wall, which is observed as pressure.

b. For constant volume and temperature, pressure is proportional to the number of particles present. Since there are four times as many particles in container B, the pressure in container B is also four times the pressure in container A.

c. Since there are four times as many particles in container B, the pressure in container B is also four times the pressure in container A. The pressure is not related to the mass of the particles, only to the number of particles.

d. The root-mean-square (rms) speed is inversely proportional to the square root of the particle's mass. Since the atom is lighter, it will have the larger rms speed. The difference in rms speeds neither supports nor contradicts the answer concerning the pressure in the container, because the force on the wall does not only depend on the speed of the particle alone. The force depends on the momentum, which is the product of mass times speed. This in turn depends only on the temperature. At constant temperature there is a constant force.

e. For an equal volume and an equal number of particles, the pressure varies directly with the absolute temperature. Since the temperature in container F is double the temperature in container E, the pressure in container F is double the pressure in container E.

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f. Since the temperature in container H is double the pressure in container G, the pressure in container H is double the pressure in container G. The pressure is not related to the mass of the particles, only to the number of particles.

g. Pressure is directly related to the number of particles and directly related to the absolute temperature. Here, the number of particles in container J is double the number of particles in container I, effectively doubling the pressure. But the temperature in container J is one-half the temperature in container I, effectively reducing the pressure by one-half. Overall, the pressures in the two containers are the same.

h. Here, the number of particles in container K is three times the number of particles in container L, and the temperature in container K is double the temperature in container L, so overall the pressure in container K is six times the pressure in container L.

■ ANSWERS TO CONCEPTUAL PROBLEMS

5.29.

a. The volume of the tire and the amount of air in the tire remain constant. From the ideal gas law, $PV = nRT$, under these conditions the pressure will vary directly with the temperature ($P \propto T$). Thus, on a cold day, you would expect the pressure in the tires to decrease, and they would appear flatter.

b. Aerosol cans are filled with a fixed amount of gas in a constant volume. From the ideal gas law, under these conditions the pressure will vary directly with the temperature ($P \propto T$). If you put an aerosol can in a fire, you will increase the temperature and thus the pressure. If the pressure gets high enough, the can will explode.

c. As the water bottle sits in the sun, the liquid water warms up. As the temperature of the water increases, so does its vapor pressure (Table 5.6). If the pressure gets high enough, it will pop the lid off the bottle.

d. The amount of air in the balloon and the temperature remain constant. From the ideal gas law, under these conditions the pressure is inversely proportional to the volume ($P \propto 1/V$). Thus, as you squeeze the balloon, you decrease the volume, resulting in an increase in pressure. If you squeeze hard enough and make the volume small enough, the balloon will pop.

5.30. Since the flasks are identical and contain the same amount of gas, the initial pressures in the N_2 flask, the O_2 flask, and the He flask will be the same. After the changes, the pressure in the He flask would be highest, with a pressure equal to three times the original. Next would be the O_2 flask, with a pressure equal to two times the original. Last would be the N_2 flask, with a pressure equal to one-half the original.

5.31.

a. The pressure and volume of a gas are inversely proportional; therefore, an increase by a factor of 2 in pressure would decrease the volume by ½ (C to D).

b. The pressure and volume of a gas are inversely proportional; therefore, a decrease by a factor of 2 in pressure would double the volume (C to A).

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c. The volume and temperature of a gas are directly proportional; therefore an increase in kelvin temperature by a factor of 1.5 would result in an increase in volume by a factor of 1.5 (C to B).

d. Since the piston can move, the pressure would not change (it would be equal to the starting pressure). The volume of gas is directly proportional to the number of moles; therefore, an increase in the number of moles by a factor of 2 would cause the volume increase by a factor of 2 (C to A).

5.32.

a. Since 1.0 out of the 3.0 moles of gas in the container is N_2, the fraction of the pressure due to N_2 is 1/3.

b. Mole fractions are not a function of temperature, so nothing would happen.

c. You would expect the pressure to be higher for two reasons. First, the water would occupy some volume, reducing the volume available for the gas to occupy. Thus, according to Boyle's law, as volume decreases, pressure increases. Second, after a time, the water would evaporate, and the vapor pressure due to the water would contribute to the total pressure, thereby increasing it.

d. Yes, there is enough information in the problem to calculate the pressure in the flask, but you would also need to know the vapor pressure of water at 22.0°C (Table 5.6).

5.33.

a. The container with the O_2 has the greater density, since the molar mass of O_2 (32.00 g/mol) is greater than that of H_2 (2.016 g/mol).

b. Since the H_2 molecules are lighter, they will be moving faster.

c. Both containers have the same number of molecules (Avogadro's law).

d. The pressure in each of the containers will not change when the valve is opened. Each container starts with the same pressure. Since the total volume remains constant, the pressure will not change.

e. The fraction of the total pressure due to the H_2 would now be 1/4.

5.34.

a. Pressure decreases as you increase in altitude. Thus, the pressure at 6000 m is less than the pressure at 3000 m. For two identical balloons, the balloon at 6000 m will have the greater volume (Boyle's law).

b. In order to calculate the volume of each balloon, you would need the temperature and pressure on the ground and the temperature and pressure at their respective heights.

5.35. In order to double the volume, you could reduce the pressure by 1/2. You could also double the temperature in Kelvin scale, but you cannot determine the final temperature without knowing the initial temperature.

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5.36.

a. If you assume that the flasks are at ordinary room temperature, say 25°C, then there would be approximately 1 mol of He (at 1.0 atm) and 1.5 mol of Xe (at 1.5 atm). Thus, the F_2 flask (with 2.0 mol) would contain the greater number of moles of gas.

b. You could decrease the temperature or remove some gases from the other two containers.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

5.37. Use the conversion factor 1 atm = 760 mmHg.

$$0.047 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 3\underline{5}.7 = 36 \text{ mmHg}$$

5.38. Use the conversion factors 1 atm = 760 mmHg and 1 atm = 101325 Pa, or 101.325 kPa.

$$259 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 34.\underline{5}3 = 34.5 \text{ kPa}$$

5.39. Using Boyle's law, solve for V_f of the neon gas at 1.292 atm pressure.

$$V_f = V_i \times \frac{P_i}{P_f} = 3.15 \text{ L} \times \frac{0.951 \text{ atm}}{1.292 \text{ atm}} = 2.3\underline{1}8 = 2.32 \text{ L}$$

5.40. Using Boyle's law, solve for V_f of the helium gas at 632 mmHg.

$$V_f = V_i \times \frac{P_i}{P_f} = 2.68 \text{ L} \times \frac{789 \text{ mmHg}}{632 \text{ mmHg}} = 3.3\underline{4}57 = 3.35 \text{ L}$$

5.41. Using Boyle's law, let V_f = volume at 0.974 atm (P_f), V_i = 50.0 L, and P_i = 19.8 atm.

$$V_f = V_i \times \frac{P_i}{P_f} = 50.0 \text{ L} \times \frac{19.8 \text{ atm}}{0.974 \text{ atm}} = 10\underline{1}6.4 = 1.02 \times 10^3 \text{ L}$$

5.42. Using Boyle's law, let V_f = volume at 1.212 atm (P_f), V_i = 8.58 m^3, and P_i = 1.020 atm.

$$V_f = V_i \times \frac{P_i}{P_f} = 8.58 \text{ m}^3 \times \frac{1.020 \text{ atm}}{1.212 \text{ atm}} = 7.2\underline{2}0 = 7.22 \text{ m}^3$$

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5.43. Using Boyle's law, let P_i = pressure of 315 cm^3 of gas, and solve for it.

$$P_i = P_f \text{ x } \frac{V_f}{V_i} = 2.51 \text{ kPa x } \frac{0.0457 \text{ cm}^3}{315 \text{ cm}^3} = 3.641 \text{ x } 10^{-4} = 3.64 \text{ x } 10^{-4} \text{ kPa}$$

5.44. Using Boyle's law, let P_f = final pressure of 27.0 dm^3 of gas, and solve for it.

$$P_f = P_i \text{ x } \frac{V_i}{V_f} = 101 \text{ kPa x } \frac{456 \text{ dm}^3}{27.0 \text{ dm}^3} = 1705.7 = 1.71 \text{ x } 10^3 \text{ kPa}$$

5.45. Use Charles's law: T_i = 18°C + 273 = 291 K, and T_f = 0°C + 273 = 273 K.

$$V_f = V_i \text{ x } \frac{T_f}{T_i} = 3.92 \text{ mL x } \frac{273 \text{ K}}{291 \text{ K}} = 3.677 = 3.68 \text{ mL}$$

5.46. Use Charles's law: T_i = 0°C + 273 = 273 K, and T_f = 20°C + 273 = 293 K.

$$V_f = V_i \text{ x } \frac{T_f}{T_i} = 22.41 \text{ L x } \frac{293 \text{ K}}{273 \text{ K}} = 24.051 = 24.1 \text{ L}$$

5.47. Use Charles's law: T_i = 22°C + 273 = 295 K, and T_f = −197°C + 273 = 76 K.

$$V_f = V_i \text{ x } \frac{T_f}{T_i} = 2.54 \text{ L x } \frac{76 \text{ K}}{295 \text{ K}} = 0.654 = 0.65 \text{ L}$$

5.48. Use Charles's law: T_i = 0°C + 273 = 273 K, and T_f = 25°C + 273 = 298 K.

$$V_f = V_i \text{ x } \frac{T_f}{T_i} = 4.83 \text{ L x } \frac{298 \text{ K}}{273 \text{ K}} = 5.272 = 5.27 \text{ L}$$

5.49. Use Charles's law: T_i = 25°C + 273 = 298 K, and V_f is the difference between the vessel's volume of 39.5 cm^3 and the 7.7 cm^3 of ethanol that is forced into the vessel.

$$T_f = T_i \text{ x } \frac{V_f}{V_i} = 298 \text{ K x } \frac{(39.5 - 7.7) \text{ cm}^3}{39.5 \text{ cm}^3} = 239.9 \text{ K } (-33.2 \text{ or } -33°\text{C})$$

5.50. Use Charles's law: T_i = 18°C + 273 = 291 K, V_i = 62.3 cm^3, and V_f = 61.2 cm^3.

$$T_f = T_i \text{ x } \frac{V_f}{V_i} = 291 \text{ K x } \frac{61.2 \text{ cm}^3}{62.3 \text{ cm}^3} = 285.8 = 286 \text{ K } (12.7 \text{ or } 13°\text{C})$$

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5.51. Use the combined law: $T_i = 31°C + 273 = 304$ K, and $T_f = 0°C + 273 = 273$ K.

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i} = 35.5 \text{ mL} \times \frac{753 \text{ mmHg}}{760 \text{ mmHg}} \times \frac{273 \text{ K}}{304 \text{ K}} = 31.\underline{5}8 = 31.6 \text{ mL}$$

5.52. Use the combined law: $T_i = 23°C + 273 = 296$ K, and $T_f = 0°C + 273 = 273$ K.

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i} = 3.84 \text{ mL} \times \frac{785 \text{ mmHg}}{760 \text{ mmHg}} \times \frac{273 \text{ K}}{296 \text{ K}} = 3.6\underline{5}8 = 3.66 \text{ mL}$$

5.53. The balanced equation is

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The ratio of moles of NH_3 to moles of NO is 4 to 4, or 1 to 1, so one volume of NH_3 will produce one volume of NO at the same temperature and pressure.

5.54. The balanced equation is

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The ratio of moles of H_2 to moles of CO_2 is 3 to 1, so three volumes of H_2 are required to react with one volume of CO_2 at the same temperature and pressure.

5.55. Solve the ideal gas law for V:

$$V = \frac{nRT}{P} = nRT\left(\frac{1}{P}\right)$$

If the temperature and number of moles are held constant, then the product nRT is constant, and volume is inversely proportional to pressure:

$$V = \text{constant} \times \frac{1}{P}$$

5.56. Solve the ideal gas law for V:

$$V = \frac{nR}{P} \times T$$

If n and P are held constant, the nR/P quotient is a constant. The equation may now be written

$$V = \text{constant} \times T$$

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5.57. Calculate the moles of oxygen, and then solve the ideal gas law for P:

$$n = 91.3 \text{ g} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 2.8\underline{5}3 \text{ mol } O_2$$

$$P = \frac{nRT}{V} = \frac{(2.8\underline{5}3 \text{ mol})\,(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{ mol})\,(294 \text{ K})}{8.58 \text{ L}} = 8.0\underline{2}2 = 8.02 \text{ atm}$$

5.58. Calculate the moles of methane, and then solve the ideal gas law for P:

$$n = 7.13 \text{ g} \times \frac{1 \text{ mol } CH_4}{16.0 \text{ g } CH_4} = 0.44\underline{5}6 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{(0.4456 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(292 \text{ K})}{5.00 \text{ L}}$$

$$= 2.1\underline{3}55 = 2.14 \text{ atm}$$

5.59. Using the moles of chlorine, solve the ideal gas law for V:

$$V = \frac{nRT}{P} = \frac{(3.50 \text{ mol})\,(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})\,(307 \text{ K})}{4.00 \text{ atm}} = 22.\underline{0}4 = 22.0 \text{ L}$$

5.60. Calculate the moles of oxygen, and then solve the ideal gas law for V:

$$n = 5.67 \text{ g} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.17\underline{7}18 \text{ mol}$$

$$V = \frac{nRT}{P} = \frac{(0.17718 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(296 \text{ K})}{0.985 \text{ atm}}$$

$$= 4.3\underline{6}9 = 4.37 \text{ L}$$

5.61. Solve the ideal gas law for temperature in K, and convert to °C:

$$T = \frac{PV}{nR} = \frac{(3.50 \text{ atm})\,(4.00 \text{ L})}{(0.410 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})} = 41\underline{6}.1 = 416 \text{ K}$$

$$°\text{C} = 416 - 273 = 143°\text{C}$$

5.62. Find the moles of C_3H_8, solve the ideal gas law for temperature in K, and convert to °C:

$$n = 5.65 \text{ g} \times \frac{1 \text{ mol } C_3H_8}{44.09 \text{ g } C_3H_8} = 0.12\underline{8}14 \text{ mol}$$

$$T = \frac{PV}{nR} = \frac{(741/760 \text{ atm})\,(2.50 \text{ L})}{(0.12\underline{8}14 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})} = 23\underline{1}.79 \text{ K}$$

$$°\text{C} = 23\underline{1}.79 - 273 = -4\underline{1}.20 = -41°\text{C}$$

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5.63. Because density equals mass per unit volume, calculating the mass of 1 L (exact number) of gas will give the density of the gas. Start from the ideal gas law, and calculate *n*; then convert the moles of gas to grams using the molar mass.

$$n = \frac{PV}{RT} = \frac{(751/760 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(304 \text{ K})} = 0.039\underline{6}1 \text{ mol}$$

$$0.039\underline{6}1 \text{ mol} \times \frac{17.03 \text{ g}}{1 \text{ mol}} = 0.67\underline{4}58 = 0.675 \text{ g}$$

Therefore, the density of NH_3 at 31°C is 0.675 g/L.

5.64. As in the previous problem, calculate the mass of 1 L (exact number) of gas to obtain the density of the gas. Start from the ideal gas law, and calculate *n*; then convert to grams.

$$n = \frac{PV}{RT} = \frac{(967/760 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(329 \text{ K})} = 0.047\underline{1}2 \text{ mol}$$

$$0.04712 \text{ mol} \times \frac{34.08 \text{ g}}{1 \text{ mol}} = 1.6\underline{0}58 \text{ g}$$

Therefore, the density of H_2S at 56°C is 1.61 g/L.

5.65. Calculate the mass of 1 L (exact number) using the ideal gas law; convert to mass.

$$n = \frac{PV}{RT} = \frac{(0.897 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(297 \text{ K})} = 0.036\underline{8}04 \text{ mol}$$

$$0.036804 \text{ mol} \times \frac{58.12 \text{ g}}{1 \text{ mol}} = 2.1\underline{3}9 = 2.14 \text{ g}$$

Therefore, the density of C_4H_{10} is 2.14 g/L.

5.66. Calculate the mass of 1 L (exact number) using the ideal gas law; convert to mass.

$$n = \frac{PV}{RT} = \frac{(797/760 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(371 \text{ K})} = 0.034\underline{4}46 \text{ mol}$$

$$0.034446 \text{ mol} \times \frac{119.5 \text{ g}}{1 \text{ mol}} = 4.1\underline{1}6 = 4.12 \text{ g}$$

Therefore, the density of $CHCl_3$ at 98°C is 4.12 g/L.

5.67. The ideal gas law gives *n* moles, which then are divided into the mass of 1.585 g for molar mass.

$$n = \frac{PV}{RT} = \frac{(753/760 \text{ atm})(1 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(363 \text{ K})} = 0.033\underline{2}62 \text{ mol}$$

$$\text{Molar mass} = \frac{1.585 \text{ g}}{0.033262 \text{ mol}} = 47.\underline{6}51 \text{ g/mol}$$

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The molecular weight is 47.7 amu.

5.68. The moles in 237 mL (0.237 L) of the compound are obtained from the ideal gas law. Dividing the mass (0.548 g) of the gas by the moles gives the molar mass and molecular mass.

$$n = \frac{PV}{RT} = \frac{(755/760 \text{ atm})\,(0.237 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})\,(373 \text{ K})} = 0.007692 \text{ mol}$$

$$\text{Molar mass} = \frac{0.548 \text{ g}}{0.007692 \text{ mol}} = 71.24 \text{ g/mol}$$

The molecular mass is 71.2 amu.

5.69. The moles in 250 mL (0.250 L) of the compound are obtained from the ideal gas law. The 2.56-g mass of the gas then is divided by the moles to obtain the molar mass and molecular mass.

$$n = \frac{PV}{RT} = \frac{(786/760 \text{ atm})\,(0.250 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})\,(394 \text{ K})} = 0.007996 \text{ mol}$$

$$\text{Molar mass} = \frac{2.56 \text{ g}}{0.007996 \text{ mol}} = 3.201 \times 10^2 = 3.20 \times 10^2 \text{ g/mol}$$

The molecular mass is 3.20×10^2 amu.

5.70. The moles in 345 mL (0.345 L) of the compound are obtained from the ideal gas law. The 2.30-g mass of the gas then is divided by the moles to obtain the molar mass and molecular mass.

$$n = \frac{PV}{RT} = \frac{(985/760 \text{ atm})\,(0.345 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})\,(421 \text{ K})} = 0.01294 \text{ mol}$$

$$\text{Molar mass} = \frac{2.30 \text{ g}}{0.01294 \text{ mol}} = 177.7 \text{ g/mol}$$

The molecular mass is 178 amu.

5.71. For a gas at a given temperature and pressure, the density depends on molecular mass (or, for a mixture, on average molecular mass). Thus, at the same temperature and pressure, the density of NH_4Cl gas would be greater than that of a mixture of NH_3 and HCl, because the average molecular mass of NH_3 and HCl would be lower than that of NH_4Cl.

5.72. For a gas at a given temperature and pressure, the density depends on molecular mass (or, for a mixture, on average molecular mass). Thus, at the same temperature and pressure, the density of PCl_5 gas would be greater than that of a mixture of PCl_3 and Cl_2 formed by the decomposition of PCl_5, because the average molecular mass of PCl_3 and Cl_2 would be lower than that of PCl_5.

5.73. The 0.050 mol CaC_2 will form 0.050 mol C_2H_2. The volume is found from the ideal gas law:

$$V = \frac{(0.050 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(299 \text{ K})}{684/760 \text{ atm}} = 1.36 = 1.4 \text{ L}$$

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5.74. The 0.0840 mol Mg will form 0.0840 mol of H_2. The volume is found from the ideal gas law:

$$V = \frac{(0.0840 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(306 \text{ K})}{665/760 \text{ atm}} = 2.4\underline{1}0 = 2.41 \text{ L}$$

5.75. Use the equation to obtain the moles of CO_2 and then the ideal gas law to obtain the volume.

$$2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(aq) + H_2O(l)$$

$$327 \text{ g LiOH} \times \frac{1 \text{ mol LiOH}}{23.95 \text{ g LiOH}} \times \frac{1 \text{ mol } CO_2}{2 \text{ mol LiOH}} = 6.8\underline{2}67 \text{ mol } CO_2$$

$$V = \frac{(6.8\underline{2}67 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(294 \text{ K})}{781/760 \text{ atm}} = 16\underline{0}.2 = 160. \text{ L}$$

5.76. Use the equation to obtain the moles of ammonia and then the ideal gas law to obtain the volume.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

$$4.56 \text{ g } Mg_3N_2 \times \frac{1 \text{ mol } Mg_3N_2}{100.9 \text{ g } Mg_3N_2} \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } Mg_3N_2} = 0.090\underline{3}86 \text{ mol } NH_3$$

$$V = \frac{(0.090386 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(297 \text{ K})}{(753/760) \text{ atm}} = 2.2\underline{2}3 = 2.22 \text{ L}$$

5.77. Use the equation to obtain the moles of ammonia and then the ideal gas law to obtain the volume.

$$2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$$

$$908 \text{ g urea} \times \frac{1 \text{ mol urea}}{60.06 \text{ g urea}} \times \frac{2 \text{ mol } NH_3}{1 \text{ mol urea}} = 30.\underline{2}3 \text{ mol } NH_3$$

$$V = \frac{(30.\underline{2}3 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(298 \text{ K})}{3.00 \text{ atm}} = 24\underline{6}.4 = 246 \text{ L}$$

5.78. Use the equation to obtain the moles of ammonia and then the ideal gas law to obtain the volume.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

$$50.0 \text{ g NO} \times \frac{1 \text{ mol NO}}{30.0 \text{ g NO}} \times \frac{5 \text{ mol } O_2}{4 \text{ mol NO}} = 2.0\underline{8}3 \text{ mol } O_2$$

$$V = \frac{(2.083 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(308 \text{ K})}{2.15 \text{ atm}} = 24.\underline{4}87 = 24.5 \text{ L}$$

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5.79. Use the equation to obtain the moles of ammonia and then the ideal gas law to obtain the volume.

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

$$150.0 \text{ g } (NH_4)_2SO_4 \times \frac{1 \text{ mol } (NH_4)_2SO_4}{132.1 \text{ g } (NH_4)_2SO_4} \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } (NH_4)_2SO_4}$$

$$= 2.2\underline{7}10 \text{ mol } NH_3$$

$$V = \frac{nRT}{P} = \frac{(2.2710 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(288 \text{ K})}{1.15 \text{ atm}} = 46.\underline{6}7 = 46.7 \text{ L}$$

5.80. Use the equation to obtain the moles of ammonia, and then the ideal gas law to obtain the volume.

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

$$26.8 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.0 \text{ g } NaHCO_3} \times \frac{1 \text{ mol } CO_2}{2 \text{ mol } NaHCO_3} = 0.15\underline{9}52 \text{ mol } CO_2$$

$$V = \frac{nRT}{P} = \frac{(0.15952 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(350 \text{ K})}{(756/760) \text{ atm}} = 4.6\underline{0}59 = 4.61 \text{ L}$$

5.81. Calculate the partial pressure of each gas; then add the pressures since the total pressure is equal to the sum of the partial pressures:

$$P(\text{He}) = \frac{(0.0200 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(283 \text{ K})}{2.50 \text{ L}} = 0.18\underline{5}78 \text{ atm}$$

$$P(H_2) = \frac{(0.0100 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(283 \text{ K})}{2.50 \text{ L}} = 0.092\underline{8}9 \text{ atm}$$

Total pressure = 0.18587 = 0.092$\underline{8}$9 = 0.27$\underline{8}$67 = 0.279

5.82. Calculate the partial pressure of each gas; then add the pressures since the total pressure is equal to the sum of the partial pressures:

$$P(\text{He}) = \frac{(0.0300 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(293 \text{ K})}{4.00 \text{ L}} = 0.18\underline{0}3 \text{ atm}$$

$$P(O_2) = \frac{(0.0200 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(293 \text{ K})}{4.00 \text{ L}} = 0.12\underline{0}2 \text{ atm}$$

Total pressure = 0.18$\underline{0}$3 + 0.12$\underline{0}$2 = 0.30$\underline{0}$5 = 0.301 atm

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5.83. Convert mass of O_2 and mass of He to moles. Use the ideal gas law to calculate the partial pressures, and then add to obtain the total pressures.

$$0.00103 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 3.2\underline{1}9 \times 10^{-5} \text{ mol } O_2$$

$$0.00056 \text{ g He} \times \frac{1 \text{ mol He}}{4.00 \text{ g He}} = 1.\underline{4}0 \times 10^{-4} \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{(3.219 \times 10^{-5} \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(288 \text{ K})}{0.2000 \text{ L}}$$

$$= 0.003\underline{8}04 \text{ atm } O_2$$

$$P = \frac{nRT}{V} = \frac{(1.\underline{4}0 \times 10^{-4} \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(288 \text{ K})}{0.2000 \text{ L}}$$

$$= 0.01\underline{6}54 \text{ atm He}$$

$$P = P_{O_2} + P_{He} = 0.003\underline{8}04 \text{ atm} + 0.01\underline{6}54 \text{ atm} = 0.02\underline{0}3 = 0.020 \text{ atm}$$

5.84. Obtain the partial pressure of helium using Dalton's law; then use the ideal gas law to obtain the mass of helium.

$$P_{He} = P - P_{O_2} = 3.00 \text{ atm} - 0.200 \text{ atm} = 2.8\underline{0}0 \text{ atm}$$

$$n_{He} = \frac{P_{He}V}{RT} = \frac{(2.80 \text{ atm})(10.0 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(293 \text{ K})} = 1.1\underline{6}45 \text{ mol He}$$

$$\text{Mass}_{He} = 1.1645 \text{ mol He} \times \frac{4.003 \text{ g He}}{1 \text{ mol He}} = 4.6\underline{6}1 = 4.66 \text{ g He}$$

5.85. For each gas, $P(\text{gas}) = P \times$ (mole fraction of gas).

$P(H_2)$	= 760 mmHg x 0.250 = 19$\underline{0}$.0	= 190 mmHg
$P(CO_2)$	= 760 mmHg x 0.650 = 49$\underline{4}$.0	= 494 mmHg
$P(HCl)$	= 760 mmHg x 0.054 = 4$\underline{1}$.04	= 41 mmHg
$P(HF)$	= 760 mmHg x 0.028 = 2$\underline{1}$.28	= 21 mmHg
$P(SO_2)$	= 760 mmHg x 0.017 = 1$\underline{2}$.92	= 13 mmHg
$P(H_2S)$	= 760 mmHg x 0.001 = 0.$\underline{7}$6	= 0.8 mmHg

5.86. For each gas, $P(\text{gas}) = P \times$ (mole fraction of gas).

$P(He)$	= 6.91 atm x 0.790	= 5.4$\underline{5}$89	= 5.46 atm
$P(N_2)$	= 6.91 atm x 0.170	= 1.1$\underline{7}$47	= 1.17 atm
$P(O_2)$	= 6.91 atm x 0.040	= 0.2$\underline{7}$64	= 0.28 atm

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5.87. The total pressure is the sum of the partial pressures of CO and H_2O, so

$$P_{CO} = P - P_{water} = 689 \text{ mmHg} - 23.8 \text{ mmHg} = 665.2 \text{ mmHg}$$

$$n_{CO} = \frac{P_{CO}V}{RT} = \frac{(665/760 \text{ atm})(3.85 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(298 \text{ K})} = 0.1378 \text{ mol CO}$$

$$0.1378 \text{ mol CO} \times \frac{1 \text{ mol HCOOH}}{1 \text{ mol CO}} \times \frac{46.03 \text{ g HCOOH}}{1 \text{ mol HCOOH}} = 6.342 = 6.34 \text{ g HCOOH}$$

5.88. The total pressure is the sum of the partial pressures of N_2 and H_2O, so

$$P_{N_2} = P - P_{H_2O} = 97.8 \text{ kPa} \times \left(\frac{1 \text{ atm}}{101.3 \text{ kPa}}\right) - 25.2 \text{ mmHg} \times \left(\frac{1 \text{ atm}}{760 \text{ mmHg}}\right)$$

$$= 0.9322 \text{ atm}$$

$$n_{N_2} = \frac{P_{N_2}V}{RT} = \frac{(0.9322 \text{ atm})\ (3.75 \text{ L})}{0.08206 \text{ L} \bullet \text{atm/ K} \bullet \text{mol})\ (299 \text{ K})} = 0.1424 \text{ mol } N_2$$

$$0.1424 \text{ mol } N_2 \times \frac{1 \text{ mol } NH_4NO_2}{1 \text{ mol } N_2} \times \frac{64.04 \text{ g } NH_4NO_2}{1 \text{ mol } NH_4NO_2} = 9.124 = 9.12 \text{ g } NH_4NO_3$$

5.89. Substitute 298 K (25°C) and 398 K (125°C) into Maxwell's distribution:

$$u_{25} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \times 8.31 \text{ kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \times 298 \text{ K}}{28.02 \times 10^{-3} \text{ kg/mol}}\right)^{1/2}$$

$$= 5.149 \times 10^2 = 5.15 \times 10^2 \text{ m/s}$$

$$u_{125} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \times 8.31 \text{ kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \times 398 \text{ K}}{28.02 \times 10^{-3} \text{ kg/mol}}\right)^{1/2}$$

$$= 5.9507 \times 10^2 = 5.95 \times 10^2 \text{ m/s}$$

Graph as in Figure 5.25.

5.90. Substitute 296 K (23°C) into Maxwell's distribution:

$$u_{23} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \times 8.31 \text{ kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \times 296 \text{ K}}{159.8 \times 10^{-3} \text{ kg/mol}}\right)^{1/2} = 214.8 = 215 \text{ m/s}$$

The rms speed is the same at 1.50 atm as at 1.00 atm because the temperature is the same.

5.91. Substitute 330 K (57°C) into Maxwell's distribution:

$$u_{330\text{ K}} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3 \times 8.31 \text{ kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \times 330 \text{ K}}{352 \times 10^{-3} \text{ kg/mol}}\right)^{1/2}$$

$$= 1.528 \times 10^2 = 1.53 \times 10^2 \text{ m/s}$$

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5.92. Substitute 365 K into Maxwell's distribution:

$$u_{365\ \mathrm{K}} = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3\ \text{x}\ 8.31\ \mathrm{kg \bullet m^2/(s^2 \bullet K \bullet mol)}\ \text{x}\ 365\ \mathrm{K}}{2.016\ \text{x}\ 10^{-3}\ \mathrm{kg/mol}}\right)^{1/2}$$

$$= 2.1\underline{2}4 \text{ x } 10^3 = 2.12 \text{ x } 10^3 \text{ m/s}$$

This is equal to 2.12 km/s, which is less than the escape velocity.

5.93. Because $u(CO_2) = u(H_2)$, we can equate the two right-hand sides of the Maxwell distributions:

$$\left(\frac{3RT(\mathrm{CO_2})}{M_m(\mathrm{CO_2})}\right)^{1/2} = \left(\frac{3RT(\mathrm{H_2})}{M_m(\mathrm{H_2})}\right)^{1/2}$$

Squaring both sides, rearranging to solve for $T(CO_2)$, and substituting numerical values, we have

$$T(\mathrm{CO_2}) = T(\mathrm{H_2}) \text{ x } \frac{M_m(\mathrm{CO_2})}{M_m(\mathrm{H_2})} = 298\ \mathrm{K} \text{ x } \frac{44.01\ \mathrm{g/mol}}{2.016\ \mathrm{g/mol}} = 65\underline{0}5.4\ \mathrm{K}$$

Thus the temperature is

$$T = 65\underline{0}5.4 - 273 = 62\underline{3}2 = 6.23 \text{ x } 10^3\ ^\circ\mathrm{C}$$

5.94. Substitute 375 m/s into the Maxwell distribution, square both sides, and solve for T:

$$u = 400\ \mathrm{m/s} = \left(\frac{3\ \text{x}\ 8.31\ \mathrm{kg \bullet m^2/(s^2 \bullet K \bullet mol)}\ \text{x}\ T}{32.00\ \text{x}\ 10^{-3}\ \mathrm{kg/\ mol}}\right)^{1/2}$$

$$(400)^2 = 160000 = \frac{3 \text{ x } 8.31 \text{ x } T}{32.00 \text{ x } 10^{-3}\ \mathrm{K}}$$

$$T = 20\underline{5}.37\ \mathrm{K} = -67.\underline{7}7 = -67.8\ ^\circ\mathrm{C}$$

5.95. The rates of effusion are directly related to the rms speed. Assume the temperature is the same for both, and write a ratio of two Maxwell distributions.

$$\frac{u_{\mathrm{N_2}}}{u_{\mathrm{O_2}}} = \frac{\left(\frac{3RT}{M_m(\mathrm{N_2})}\right)^{1/2}}{\left(\frac{3RT}{M_m(\mathrm{O_2})}\right)^{1/2}} = \left(\frac{M_m(\mathrm{O_2})}{M_m(\mathrm{N_2})}\right)^{1/2} = \left(\frac{32.00\ \mathrm{g/mol}}{28.02\ \mathrm{g/mol}}\right)^{1/2}$$

$$= 1.06\underline{8}6 = 1.069$$

Thus the ratio of the rates of effusion of N_2 and O_2 is 1.069 to 1.

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5.96. The rates of effusion are directly related to the rms speed. Assume the temperature is the same for both, and write a ratio of two Maxwell distributions.

$$\frac{u_{H_2}}{u_{H_2Se}} = \frac{\left(\frac{3RT}{M_m(H_2)}\right)^{1/2}}{\left(\frac{3RT}{M_m(H_2Se)}\right)^{1/2}} = \left(\frac{M_m(H_2Se)}{M_m(H_2)}\right)^{1/2} = \left(\frac{80.976\ \text{g/mol}}{2.016\ \text{g/mol}}\right)^{1/2} = 6.33\underline{7}7 = 6.338$$

Thus the ratio of the rates of effusion of H_2 and H_2Se is 6.338 to 1.

5.97. The rates of effusion are directly related to the rms speed. Assume the temperature is the same for both, and write a ratio of two Maxwell distributions.

$$\frac{u_{H_2}}{u_{I_2}} = \left(\frac{M_m(I_2)}{M_m(H_2)}\right)^{1/2} = \left(\frac{253.8\ \text{g/mol}}{2.016\ \text{g/mol}}\right)^{1/2} = 11.2\underline{2}0 = 11.22$$

Because hydrogen diffuses 11.22 times as fast as iodine, the time it would take would be 1/11.22 of the time required for iodine:

$$t(H_2) = 39\ \text{s} \times (1/11.22) = 3.\underline{4}7 = 3.5\ \text{s}$$

5.98. The rates of effusion are directly related to the rms speed. Assume the temperature is the same for both, and write a ratio of two Maxwell distributions.

$$\frac{u_{He_2}}{u_{N_2}} = \left(\frac{M_m(N_2)}{M_m(He)}\right)^{1/2} = \left(\frac{28.02\ \text{g/mol}}{4.003\ \text{g/mol}}\right)^{1/2} = 2.64\underline{5}7 = 2.646$$

Because helium diffuses 2.646 times as fast as nitrogen, the time it would take would be 1/2.646 of the time required for nitrogen:

$$t(He) = 10.6\ \text{hr} \times (1/2.646) = 4.0\underline{0}6 = 4.01\ \text{hr}$$

5.99. Since the volume of gas produced is directly related to the rate of effusion, the ratio of the volumes of gas can be written in terms of the ratio of the rms speeds. This in turn can be written in terms of the masses of the particles.

$$\frac{4.83\ \text{mL gas}}{9.23\ \text{mL Ar}} = \frac{u_{gas}}{u_{Ar}} = \left(\frac{M_m(Ar)}{M_m(gas)}\right)^{1/2} = \left(\frac{39.95\ \text{g/mol}}{M_m(gas)}\right)^{1/2}$$

Squaring both sides gives

$$0.27\underline{3}83 = \frac{39.95\ \text{g/mol}}{M_m(gas)}$$

Solving for the molar mass gives

$$M_m(gas) = \frac{39.95\ \text{g/mol}}{0.27383} = 14\underline{5}.8\ \text{g/mol};\ \text{molecular mass} = 146\ \text{amu}$$

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5.100. The time it takes for a fixed volume of gas to effuse through a hole is inversely related to the rate of effusion. The ratio of the times can thus be written in terms of the rms speeds and, in turn, the molar masses.

$$\frac{68.3 \text{ s } (N_2)}{85.6 \text{ s (gas)}} = \frac{u_{gas}}{u_{N_2}} = \left(\frac{M_m(N_2)}{M_m(gas)}\right)^{1/2} = \left(\frac{28.02 \text{ g/mol}}{M_m(gas)}\right)^{1/2}$$

Squaring both sides gives

$$0.63\underline{6}639 = \frac{28.02 \text{ g/mol}}{M_m(gas)}$$

Solving for the molar mass gives

$$M_m(gas) = \frac{28.02 \text{ g/mol}}{0.636639} = 44.\underline{0}1 \text{ g/mol; molecular mass} = 44.0 \text{ amu}$$

5.101. Solving the van der Waals equation for $n = 1$ and $T = 355.2$ K for P gives

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} = \frac{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(355.2 \text{ K})}{(30.00 \text{ L} - 0.08710 \text{ L})} - \frac{12.56 \text{ L}^2 \bullet \text{atm}}{(30.00 \text{ L})^2}$$

$$P = 0.974\underline{4}19 - 0.013\underline{9}555 = 0.960\underline{4}6 = 0.9605 \text{ atm}$$

$$P(\text{ideal gas law}) = 0.971\underline{5}9 \text{ atm}$$

5.102. Solving the van der Waals equation for $n = 1$ and $T = 393.2$ K for P gives

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} = \frac{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(393.2 \text{ K})}{(32.50 \text{ L} - 0.03049 \text{ L})} - \frac{5.537 \text{ L}^2 \bullet \text{atm}}{(32.50 \text{ L})^2}$$

$$P = 0.993\underline{7}3 - 0.005\underline{2}421 = 0.988\underline{4}90 = 0.9885 \text{ atm}$$

$$P(\text{ideal gas law}) = 0.992\underline{7}9 \text{ atm}$$

5.103. To calculate a/V^2 in the van der Waals equation, we obtain V from the ideal gas law at 1.00 atm:

$$V = \frac{RT}{P} = \frac{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(273 \text{ K})}{1.00 \text{ atm}} = 22.40 \text{ L}$$

$$\frac{a}{V^2} = \frac{5.570}{(22.4 \text{ L})^2} = 1.1\underline{1}0 \times 10^{-2}$$

At 1.00 atm, $V = 22.4$ L, and $a/V^2 = 1.110 \times 10^{-2}$. Substituting into the van der Waals equation:

$$V = \frac{RT}{P + \frac{a}{V^2}} + b = \frac{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(273 \text{ K})}{(1.00 + 1.110 \times 10^{-2}) \text{ atm}} + 0.06499 = 22.\underline{2}2 = 22.2 \text{ L}$$

At 10.0 atm, the van der Waals equation gives 2.08 L. The ideal gas law gives 22.4 L for 1.00 atm and 2.24 L for 10.0 atm.

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5.104. To substitute for a/V^2 in the van der Waals equation, we obtain V from the ideal gas law at 1.00 atm:

$$V = \frac{RT}{P} = \frac{(0.08206\ \text{L} \bullet \text{atm/K} \bullet \text{mol})(273\ \text{K})}{1.00\ \text{atm}} = 22.40\ \text{L}$$

$$\frac{a}{V^2} = \frac{1.382}{(22.4\ \text{L})^2} = 2.7\underline{5}4 \times 10^{-3}$$

At 1.00 atm, $V = 22.4$ L, and $a/V^2 = 2.75 \times 10^{-3}$. Substituting into the van der Waals equation:

$$V = \frac{RT}{P + \frac{a}{V^2}} + b = \frac{(0.08206\ \text{L} \bullet \text{atm/K} \bullet \text{mol})(273\ \text{K})}{(1.00 + 2.75 \times 10^{-3})\ \text{atm}} + 0.03186 = 22.\underline{3}7 = 22.4\ \text{L}$$

At 10.0 atm, the van der Waals equation gives 2.21 L. The ideal gas law gives 22.4 L for 1.00 atm and 2.24 L for 10.0 atm.

■ SOLUTIONS TO GENERAL PROBLEMS

5.105. Calculate the mass of 1 cm^2 of the 20.5 m of water above the air in the glass. The volume is the product of the area of 1 cm^2 and the height of 20.5×10^2 cm (20.5 m) of water. The density of 1.00 g/cm^3 must be used to convert volume to mass:

$$m = d \times V$$

$$m = 1.00\ \text{g/cm}^3 \times (1.00\ \text{cm}^2 \times 20.5 \times 10^2\ \text{cm}) = 2.05 \times 10^3\ \text{g, or } 2.05\ \text{kg}$$

The pressure exerted on an object at the bottom of the column of water is

$$P = \frac{\text{force}}{\text{area}} = \frac{(m)(\text{g})}{\text{area}} = \frac{(2.05\ \text{kg})(9.807\ \text{m/s}^2)}{(1.00\ \text{cm}^2)\left(\frac{10^{-2}\ \text{m}}{1\ \text{cm}}\right)^2} = 2.01 \times 10^5\ \text{kg/ms}^2$$

$$= 2.01 \times 10^5\ \text{Pa}$$

The total pressure on the air in the tumbler equals the sum of the barometric pressure and the water pressure:

$$P = 1.00 \times 10^2\ \text{kPa} + 2.01 \times 10^2\ \text{kPa} = 3.01 \times 10^2\ \text{kPa}$$

Multiply the initial volume by a factor accounting for the change in pressure to find V_f:

$$V_f = V_i \times \frac{P_i}{P_f} = 243\ \text{cm}^3 \times \left(\frac{1.00 \times 10^2\ \text{kPa}}{3.01 \times 10^2\ \text{kPa}}\right) = 80.\underline{7}3 = 80.7\ \text{cm}^3$$

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5.106. The volume of 1 m^2 of the 40.0 m of water above the air is 40.0 m^3. The mass of water above this area is

$$m = d \text{ x } V = \frac{1.025 \text{ g}}{1 \text{ cm}^3} \text{ x } \left(\frac{1 \text{ cm}}{10^{-2} \text{ m}}\right)^3 \text{ x } 40.0 \text{ m}^3 = 4.1\underline{0}00 \text{ x } 10^7 \text{ g } (4.1\underline{0}00 \text{ x } 10^4 \text{ kg})$$

The pressure on this area is

$$P = \frac{\text{force}}{\text{area}} = \frac{(m)(g)}{\text{area}} = \frac{(4.100 \text{ x } 10^4 \text{ kg})(9.807 \text{ m/s}^2)}{1 \text{ m}^2} = 4.0\underline{2}08 \text{ x } 10^5 \text{ kg/ ms}^2 \text{ or Pa}$$

$$P = 4.0208 \text{ x } 10^5 \text{ Pa x } \frac{1 \text{ atm}}{1.013 \text{ x } 10^5 \text{ Pa}} = 3.9\underline{6}92 \text{ atm}$$

The total pressure at 40.0 m is

$$P = P_{air} + P_{water} = 1.00 \text{ atm} + 3.9692 \text{ atm} = 4.9\underline{6}92 \text{ atm}$$

The density of a gas is directly proportional to the pressure, so

$$d_2 = d_1 \text{ x } \frac{P_2}{P_1} = (1.205 \text{ g/L}) \text{ x } \left(\frac{4.9692 \text{ atm}}{1.00 \text{ atm}}\right) = 5.9\underline{8}7 = 5.99 \text{ g/L}$$

5.107. Use the combined gas law and solve for V_f:

$$V_f = V_i \text{ x } \frac{P_i}{P_f} \text{ x } \frac{T_f}{T_i} = 201 \text{ mL x } \frac{738 \text{ mmHg}}{760 \text{ mmHg}} \text{ x } \frac{273 \text{ K}}{294 \text{ K}} = 18\underline{1}.24 = 181 \text{ mL}$$

5.108. Use the combined gas law and solve for V_f:

$$V_f = V_i \text{ x } \frac{P_i}{P_f} \text{ x } \frac{T_f}{T_i} = 12.0 \text{ L x } \frac{11.0 \text{ atm}}{1.00 \text{ atm}} \text{ x } \frac{273 \text{ K}}{293 \text{ K}} = 12\underline{2}.98 = 123 \text{ L}$$

5.109. Use the combined gas law and solve for V_f:

$$V_f = V_i \text{ x } \frac{P_i}{P_f} \text{ x } \frac{T_f}{T_i} = 5.0 \text{ dm}^3 \text{ x } \frac{100.0 \text{ kPa}}{79.0 \text{ kPa}} \text{ x } \frac{293 \text{ K}}{287 \text{ K}} = 6.\underline{4}6 = 6.5 \text{ dm}^3$$

5.110. Let V_i = 1 volume (vol) in the combined gas law; solving for V_f will give the relative final volume, or factor, for the increase:

$$V_f = V_i \text{ x } \frac{P_i}{P_f} \text{ x } \frac{T_f}{T_i} = 1 \text{ vol x } \frac{1.00 \text{ atm}}{1.00 \text{ x } 10^{-3} \text{ atm}} \text{ x } \frac{252 \text{ K}}{288 \text{ K}} = 87\underline{5}.0 \text{ vol, or 875 times}$$

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5.111. Use the ideal gas law to calculate the moles of helium, and combine this with Avogadro's number to obtain the number of helium atoms:

$$n = \frac{PV}{RT} = \frac{(765/760 \text{ atm})(0.01205 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(296 \text{ K})} = 4.9\underline{9}3 \times 10^{-4} \text{ mol}$$

$$4.993 \times 10^{-4} \text{ mol He} \times \frac{6.022 \times 10^{23} \text{ He}^{2+} \text{ ions}}{1 \text{ mol He}} \times \frac{1 \text{ atom}}{1 \text{ He}^{2+} \text{ ion}} = 3.0\underline{0}67 \times 10^{20}$$

$$= 3.01 \times 10^{20} \text{ atoms}$$

5.112. Use the ideal gas law to calculate the moles of nitrogen, and combine this with the molar mass to obtain the mass of nitrogen. Then calculate the mass percentage:

$$n = \frac{PV}{RT} = \frac{(749/760 \text{ atm})(0.00159 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 6.4\underline{0}7 \times 10^{-5} \text{ mol}$$

$$6.4\underline{0}7 \times 10^{-5} \text{ mol } N_2 \times \frac{28.02 \text{ g } N_2}{1 \text{ mol } N_2} = 1.7\underline{9}55 \times 10^{-3} \text{ g N} \quad (1.7\underline{9}55 \text{ mg N})$$

$$\text{Percent N} = \frac{\text{mass N}}{\text{mass comp.}} \times 100\% = \frac{1.7955 \text{ mg N}}{8.75 \text{ mg}} \times 100\% = 20.\underline{5}2 = 20.5\%$$

5.113. Calculate the molar mass, M_m, by dividing the mass of 1 liter of air by the moles of the gas from the ideal gas equation:

$$M_m = \frac{\text{mass}}{n} = 1.2929 \text{ g air} \times \frac{(0.082058 \text{ L} \cdot \text{atm/K} \cdot \text{ mol})\ (273.15 \text{ K})}{(1 \text{ atm})(1 \text{ L})}$$

$$= 28.97\underline{9}2 \text{ g/mol} = 28.979 \text{ g/ mol (amu)}$$

5.114. First, calculate the molar mass, M_m, by dividing the mass of 1 liter of air by the moles of the gas from the ideal gas equation:

$$M_m = \frac{\text{mass}}{n} = 1.22 \text{ g gas} \times \frac{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{ mol})\ (293 \text{ K})}{(1 \text{ atm})(1 \text{ L})} = 29.\underline{3}3 \text{ g/mol}$$

Find the empirical formula from the 80.0% C and 20% H by assuming 1 g of compound and calculating the moles:

$$0.800 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.06661 \text{ mol C}$$

$$0.200 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.1984 \text{ mol H}$$

$$\frac{0.06661 \text{ mol C}}{0.06661} = 1.00, \text{ or } 1 \text{ mol C}; \qquad \frac{0.1984 \text{ mol H}}{0.06661} = 2.98, \text{ or } 3 \text{ mol H}$$

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The simplest formula is CH_3, whose empirical formula mass is 15.03 g/mol. The number of CH_3 units contained in the molecular mass of 29.33 is

$$\frac{\text{Molecular mass}}{\text{Formula mass}} = \frac{29.33}{15.03} = 1.95, \text{ or } 2$$

The molecular formula is $(CH_3)_2$, or C_2H_6.

5.115. Use the ideal gas law to calculate the moles of CO_2. Then convert to mass of LiOH.

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(5.8 \times 10^2 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(273 \text{ K})} = 2\underline{5}.89 \text{ mol } CO_2$$

$$2\underline{5}.89 \text{ mol } CO_2 \times \frac{2 \text{ mol LiOH}}{1 \text{ mol } CO_2} \times \frac{23.95 \text{ g LiOH}}{1 \text{ mol LiOH}} = 1\underline{2}40 = 1.2 \times 10^3 \text{ g LiOH}$$

5.116. Use the ideal gas law to calculate moles of CO_2. Then convert to mass of pyruvic acid.

$$n = \frac{PV}{RT} = \frac{(349/760 \text{ atm})(0.0212 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(303 \text{ K})} = 3.9\underline{1}5 \times 10^{-4} \text{ mol } CO_2$$

$$3.915 \times 10^{-4} \text{ mol } CO_2 \times \frac{1 \text{ mol } C_3H_4O_3}{1 \text{ mol } CO_2} \times \frac{88.06 \text{ g } C_3H_4O_3}{1 \text{ mol } C_3H_4O_3}$$

$$= 0.034\underline{4}7 = 0.0345 \text{ g } C_3H_4O_3$$

5.117. Convert mass to moles of $KClO_3$, and then use the equation below to convert to moles of O_2. Use the ideal gas law to convert moles of O_2 to pressure at 25°C (298 K).

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

$$170.0 \text{ g } KClO_3 \times \frac{1 \text{ mol } KClO_3}{122.55 \text{ g } KClO_3} \times \frac{3 \text{ mol } O_2}{2 \text{ mol } KClO_3} = 2.0\underline{8}0 \text{ mol } O_2$$

$$P = \frac{nRT}{V} = \frac{(2.0\underline{8}0 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(298 \text{ K})}{2.50 \text{ L}} = 20.\underline{3}53 = 20.4 \text{ atm } O_2$$

5.118. Convert mass to moles of $KCHO_2$, and then use the equation below to convert to moles of H_2. Use the ideal gas law to convert moles of H_2 to pressure at 25°C (298 K).

$$KCHO_2(s) + KOH(s) \rightarrow K_2CO_3(s) + H_2(g)$$

$$50.0 \text{ g } KCHO_2 \times \frac{1 \text{ mol } KCHO_2}{84.12 \text{ g } KCHO_2} = 0.59\underline{4}38 \text{ mol } KCHO_2$$

From the equation, 0.59438 mol of $KCHO_2$ produces 0.59438 mol of H_2.

$$P = \frac{nRT}{V} = \frac{(0.59438 \text{ mol } O_2)(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(298 \text{ K})}{2.50 \text{ L}} = 5.8\underline{1}4 = 5.81 \text{ atm } H_2$$

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5.119. Find the number of moles of CO_2 first. Then convert this to moles of HCl and molarity of HCl.

$$n = \frac{(727 / 760 \text{ atm}) \text{ x } 0.141 \text{ L}}{0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol} \text{ x } 300 \text{ K}} = 0.0054\underline{7}88 \text{ mol}$$

$$\text{mol HCl} = 0.0054788 \text{ mol } CO_2 \text{ x } (2 \text{ mol HCl} / 1 \text{ mol } CO_2) = 0.010\underline{9}57 \text{ mol}$$

$$M \text{ HCl} = 0.010\underline{9}57 \text{ mol HCl} \div 0.0249 \text{ L HCl} = 0.44\underline{0}0 = 0.440 \text{ mol/L HCl}$$

5.120. Find the number of moles of CO_2 first. Then convert this to moles of HCl and molarity of HCl.

$$n = \frac{731/760 \text{ atm} \text{ x } 0.159 \text{ L}}{0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol} \text{ x } 296 \text{ K}} = 0.006\underline{2}96 \text{ mol}$$

$$\text{mol HCl} = 0.006296 \text{ mol } CO_2 \text{ x } \frac{2 \text{ mol HCl}}{1 \text{ mol } CO_2} = 0.012\underline{5}9 \text{ mol}$$

$$\text{Molarity} = \frac{0.01259 \text{ mol}}{0.0186 \text{ L}} = 0.67\underline{7}0 = 0.677 \text{ } M \text{ HCl}$$

5.121. The number of moles of carbon dioxide is

$$n = \frac{646 / 760 \text{ atm} \text{ x } 0.1500 \text{ L}}{0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol} \text{ x } 300 \text{ K}} = 0.005\underline{1}79 \text{ mol}$$

The number of moles of molecular acid used is

$$0.1250 \text{ mol/L} \text{ x } 0.04141 \text{ L} = 0.005176 \text{ mol acid}$$

Thus, the acid is H_2SO_4 since 1 mole of H_2SO_4 reacts to form 1 mole of CO_2

5.122. The number of moles of carbon dioxide is

$$n = \frac{722 / 760 \text{ atm} \text{ x } 0.1250 \text{ L}}{0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol} \text{ x } 290 \text{ K}} = 0.004\underline{9}90 \text{ mol}$$

The number of moles of molecular acid used is

$$0.2040 \text{ mol/L} \text{ x } 0.04990 \text{ L} = 0.0099756 \text{ mol acid}$$

Thus, the acid is HCl since the ratio of acid to CO_2 is $0.0099756 \div 0.004990 = 2.00$ to 1.

5.123. Use Maxwell's distribution to calculate the temperature in kelvins; then convert to °C.

$$T = \frac{u^2 M_m}{3R} = \frac{(0.605 \text{ x } 10^3 \text{ m/s})^2 \text{ } (17.03 \text{ x } 10^{-3} \text{ kg/mol})}{3 \text{ } (8.31 \text{ kg} \bullet \text{m}^2/\text{s}^2 \bullet \text{K} \bullet \text{mol})} = 25\underline{0}.0 = 250. \text{ K } (-23°\text{C})$$

5.124. Use Maxwell's distribution to calculate the temperature in kelvins.

$$T = \frac{u^2 M_m}{3R} = \frac{(3.53 \text{ x } 10^3 \text{ m/s})^2 \text{ } (4.003 \text{ x } 10^{-3} \text{ kg/mol})}{3 \text{ } (8.31 \text{ kg} \bullet m^2 / s^2 \bullet K \bullet mol)} = 2.0\underline{0}08 \text{ x } 10^3 = 2.00 \text{ x } 10^3 \text{ K}$$

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5.125. Calculate the ratio of the root-mean-square (rms) molecular speeds, which is the same as the ratio of the rates of effusion:

$$\frac{u\,[\mathrm{U(235)F_6}]}{u\,[\mathrm{U(238)F_6}]} = \left(\frac{M_m[\mathrm{U(238)F_6}]}{M_m[\mathrm{U(235)F_6}]}\right)^{1/2} = \left(\frac{352.04\ \mathrm{g/\ mol}}{349.03\ \mathrm{g/\ mol}}\right)^{1/2} = 1.004\underline{3}02 = 1.0043$$

5.126. Calculate the ratio of the root-mean-square (rms) molecular speeds, which is the same as the ratio of the rates of effusion through the barrier:

$$\frac{u\,[\mathrm{H_2}(1,1)]}{u\,[\mathrm{H_2}(1,2)]} = \left(\frac{M_m[\mathrm{H_2}(1,2)]}{M_m[\mathrm{H_2}(1,1)]}\right)^{1/2} = \left(\frac{3.0219\ \mathrm{g/\ mol}}{2.0156\ \mathrm{g/\ mol}}\right)^{1/2} = 1.22\underline{4}4 = 1.1224$$

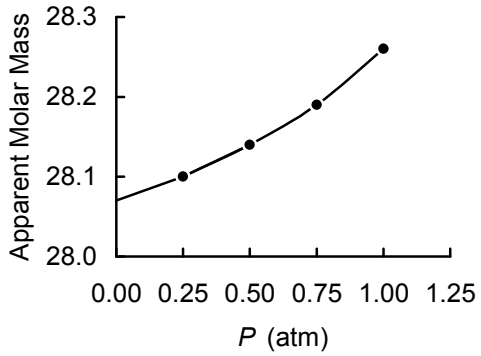
5.127. First, calculate the apparent molar masses at each pressure using the ideal gas law. Only the calculation of the apparent molar mass for 0.2500 atm will be shown; the other values will be summarized in a table.

$$n = \frac{PV}{RT} = \frac{(0.2500\ \mathrm{atm})\,(3.1908\ \mathrm{L})}{(0.082057\ \mathrm{L \bullet atm/K \bullet mol})\,(273.15\ \mathrm{K})} = 3.55\underline{8}96 \times 10^{-2}\ \mathrm{mol}$$

$$\text{Apparent molar mass} = \frac{1.000\ \mathrm{g}}{3.55896 \times 10^{-2}\ \mathrm{mol}} = 28.0\underline{9}8 = 28.10\ \mathrm{g/mol}$$

The following table summarizes the apparent molar masses calculated as above for all P's; these data are plotted in the graph to the right of the table.

P **(atm)**	**App. Molar Mass (g/mol)**
0.2500	28.10
0.5000	28.14
0.7500	28.19
1.0000	28.26



Extrapolation back to $P = 0$ gives 28.07 g/mol for the molar mass of the unknown gas (CO).

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5.128. First, calculate the apparent molar mass at each pressure using the ideal gas law. Only the calculation of the molar mass at 0.2500 atm will be shown; the other values will be summarized in a table.

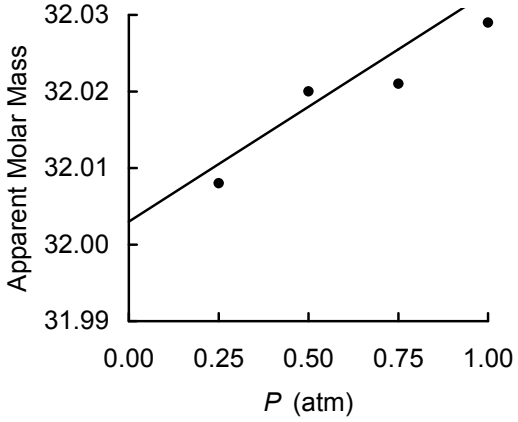
$$n = \frac{PV}{RT} = \frac{(0.2500 \text{ atm})(2.801 \text{ L})}{(0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273.15 \text{ K})} = 3.12\underline{4}2 \times 10^{-2} \text{ mol}$$

$$\text{Apparent molar mass} = \frac{1.000 \text{ g}}{3.1242 \times 10^{-2} \text{ mol}} = 32.0\underline{0}8 = 32.01 \text{ g/mol}$$

The following table summarizes the apparent molar masses calculated as above for all *P*'s; these data are plotted in the graph to the right of the table.

***P* (atm)**	**App. Molar Mass (g/mol)**
0.2500	32.008
0.5000	32.020
0.7500	32.021
1.0000	32.029

Extrapolation back to $P = 0$ gives close to 32.00 g/mol for the molar mass of O_2.



5.129. Use $CO + 1/2O_2 \rightarrow CO_2$, instead of 2CO. First, find the moles of CO and O_2 by using the ideal gas law.

$$n_{CO} = \frac{PV}{RT} = \frac{(0.500 \text{ atm})(2.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})} = 0.040\underline{6}2 \text{ mol}$$

$$n_{O_2} = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})} = 0.040\underline{6}2 \text{ mol}$$

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There are equal amounts of CO and O_2, but (from the equation) only half as many moles of O_2 as CO are required for the reaction. Therefore, when 0.04062 mol CO has been consumed, only 0.04062/2 mol O_2 will have been used up. Then 0.04062/2 mol O_2 will remain, and 0.04062 mol CO_2 will have been produced. At the end,

$$n_{CO} = 0 \text{ mol}; \quad n_{O_2} = 0.0202 \text{ mol}; \text{ and } n_{CO_2} = 0.04062 \text{ mol}$$

However, the total volume with the valve open is 3.00 L, so the partial pressures of O_2 and CO_2 must be calculated from the ideal gas law for each:

$$\frac{nRT}{V} = \frac{(0.0203 \text{ mol } O_2)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})}{3.00 \text{ L}} = 0.16\underline{6}58 = 0.167 \text{ atm } O_2$$

$$\frac{nRT}{V} = \frac{(0.04062 \text{ mol } CO_2)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})}{3.00 \text{ L}}$$

$$= 0.33\underline{3}32 = 0.333 \text{ atm } CO_2$$

5.130. Use $H_2 + 1/2O_2 \rightarrow H_2O$. First, find the moles of H_2 and O_2 by using the ideal gas law.

$$n_{H_2} = \frac{PV}{RT} = \frac{(0.500 \text{ atm})(2.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})} = 0.040\underline{6}2 \text{ mol}$$

$$n_{O_2} = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})} = 0.040\underline{6}2 \text{ mol}$$

When all the H_2 has been consumed, half of the O_2 will remain. At the end, there will be 0.040$\underline{6}$2 mol H_2O formed. However, the final volume is 3.00 L, so the partial pressures of H_2O and O_2 must each be calculated from the ideal gas law:

$$\frac{nRT}{V} = \frac{(0.04062 \text{ mol } H_2O)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})}{3.00 \text{ L}}$$

$$= 0.33\underline{3}3 = 0.333 \text{ atm } H_2O$$

$$\frac{nRT}{V} = \frac{(0.02031 \text{ mol } O_2)(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})}{3.00 \text{ L}}$$

$$= 0.16\underline{6}66 = 0.167 \text{ atm } O_2$$

5.131. Cells in the lining of arteries detect increased blood pressure and respond by producing nitric oxide. NO rapidly diffuses through the artery wall to cells in the surrounding muscle tissue. In response, the muscle tissue relaxes, the blood vessel expands, and the blood pressure drops.

5.132. Angina results from reduced blood flow to the heart muscle. Nitroglycerin breaks down in the body to form nitric oxide, which relaxes the arteries, allowing greater blood flow to the heart.

5.133. Svante Arrhenius was the first to show how sensitive the temperature of the earth might be to the percentage of carbon dioxide in the atmosphere.

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5.134. The principal gases in the atmosphere are oxygen, O_2, and nitrogen, N_2. These gases are transparent to visible light from the sun, and when the light reaches the surface of the earth, it is absorbed and converted to heat. The heat causes atoms in the earth's surface to vibrate, which then radiate the heat energy as infrared radiation, or heat rays. Neither oxygen nor nitrogen absorbs infrared radiation, but other gases, especially carbon dioxide, do absorb infrared radiation, and it is this absorption that warms the atmosphere, giving a greenhouse effect.

■ SOLUTIONS TO STRATEGY PROBLEMS

5.135. First calculate the moles of carbon dioxide that formed.

$$n = \frac{PV}{RT} = \frac{(738/760 \text{ atm})(183 \times 10^{-3} \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(297.15 \text{ K})} = 0.007287 \text{ mol} CO_2$$

Now, find the molarity.

$$\frac{0.007287 \text{ mol } CO_2}{24.6 \times 10^{-3} \text{ L}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } CO_2} = 0.5924 = 0.592 \, M$$

5.136.

a. The taller, narrower curve, with a maximum value near 500 m/s, is for the heaver particles, neon. The flatter, wider curve, with a maximum value near 1500 m/s, is for the lighter particles, hydrogen.

b. $$u_{Ne} = \left(\frac{3 \times 8.31 \text{ kg} \cdot \text{m}^2/(\text{s}^2 \cdot \text{K} \cdot \text{mol}) \times 200 \text{ K}}{20.18 \times 10^{-3} \text{ kg/mol}} \right)^{1/2} = 497.06 = 497 \text{ m/s}$$

$$u_{H_2} = \left(\frac{3 \times 8.31 \text{ kg} \cdot \text{m}^2/(\text{s}^2 \cdot \text{K} \cdot \text{mol}) \times 200 \text{ K}}{2.016 \times 10^{-3} \text{ kg/mol}} \right)^{1/2} = 1573 = 1.57 \times 10^3 \text{ m/s}$$

c. Since hydrogen has the higher rms speed, it will have a greater effusion rate. Molecules moving faster collide with the hole in the container more often and have a higher probability of effusing.

d. $$T = \frac{u^2 M_m}{3R} = \frac{(497.06 \text{ m/s})^2 \ (2.016 \times 10^{-3} \text{ kg/mol})}{3 \ (8.31 \text{ kg} \cdot m^2 / s^2 \cdot K \cdot mol)} = 19.98 = 20.0 \text{ K}$$

5.137. $$P_f = \frac{P_i V_i T_f}{V_f T_i} = \frac{(1 \text{ atm}) \ (162 \text{ L}) \ (279.07 \text{ K})}{(18.8 \text{ L}) \ (294.15 \text{ K})} = 8.1752 = 8.18 \text{ atm}$$

5.138. $$V_f = \frac{P_i V_i T_f}{P_f T_i} = \frac{(740 \text{ mmHg}) \ (435 \text{ mL}) \ (273.15 \text{ K})}{(760 \text{ mmHg}) \ (298.15 \text{ K})} = 388.03 = 388 \text{ mL}$$

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5.139. First note that 16.0 g O_2 represents 0.500 mol O_2 and that 14.0 g N_2 represents 0.500 mol N_2. Altogether, then, there is 1.00 mol of gas present in the container.

a. At STP 1.00 mol of gas occupies 22.4 L.

b. $$P_{O_2} = X_{O_2} \text{ x } P_{tot} = \frac{0.500 \text{ mol } O_2}{0.500 \text{ mol } O_2 + 0.500 \text{ mol } N_2} \text{ x } 1 \text{ atm} = 0.500 \text{ atm}$$

c. $$X_{N_2} = \frac{0.500 \text{ mol } N_2}{0.500 \text{ mol } O_2 + 0.500 \text{ mol } N_2} = 0.500 \quad (50.0\% \text{ mole percent})$$

5.140.

a. The molar mass of C_4H_7S is 87.166 g/mol.

$$u = \left(\frac{3 \text{ x } 8.31 \text{ kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{K} \bullet \text{mol}) \text{ x } 298.15 \text{ K}}{87.166 \text{ x } 10^{-3} \text{ kg/mol}} \right)^{1/2} = 29\underline{2}.08 = 292 \text{ m/s}$$

b. $$t = \frac{150 \text{ m}}{292 \text{ m/s}} = 0.51\underline{3}5 = 0.514 \text{ s}$$

c. This is probably not a good estimate because molecules do not travel in straight lines over such distances without undergoing numerous collisions. The actual path is random and irregular, and the time it would take cannot be estimated accurately.

5.141. The density of a gas can be calculated by using $d = PM_m/RT$. For two different gases under the same conditions of temperature and pressure, this reduces to

$$\frac{d_2}{d_1} = \frac{M_2}{M_1} = \frac{146.07 \text{ g/mol}}{29.0 \text{ g/mol}} = 5.0\underline{3}6 = 5.04$$

Thus, the density of SF_6 is 5.04 times the density of air.

5.142.

a. $$P = \frac{(1.0 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(348.15 \text{ K})}{1.0 \text{ L}} \text{ x } \frac{760 \text{ mmHg}}{1 \text{ atm}}$$

$$= 2.\underline{1}71 \text{ x } 10^4 = 2.2 \text{ x } 10^4 \text{ mmHg}$$

b. The molecules are undergoing constant random motion and are colliding with each other and with the walls of the container. The pressure in the container is caused by collisions of the molecules with the walls.

c. If the temperature of the container is increased to 150°C, the average speed of the molecules will increase, and the number of collisions with other molecules and with the walls of the container will also increase. This will result in an increase in the pressure.

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5.143. The moles of H_2S gas formed is

$$n = \frac{(12.0 \text{ atm})(0.600 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(398 \text{ K})} = 0.22\underline{0}45 \text{ mol } H_2S$$

The mass can now be calculated.

$$0.22045 \text{ mol } H_2S \times \frac{1 \text{ mol } S_8}{8 \text{ mol } H_2S} \times \frac{256.56 \text{ g}}{1 \text{ mol } S_8} = 7.0\underline{6}9 = 7.07 \text{ g } S_8$$

5.144.

a. Since the piston is movable, the pressure inside each flask is the same as the pressure outside, 1.0 atm.

b. Since containers A and B have the same volume, and since container B has twice as many particles, the absolute temperature in container B is one-half the temperature in container A. Container C has twice the volume of container A and also twice as many particles. Thus, the temperature in container C is the same as the temperature in container A.

c. Since the piston is movable, the pressure inside each flask will remain the same as before, 1.0 atm. Now the volume is directly proportional to the amount of gas present, so the volumes of containers B and C will be equal, and the volume of container A will be one-half as much.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

5.145. Assume a 100.0-g sample, giving 85.2 g CH_4 and 14.8 g C_2H_6. Convert each to moles:

$$85.2 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} = 5.3\underline{1}1 \text{ mol } CH_4$$

$$14.8 \text{ g } C_2H_6 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} = 0.49\underline{2}1 \text{ mol } C_2H_6$$

$$V_{CH_4} = \frac{(5.311 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(291 \text{ K})}{(771/760) \text{ atm}} = 12\underline{5}.03 \text{ L}$$

$$V_{C_2H_6} = \frac{(0.4921 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(291 \text{ K})}{(771/760) \text{ atm}} = 11.\underline{5}8 \text{ L}$$

The density is calculated as follows:

$$d = \frac{85.2 \text{ g } CH_4 + 14.8 \text{ g } C_2H_6}{(125.03 + 11.58) \text{ L}} = 0.73\underline{1}9 = 0.732 \text{ g/L}$$

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5.146. Assume a 100.0-g sample, giving 34.3 g He, 51.7 g N_2, and 14.0 g O_2. Convert to moles:

$$34.3 \text{ g He} \times \frac{1 \text{ mol He}}{4.00 \text{ g}} = 8.5\underline{7}50 \text{ mol He}$$

$$51.7 \text{ g } N_2 \times \frac{1 \text{ mol } N_2}{28.02 \text{ g}} = 1.8\underline{4}51 \text{ mol } N_2$$

$$14.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.43\underline{7}50 \text{ mol } O_2$$

$$V_{He} = \frac{(8.575 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})}{(755/760) \text{ atm}} = 208.\underline{9} \text{ L}$$

$$V_{N_2} = \frac{(1.8451 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})}{(755/760) \text{ atm}} = 44.\underline{9}6 \text{ L}$$

$$V_{O_2} = \frac{(0.4375 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})}{(755/760) \text{ atm}} = 10.\underline{6}6 \text{ L}$$

The density is calculated as follows:

$$d = \frac{34.3 \text{ g He} + 51.7 \text{ g } N_2 + 14.0 \text{ g } O_2}{(208.9 + 44.96 + 10.66) \text{ L}} = 0.37\underline{8}02 = 0.378 \text{ g/L}$$

5.147. First, subtract the height of mercury equivalent to the 25.00 cm (250 mm) of water inside the tube from 771 mmHg to get P_{gas}. Then subtract the vapor pressure of water, 18.7 mmHg, from P_{gas} to get P_{O_2}

$$h_{Hg} = \frac{(h_W)(d_W)}{d_{Hg}} = \frac{250 \text{ mm} \times 0.99987 \text{ g/cm}^3}{13.596 \text{ g/cm}^3} = 18.\underline{3}8 \text{ mmHg}$$

$$P_{gas} = P - P_{25 \text{ cm water}} = 771 \text{ mmHg} - 18.38 \text{ mmHg} = 75\underline{2}.62 \text{ mmHg}$$

$$P_{O_2} = 75\underline{2}.62 \text{ mmHg} - 18.7 \text{ mmHg} = 73\underline{3}.92 \text{ mmHg}$$

$$n = \frac{PV}{RT} = \frac{(733.92/760 \text{ atm})(0.0310 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(294 \text{ K})} = 0.0012\underline{4}08 \text{ mol } O_2$$

$$\text{Mass} = (2 \times 0.0012408) \text{ mol } Na_2O_2 \times \frac{77.98 \text{ g } Na_2O_2}{1 \text{ mol } Na_2O_2} = 0.19\underline{3}5 = 0.194 \text{ g } Na_2O_2$$

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5.148. Proceed as in the previous problem, subtracting the height of the water and then the vapor pressure to find P_{H_2}.

$$h_{Hg} = \frac{(h_W)(d_W)}{d_{Hg}} = \frac{310 \text{ mm x } 0.99987 \text{ g/cm}^3}{13.596 \text{ g/cm}^3} \quad 22.\underline{8}0 \text{ mmHg}$$

$$P_{gas} = P - P_{31 \text{ cm water}} = 751 \text{ mmHg} - 22.80 \text{ mmHg} = 72\underline{8}.2 \text{ mmHg}$$

$$P_{H_2} = (728.2 - 14.5) \text{ mmHg} = 71\underline{3}.7 \text{ mmHg}$$

$$n = \frac{PV}{RT} = \frac{(713.7 / 760 \text{ atm})\,(0.0221 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(290 \text{ K})} = 0.00087\underline{2}09 \text{ mol } H_2$$

$$\text{Mass} = 0.00087\underline{209} \text{ mol } H_2 \text{ x } \frac{1 \text{ mol Zn}}{1 \text{ mol } H_2} \text{ x } \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 0.057\underline{0}26 = 0.0570 \text{ g Zn}$$

5.149. First find the moles of CO_2:

$$n = \frac{PV}{RT} = \frac{(785/760 \text{ atm})\,(1.94 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})\,(298 \text{ K})} = 0.081\underline{9}4 \text{ mol CO}$$

Set up one equation in one unknown: x = mol $CaCO_3$; $(0.08194 - x)$ = mol $MgCO_3$.

$$7.85 \text{ g} = (100.1 \text{ g/mol})x + (84.32 \text{ g/mol})(0.08194 - x)$$

$$x = \frac{(7.85 - 6.9092)}{(100.1 - 84.32)} = 0.05\underline{9}62 \text{ mol } CaCO_3$$

$$(0.08194 - x) = 0.02\underline{2}32 \text{ mol } MgCO_3$$

$$CaCO_3 = \frac{0.05962 \text{ mol } CaCO_3 \text{ x } 100.1 \text{ g/mol}}{7.85 \text{ g}} \text{ x } 100\% = 7\underline{6}.02 = 76\%$$

$$\text{Percent } MgCO_3 = 100.00\% - 76.02\% = 2\underline{3}.98 = 24\%$$

5.150. First find the moles of H_2S:

$$n = \frac{PV}{RT} = \frac{(745/760 \text{ atm})\,(1.049 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})\,(296 \text{ K})} = 0.042\underline{3}3 \text{ mol } H_2S$$

Set up one equation in one unknown: x = mol ZnS; $(0.04233 - x)$ = mol PbS.

$$6.12 \text{ g} = (97.46 \text{ g/mol})x + (239.25 \text{ g/mol})(0.04233 - x)$$

$$x = \frac{(6.12 - 10.127)}{(97.46 - 239.25)} = 0.028\underline{2}6 \text{ mol ZnS}$$

$$(0.04233 - x) = 0.014\underline{0}70 \text{ mol PbS}$$

$$\text{Percent ZnS} = \frac{0.02826 \text{ mol ZnS x } 97.46 \text{ g/mol}}{6.12 \text{ g}} \text{ x } 100\% = 45.\underline{0}0 = 45.0\%$$

$$\text{Percent PbS} = 55.0\%$$

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5.151. Write a mass-balance equation to solve for the moles of each gas, using 28.01 g/mol for the molar mass of N_2 and 20.18 g/mol for the molar mass of Ne. Let y equal moles of each gas:

$28.01\,y + 20.18\,y = 10.0$ g

$y = (10.0 \div 48.19) = 0.20\underline{7}51$ mol

Total moles (n) = 0.41502 mol (use below)

Use the ideal gas law to calculate the volume, which can then be used to calculate density.

$$\frac{(0.41502\text{ mol})(0.08206\text{ L}\bullet\text{atm/K}\bullet\text{mol})(500\text{ K})}{15.00\text{ atm}} = 1.1\underline{3}52\text{ L}$$

$d = 10.0\text{ g} \div 1.1352\text{ L} = 8.8\underline{0}8 = 8.81$ g/L

5.152. Write a mass-balance equation to solve for moles of each, using 39.95 g/mol for the molar mass of Ar and 20.18 g/mol for the molar mass of Ne. Let y equal moles of Ar and $2y$ equal moles of Ne:

$39.95\,y + 20.18\,(2y) = 50.0$ g

$y = (50.0 \div 80.31) = 0.62\underline{2}5$ mol

Total moles (n) = mol Ar + mol Ne = $0.6225 + (2)(0.6225) = 1.86\underline{7}7$ mol (use below)

Volume of the mixture = 50.0 g ÷ 4.00 g/L = 12.5 L

Use the ideal gas law to calculate the total pressure.

$$P(\text{total}) = \frac{(1.8677\text{ mol})(0.08206\text{ L}\bullet\text{atm/K}\bullet\text{mol})(350\text{ K})}{12.5\text{ L}} = 4.2\underline{9}2\text{ atm}$$

Partial pressure of Ne = $2/3\,P(\text{total}) = 2/3(4.292\text{ atm}) = 2.8\underline{6}1 = 2.86$ atm

5.153. Rearrange the equation $PM_m = dRT$ to find the quantity RT/M_m. Then plug into the equation for the root-mean-square speed.

$$\frac{RT}{M_m} = \frac{P}{d}$$

$$u = \left(\frac{3RT}{M_m}\right)^{1/2} = \left(\frac{3P}{d}\right)^{1/2} = \left(\frac{3\left(\frac{675}{760}\right)\text{ atm x }(8.31\text{ kg}\bullet\text{m}^2/\text{s}^2\bullet\text{K}\bullet\text{mol})}{(3.00\text{ x }10^{-3}\text{ kg/L})(0.08206\text{ L}\bullet\text{atm/K}\bullet\text{mol})}\right)^{1/2}$$

$$= 2.9\underline{9}90\text{ x }10^2 = 3.00\text{ x }10^2\text{ m/s}$$

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5.154. Rearrange the equation for the root-mean-square speed to get $M_m = 3RT/u^2$.

$$M_m = \frac{(3)(8.31\ \text{kg} \bullet \text{m}^2/(\text{s}^2 \bullet \text{mol} \bullet \text{K})(298.2\ \text{K})}{(5.00 \times 10^2\ \text{m/s})^2} = 0.029\underline{7}37\ \text{kg/mol} = 29.\underline{7}4\ \text{g/mol}$$

Now, rearrange the equation $PM_m = dRT$ to find the density, $d = PM_m/RT$.

$$d = \frac{PM_m}{RT} = \frac{(2.50\ \text{atm})(29.74\ \text{g/mol})}{(0.08206\ \text{L} \bullet \text{atm/K} \bullet \text{mol})(298.2\ \text{K})} = 3.0\underline{3}8 = 3.04\ \text{g/L}$$

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CHAPTER 6

Thermochemistry

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

6.1. Substitute into the formula $E_k = 1/2\ mv^2$ using SI units:

$$E_k = 1/2 \times 9.11 \times 10^{-31}\ \text{kg} \times (5.0 \times 10^6\ \text{m/s})^2 = 1.\underline{1}3 \times 10^{-17} = 1.1 \times 10^{-17}\ \text{J}$$

$$1.13 \times 10^{-17}\ \text{J} \times \frac{1\ \text{cal}}{4.184\ \text{J}} = 2.\underline{7}2 \times 10^{-18} = 2.7 \times 10^{-18}\ \text{cal}$$

6.2. Heat is evolved; therefore, the reaction is exothermic. The value of q is −1170 kJ.

6.3. The thermochemical equation is

$$2N_2H_4(l) + N_2O_4(l) \rightarrow 3N_2(g) + 4H_2O(g);\ \Delta H = -1049\ \text{kJ}$$

ΔH equals −1049 kJ for 1 mol N_2H_4 and for 2 mol N_2H_4.

6.4.

a. $N_2H_4(l) + 1/2N_2O_4(l) \rightarrow 3/2N_2(g) + 2H_2O(g);\ \Delta H = -524.5\ \text{kJ}$

b. $4H_2O(g) + 3N_2(g) \rightarrow 2N_2H_4(l) + N_2O_4(l);\ \Delta H = 1049\ \text{kJ}$

6.5. The reaction is

$$2N_2H_4(l) + N_2O_4(l) \rightarrow 3N_2(g) + 4H_2O(g);\ \Delta H = -1049\ \text{kJ}$$

$$10.0\ \text{g}\ N_2H_4 \times \frac{1\ \text{mol}\ N_2H_4}{32.02\ \text{g}} \times \frac{1\ \text{mol}\ N_2O_4}{2\ \text{mol}\ N_2H_4} \times \frac{-1049\ \text{kJ}}{1\ \text{mol}\ N_2O_4} = -16\underline{3}.80 = -164\ \text{kJ}$$

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6.6. Substitute into the equation $q = s \times m \times \Delta t$ to obtain the heat transferred. The temperature change is

$$\Delta t = t_f - t_i = 100.0°C - 20.0°C = 80.0°C$$

Therefore,

$$q = s \times m \ \Delta t = 0.449 J/(g \bullet °C) \times 5.00 \text{ g} \times 80.0°C = 1.796 \times 10^2 = 1.80 \times 10^2 \text{ J}$$

6.7. The total mass of the solution is obtained by adding the volumes together and by using the density of water (1.000 g/mL). This gives 33 + 42 = 75 mL, or 75 g. The heat absorbed by the solution is

$$q = s \times m \times \Delta t = 4.184 J/(g \bullet °C) \times 75 \text{ g} \times (31.8°C - 25.0°C) = 2133.8 \text{ J}$$

The heat released by the reaction, q_{rxn}, is equal to the negative of this value, or −2133.8 J. To obtain the enthalpy change for the reaction, you need to calculate the moles of HCl that reacted. This is

$$\text{Mol HCl} = 1.20 \text{ mol/L} \times 0.033 \text{ L} = 0.0396 \text{ mol}$$

The enthalpy change for the reaction can now be calculated.

$$\Delta H = \frac{-2133.8 \text{ J}}{0.0396 \text{ mol}} = -53884 \text{ J/mol} = -54 \text{ kJ/mol}$$

Expressing this result as a thermochemical equation, you have

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l); \quad \Delta H = -54 \text{ kJ}$$

6.8. Use Hess's law to find ΔH for $4Al(s) + 3MnO_2(s) \rightarrow 2Al_2O_3(s) + 3Mn(s)$ from the following data for equations 1 and 2:

$$2Al(s) + 3/2O_2(g) \rightarrow Al_2O_3(s); \quad \Delta H = -1676 \text{ kJ} \quad (1)$$

$$Mn(s) + O_2(g) \rightarrow MnO_2(s); \quad \Delta H = -520 \text{ kJ} \quad (2)$$

If you take equation 1 and multiply it by 2, you obtain

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s); \quad \Delta H = 2 \times (-1676 \text{ kJ}) = -3352 \text{ kJ}$$

Since the desired reaction has three MnO_2 on the left side, reverse equation 2 and multiply it by 3. The result is

$$3MnO_2(s) \rightarrow 3Mn(s) + 3O_2(g) \quad \Delta H = -3 \times (-520 \text{ kJ}) = 1560 \text{ kJ}$$

If you add the two equations and corresponding enthalpy changes, you obtain the enthalpy change of the desired equation.

$4Al(s) + 3O_2(g)$	$\rightarrow$	$2Al_2O_3(s)$	$\Delta H = -3352$ kJ
$3MnO_2(s)$	$\rightarrow$	$3Mn(s) + 3O_2(g)$	$\Delta H = 1560$ kJ
$4Al(s) + 3MnO_2(s)$	$\rightarrow$	$2Al_2O_3(s) + 3Mn(s)$	$\Delta H = -1792$ kJ

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6.9. The vaporization process, with the $\Delta H°_f$ values given below the substances, is

$$\begin{array}{ccc} H_2O(l) & \rightarrow & H_2O(g) \\ -285.8 & & -241.8 \quad \text{(kJ)} \end{array}$$

The calculation is

$$\Delta H^\circ_{vap} = \Sigma n\,\Delta H^\circ_f\,(\text{products}) - \Sigma m\,\Delta H^\circ_f\,(\text{reactants}) = \Delta H^\circ_f\,[H_2O(g)] - \Delta H^\circ_f\,[H_2O(l)]$$

$$= (-241.8\text{ kJ}) - (-285.8\text{ kJ}) = 44.0\text{ kJ}$$

6.10. The reaction, with the $\Delta H°_f$ values given below the substances, is

$$\begin{array}{ccccccc} 3NO_2(g) & + & H_2O(l) & \rightarrow & 2HNO_3(aq) & + & NO(g) \\ 33.10 & & -285.8 & & -207.4 & & 90.29 \quad \text{(kJ)} \end{array}$$

The calculation is

$$\Delta H^\circ_{rxn} = \Sigma n\,\Delta H^\circ_f\,(\text{products}) - \Sigma m\,\Delta H^\circ_f\,(\text{reactants})$$

$$= [2\,\Delta H^\circ_f\,(HNO_3) + \Delta H^\circ_f\,(NO)] - [3\,\Delta H^\circ_f\,(NO_2) + \Delta H^\circ_f\,(H_2O)]$$

$$= [2(-207.4) + (90.29)]\text{ kJ} - [3(33.10) + (-285.8)]\text{ kJ} = -138.\underline{0}1 = -138.0\text{ kJ}$$

6.11. The net chemical reaction, with the $\Delta H°_f$ values given below the substances, is

$$\begin{array}{ccccccc} 2\,NH_4^+(aq) & + & 2OH^-(aq) & \rightarrow & 2NH_3(g) & + & 2H_2O(l) \\ 2(-132.5) & & 2(-230.0) & & 2(-45.90) & & 2(-285.8) \quad \text{(kJ)} \end{array}$$

The calculation is

$$\Delta H^\circ_{rxn} = [2\,\Delta H^\circ_f\,(NH_3) + 2\,\Delta H^\circ_f\,(H_2O)] - [2\,\Delta H^\circ_f\,(NH_4^+) + 2\,\Delta H^\circ_f\,(OH^-)]$$

$$= [2(-45.90) + 2(-285.8)] - [2(-132.5) + 2(-230.0)] = 61.\underline{6}0 = 61.6\text{ kJ}$$

■ ANSWERS TO CONCEPT CHECKS

6.1. The photovoltaic cells collect the sun's energy, converting it to electrical energy. This electrical energy is stored in the battery as chemical energy, which is later changed back to electrical energy that runs a motor. As the motor rotates, it changes the electrical energy to kinetic energy (energy of motion) of the motor, then of water, which in turn is changed to potential energy (energy of position) of water as the water moves upward in the gravitational field of earth.

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6.2.

a. This reaction is the one shown in the problem, and it has a positive ΔH, so the reaction is endothermic.

b. This reaction is simply twice reaction a, so it is also endothermic.

c. This reaction is the reverse of reaction a, so it is exothermic.

d. This reaction is simply twice reaction c, so it is more exothermic than reaction c.

Thus, reaction d is the most exothermic reaction.

6.3. You can think of the sublimation of ice as taking place in two stages. First, the solid melts to liquid; then the liquid vaporizes. The first process has an enthalpy ΔH_{fus}. The second process has an enthalpy ΔH_{vap}. Therefore, the total enthalpy, which is the enthalpy of sublimation, is the sum of these two enthalpies:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

6.1. Energy is the potential or capacity to move matter. Kinetic energy is the energy associated with an object by virtue of its motion. Potential energy is the energy an object has by virtue of its position in a field of force. Internal energy is the sum of the kinetic and potential energies of the particles making up a substance.

6.2. In terms of SI base units, a joule is $kg \cdot m^2/s^2$.

6.3. Originally, a calorie was defined as the amount of energy required to raise the temperature of one gram of water by one degree Celsius. At present, the calorie is defined as 4.184 J.

6.4. At either of the two highest points above the earth in a pendulum's cycle, the energy of the pendulum is all potential energy and is equal to the product mgh (m = mass of pendulum, g = constant acceleration of gravity, and h = height of pendulum). As the pendulum moves downward, its potential energy decreases from mgh to near zero, depending on how close it comes to the earth's surface. During the downward motion, its potential energy is converted to kinetic energy. When it reaches the lowest point (middle) of its cycle, the pendulum has its maximum kinetic energy and minimum potential energy. As it rises above the lowest point, its kinetic energy begins to be converted to potential energy. When it reaches the other high point in its cycle, the energy of the pendulum is again all potential energy. By the law of conservation of energy, this energy cannot be lost, only converted to other forms. At rest, the energy of the pendulum has been transferred to the surroundings in the form of heat.

6.5. As the heat flows into the gas, the gas molecules gain energy and move at a greater average speed. The internal energy of the gas increases.

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6.6. An exothermic reaction is a chemical reaction or a physical change in which heat is evolved (q is negative). For example, burning one mole of methane, $CH_4(g)$, yields carbon dioxide, water, and 890 kJ of heat. An endothermic reaction is a chemical reaction or physical change in which heat is absorbed (q is positive). For example, the reaction of one mole of barium hydroxide with ammonium nitrate absorbs 170.8 kJ of heat in order to form ammonia, water, and barium nitrate.

6.7. Changes in internal energy depend only on the initial and final states of the system, which are determined by variables such as temperature and pressure. Such changes do not depend on any previous history of the system.

6.8. The enthalpy change equals the heat of reaction at constant pressure.

6.9. At constant pressure, the enthalpy change is positive (the enthalpy increases) for an endothermic reaction.

6.10. It is important to give the states when writing an equation for ΔH because ΔH depends on the states of all reactants and products. If any state changes, ΔH changes.

6.11. When the equation for the reaction is doubled, the enthalpy is also doubled. When the equation is reversed, the sign of ΔH is also reversed.

6.12. First, convert the 10.0 g of water to moles of water, using its molar mass (18.02 g/mol). Next, using the equation, multiply the moles of water by the appropriate mole ratio (1 mol CH_4 / 2 mol H_2O). Finally, multiply the moles of CH_4 by the heat of the reaction (−890.3 kJ/mol CH_4).

6.13. The heat capacity (C) of a substance is the quantity of heat needed to raise the temperature of the sample of substance one degree Celsius (or one kelvin). The specific heat of a substance is the quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (or one kelvin) at constant pressure.

6.14. A simple calorimeter consists of an insulated container (for example, a pair of styrene coffee cups as in Figure 6.12) with a thermometer. The heat of the reaction is obtained by conducting the reaction in the calorimeter. The temperature of the mixture is measured before and after the reaction, and since this is a constant-pressure process, the heat is directly related to the enthalpy change, ΔH.

6.15. Hess's law states that for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is the sum of the enthalpy changes for the individual steps. In other words, no matter how you go from reactants to products, the enthalpy change for the overall chemical change is the same. This is because enthalpy is a state function.

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6.16. No, you can still obtain the enthalpy for the desired reaction. You will need to come up with a system of reactions that can be combined to give the desired reaction and will need to know the enthalpy changes for each of the steps. Then, using Hess's law, you can obtain the enthalpy change for the reaction under study.

6.17. The thermodynamic standard state consists of the standard thermodynamic conditions chosen for substances when listing or comparing thermodynamic data: one atm pressure and the specified temperature (usually 25°C).

6.18. The reference form of an element is the most stable form (physical state and allotrope) of the element under standard thermodynamic conditions. The standard enthalpy of formation of an element in its reference form is zero.

6.19. The standard enthalpy of formation of a substance, $\Delta H°_f$, is the enthalpy change for the formation of one mole of the substance in its standard state from its elements in their reference form and in their standard states.

6.20. The equation for the formation of $H_2S(g)$ is

$$H_2(g) + 1/8S_8(\text{rhombic}) \rightarrow H_2S(g)$$

6.21. The reaction of $C(g) + 4H(g) \rightarrow CH_4(g)$ is not an appropriate equation for calculating the $\Delta H°_f$ of methane because the most stable form of each element is not used. Both $H_2(g)$ and C(graphite) should be used instead of $H(g)$ and $C(g)$, respectively.

6.22. A fuel is any substance that is burned or similarly reacted to provide heat and other forms of energy. The fossil fuels are petroleum (oil), gas, and coal. They were formed millions of years ago when aquatic plants and animals were buried and compressed by layers of sediment at the bottoms of swamps and seas. Over time, this organic matter was converted by bacterial decay and pressure to fossil fuels.

6.23. One of the ways of converting coal to methane involves the water-gas reaction.

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

In this reaction, steam is passed over hot coal. This mixture is then reacted over a catalyst to give methane.

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$

6.24. Some possible rocket fuel/oxidizer combinations are H_2/O_2 and hydrazine/dinitrogen tetroxide. The chemical equations for their reactions are

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g); \quad \Delta H° = -242 \text{ kJ}$$

$$2N_2H_4(l) + N_2O_4(l) \rightarrow 3N_2(g) + 4H_2O(g); \quad \Delta H° = -1049 \text{ kJ}$$

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6.25. The answer is d, burning enough butane to produce one mole of water.

6.26. The answer is b, 40.°C.

6.27. The answer is c, endothermic, and the temperature of the resulting solution falls.

6.28. The answer is c, the water with the mercury will be the hottest.

■ ANSWERS TO CONCEPT EXPLORATIONS

6.29. Part 1

a. The temperature change for the hot water is $\Delta t = 60°C - 80°C = -20°C$. The temperature change for the cold water is $\Delta t = 60°C - 20°C = 40°C$. The magnitude of the temperature change for the cold water is twice the magnitude of the temperature change for the hot water.

b. The heat transferred from the hot water to the cold water.

c. $q = s \times m \times \Delta t = (4.18\ J/g{\bullet}°C)(100.\ g)(40°C) = 1.672 \times 10^4 = 1.67 \times 10^4\ J = 16.7\ kJ$

d. The quantity of heat transferred from the hot-water sample is equal to the quantity of heat transferred to the cold-water sample.

e. Since both samples are water, the specific heat capacities of both samples are the same. Also, the quantity of heat is the same for both. Thus $m_{hot}\Delta t_{hot} = m_{cold}\Delta t_{cold}$. Since the cold water has one-half the mass of the hot water, it will have twice the temperature change.

f. Since the hot water has one-half the mass of the cold water, it will have twice the temperature change of the cold water.

g. Since the first sample (cold water) increases by one-third the temperature change of the second sample (hot water), the first sample (cold water) has three times the mass of the second sample (hot water).

h. $$\frac{\Delta t_{cold}}{\Delta t_{hot}} = \frac{m_{hot}}{m_{cold}} = \frac{7\ g}{3\ g} = 2.33$$

Therefore, the cold water will have a temperature change 2.3 times the temperature change for the hot water.

Part 2

The amount of heat added cannot be calculated. In order to perform this calculation, it is necessary to know the mass of the water.

Part 3

Since $q = s \times m \times \Delta t$, for two samples of water with an identical temperature change, the heat required is directly proportional to the mass of the solution. If the second solution requires double the heat of the first solution, then it has double the mass of the first solution.

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6.30.

a. $q = (4.18\ \text{J/g•°C}) \times (100.\ \text{g}) \times (41°\text{C} - 21°\text{C}) = 8360\ \text{J} = 8.4 \times 10^3\ \text{J} = 8.4\ \text{kJ}$

b. $q_{rxn} = -q_{water} = -(4.18\ \text{J/g•°C}) \times (100.\ \text{g}) \times (31°\text{C} - 21°\text{C}) = -4180\ \text{J}$

$= -4.2 \times 10^3\ \text{J} = -4.2\ \text{kJ}$

This is one-half of the value of q in part a.

c. In parts a and b, you see that for each 10°C temperature change, 4.2 kJ of heat is required. Thus, for a temperature change of 30°C (from 21°C to 51°C), three times as much heat is required. This is 4.2 kJ x 3, or 12.6 kJ.

d. You should need three times as much as for part b, or 0.06 mol of X and 0.03 mol of Y.

e. There is 4.2 kJ for each 0.01 mol of Y. This gives 420 kJ for one mole of Y, which is the enthalpy of the reaction.

■ ANSWERS TO CONCEPTUAL PROBLEMS

6.31. Kinetic energy is proportional to mass and to speed squared. Compare the kinetic energy of the smaller car with that of the larger car (twice the mass), assuming both are traveling at the same speed. The larger car would have twice the kinetic energy of the smaller car. Or we could say that the smaller car has only half the kinetic energy of the larger car. Now suppose the speed of the smaller is increased by a factor of 2 (so it is now moving at twice its original speed). Its kinetic energy is increased by a factor of 4. Therefore, the smaller car now has one-half times four times, or twice, the kinetic energy of the larger car. The smaller car has the greater kinetic energy.

6.32. The equation says that 1 mol of butane reacts with 13/2 mol of oxygen to yield 4 mol of carbon dioxide and 5 mol of water. The reaction yields a certain amount of heat, which you can symbolize as q. So choice a yields heat q. On the other hand, choice b is only 1 mol of oxygen, not 13/2 mol. So, choice b yields heat equal to 2/13 q. This result might be easier to see by first looking at choice c. Note that the 1 mol of carbon dioxide stated in choice c is only one-fourth that given in the equation. This means that choice c yields one-fourth q (just the inverse of the coefficient of the equation). Similarly, choice d yields one-fifth q. Therefore, choice b yields the least heat.

6.33.

a. After the water is placed into the freezer, it will lose heat to the freezer, so q_{sys} is negative.

b. The water will have turned to ice.

c. The initial enthalpy (of the water) is higher than the final enthalpy (of the ice).

d. After several hours, the temperature of the water will be −20°C.

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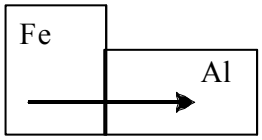
6.34.

a. Heat will flow from the iron block to the aluminum block.



b. The aluminum block will be absorbing heat, so q_{sys} will be positive.

c. The temperatures of the aluminum block and the iron block will both be the same.

d. The heat gained by the aluminum will equal the heat lost by the iron. Each heat term will be equal to s x m x Δt. This gives

$$(0.901 \text{ J/g}\bullet^\circ\text{C})(20.0 \text{ g})(t_f - 45.0^\circ\text{C}) = (0.449 \text{ J/g}\bullet^\circ\text{C})(20.0 \text{ g})(50.0^\circ\text{C} - t_f)$$

You can cancel the mass and the units from both sides to give a simplified expression.

$$(0.901)(t_f - 45.0^\circ\text{C}) = (0.449)(50.0^\circ\text{C} - t_f)$$

This can be simplified to give $1.350\ t_f = 62.995$, or $t_f = 46.\underline{6}6 = 46.7^\circ\text{C}$.

6.35. You can imagine this process taking place in two steps: first, the preparation of water vapor from the elements, and second, the change of the vapor to liquid. Here are the equations:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g);\ \Delta H_f$$

$$H_2O(g) \rightarrow H_2O(l);\ -\Delta H_{vap}$$

The last equation is the reverse of the vaporization of water, so the enthalpy of the step is the negative of the enthalpy of vaporization. The enthalpy change for the preparation of one mole of liquid water, ΔH, is the sum of the enthalpy changes for these two steps:

$$\Delta H = \Delta H_f + (-\Delta H_{vap}) = \Delta H_f - \Delta H_{vap}$$

6.36. The expression for the heat is $q = s$ x m x Δt. For the same amount of heat and mass, the product s x Δt must be constant. The metal with the smaller specific heat will have the larger Δt. Since the specific heat for aluminum (0.901 J/g•°C) is larger than that for iron (0.449 J/g•°C), the block of iron will have the larger Δt and be warmer.

6.37.

a. The heat lost by the metal is equal to the heat gained by the water. Since $q = s$ x m x Δt, the heat gained by the water is directly proportional to Δt. Since Δt is larger for water with metal A, metal A lost more heat. Now, each metal has the same mass and Δt, so the specific heat is directly proportional to q. Since q is larger for A, the specific heat is larger for A.

b. The metal with the higher specific heat will have absorbed more heat to reach the starting temperature of 95°C; therefore, it will release more heat to the water, causing the water to reach a higher temperature. The beaker with metal A will rise to the higher temperature.

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6.38. Silver metal reacts with a halogen to produce the corresponding silver halide. For example, silver reacts with fluorine to produce silver fluoride. Each reaction corresponds to the reaction forming the silver halide, so you look in the table of enthalpies of formation of compounds (Table 6.2). The most exothermic reaction would be the one with the most negative enthalpy of formation. That would be the reaction for the formation of silver fluoride.

6.39. Let us write ΔH_{rxn} for the enthalpy change when one mole of P_4S_3 burns in O_2 to give P_4O_{10} and SO_2. In principle, you could calculate ΔH_{rxn} from enthalpies of formation for the reactants and products of this reaction. You would require the values for P_4S_3, O_2 (which equals zero), P_4O_{10}, and SO_2. Enthalpies of formation for the products, P_4O_{10} and SO_2, are given in Table 6.2 in the text. This means that if you have measured ΔH_{rxn}, you can use the enthalpies of formation of P_4O_{10} and SO_2 to calculate the enthalpy of formation for P_4S_3. What you have done is this: you have used enthalpies of combustion to calculate enthalpies of formation. This is the idea most often used to obtain enthalpies of formation.

6.40.

a. Since ΔH is positive, the reaction is endothermic, and the solution will be colder.

b. While the salt dissolves, heat will flow into the beaker to raise the temperature of the water back to the initial temperature.

c. After the water returns to room temperature, q for the system will be zero.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

6.41. The heat released, in kilocalories, is

$$-445.1 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ cal}}{4.184 \text{ J}} \times \frac{1 \text{ kcal}}{1000 \text{ cal}} = -106.\underline{3}8 = -106.4 \text{ kcal}$$

6.42. The heat released, in kilocalories, is

$$-309.1 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ cal}}{4.184 \text{ J}} \times \frac{1 \text{ kcal}}{1000 \text{ cal}} = -73.8\underline{7}6 = -73.88 \text{ kcal}$$

6.43. The kinetic energy, in joules, is

$$E_k = 1/2 \times 4.85 \times 10^3 \text{ lb} \times \frac{0.4536 \text{ kg}}{1 \text{ lb}} \times \left[\frac{57 \text{ mi}}{1 \text{ h}}\right]^2 \times \left[\frac{1609 \text{ m}}{1 \text{ mi}}\right]^2 \times \left[\frac{1 \text{ h}}{3600 \text{ s}}\right]^2$$

$$= 7.\underline{1}3 \times 10^5 = 7.1 \times 10^5 \text{ J}$$

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The kinetic energy, in calories, is

$$E_k = 7.\underline{1}3 \times 10^5 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 1.\underline{7}0 \times 10^5 = 1.7 \times 10^5 \text{ cal}$$

6.44. The kinetic energy, in joules, is

$$E_k = 1/2 \times 245 \text{ gr} \times \frac{0.0000648 \text{ kg}}{1 \text{ gr}} \times \left[\frac{2520 \text{ ft}}{1 \text{ s}}\right]^2 \times \left[\frac{1 \text{ yd}}{3 \text{ ft}}\right]^2 \times \left[\frac{0.9144 \text{ m}}{1 \text{ yd}}\right]^2$$

$$= 46\underline{8}3 = 4.68 \times 10^3 \text{ J}$$

The kinetic energy, in calories, is

$$E_k = 4683 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 11\underline{1}9 = 1.12 \times 10^3 \text{ cal}$$

6.45. To insert the mass of one molecule of ClO_2 in the formula, multiply the molar mass by the reciprocal of Avogadro's number. The kinetic energy in joules is

$$E_k = 1/2 \times \frac{67.45 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molec.}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left[\frac{306 \text{ m}}{1 \text{ s}}\right]^2$$

$$= 5.2\underline{4}3 \times 10^{-21} = 5.24 \times 10^{-21} \text{ J/molec.}$$

6.46. To insert the mass of one molecule of N_2O in the formula, multiply the molar mass by the reciprocal of Avogadro's number. The kinetic energy in joules is

$$E_k = 1/2 \times \frac{44.02 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molec.}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left[\frac{379 \text{ m}}{1 \text{ s}}\right]^2$$

$$= 5.2\underline{4}9 \times 10^{-21} = 5.25 \times 10^{-21} \text{ J/molec.}$$

6.47. Endothermic reactions absorb heat, so the sign of q will be positive because energy must be gained by the system from the surroundings. The flask will feel cold to the touch.

6.48. Exothermic reactions evolve heat, so the sign of q will be negative because energy is lost from the system to the surroundings. The flask will feel hot to the touch.

6.49. The gain of 66.2 kJ of heat per 2 mol NO_2 means the reaction is endothermic. Because energy is gained by the system from the surroundings, q is positive and is +66.2 kJ for 2 mol NO_2 reacting.

6.50. The release of 939 kJ of heat per 2 mol HCN means the reaction is exothermic. Because energy is lost from the system to the surroundings, q is negative, and because the reaction involves 2 mol HCN, q for the reaction is −939 kJ.

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6.51. The reaction of Fe(*s*) with HCl must yield H_2 and $FeCl_2$. To balance the hydrogen, 2HCl must be written as a reactant:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

To write a thermochemical equation, the sign of ΔH must be negative because heat is evolved:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g); \quad \Delta H = -89.1 \text{ kJ}$$

6.52. The decomposition of 2 mol $KClO_3$ to KCl and O_2 must yield 2 mol KCl to balance the potassium and chlorine. To balance the oxygen, 3 mol O_2 must be written as a product:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

To write a thermochemical equation, the sign of ΔH must be negative because heat is evolved:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g); \quad \Delta H = -78.0 \text{ kJ}$$

6.53. The first equation is

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s); \quad \Delta H = -3010 \text{ kJ}$$

The second equation is

$$P_4O_{10}(s) \rightarrow P_4(s) + 5O_2(g); \quad \Delta H = ?$$

The second equation has been obtained by reversing the first equation. Therefore, to obtain ΔH for the second equation, ΔH for the first equation must be reversed in sign: $-(-3010) = +3010$ kJ.

6.54. The first equation is

$$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g); \quad \Delta H = -1077 \text{ kJ}$$

The second equation is

$$1/2CS_2(l) + 3/2O_2(g) \rightarrow 1/2CO_2(g) + SO_2(g); \quad \Delta H = ?$$

The second equation has been obtained by dividing each coefficient in the first equation by 2. Therefore, to obtain ΔH for the second equation, ΔH for the first equation must be divided by 2; that is, $(-1077) \div 2 = -538.5$ kJ.

6.55. The first equation is

$$1/4P_4O_{10}(s) + 3/2H_2O(l) \rightarrow H_3PO_4(aq); \quad \Delta H = -96.2 \text{ kJ}$$

The second equation is

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq); \quad \Delta H = ?$$

The second equation has been obtained from the first by multiplying each coefficient by 4. Therefore, to obtain the ΔH for the second equation, the ΔH for the first equation must be multiplied by 4; that is, $-96.2 \times 4 = -384.8 = 385$ kJ

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6.56. The first equation is

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g); \quad \Delta H = -906 \text{ kJ}$$

The second equation is

$$NO(g) + 3/2H_2O(g) \rightarrow NH_3(g) + 5/4O_2(g); \quad \Delta H = ?$$

The second equation has been obtained by reversing the first equation and dividing each coefficient by 4. Therefore, to obtain ΔH for the second equation, the ΔH for the first equation must be reversed in sign and divided by 4; that is, $+906 \div 4 = 226.50 = 227$ kJ.

6.57. Because nitric oxide is written as NO in the equation, the molar mass of NO equals 30.01 g per mol NO. From the equation, 2 mol NO evolve 114 kJ heat. Divide the 114 kJ by the 2 mol NO and by the 30.01 g/mol NO to obtain the amount of heat evolved per gram of NO:

$$\frac{-114 \text{ kJ}}{2 \text{ mol NO}} \times \frac{1 \text{ mol NO}}{30.01 \text{ g NO}} = 1.899 = \frac{-1.90 \text{ kJ}}{\text{g NO}}$$

6.58. Because hydrogen is written as H_2 in the equation, the molar mass of H_2 equals 2.016 g per mol H_2. From the equation, 2 mol H_2 evolve 484 kJ heat. Divide this by the 2 mol H_2 and by the 2.016 g/mol H_2 to obtain the amount of heat evolved per gram of hydrogen:

$$\frac{-484 \text{ kJ}}{2 \text{ mol } H_2} \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} = -120.03 = \frac{-120 \text{ kJ}}{\text{g } H_2}$$

6.59. The molar mass of ammonia is 17.03 g/mol. From the equation, 4 mol NH_3 evolve 1267 kJ of heat. Divide 35.8 g NH_3 by its molar mass and the 4 mol NH_3 in the equation to obtain the amount of heat evolved:

$$35.8 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} \times \frac{-1267 \text{ kJ}}{4 \text{ mol } NH_3} = -6.658 \times 10^2 = -6.66 \times 10^2 \text{ kJ}$$

6.60. The molar mass of H_2S is 34.08 g/mol. From the equation, 2 mol H_2S evolve 1036 kJ of heat. This gives

$$28.5 \text{ g } H_2S \times \frac{1 \text{ mol } H_2S}{34.08 \text{ g } H_2S} \times \frac{-1036 \text{ kJ}}{2 \text{ mol } H_2S} = -433.18 = -433 \text{ kJ}$$

6.61. The molar mass of C_3H_8 is 44.06 g/mol. From the equation, 1 mol C_3H_8 evolves 2043 kJ heat. This gives

$$-369 \text{ kJ} \times \frac{1 \text{ mol } C_3H_8}{-2043 \text{ kJ}} \times \frac{44.06 \text{ g } C_3H_8}{1 \text{ mol } C_3H_8} = 7.957 = 7.96 \text{ g } C_3H_8$$

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6.62. The molar mass of C_2H_5OH is 46.05 g/mol. From the equation, 1 mol C_2H_5OH evolves 1235 kJ heat. This gives

$$-358 \text{ kJ} \times \frac{1 \text{ mol } C_2H_5OH}{-1235 \text{ kJ}} \times \frac{46.05 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH} = 13.\underline{3}48 = 13.3 \text{ g } C_2H_5OH$$

6.63. Multiply the 180 g (0.180 kg) of water by the specific heat of 4.18 J/(g•°C) and by Δt to obtain heat in joules:

$$180 \text{ g} \times (96°C - 19°C) \times \frac{4.18 \text{ J}}{1 \text{ g} \bullet °C} = 5\underline{7}934 = 5.8 \times 10^4 \text{ J}$$

6.64. Multiply the 1.28×10^3 g (1.28 kg) iron by the specific heat of 0.449 J/(g•°C) and by Δt to obtain heat in joules:

$$1.28 \times 10^3 \text{ g} \times (178°C - 21°C) \times \frac{0.449 \text{ J}}{1 \text{ g} \bullet °C} = 90\underline{2}31 = 9.02 \times 10^4 \text{ J}$$

6.65. Use the 2.26×10^3 J/g (2.26 kJ/g) heat of vaporization to calculate the heat of condensation. Then use it to calculate Δt, the temperature change.

$$\text{Heat of condensation} = \frac{2.26 \times 10^3 \text{ J}}{1 \text{ g}} \times 168 \text{ g} = 3.7\underline{9}68 \times 10^5 \text{ J}$$

$$\text{Temperature change} = \Delta t = \frac{3.7\underline{9}68 \times 10^5 \text{ J}}{6.44 \times 10^4 \text{ g}} \times \frac{1 \text{ g} \bullet °C}{1.015 \text{ J}} = 5.8\underline{0}85 = 5.81°C$$

6.66. Use the 334 J/g (0.334 kJ/g) heat of fusion to calculate the heat of melting. Then use the heat of melting to calculate Δt, the temperature change.

$$\text{Heat of melting} = \times 31.5 \text{ g} \times \frac{334 \text{ J}}{1 \text{ g}} = 10\underline{5}21 \text{ J}$$

Heat melting + heat warming = heat lost by 210 g H_2O

Let t = the final temperature, and substitute into the above equation:

$$10521 \text{ J} + \left[\frac{4.18 \text{ J}}{1 \text{ g} \bullet °C}\right] \times 31.5 \text{ g} \times (t - 0°C) = \left[\frac{4.18 \text{ J}}{1 \text{ g} \bullet °C}\right] \times 210 \text{ g} \times (21.0°C - t)$$

Solve the above equation for t.

$$10521 \text{ J} + 131.67t = 18433.8 \text{ J} - 877.8t$$

$$t = \frac{18433.8 \text{ J} - 10521 \text{ J}}{(131.67 + 877.8) \text{ J/°C}} = 7.8\underline{3}8 = 7.84°C$$

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6.67. The enthalpy change for the reaction is equal in magnitude and opposite in sign to the heat-energy change occurring from the cooling of the solution and calorimeter.

$$q_{calorimeter} = (1071 \text{ J/°C})(21.56°\text{C} - 25.00°\text{C}) = -3684.2 \text{ J}$$

Thus, 15.3 g $NaNO_3$ is equivalent to −3684.2 J heat energy. The amount of heat absorbed by 1.000 mol $NaNO_3$ is calculated from +3684.2 J (opposite sign):

$$1.000 \text{ mol } NaNO_3 \times \frac{85.00 \text{ g } NaNO_3}{1 \text{ mol } NaNO_3} \times \frac{3684.2 \text{ J}}{15.3 \text{ g } NaNO_3} = 2.0468 \times 10^4 \text{ J}$$

Thus, the enthalpy change, ΔH, for the reaction is 2.05×10^4 J, or 20.5 kJ, per mol $NaNO_3$.

6.68. The enthalpy change for the reaction is equal in magnitude and opposite in sign to the heat energy produced from the warming of the solution and the calorimeter.

$$q_{calorimeter} = (1258 \text{ J/°C})(38.7°\text{C} - 25.0°\text{C}) = +1.7234 \times 10^4 \text{ J}$$

Thus, 23.6 g $CaCl_2$ is equivalent to 1.7234×10^4 J heat energy. The amount of heat released by 1.20 mol $CaCl_2$ is calculated from -1.7234×10^4 J (opposite sign):

$$1.20 \text{ mol } CaCl_2 \times \frac{110.98 \text{ g } CaCl_2}{1 \text{ mol } CaCl_2} \times \frac{-1.7234 \times 10^4 \text{ J}}{23.6 \text{ g } CaCl_2} = -9.7255 \times 10^4 \text{ J}$$

Thus, the enthalpy change, ΔH, for the reaction is -9.73×10^4 J, or −97.3 kJ, per mol $CaCl_2$.

6.69. The energy change for the reaction is equal in magnitude and opposite in sign to the heat energy produced from the warming of the solution and the calorimeter.

$$q_{calorimeter} = (9.63 \text{ kJ/°C})(33.73 - 25.00°\text{C}) = +84.069 \text{ kJ}$$

Thus, 2.84 g C_2H_5OH is equivalent to 84.069 kJ heat energy. The amount of heat released by 1.000 mol C_2H_5OH is calculated from −84.069 kJ (opposite sign):

$$1.00 \text{ mol } C_2H_5OH \times \frac{46.07 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH} \times \frac{-84.069 \text{ kJ}}{2.84 \text{ g } C_2H_5OH} = -1363.75 \text{ kJ}$$

Thus, the enthalpy change, ΔH, for the reaction is -1.36×10^3 kJ/mol ethanol.

6.70. The energy change for the reaction is equal in magnitude and opposite in sign to the heat energy produced from the warming of the solution and the calorimeter.

$$q_{calorimeter} = (12.05 \text{ kJ/°C})(37.18°\text{C} - 25.00°\text{C}) = +146.769 \text{ kJ}$$

Thus, 3.51 g C_6H_6 is equivalent to 146.769 kJ heat energy. The amount of heat released by 1.25 mol C_6H_6 is calculated from −146.769 kJ (opposite sign):

$$1.25 \text{ mol } C_6H_6 \times \frac{78.11 \text{ g } C_6H_6}{1 \text{ mol } C_6H_6} \times \frac{-146.769 \text{ kJ}}{3.51 \text{ g } C_6H_6} = -4082.6$$

Thus, the enthalpy change, ΔH, for the reaction is -4.08×10^3 kJ/mol benzene.

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6.71. Using the equations in the data, reverse the direction of the first reaction, and reverse the sign of its ΔH. Then multiply the second equation by 2, multiply its ΔH by 2, and add. Setup:

$N_2(g) + 2H_2O(l) \rightarrow N_2H_4(l) + O_2(g)$; $\Delta H = (-622.2 \text{ kJ}) \times (-1)$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; $\Delta H = (-285.8 \text{ kJ}) \times (2)$

$N_2(g) + 2H_2(g) \rightarrow N_2H_4(l)$; $\Delta H = 50.6 \text{ kJ}$

6.72. Using the equations in the data, reverse the direction of the first reaction, and reverse the sign of its ΔH. Then divide the reversed first equation by 2, divide its ΔH by 2, and add to the second equation. Setup:

$H_2O(l) + /2O_2(g) \rightarrow H_2O_2(l)$; $\Delta H = (-196.0 \text{ kJ}) \times (-1/2)$

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$; $\Delta H = (-285.8 \text{ kJ})$

$H_2(g) + O_2(g) \rightarrow H_2O_2(l)$; $\Delta H = -187.8 \text{ kJ}$

6.73. Using the equations in the data, multiply the second equation by 2, and reverse its direction; do the same to its ΔH. Then multiply the first equation by 2 and its ΔH by 2. Finally, multiply the third equation by 3 and its ΔH by 3. Then add. Setup:

$4NH_3(g) \rightarrow 2N_2(g) + 6H_2(g)$; $\Delta H = (-91.8 \text{ kJ}) \times (-2)$

$2N_2(g) + 2O_2(g) \rightarrow 4NO(g)$; $\Delta H = (180.6 \text{ kJ}) \times (2)$

$6H_2(g) + 3O_2(g) \rightarrow 6H_2O(g)$; $\Delta H = (-483.7 \text{ kJ}) \times (3)$

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$; $\Delta H = -906.3 \text{ kJ}$

6.74. Using the equations in the data, reverse the direction of the second equation and reverse the sign of its ΔH. Then, reverse the direction of the first equation and multiply by 1/2; do the same to its ΔH. Finally, multiply the third equation and its ΔH by 1/2. Add all three equations. Setup:

$CH_4(g) \rightarrow C(\text{graph}) + 2H_2(g)$; $\Delta H = (-74.9 \text{ kJ}) \times (-1)$

$NH_3(g) \rightarrow 1/2N_2(g) + 3/2H_2(g)$; $\Delta H = (-91.8 \text{ kJ}) \times (-1/2)$

$1/2H_2(g) + C(\text{graph}) + 1/2N_2(g) \rightarrow HCN(g)$; $\Delta H = (270.3 \text{ kJ}) \times (1/2)$

$CH_4(g) + NH_3(g) \rightarrow HCN(g) + 3H_2(g)$; $\Delta H = 255.\underline{9}5 = 256.0 \text{ kJ}$

6.75. After reversing the second equation in the data, add all the equations. Setup:

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta H = (-1411 \text{ kJ})$

$2CO_2(g) + 3H_2O(l) \rightarrow C_2H_6(g) + 7/2O_2(g)$; $\Delta H = (-1560) \times (-1)$

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$; $\Delta H = (-286 \text{ kJ})$

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$; $\Delta H = -137 \text{ kJ}$

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6.76. After reversing the first equation, double the second and third equations, and then add. Setup:

$2CO_2(g) + 2H_2O(l)$	$\rightarrow CH_3COOH(l) + 2O_2(g);$	$\Delta H = (-874 \text{ kJ}) \times (-1)$
$2C(\text{graph}) + 2O_2(g)$	$\rightarrow 2CO_2(g);$	$\Delta H = (-394 \text{ kJ}) \times (2)$
$2H_2(g) + O_2(g)$	$\rightarrow 2H_2O(l);$	$\Delta H = (-286 \text{ kJ}) \times (2)$
$2C(\text{graph}) + 2H_2(g) + O_2(g)$	$\rightarrow CH_3COOH(l);$	$\Delta H = -486 \text{ kJ}$

6.77. Write the $\Delta H°$ values (Appendix C) underneath each compound in the balanced equation:

$$\underset{-277.7}{C_2H_5OH(l)} \rightarrow \underset{-235.4}{C_2H_5OH(g)} \quad \text{(kJ)}$$

$$\Delta H°_{vap} = [\Delta H°_f(C_2H_5OH(g))] - [\Delta H°_f(C_2H_5OH(l))] = [-235.4] - [-277.7] = +42.3 \text{ kJ}$$

6.78. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation:

$$\underset{-135.4}{CCl_4(l)} \rightarrow \underset{-95.98}{CCl_4(g)} \quad \text{(kJ)}$$

$$\Delta H°_{vap} = [\Delta H°_f(CCl_4(g))] - [\Delta H°_f(CCl_4(l))] = [-95.98] - [-135.4] \text{ kJ} = +39.4 \text{ kJ}$$

6.79. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation:

$$\underset{2(-20.50)}{2H_2S(g)} + \underset{3(0)}{3O_2(g)} \rightarrow \underset{2(-285.8)}{2H_2O(l)} + \underset{2(-296.8)}{2SO_2(g)} \quad \text{(kJ)}$$

$$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$$
$$= [2(-285.8) + 2(-296.8)] - [2(-20.50) + 3(0)] \text{ kJ} = -1124.\underline{2}0 = -1124.2 \text{ kJ}$$

6.80. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation:

$$\underset{89.70}{CS_2(l)} + \underset{3(0)}{3O_2(g)} \rightarrow \underset{-393.5}{CO_2(g)} + \underset{2(-296.8)}{2SO_2(g)} \quad \text{(kJ)}$$

$$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$$
$$= [(-393.5) + 2(-296.8)] - [(89.70) + 3(0)] = -1076.8 \text{ kJ}$$

6.81. Write the $\Delta H°$ values (Appendix C) underneath each compound in the balanced equation:

$$\underset{-825.5}{Fe_2O_3(s)} + \underset{3(-110.5)}{3CO(g)} \rightarrow \underset{2(0)}{2Fe(s)} + \underset{3(-393.5)}{3CO_2(g)} \quad \text{(kJ)}$$

$$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$$
$$= [2(0) + 3(-393.5)] - [(-825.5) + 3(-110.5)] = -23.5 \text{ kJ}$$

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6.82. Write the $\Delta H°$ values (Appendix C) underneath each compound in the balanced equation:

$$\begin{array}{llcll} 2PbS(s) & 3O_2(g) & \rightarrow & 2SO_2(g) & 2PbO(s) \\ 2(-98.32) & 3(0) & & 2(-296.8) & 2(-219.4) \quad \text{(kJ)} \end{array}$$

$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$

$= [2(-296.8) + 2(-219.4)] - [2(-98.32) + 3(0)] = -835.\underline{7}6 = -835.8 \text{ kJ}$

6.83. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation:

$$\begin{array}{lcll} HCl(g) & \rightarrow & H^+(aq) & Cl^-(aq) \\ -92.31 & & 0 & -167.2 \text{ (kJ)} \end{array}$$

$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$

$= [(0) + (-167.2)] - [-92.31] = -74.\underline{8}9 = -74.9 \text{ kJ}$

6.84. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation:

$$\begin{array}{lcllcll} CaCO_3(s) & + & CO_2(g) + H_2O(l) & \rightarrow & Ca^{2+}(aq) & + & 2HCO_3^-(aq) \\ -1206.9 & & -393.5 \quad -285.8 & & -542.8 & & 2(-692.0) \quad \text{(kJ)} \end{array}$$

$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$

$= [(-542.8) + 2(-692.0)] - [(-1206.9) + (-393.5) + (-285.8)] = -40.6 \text{ kJ}$

6.85. Calculate the molar heat of formation from the equation with the $\Delta H°$ values below each substance; then convert to the heat for 10.0 g of $MgCO_3$ using the molar mass of 84.3.

$$\begin{array}{lcll} MgCO_3(s) & \rightarrow & MgO(s) + CO_2(g) & \\ -1111.7 & & -601.2 \quad -393.5 & \text{(kJ)} \end{array}$$

$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$

$\Delta H° = -601.2 \text{ kJ} + (-393.5 \text{ kJ}) - (-1111.7 \text{ kJ}) = 11\underline{7}.0 \text{ kJ}$

$$\text{Heat} = 10.0 \text{ g} \times \frac{1 \text{ mol}}{84.3 \text{ g}} \times \frac{117.0 \text{ kJ}}{\text{mol}} = 13.\underline{8}7 = 13.9 \text{ kJ}$$

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6.86. Calculate the molar heat of formation from the equation with the $\Delta H°$ values below each substance; then convert to the heat for 10.0 g of $BaCO_3$ using the molar mass of 197.3.

$$\begin{array}{ccccc} BaCO_3(s) & \rightarrow & BaO(s) & + & CO_2(g) \\ -1216.3 & & -548.1 & & -393.5 \quad \text{(kJ)} \end{array}$$

$$\Delta H° = \Sigma n\Delta H°_f(\text{products}) - \Sigma m\Delta H°_f(\text{reactants})$$

$$\Delta H° = -548.1 \text{ kJ} + (-393.5 \text{ kJ}) - (-1216.3 \text{ kJ}) = 27\underline{4}.7 \text{ kJ}$$

$$\text{Heat} = 10.0 \text{ g} \times \frac{1 \text{ mol}}{197.3 \text{ g}} \times \frac{274.7 \text{ kJ}}{\text{mol}} = 13.\underline{9}2 = 13.9 \text{ kJ}$$

■ SOLUTIONS TO GENERAL PROBLEMS

6.87. The SI units of force must be kg•m/s^2 (= newton, N) to be consistent with the joule, the SI unit of energy:

$$\frac{\text{kg} \bullet \text{m}}{\text{s}^2} \times \text{m} = \frac{\text{kg} \bullet \text{m}^2}{\text{s}^2} = \text{joule, J}$$

6.88. Solving $E_p = mgh$, you obtain $g = E_p/mh$. Thus, the SI unit of g is (kg•m^2/s^2)/(kg•m) = m/s^2.

6.89. Using Table 1.5 and 4.184 J/cal, convert the 686 Btu/lb to J/g:

$$\frac{686 \text{ Btu}}{1 \text{ lb}} \times \frac{252 \text{ cal}}{1 \text{ Btu}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} \times \frac{1 \text{ lb}}{0.4536 \text{ kg}} \times \frac{1 \text{ kg}}{10^3 \text{ g}}$$

$$= 1.5\underline{9}4 \times 10^3 = 1.59 \times 10^3 \text{ J/g}$$

6.90. Using Table 1.5 and 4.184 J/cal, convert the 51600 Btu/lb to J/g:

$$\frac{51600 \text{ Btu}}{1 \text{ lb}} \times \frac{252 \text{ cal}}{1 \text{ Btu}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} \times \frac{1 \text{ lb}}{0.4536 \text{ kg}} \times \frac{1 \text{ kg}}{10^3 \text{ g}}$$

$$= 1.1\underline{9}9 \times 10^5 = 1.20 \times 10^5 \text{ J/g}$$

6.91. Substitute into the equation $E_p = mgh$, and convert to SI units.

$$E_p = 1.00 \text{ lb} \times \frac{9.807 \text{ m}}{\text{s}^2} \times 167 \text{ ft} \times \frac{0.4536 \text{ kg}}{1 \text{ lb}} \times \frac{0.9144 \text{ m}}{3 \text{ ft}}$$

$$= \frac{22\underline{6}.433 \text{ kg} \bullet \text{m}^2}{\text{s}^2} = 226 \text{ J}$$

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At the bottom, all the potential energy is converted to kinetic energy, so $E_k = 226.433\ \text{kg}\bullet\text{m}^2/\text{s}^2$. Because $E_k = 1/2mv^2$, solve for v, the speed (velocity):

$$v = \sqrt{\frac{E_k}{1/2 \text{ x } m}} = \sqrt{\frac{226.433\ \text{kg} \bullet \text{m}^2/\text{s}^2}{1/2 \text{ x } 1.00\ \text{lb x } 0.4536\ \text{kg/lb}}} = 31.\underline{6}0 = 31.6\ \text{m/s}$$

6.92. Substitute into the equation $E_k = 1/2mv^2$, and convert to SI units.

$$E_k = 1/2 \text{ x } 2354\ \text{lb x } \frac{0.4536\ \text{kg}}{1\ \text{lb}} \text{ x } \left(\frac{11.2\ \text{km}}{\text{s}} \text{ x } \frac{10^3\ \text{m}}{1\ \text{km}}\right)^2$$

$$= 6.6\underline{9}7 \text{ x } 10^{10}\ \text{kg}\bullet\text{m}^2/\text{s}^2 = 6.70 \text{ x } 10^{10}\ \text{J}$$

6.93. The equation is

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g); \quad \Delta H = 177.9\ \text{kJ}$$

Use the molar mass of 100.08 g/mol to convert the heat per mole to heat per 27.3 g.

$$21.3\ \text{g } CaCO_3 \text{ x } \frac{1\ \text{mol } CaCO_3}{100.08\ \text{g } CaCO_3} \text{ x } \frac{177.9\ \text{kJ}}{1\ \text{mol } CaCO_3} = 37.\underline{8}6 = 37.9\ \text{kJ}$$

6.94. The equation is

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s); \quad \Delta H = -65.2\ \text{kJ}$$

Use the molar mass in the conversion.

$$24.5\ \text{g CaO} \text{ x } \frac{1\ \text{mol CaO}}{56.08\ \text{g CaO}} \text{ x } \frac{-65.2\ \text{kJ}}{1\ \text{mol CaO}} = -28.\underline{4}8 = -28.5\ \text{kJ}$$

The heat released is 28.5 kJ.

6.95. The equation is

$$2HCHO_2(l) + O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

Use the molar mass of 46.03 g/mol to convert −30.3 kJ/5.48 g to ΔH per mole of acid.

$$\frac{-30.3\ \text{kJ}}{5.48\ \text{g } HCHO_2} \text{ x } \frac{46.03\ \text{g } HCHO_2}{1\ \text{mol } HCHO_2} = -25\underline{4}.508 = -255\ \text{kJ/mol}$$

6.96. The equation is

$$HC_2H_3O_2(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

Use the molar mass of 60.05 g/mol to convert −52.0 kJ/3.58 g to ΔH per mole of acid.

$$\frac{-52.0\ \text{kJ}}{3.58\ \text{g } HC_2H_3O_2} \text{ x } \frac{60.05\ \text{g } HC_2H_3O_2}{1\ \text{mol } HC_2H_3O_2} = -87\underline{2}.2 = -872\ \text{kJ/mol}$$

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6.97. The heat gained by the water at the lower temperature equals the heat lost by the water at the higher temperature. Each heat term is s x m x Δt. This gives

$$(4.184 \text{ J/g•°C})(54.9 \text{ g})(t_f - 31.5°\text{C}) = (4.184 \text{ J/g•°C})(21.0 \text{ g})(52.7°\text{C} - t_f)$$

The specific heat and the units can be canceled from both sides to give

$$(54.9)(t_f - 31.5°\text{C}) = (21.0)(52.7°\text{C} - t_f)$$

After rearranging, you get $75.9\ t_f = 2836.05$. This gives $t_f = 37.\underline{3}6 = 37.4°\text{C}$.

6.98. The heat gained by the water at the lower temperature equals the heat lost by the water at the higher temperature. Each heat term is s x m x Δt. This gives

$$(4.184 \text{ J/g•°C})(45.4 \text{ g})(t_f - 35.7°\text{C}) = (4.184 \text{ J/g•°C})(20.5 \text{ g})(66.2°\text{C} - t_f)$$

The specific heat and the units can be canceled from both sides to give

$$(45.4)(t_f - 35.7°\text{C}) = (20.5)(66.2°\text{C} - t_f)$$

After rearranging, you get $65.9\ t_f = 2977.88$. This gives $t_f = 45.\underline{1}8 = 45.2°\text{C}$.

6.99. Divide the 235 J heat by the mass of lead and the Δt to obtain the specific heat.

$$\text{Specific heat} = \frac{235 \text{ J}}{121.6 \text{ g } (35.5°\text{C} - 20.4°\text{C})} = 0.12\underline{7}98 = \frac{0.128 \text{ J}}{\text{g} \bullet °C}$$

6.100. Divide the 47.0 J heat by the mass of copper and the Δt to obtain the specific heat.

$$\text{Specific heat} = \frac{47.0 \text{ J}}{35.4 \text{ g } (3.45°\text{C})} = 0.38\underline{4}8 = \frac{0.385 \text{ J}}{\text{g} \bullet °C}$$

6.101. The energy used to heat the Zn comes from cooling the water. Calculate q for water:

$$q_{wat} = \text{specific heat x mass x } \Delta t$$

$$q_{wat} = \frac{4.18 \text{ J}}{\text{g} \bullet °C} \text{ x } 50.0 \text{ g x } (96.68°\text{C} - 100.00°\text{C}) = -69\underline{3}.88 \text{ J}$$

The sign of q for the Zn is the reverse of the sign of q for water because the Zn is absorbing heat:

$$q_{met} = -(q_{wat}) = -(-693.88) = 69\underline{3}.88 \text{ J}$$

$$\text{Specific heat} = \frac{693.88 \text{ J}}{25.3 \text{ g } (96.68°\text{C} - 25.00°\text{C})} = 0.38\underline{2}6 = \frac{0.383 \text{ J}}{\text{g} \bullet °C}$$

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6.102. The energy given up by the metal is used to heat the water. Calculate q for water:

q_{wat} = specific heat x mass x Δt

$$q_{wat} = \frac{4.18\ \text{J}}{\text{g} \bullet {}^\circ C} \times 26.7\ \text{g} \times (30.00^\circ\text{C} - 25.00^\circ\text{C}) = 55\underline{8}.03\ \text{J}$$

The sign of q for the metal is the reverse of the sign of q for water because the metal is giving up heat:

$q_{met} = -(q_{wat}) = -55\underline{8}.03$ J

$$\text{Specific heat} = \frac{-558.03\ \text{J}}{19.6\ \text{g}\ (30.00^\circ\text{C} - 61.67^\circ\text{C})} = 0.89\underline{8}9 = \frac{0.899\ \text{J}}{\text{g} \bullet {}^\circ C}$$

6.103. First, multiply the molarities by the volumes, in liters, to get the moles of NaOH and the moles of HCl, and thus determine the limiting reactant.

Mol NaOH = M x V = 0.996 M x 0.0141 L = 0.014$\underline{0}$4 mol

Mol HCl = M x V = 0.905 M x 0.0323 L = 0.029$\underline{2}$3 mol

Therefore, NaOH is the limiting reactant. The total volume of the system is 14.1 mL + 32.3 mL = 46.4 mL. Since the density of water is 1.00 g/mL, the total mass of the system is 46.4 g. Next, set the heat released by the reaction (mol x enthalpy of reaction) equal to the heat absorbed by the water (s x m x Δt). This gives

(0.01404 mol)(55.8 x 10^3 J/mol) = (4.184 J/g•°C)(46.4 g)(t_f − 21.6°C)

After dividing, this gives t_f − 21.6°C = 4.035°C, or t_f = 25.$\underline{6}$3 = 25.6°C.

6.104. First, multiply the molarities by the volumes, in liters, to get the moles of KOH and the moles of HBr and thus determine the limiting reactant.

Mol KOH = M x V = 1.05 M x 0.0291 L = 0.030$\underline{5}$55 mol

Mol HBr = M x V = 1.07 M x 0.0209 L = 0.022$\underline{3}$63 mol

Therefore, HBr is the limiting reactant. The total volume of the system is 29.1 mL + 20.9 mL = 50.0 mL. Since the density of water is 1.00 g/mL, the total mass of the system is 50.0 g. Next, set the heat released by the reaction (mol x enthalpy of reaction) equal to the heat absorbed by the water (s x m x Δt). This gives

(0.022363 mol)(55.8 x 10^3 J/mol) = (4.184 J/g•°C)(50.0 g)(t_f − 21.8°C)

After dividing, this gives t_f − 21.8°C = 5.964°C, or t_f = 27.$\underline{7}$6 = 27.8°C.

6.105. Use Δt and the heat capacity of 547 J/°C to calculate q:

$q = C\Delta t$ = (547 J/°C)(36.66 − 25.00)°C = 6.3$\underline{7}$8 x 10^3 J (6.3$\underline{7}$8 kJ)

Energy is released in the solution process in raising the temperature, so ΔH is negative:

$$\Delta H = \frac{-6.378\ \text{kJ}}{6.48\ \text{g LiOH}} \times \frac{23.95\ \text{g LiOH}}{1\ \text{mol LiOH}} = -23.\underline{5}7 = -23.6\ \text{kJ/mol}$$

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6.106. Use Δt and the heat capacity of 682 J/°C to calculate q:

$$q = C\Delta t = (682 \text{ J/°C})(14.14 - 25.00)\text{°C} = -7.4\underline{0}65 \text{ x } 10^3 \text{ J } (-7.4\underline{0}65 \text{ kJ})$$

Energy is absorbed in the solution process in lowering the temperature, so the sign of ΔH must be reversed, making the heat positive:

$$\Delta H = \frac{7.4065 \text{ kJ}}{21.45 \text{ g KNO}_3} \text{ x } \frac{101.1 \text{ g KNO}_3}{1 \text{ mol KNO}_3} = 34.\underline{9}1 = 34.9 \text{ kJ/mol}$$

6.107. Use Δt and the heat capacity of 13.43 kJ/°C to calculate q:

$$q = C\Delta t = (13.43 \text{ kJ/°C})(35.84 - 25.00)\text{°C} = 145.\underline{5}81 \text{ kJ}$$

As in the previous two problems, the sign of ΔH must be reversed, making the heat negative:

$$\Delta H = \frac{-145.581 \text{ kJ}}{10.00 \text{ g HC}_2\text{H}_3\text{O}_2} \text{ x } \frac{60.05 \text{ g HC}_2\text{H}_3\text{O}_2}{1 \text{ mol HC}_2\text{H}_3\text{O}_2} = -874.\underline{2}1 = -874.2 \text{ kJ/mol}$$

6.108. Use Δt and the heat capacity of 15.8 kJ/°C to calculate q:

$$q = C\Delta t = (15.8 \text{ kJ/°C})(20.54 - 20.00)\text{°C} = 8.\underline{5}3 \text{ kJ}$$

As in the previous three problems, the sign of ΔH must be reversed, making the heat negative:

$$\Delta H = \frac{-8.53 \text{ kJ}}{0.548 \text{ g sugar}} \text{ x } \frac{150.1 \text{ g sugar}}{1 \text{ mol sugar}} = -2.\underline{3}36 \text{ x } 10^3 = -2.3 \text{ x } 10^3 \text{ kJ/mol}$$

6.109. Using the equations in the data, reverse the direction of the first reaction, and reverse the sign of its ΔH. Then add the second and third equations and their ΔH's.

$H_2O(g)$ +	$SO_2(g)$	$\rightarrow$	$H_2S(g)$ + $3/2O_2(g)$;	$\Delta H = (-518 \text{ kJ}) \text{ x } (-1)$
$H_2(g)$ +	$1/2O_2(g)$	$\rightarrow$	$H_2O(g)$;	$\Delta H = (-242 \text{ kJ})$
$1/8S_8$(rh.) +	$O_2(g)$	$\rightarrow$	$SO_2(g)$;	$\Delta H = (-297 \text{ kJ})$
$H_2(g)$ +	$1/8S_8(rh.)$	$\rightarrow$	$H_2S(g)$;	$\Delta H = -21 \text{ kJ}$

6.110. Using the equations in the data, reverse the direction of the reaction involving oxidation of the glycol, and reverse the sign of its ΔH. Then add half of the reaction involving oxidation of C_2H_4O, and half of its ΔH.

$2CO_2(g) + 3H_2O(l)$	$\rightarrow$	$HOC_2H_4OH(l) + 5/2O_2(g)$;	$\Delta H = (-1189.8 \text{ kJ}) \text{ x } (-1)$
$C_2H_4O(g) + 5/2O_2(g)$	$\rightarrow$	$2CO_2(g) + 2H_2O(l)$;	$\Delta H = (-2612.2 \text{ kJ}) \text{ x } (1/2)$
$C_2H_4O(g) + H_2O(l)$	$\rightarrow$	$HOC_2H_4OH(l)$;	$\Delta H = -116.3 \text{ kJ}$

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6.111. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation.

$$\underset{-74.9}{CH_4(g)} + \underset{-241.8}{H_2O(g)} \rightarrow \underset{-110.5}{CO(g)} + \underset{3(0)}{3H_2(g)} \quad (kJ)$$

$\Delta H° = [-110.5 + 3(0)] - [(-74.87) + (-241.8)] = 206.\underline{1}7 = 206.2$ kJ

6.112. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation.

$$\underset{2(-74.87)}{2CH_4(g)} \quad \underset{0}{O_2(g)} \rightarrow \underset{2(-110.5)}{2CO(g)} \quad \underset{4(0)}{4H_2(g)} \quad (kJ)$$

$\Delta H° = [2(-110.5) + 4(0)] - [2(-74.87) + 0] = -71.\underline{2}6 = -71.3$ kJ

6.113. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation. The $\Delta H_f°$ of −635 kJ/mol CaO is given in the problem.

$$\underset{-1206.9}{CaCO_3(s)} \rightarrow \underset{-635}{CaO(s)} + \underset{-393.5}{CO_2(g)} \quad (kJ)$$

$\Delta H° = [(-635) + (-393.5)] - [-1206.9] = 17\underline{8}.4 = 178$ kJ

6.114. Write the $\Delta H°$ values (Table 6.2) underneath each compound in the balanced equation.

$$\underset{2(-950.8)}{2NaHCO_3(s)} \rightarrow \underset{-1130.8}{Na_2CO_3(s)} + \underset{-241.8}{H_2O(g)} + \underset{-393.5}{CO_2(g)} \quad (kJ)$$

$\Delta H° = [(-1130.8) + (-241.8) + (-393.5)] - [2(-950.8)] = 135.5$ kJ

6.115. Calculate the molar heat of reaction from the equation with the $\Delta H°$ values below each substance; then convert to the heat for the reaction at 25°C.

$$\underset{0.0\ kJ}{2H_2(g)} + \underset{0.0\ kJ}{O_2(g)} \rightarrow \underset{-285.8\ kJ}{2H_2O(l)}$$

$\Delta H° = 2 \times (-285.8\ kJ) - 0 - 0 = -571.6$ kJ

The moles of oxygen in 2.000 L with a density of 1.11 g/L is

$$2.000\ L\ O_2 \times \frac{1.11\ g\ O_2}{1\ L\ O_2} \times \frac{1\ mol\ O_2}{32.0\ g\ O_2} = 0.0693\underline{7}\ mol\ O_2$$

The heat of reaction from 0.06937 mol O_2 is

$$0.69\underline{3}7\ mol\ O_2 \times \frac{-571.6\ kJ}{mol\ O_2} = -39.\underline{6}54 = -39.7\ kJ$$

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6.116. Calculate the molar heat of reaction from the equation with the $\Delta H°$ values below each substance; then convert to the heat for the reaction at 25°C.

$$Cl_2(g) + 2Na(s) \rightarrow 2NaCl(s)$$

0.0 kJ 0.0 kJ - 411.1 kJ

$$\Delta H° = 2 \text{ x } (-411.1 \text{ kJ}) - 0 - 0 = -822.2 \text{ kJ}$$

The moles of chlorine in 4.000 L Cl_2 with a density of 2.46 g/L is

$$4.000 \text{ L } Cl_2 \text{ x } \frac{2.46 \text{ g } Cl_2}{\text{L } Cl_2} \times \frac{1 \text{ mol } Cl_2}{70.9 \text{ g } Cl_2} = 0.1387 \text{ mol } Cl_2$$

The heat of reaction from 0.1387 mol Cl_2 is

$$0.1387 \text{ mol } Cl_2 \text{ x } \frac{-822.2 \text{ kJ}}{\text{mol } Cl_2} = -114.03 = -114 \text{ kJ}$$

6.117. Let $\Delta H_f°$ = the unknown standard enthalpy of formation for sucrose. Then write this symbol and the other $\Delta H_f°$ values underneath each compound in the balanced equation, and solve for $\Delta H_f°$ using the $\Delta H°$ of −5641 kJ for the reaction.

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$$

$\Delta H_f°$ 12(0) 12(-393.5) 11(-285.8) (kJ)

$$\Delta H° = -5641 = [12(-393.5) + 11(-285.8)] - [\Delta H_f° + 12(0)]$$

$$\Delta H_f° = -2225 \text{ kJ/mol sucrose}$$

6.118. Let $\Delta H_f°$ = the unknown standard enthalpy of formation for acetone. Then write this symbol and the other $\Delta H_f°$ values underneath each compound in the balanced equation, and solve for $\Delta H_f°$ using the $\Delta H°$ of −1791 kJ for the reaction.

$$CH_3COCH_3(l) + 4O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$$

$\Delta H_f°$ 4(0) 3(-393.5) 3(-285.8) (kJ)

$$\Delta H° = -1791 = [3(-393.5) + 3(-285.8)] - [\Delta H_f° + 4(0)]$$

$$\Delta H_f° = -246.9 = -247 \text{ kJ/mol acetone}$$

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6.119. First, calculate the heat evolved from the molar amounts represented by the balanced equation. From Appendix C, obtain the individual heats of formation, and write those below the reactants and products in the balanced equation. Then multiply the molar heats of formation by the number of moles in the balanced equation, and write those products below the molar heats of formation.

$2Al(s)$	+	$3NH_4NO_3(s)$	→	$3N_2(g)$	+	$6H_2O(g)$	+	$Al_2O_3(s)$	
0.0 kJ		-365.6 kJ		0.0 kJ		-241.8		-1675.7 kJ	(kJ/mol)
0.0 kJ		-1096.8 kJ		0.0 kJ		-1450.8		-1675.7 kJ	(kJ/eqn.)

The total heat of reaction of 2 mol Al and 3 mol NH_4NO_3 is

$$\Delta H = -1450.8 - 1675.7 - (-1096.8 \text{ kJ}) = -2029.7 \text{ kJ}$$

Now, 245 kJ represents the following fraction of the total heat of reaction:

$$\frac{245 \text{ kJ}}{2029.7 \text{ kJ}} = 0.12\underline{0}7$$

Thus, 245 kJ requires the fraction 0.1207 of the moles of each reactant: 0.1207 x 2, or 0.24$\underline{1}$4, mol of Al and 0.1207 x 3, or 0.36$\underline{2}$1, mol of NH_4NO_3. The mass of each reactant and the mass of the mixture are as follows:

0.2414 mol Al x 26.98 g/mol Al = 6.5$\underline{1}$3 g of Al

0.3621 mol NH_4NO_3 x 80.04 g/mol NH_4NO_3 = 28.$\underline{9}$8 g NH_4NO_3

6.513 g Al + 28.98 g NH_4NO_3 = 35.$\underline{4}$9 = 35.5 g of the mixture

6.120. First, calculate the heat evolved from the molar amounts represented by the balanced equation. From Appendix C, obtain the individual heats of formation, and write those below the reactants and products in the balanced equation. Then multiply the molar heats of formation by the number of moles in the balanced equation, and write those products below the molar heats of formation.

$2Al(s)$	+	$Fe_2O_3(s)$	→	$2Fe(l)$	+	$Al_2O_3(s)$	
0.0 kJ		-825.5 kJ		+12.40 kJ		-1675.7 (kJ)	(kJ/mol)
0.0 kJ		-825.5 kJ		+24.80 kJ		-1675.7 (kJ)	(kJ/eqn)

The total heat of reaction of 2 mol Al and 1 mol Fe_2O_3 is

$$\Delta H = +24.80 - 1675.7 - (-825.5 \text{ kJ}) = -825.\underline{4}0 \text{ kJ}$$

Now, 348 kJ represents the following fraction of the total heat of reaction:

$$\frac{348 \text{ kJ}}{825.40 \text{ kJ}} = 0.42\underline{1}6$$

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Thus, 348 kJ requires the fraction 0.4216 of the moles of each reactant: 0.4216 x 2, or 0.8432, mol of Al and 0.4216 x 1, or 0.4216, mol of Fe_2O_3. The mass of each reactant and the mass of the mixture are as follows:

0.8432 mol Al x 26.98 g/mol Al = 22.750 g Al

0.4216 mol Fe_2O_3 x 159.7 g/mol Fe_2O_3 = 67.331 g Fe_2O_3

22.750 g Al + 67.331 g Fe_2O_3 = 90.081 = 90.1 g of the mixture

6.121. White phosphorus is a yellowish-white, waxy substance often sold in the form of sticks looking something like fat crayons. It is not found in modern matches. It was outlawed in the early 1900s because workers began to show symptoms of white phosphorus poisoning, in which the jawbone disintegrated.

6.122. The phosphorus compound in "strike anywhere" matches is tetraphosphorus trisulfide, P_4S_3. It burns in air in the very exothermic reaction

$$P_4S_3(s) + 8O_2(g) \rightarrow P_4O_{10}(s) + 3SO_2(s)$$

■ SOLUTIONS TO STRATEGY PROBLEMS

6.123. $v = \left(\frac{2E}{m}\right)^{1/2} = \left(\frac{2 \text{ x } 15.75 \text{ J}}{56.6 \text{ x } 10^{-3} \text{ kg}}\right)^{1/2} = 23.591 = 23.6 \text{ m/s}$

6.124. No other information is needed to answer either question.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g); \quad \Delta H = -198 \text{ kJ}$$

$$3SO_3(g) \rightarrow 3SO_2(g) + 3/2O_2(g); \quad \Delta H = 297 \text{ kJ}$$

6.125. The reaction is

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s); \quad \Delta H = -1651 \text{ kJ}$$

The heat released is

$$10.3 \text{ g } Fe_2O_3 \text{ x } \left(\frac{1 \text{ mol } Fe_2O_3}{159.69 \text{ g}}\right) \text{ x } \left(\frac{1651 \text{ kJ}}{2 \text{ mol } Fe_2O_3}\right) = 53.24 = 53.2 \text{ kJ}$$

If ozone gas was burned instead, you would need to know the heat of the following reaction:

$$2O_3(g) \rightarrow 3O_2(g)$$

6.126. $7.60 \text{ kJ x } \left(\frac{1 \text{ mol } O_2}{484 \text{ kJ}}\right) \text{ x } \left(\frac{32.00 \text{ g}}{1 \text{ mol } O_2}\right) = 0.5024 = 0.502 \text{ g}$

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6.127. For 2 mol water produced, 2 mol H_2 reacted. This is 2 x 2.016 g/mol = 4.032 g.

6.128. The heat lost by metal is equal to the heat gained by calorimeter.

$$(0.449\ \text{J/g•°C})(m)(95.4°\text{C} - 51.9°\text{C}) = (4.18\ \text{J/g•°C})(284\ \text{g})(51.9°\text{C} - 32.2°\text{C})$$

Solve for the mass of iron.

$$m = \frac{(4.18\ \text{J/g•°C})(284\ \text{g})(51.9°\text{C} - 32.2°\text{C})}{(0.449\ \text{J/g•°C})(95.4°\text{C} - 51.9°\text{C})} = 1197.3 = 1.20 \times 10^3\ \text{g}$$

6.129. The heat released in the reaction is equal to the heat gained by the calorimeter.

$$m \times \left(\frac{1\ \text{mol}\ C_6H_5COOH}{122.12\ \text{g}}\right) \times (3226\ \text{kJ/mol}) = (12.41\ \text{kJ/°C})(27.65°\text{C} - 23.44°\text{C})$$

Solve for the mass of benzoic acid.

$$m = \frac{(12.41\ \text{kJ/°C})(27.65°\text{C} - 23.44°\text{C})(122.12\ \text{g/mol})}{3226\ \text{kJ/mol}} = 1.977 = 1.98\ \text{g}$$

6.130. Multiply the first reaction by 2. Then reverse the second reaction, and multiply it by 2. Finally, multiply the third reaction by 3. Add the resulting equations together to get the reaction of interest.

2A + 2B	→	4C	$\Delta H = (-447\ \text{kJ}) \times (2)$
4E	→	2A + 6D	$\Delta H = (-484\ \text{kJ}) \times (-2)$
6D + 3B	→	6F	$\Delta H = (-429\ \text{kJ}) \times (3)$
4E + 5B	→	4C + 6F	$\Delta H = -1213\ \text{kJ}$

6.131. $\Delta H°_{comb} = \Sigma n\,\Delta H_f^\circ\,(\text{products}) - \Sigma m\,\Delta H_f^\circ\,(\text{reactants})$

$$= [\Delta H_f^\circ(P_4O_{10}) + 3\,\Delta H_f^\circ(SO_2)] - [\Delta H_f^\circ(P_4S_3) + 8\,\Delta H_f^\circ(O_2)]$$

$$-3651\ \text{kJ} = [(-3009.9\ \text{kJ}) + 3(-296.8\ \text{kJ})] - [(1\ \text{mol})\,\Delta H_f^\circ(P_4S_3) + 8(0\ \text{kJ})]$$

Solve for the enthalpy of formation of P_4S_3.

$$\Delta H_f^\circ(P_4S_3) = \frac{(-3009.9\ \text{kJ}) + (3)(-296.8\ \text{kJ}) - (-3651\ \text{kJ})}{1\ \text{mol}} = -249.3 = -249\ \text{kJ/mol}$$

The value from Appendix C is −224.6 kJ/mol, which is a difference of 10.9%.

6.132. $\Delta H°_{comb} = \Sigma n\,\Delta H_f^\circ\,(\text{products}) - \Sigma m\,\Delta H_f^\circ\,(\text{reactants})$

$$= [7\,\Delta H_f^\circ(CO_2) + 4\,\Delta H_f^\circ(H_2O)] - [\Delta H_f^\circ(C_6H_5CH_3) + 9\,\Delta H_f^\circ(O_2)]$$

$$-3908\ \text{kJ} = [7(-393.5\ \text{kJ}) + 4(-285.8\ \text{kJ})] - [(1\ \text{mol})\,\Delta H_f^\circ(C_6H_5CH_3) + 9(0\ \text{kJ})]$$

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Solve for the enthalpy of formation of $C_6H_5CH_3$.

$$\Delta H_f^\circ (C_6H_5CH_3) = \frac{(7)(-393.5\text{ kJ}) + (4)(-285.8\text{ kJ}) - (-3908\text{ kJ})}{1\text{ mol}} = 1\underline{0}.3 = 10.\text{ kJ/mol}$$

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

6.133. The heat lost, q, by the water(s) with a temperature higher than the final temperature must be equal to the heat gained, q, by the water(s) with a temperature lower than the final temperature.

q(lost by water at higher temp) = q(gained by water at lower temp)

$\Sigma (s \times m \times \Delta t) = \Sigma (s \times m \times \Delta t)$

Divide both sides of the equation by the specific heat, s, to eliminate this term, and substitute the other values. Since the mass of the water at 50.0°C is greater than the sum of the masses of the other two waters, assume the final temperature will be greater than 37°C and greater than 15°C. Use this to set up the three Δt expressions, and write one equation in one unknown, letting t equal the final temperature. Simplify by omitting the "grams" from 45.0 g, 25.0 g, and 15.0 g.

$\Sigma (m \times \Delta t) = \Sigma (m \times \Delta t)$

$45.0 \times (50.0°C - t) = 25.0 \times (t - 15.0°C) + 15.0 \times (t - 37°C)$

$2250°C - 45.0\,t = 25.0\,t - 375°C + 15.0\,t - 555.0°C$

$-85.0\,t = -3180°C$

$t = 37.\underline{4}1 = 37.4°C$ (the final temperature)

6.134. The heat lost, q, by the substances(s) with a temperature higher than the final temperature must be equal to the heat gained, q, by the substances(s) with a temperature lower than the final temperature.

q(lost) = q(gained)

$\Sigma (s \times m \times \Delta t) = \Sigma (s \times m \times \Delta t)$

Since the temperature of the iron, 95.0°C, is far larger than the temperatures of the other two substances, assume the final temperature will be greater than 35.5°C and greater than 25°C. Then, write the heat term for the iron on the left and the sum of the heat terms for water and ethanol on the right. Since the masses, m, are equal, divide both sides by m to eliminate this term, and solve one equation in one unknown, letting t equal the final temperature. (To simplify the setup, only the temperature unit is retained.)

$\Sigma (s \times \Delta t) = \Sigma (s \times \Delta t)$

$0.449 \times (95.0°C - t) = 2.43 \times (t - 35.5°C) + 4.18 \times (t - 25.0°C)$

$42.655°C - 0.449\,t = 2.43\,t - 86.265°C + 4.18\,t - 104.5°C$

$-7.059\,t = -233.42°C$

$t = 33.\underline{0}6 = 33.1°C$ (the final temperature)

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The final temperature is actually less than that of the ethanol, but rewriting the equation to account for this still gives the same final temperature.

6.135. First, calculate the mole fraction of each gas in the product, assuming 100 g product:

Mol CO = 33 g CO x 1 mol CO/28.01 g CO = 1.178 mol CO

Mol CO_2 = 67 g CO_2 x 1 mol CO_2/44.01 g CO_2 = 1.522 mol CO_2

$$\text{Mol frac. CO} = \frac{1.178 \text{ mol CO}}{(1.178 + 1.522) \text{ mol}} = 0.4363$$

$$\text{Mol frac. } CO_2 = \frac{1.522 \text{ mol } CO_2}{(1.178 + 1.522) \text{ mol}} = 0.5637$$

Now, calculate the starting moles of C, which equal the total moles of CO and CO_2:

Starting mol C(*s*) = 1.00 g C x 1 mol C/12.01 g C

= 0.08326 mol C = mol CO + CO_2

Use the mole fractions to convert mol CO + CO_2 to mol CO and mol CO_2:

$$\text{Mol CO} = \frac{0.4363 \text{ mol CO}}{1 \text{ mol total}} \text{ x } 0.08326 \text{ mol total} = 0.03633 \text{ mol CO}$$

$$\text{Mol } CO_2 = \frac{0.5637 \text{ mol } CO_2}{1 \text{ mol total}} \text{ x } 0.08326 \text{ mol total} = 0.04693 \text{ mol } CO_2$$

Now, use enthalpies of formation (Table 6.2) to calculate the heat of combustion for both:

C(*s*)	+	$1/2O_2(g)$	→	CO(*g*)
0.03633		excess		0.03633 (mol)
0		0		-110.5 (kJ/mol)
0		0		-110.5 (kJ/mol)

C(*s*)	+	$O_2(g)$	→	$CO_2(g)$
0.04693		excess		0.04693 (mol)
0		0		-393.5 (kJ/mol)
0		0		-18.47 (kJ/0.04693 mol)

Total $\Delta H = -4.014 + (-18.47) = -22.48 = -22$ kJ

Heat released = 22 kJ

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6.136. The balanced equations are

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$C_2H_6(g) + 3.5O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

First, calculate the moles of CH_4 and C_2H_6 (let 80.0% = 0.800 g and 20.0% = 0.200 g).

$$\text{Mol } CH_4 = 0.800 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} = 0.049\underline{8}7 \text{ mol } CH_4$$

$$\text{Mol } C_2H_6 = 0.200 \text{ g } C_2H_6 \times \frac{1 \text{ mol } C_2H_6}{30.07 \text{ g } C_2H_6} = 0.006\underline{6}51 \text{ mol } C_2H_6$$

Now, use the enthalpies of formation (Table 6.2) to calculate the total heat:

$CH_4(g)$	+	$2O_2(g)$	→	$CO_2(g)$	+	$2H_2O(l)$
0.04987		excess		0.04987		2(0.04987) (mol)
-74.87		0		-393.5		-285.8 (kJ/mol)
-3.7$\underline{3}$4		0		-19.$\underline{6}$2		-28.$\underline{5}$1 (kJ/eqn.)

$C_2H_6(g)$	+	$3.5O_2$	→	$2CO_2(g)$	+	$3H_2O(l)$
0.006651		excess		2(0.006651)		3(0.006651) (mol)
-84.68		0		-393.5		-285.8 (kJ/mol)
-0.56$\underline{3}$2		0		-5.2$\underline{3}$4		-5.7$\underline{0}$3 (kJ/eqn.)

For the combustion of CH_4:

$$\Delta H = [(-28.51) + (-19.62)] - [(-3.734) + 0] = -44.\underline{3}95 \text{ kJ}$$

For the combustion of C_2H_6:

$$\Delta H = [(-5.234) + (-5.703)] - [(-0.5632) + 0] = -10.3\underline{7}3 \text{ kJ}$$

For the combustion of the total (1.00 g) of CH_4 and C_2H_6:

$$\Delta H = -44.395 + (-10.373) = -54.\underline{7}68 = -54.8 \text{ kJ}$$

Heat evolved = 54.8 kJ

6.137. The $\Delta H°$ for the reactions to produce CO and CO_2 in each case is equal to the $\Delta H_f°$ of the respective gases. Thus $\Delta H°$ to produce CO is −110.5 kJ/mol, and $\Delta H°$ to produce CO_2 is −393.5 kJ/mol. Since 1 mol graphite is needed to produce 1 mol either CO or CO_2, one equation in one unknown can be written for the heat produced, using m for the moles of CO and (2.00 − m) for moles of CO_2.

$$-481 \text{ kJ} = m \times (-110.5 \text{ kJ}) + (2.00 - m) \times (-393.5 \text{ kJ})$$

$$-481 = -110.5\,m - 787 + 393.5\,m$$

$$\text{mol CO} = m = 1.0\underline{8}1; \quad \text{mass CO} = 1.081 \times 28.0 \text{ g/mol} = 30.\underline{2}6 = 30.3 \text{ g}$$

$$\text{mol } CO_2 = (2.00 - m) = 0.9\underline{1}9; \quad \text{mass } CO_2 = 0.9\underline{1}9 \text{ mol} \times 44.0 \text{ g/mol} = 4\underline{0}.4 = 40. \text{ g}$$

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6.138. The $\Delta H°$ values for each reaction are as follows:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H° = -393.5 \text{ kJ} + 2(-285.8 \text{ kJ}) - (-74.87 \text{ kJ}) - 0 = -890.\underline{2}3 \text{ kJ}$$

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

$$\Delta H° = 2(-393.5 \text{ kJ}) + 2(-285.8 \text{ kJ}) - (52.47 \text{ kJ}) - 0 = -1411.\underline{0}7 \text{ kJ}$$

Since 10.0 g of CH_4 and C_2H_4 produce 520 kJ of heat, one equation in one unknown can be written for the heat produced, using m for the mass of CH_4 and $(10.00 - m)$ for the mass of C_2H_4. Use m /16.0 for the moles of CH_4 and $(10.00 - m)$ /28.0 for the moles of C_2H_4.

$$-520 \text{ kJ} = (m/16.0) \times (-890.23 \text{ kJ}) + [(10.00 - m)/28.0] \times (-1411.07 \text{ kJ})$$

$$-520 = -55.\underline{6}3\, m + (-503.\underline{9}5) + 50.3\underline{9}\, m$$

$$\text{Mass } CH_4 = m = 1\underline{6}.05 \div 5.24 = 3.\underline{0}62 = 3.1 \text{ g}$$

$$\text{Mass percentage } CH_4 = (3.06 \text{ g} \div 10.0 \text{ g}) \times 100\% = 3.06 = 3.1\%$$

6.139. The equation is

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g); \quad \Delta H° = -906 \text{ kJ}$$

First, determine the limiting reactant by calculating the moles of NH_3 and of O_2; then, assuming one of the reactants is totally consumed, calculate the moles of the other reactant needed for the reaction.

$$10.0 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} = 0.58\underline{7}2 \text{ mol } NH_3$$

$$20.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.62\underline{5}0 \text{ mol } O_2$$

$$0.62\underline{5}0 \text{ mol } O_2 \times \frac{4 \text{ mol } NH_3}{5 \text{ mol } O_2} = 0.500 \text{ mol } NH_3 \text{ needed}$$

Because NH_3 is present in excess of what is needed, O_2 must be the limiting reactant. Now calculate the heat released on the basis of the complete reaction of 0.622250 mol O_2:

$$\Delta H = \frac{-906 \text{ kJ}}{5 \text{ mol } O_2} \times 0.6250 \text{ mol } O_2 = -11\underline{3}.25 = -113 \text{ kJ}$$

The heat released by the complete reaction of the 20.0 g (0.6250 mol) of $O_2(g)$ is 113 kJ.

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6.140. The equation is

$$CS_2(g) + 3Cl_2(g) \rightarrow S_2Cl_2(g) + CCl_4(g); \quad \Delta H° = -230 \text{ kJ}$$

First, determine the limiting reactant by calculating the moles of CS_2 and of Cl_2; then, assuming one of the reactants is totally consumed, calculate the moles of the other reactant needed for the reaction.

$$10.0 \text{ g } CS_2 \times \frac{1 \text{ mol } CS_2}{76.13 \text{ g } CS_2} = 0.13\underline{1}4 \text{ mol } CS_2$$

$$10.0 \text{ g } Cl_2 \times \frac{1 \text{ mol } Cl_2}{70.91 \text{ g } Cl_2} = 0.14\underline{1}0 \text{ mol } Cl_2$$

$$0.1410 \text{ mol } Cl_2 \times \frac{1 \text{ mol } CS_2}{3 \text{ mol } Cl_2} = 0.047\underline{0}0 \text{ mol } CS_2$$

Because CS_2 is present in excess of what is needed, Cl_2 must be the limiting reactant. Now calculate the heat released on the basis of the complete reaction of 0.1410 mol Cl_2.

$$\Delta H = \frac{-230 \text{ kJ}}{3 \text{ mol } Cl_2} \times 0.1410 \text{ mol } Cl_2 = -10.\underline{8}10 = -10.8 \text{ kJ}$$

The heat released by the complete reaction of 10.0 g of $Cl_2(g)$ is 10.8 kJ.

6.141. The equation is

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \quad \Delta H° = -91.8 \text{ kJ}$$

a. To find the heat evolved from the production of 1.00 L of NH_3, convert the 1.00 L to mol NH_3 using the density and molar mass (17.03 g/mol). Then convert the moles to heat (ΔH) using $\Delta H°$.

$$\text{Mol } NH_3 = \frac{d \times V}{M_M} = \frac{0.696 \text{ g/L} \times 1 \text{ L}}{17.03 \text{ g/mol}} = 0.040\underline{8}7 \text{ mol } NH_3$$

$$\Delta H = \frac{-91.8 \text{ kJ}}{2 \text{ mol } NH_3} \times 0.040\underline{8}7 \text{ mol } NH_3 = -1.8\underline{7}6 \text{ (1.88 kJ heat evolved)}$$

b. First, find the moles of N_2 using the density and molar mass (28.02 g/mol). Then convert to the heat needed to raise the N_2 from 25°C to 400°C.

$$\text{Mol } N_2 = \frac{d \times V}{M_M} = \frac{1.145 \text{ g/L} \times 0.500 \text{ L}}{28.02 \text{ g/mol}} = 0.020\underline{4}3 \text{ mol } N_2$$

$$0.020\underline{4}3 \text{ mol } N_2 \times \frac{29.12 \text{ J}}{\text{mol} \bullet °C} \times (400 - 25)°C = 22\underline{3}.2 \text{ J } (0.22\underline{3}2 \text{ kJ})$$

$$\text{Percent heat for } N_2 = \frac{0.2232 \text{ kJ}}{1.876 \text{ kJ}} \times 100\% = 11.\underline{8}9 = 11.9\%$$

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6.142. The equation is

$$2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2SO_2(g); \quad \Delta H° = -1124 \text{ kJ}$$

a. First, calculate the moles of SO_2 using the density and molar mass (64.07 g/mol). Then convert the moles to heat (ΔH) using $\Delta H°$.

$$\text{Mol } SO_2 = \frac{d \text{ x } V}{M_M} = \frac{2.62 \text{ g/L x } 1 \text{ L}}{64.07 \text{ g/mol}} = 0.04089 \text{ mol } SO_2$$

$$\Delta H = \frac{-1124 \text{ kJ}}{2 \text{ mol } SO_2} \text{ x } 0.04089 \text{ mol } SO_2 = -22.98 \text{ (23.0 kJ heat evolved)}$$

b. Recall that 1.000 L of SO_2 = 0.04089 mol SO_2. Use this with the molar heat capacity of 30.2 J/(mol•°C) to calculate the heat needed to raise the temperature of SO_2 from 25°C to 500°C.

$$0.04089 \text{ mol } SO_2 \text{ x } \frac{30.2 \text{ J}}{(\text{mol} \bullet °C)} \text{ x } (500 - 25)°C = 586.6 \text{ J } (0.5866 \text{ kJ})$$

$$\text{Percent heat for } SO_2 = \frac{0.5866 \text{ kJ}}{22.98 \text{ kJ}} \text{ x } 100\% = 2.552 = 2.55\%$$

6.143. The glucose equation is

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O; \quad \Delta H° = -2802.8 \text{ kJ}$$

Convert the 2.50×10^3 kcal to mol of glucose using the $\Delta H°$ of −2802.8 kJ for the reaction and the conversion factor of 4.184 kJ/kcal:

$$2.50 \times 10^3 \text{ kcal x } \frac{4.184 \text{ kJ}}{1.000 \text{ kcal}} \text{ x } \frac{1 \text{ mol glucose}}{2802.8 \text{ kJ}} = 3.7319 \text{ mol glucose}$$

Next, convert mol glucose to mol LiOH using the above equation for glucose and the equation for LiOH:

$$2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(s) + H_2O(l)$$

$$3.7319 \text{ mol glucose x } \frac{6 \text{ mol } CO_2}{1 \text{ mol glucose}} \text{ x } \frac{2 \text{ mol LiOH}}{1 \text{ mol } CO_2} = 44.783 \text{ mol LiOH}$$

Finally, use the molar mass of LiOH to convert moles to mass:

$$44.783 \text{ mol LiOH x } \frac{23.95 \text{ g LiOH}}{1 \text{ mol LiOH}} = 1.0725 \times 10^3 \text{ g (1.07 kg) LiOH}$$

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6.144. Using $\Delta H_f^\circ = -1273$ kJ for glucose, the conversion of glucose to heat and ΔH° in the body is

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l); \quad \Delta H^\circ = -2802.8 \text{ kJ}$$

Convert the 1.00×10^2 kcal to mol of glucose, using the ΔH° of −2802.8 kJ:

$$100 \text{ kcal} \times \frac{4.184 \text{ kJ}}{1.000 \text{ kcal}} \times \frac{1 \text{ mol glucose}}{2802.8 \text{ kJ}} = 0.14927 \text{ mol glucose}$$

Next, convert mol glucose to mol KO_2 using the above equation for glucose and the equation for KO_2:

$$4KO_2(s) + 2H_2O(l) \rightarrow 4KOH(s) + 3O_2(g)$$

$$0.14927 \text{ mol glucose} \times \frac{6 \text{ mol } O_2}{1 \text{ mol glucose}} \times \frac{4 \text{ mol } KO_2}{3 \text{ mol } O_2} = 1.1942 \text{ mol } KO_2$$

$$1.1942 \text{ mol } KO_2 \times \frac{71.1 \text{ g } KO_2}{1 \text{ mol } KO_2} = 84.91 = 84.9 \text{ g } KO_2$$

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CHAPTER 7

Quantum Theory of the Atom

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

7.1. Rearrange the equation $c = \nu\lambda$, which relates wavelength to frequency and the speed of light (3.00×10^8 m/s):

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{3.91 \times 10^{14} \text{ /s}} = 7.6\underline{7}2 \times 10^{-7} = 7.67 \times 10^{-7} \text{ m, or } 767 \text{ nm}$$

7.2. Rearrange the equation $c = \nu\lambda$, which relates frequency to wavelength and the speed of light (3.00×10^8 m/s). Recognize that 456 nm = 4.56×10^{-7} m.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{4.56 \times 10^{-7} \text{ m}} = 6.5\underline{7}8 \times 10^{14} = 6.58 \times 10^{14} \text{ /s}$$

7.3. First, use the wavelengths to calculate the frequencies from $c = \nu\lambda$. Then calculate the energies using $E = h\nu$.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.0 \times 10^{-6} \text{ m}} = 3.\underline{0}0 \times 10^{14} \text{ /s}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.0 \times 10^{-8} \text{ m}} = 3.\underline{0}0 \times 10^{16} \text{ /s}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.0 \times 10^{-10} \text{ m}} = 3.\underline{0}0 \times 10^{18} \text{ /s}$$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J•s} \times 3.00 \times 10^{14} \text{ /s} = 1.\underline{9}89 \times 10^{-19} = 2.0 \times 10^{-19} \text{ J (IR)}$$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J•s} \times 3.00 \times 10^{16} \text{ /s} = 1.\underline{9}89 \times 10^{-17} = 2.0 \times 10^{-17} \text{ J (UV)}$$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J•s} \times 3.00 \times 10^{18} \text{ /s} = 1.\underline{9}89 \times 10^{-15} = 2.0 \times 10^{-15} \text{ J (x ray)}$$

The x-ray photon (shortest wavelength) has the greatest amount of energy; the infrared photon (longest wavelength) has the least amount of energy.

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7.4. From the formula for the energy levels, $E = -R_H/n^2$, obtain the expressions for both E_i and E_f. Then calculate the energy change for the transition from $n = 3$ to $n = 1$ by subtracting the lower value from the upper value. Set this equal to $h\nu$. The result is

$$\left[\frac{-R_H}{9}\right] - \left[\frac{-R_H}{1}\right] = \frac{8R_H}{9} = h\nu$$

The frequency of the emitted radiation is

$$\nu = \frac{8R_H}{9} = \frac{8}{9} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.63 \times 10^{-34}\ \text{J} \bullet \text{s}} = 2.921 \times 10^{15} = 2.92 \times 10^{15}\ /\text{s}$$

Since $\lambda = c/\nu$,

$$\lambda = \frac{3.00 \times 10^{8}\ \text{m/s}}{2.92 \times 10^{15}\ /\text{s}} = 1.027 \times 10^{-7} = 1.03 \times 10^{-7}\ \text{m, or } 103\ \text{nm}$$

7.5. Calculate the frequency from $c = \nu\lambda$, recognizing that 589 nm is 5.89×10^{-7} m.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{5.89 \times 10^{-7}\ \text{m}} = 5.093 \times 10^{14} = 5.09 \times 10^{14}\ /\text{s}$$

Finally, calculate the energy difference.

$$E = h\nu = 6.63 \times 10^{-34}\ \text{J} \bullet \text{s} \times 5.093 \times 10^{14}\ /\text{s} = 3.3766 \times 10^{-19} = 3.38 \times 10^{-19}\ \text{J}$$

7.6. To calculate wavelength, use the mass of an electron ($m = 9.11 \times 10^{-31}$ kg), and Planck's constant ($h = 6.63 \times 10^{-34}$ J•s, or 6.63×10^{-34} kg•m^2/s).

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{9.11 \times 10^{-31}\ \text{kg} \times 2.19 \times 10^{6}\ \text{m/s}} = 3.323 \times 10^{-10}\ \text{m}\ (332\ \text{pm})$$

7.7.

a. The value of n must be a positive whole number greater than zero. Here, it is zero. Also, if n is zero, there are no allowed values for l and m_l.

b. The values for l can range only from zero to $(n - 1)$. Here, l has a value greater than n.

c. The values for m_l range from $-l$ to $+l$. Here, m_l has a value greater than l.

d. The value for m_s is either + 1/2 or −1/2. Here, it is zero.

■ ANSWERS TO CONCEPT CHECKS

7.1. The frequency and wavelength are inversely related. Therefore, if the frequency is doubled, the wavelength is halved. Red light has a wavelength around 700 nm, so doubling its frequency halves its wavelength to about 350 nm, which is in the ultraviolet range just beyond the visible spectrum.

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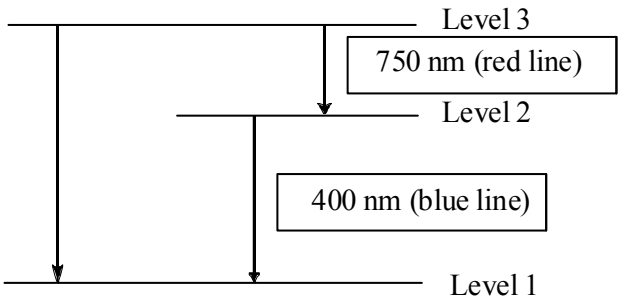
7.2. Since the transitions are between adjacent levels, the energy-level diagram must look something like the following diagram, with the red transition between two close levels and the blue transition between two more widely spaced levels. (The three levels could be spaced so the red and blue transitions are interchanged, with the blue transition above the red one.)



The transition from the top level to the lowest level would correspond to a transition that is greater in energy change than either of the other two transitions. Thus, the three transitions, from lowest to highest energy change, are in this order: red, blue, and the transition from the highest to lowest level. The last transition would have the highest frequency and therefore the shortest wavelength. It would lie just beyond the blue portion of the visible spectrum in the ultraviolet region.

7.3. The de Broglie relation says the wavelength of a particle is inversely proportional to both mass and speed. So, to maintain the wavelength constant while the mass increases would mean the speed would have to decrease. In going from a particle with the mass of an electron to one with that of a proton, the speed would have to decrease by a factor of about 2000 in order to maintain the same wavelength. The proton would have to have a speed approximately 2000 times slower than an electron of the same wavelength.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

7.1. Light is a wave, which is a form of electromagnetic radiation. In terms of waves, light can be described as a continuously repeating change, or oscillation, in electric and magnetic fields that can travel through space. Two characteristics of light are wavelength (often given in nanometers, nm) and frequency.

7.2. The relationship among the different characteristics of light waves is $c = \nu\lambda$, where ν is the frequency, λ is the wavelength, and c is the speed of light.

7.3. Starting with the shortest wavelengths, the electromagnetic spectrum consists of gamma rays, x rays, far ultraviolet (UV), near UV, visible light, near infrared (IR), far IR, microwaves, radar, and TV/FM radio waves (longest wavelengths).

7.4. The term *quantized* means the possible values of the energies of an atom are limited to only certain values. Planck was trying to explain the intensity of light of various frequencies emitted by a hot solid at different temperatures. The formula he arrived at was $E = nh\nu$, where E is energy, n is a whole number ($n = 1, 2, 3, \ldots$), h is Planck's constant, and ν is frequency.

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7.5. *Photoelectric effect* is the term applied to the ejection of electrons from the surface of a metal or from other materials when light shines on it. Electrons are ejected only when the frequency (or energy) of light is larger than a certain minimum, or threshold, value that is constant for each metal. If a photon has a frequency equal to or greater than this minimum value, then it will eject one electron from the metal surface.

7.6. The wave–particle picture of light regards the wave and particle depictions of light as complementary views of the same physical entity. In the equation $E = h\nu$, E is the energy of a light particle (photon) and ν is the frequency of the associated wave.

7.7. The equation that relates the particle properties of light is $E = h\nu$. The symbol E is energy, h is Planck's constant, and ν is the frequency of the light.

7.8. According to physical theory at Rutherford's time, an electrically charged particle revolving around a center would continuously lose energy as electromagnetic radiation. As an electron in an atom lost energy, it would spiral into the nucleus (in about 10^{-10} s). Thus, the stability of the atom could not be explained.

7.9. According to Bohr, an electron in an atom can have only specific energy values. An electron in an atom can change energy only by going from one energy level (of allowed energy) to another energy level (of allowed energy). An electron in a higher energy level can go to a lower energy level by emitting a photon of an energy equal to the difference in energy. However, when an electron is in its lowest energy level, no further changes in energy can occur. Thus, the electron does not continuously radiate energy as was thought at Rutherford's time. These features solve the difficulty alluded to in Question 7.8.

7.10. Emission of a photon occurs when an electron in a higher energy level undergoes a transition to a lower energy level. The energy lost is emitted as a photon.

7.11. Absorption, the reverse of emission, occurs when a photon of a certain required energy is absorbed by a certain electron in an atom. The energy of the photon must be equal to the energy necessary to excite the electron of the atom from a lower energy level, usually the lowest, to a higher energy level.

7.12. The quantum corral, shown in Figure 7.21, shows evidence of electron waves. A practical example of diffraction is the operation of the scanning tunneling microscope.

7.13. The square of a wave function equals the probability of finding an electron within a region of space.

7.14. The uncertainty principle says we can no longer think of the electron as having a precise orbit in an atom similar to the orbit of the planets around the sun. This principle says it is impossible to know with absolute precision both the position and the speed of a particle such as an electron.

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7.15. Quantum mechanics vastly changes Bohr's original picture of the hydrogen atom in that we can no longer think of the electron as having a precise orbit around the nucleus in this atom. Recall that Bohr's theory depended on the hydrogen electron having specific energy values and thus specific positions and speeds around the nucleus. But quantum mechanics and the uncertainty principle say it is impossible to know with absolute precision both the speed and the position of an electron. So Bohr's energy levels are only the most probable paths of the electrons.

7.16.

a. The principal quantum number can have an integer value between one and infinity.

b. The angular momentum quantum number can have any integer value between zero and $(n - 1)$.

c. The magnetic quantum number can have any integer value between $-l$ and $+l$.

d. The spin quantum number can be either +1/2 or −1/2.

7.17. The notation is 4*f*. This subshell contains seven orbitals.

7.18. An *s* orbital has a spherical shape. A *p* orbital has two lobes positioned along a straight line through the nucleus at the center of the line (a dumbbell shape).

7.19. The answer is d, an electron in the $n = 1$ level is higher in energy than an electron in the $n = 4$ level.

7.20. The answer is a, I only.

7.21. The answer is c, transition from the $n = 3$ to the $n = 1$ level.

7.22. The answer is a, 8.66×10^{-6} m.

■ ANSWERS TO CONCEPT EXPLORATIONS

7.23.

a. Red light has a greater wavelength than blue light.

b. The frequency of blue light is greater than that of red light.

c. The energy of blue light is greater than that of red light.

d. No, the speed of red light and the speed of blue light are the same, the constant speed of light.

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e. The energy of three photons of blue light is three times the energy of one photon of blue light. To compare the two energies, first note that the energy of n photons of light is $E = nh\nu$. Also, since $\nu = c/\lambda$, the energy can be written as $E = nhc/\lambda$. Now find the ratio as follows.

$$\frac{E_{blue}}{E_{red}} = \frac{\dfrac{n_{blue}hc}{\lambda_{blue}}}{\dfrac{n_{red}hc}{\lambda_{red}}} = \frac{n_{blue}\lambda_{red}}{n_{red}\lambda_{blue}} = \frac{(2)(704\text{ nm})}{(3)(451\text{ nm})} = 1.0\underline{4}0 = 1.04$$

Thus, the energy of two photons corresponding to a wavelength of 451 nm (blue light) is 1.04 times the energy of three photons corresponding to a wavelength of 704 nm (red light).

f. The frequency and energy of the light are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\text{ m/s}}{1.22 \times 10^{-6}\text{ m}} = 2.4\underline{5}9 \times 10^{14}/\text{s}$$

$$E = h\nu = (6.63 \times 10^{-34}\text{ J•s})(2.459 \times 10^{14}/\text{s}) = 1.6\underline{3}0 \times 10^{-19}\text{ J}$$

Now use the appropriate formula to determine the energy for a transition from $n = 1$ to $n = 2$, which is the minimum energy required for a transition to occur.

$$E = -R_H\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right) = -(2.179 \times 10^{-18}\text{J})\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 1.63\underline{4}5 \times 10^{-18}\text{ J}.$$

Since the available energy is less than the minimum energy required, no transition occurs.

g. One mole of hydrogen atoms would require a minimum of one mole of photons. First, use the appropriate formula to calculate the energy required for the transition.

$$E = -R_H\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right) = -(2.179 \times 10^{-18}\text{J})\left(\frac{1}{3^2} - \frac{1}{1^2}\right) = 1.93\underline{6}8 \times 10^{-18}\text{ J}.$$

The wavelength of the light is

$$\nu = \frac{E}{h} = \frac{1.9368 \times 10^{-18}\text{ J}}{6.63 \times 10^{-34}\text{ J•s}} = 2.92\underline{1} \times 10^{15}/\text{s}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\text{ m/s}}{2.921 \times 10^{15}\text{ /s}} = 1.0\underline{2}6 \times 10^{-7}\text{ m} = 1.03 \times 10^{-7}\text{ m} \quad (103\text{ nm})$$

7.24.

a. The ground-state energy levels of X and H are the same.

b. The energy of an electron in H would be lower (more negative) because $1/n^3$ is smaller than $1/n^2$.

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c. The spacing of the energy levels of hydrogen atoms is larger, because

$$\frac{1}{n^2} - \frac{1}{(n+1)^2} \text{ is greater than } \frac{1}{n^3} - \frac{1}{(n+1)^3}$$

Find the ratio of the energies as follows.

$$\frac{E_H}{E_X} = \frac{-R_H / n^2}{-R_H / n^3} = n$$

Thus, $E_H = nE_X$.

d. Since its energy-level spacings are larger, hydrogen would involve the emission of a higher frequency of light.

e. It will take the same energy to remove the electron from the ground state of H and X atoms. However, since its energy-level spacings are larger for an H atom, hydrogen would involve more energy to completely remove its electron from states other than the ground state.

f. No, since the energy spacings are different for these atoms, the amounts of energy required for a transition between the $n = 2$ and $n = 5$ levels are also different. The atoms will require photons of different energy.

■ ANSWERS TO CONCEPTUAL PROBLEMS

7.25. Wavelength and frequency are inversely related. Moreover, ultraviolet light is at higher frequency than yellow light. Doubling the frequency of a beam of light would give that beam a higher frequency than yellow light, whereas doubling the wavelength would give that beam a lower frequency than yellow light. Consequently, the beam with frequency doubled must be the one in the ultraviolet region. Here is another way to look at the problem. Energy is directly related to the frequency and inversely related to the wavelength. Thus, the beam whose frequency is doubled will increase in energy, whereas the beam whose wavelength is doubled will decrease in energy. Since yellow light is in the visible region of the spectrum, which is lower in energy than the ultraviolet region (Figure 7.5), the beam whose frequency is doubled will be higher in energy and thus in the UV region of the spectrum.

7.26. Frequency is inversely related to wavelength. Thus, the infrared radiation with a wavelength that is one thousand times larger than the visible light would have a frequency one thousand times smaller than the visible light. But, the visible light has a frequency that is one thousand times smaller than that of the X radiation. This makes the frequency of the X radiation one million times larger that the frequency of the infrared radiation. Therefore, since energy is directly related to the frequency, the energy of the X radiation would be one million times as large as the energy of the infrared radiation.

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7.27. That one color of light does not result in an ejection of electrons implies that that color has too little energy per photon. Of the two colors, red and green, red light has less energy per photon. Thus, you expect the experiment with red light to result in no ejection of photons, whereas the experiment with green light must be the one that ejects electrons. (Two red photons have more than enough energy to eject an electron, but this energy needs to be concentrated in only one photon to be effective.) In the photoelectric effect, one photon of light ejects at most one electron. Therefore, in the experiment with green light, one electron is ejected.

7.28. Ultraviolet radiation is higher in energy than red light (Figure 7.5). Since an atom that started in the ground state cannot emit more energy than it absorbed, the absorbed photon must be higher in energy than the emitted photon. This makes the emitted photon (photon 2) the red light.

7.29. Energy is inversely proportional to the wavelength of the radiation. The transition from the highest energy level to the lowest energy level would involve the greatest energy change and thus the shortest wavelength, *x* nm.

7.30. In a transition from the $n = 1$ to the $n = 5$ energy level, an atom will absorb a photon with the same energy as the photon that was emitted in the transition from the $n = 5$ to the $n = 1$ energy level. Since yellow light was emitted, the experiment using yellow light will promote the electron to the $n = 5$ level.

7.31. A proton is approximately 2000 times the weight of an electron. Also, from the de Broglie relation, $l = h/mv$, you see that the wavelength is inversely proportional to both the mass and the speed of the particle. Considering the protons in parts b and c, since the mass is the same in both parts, the proton with the smaller speed, part b, will have a longer wavelength. Now, comparing the electron in part a with the proton in part b, since both have the same speed, the electron in part a with the smaller mass will have the longer wavelength. Therefore, the electron in part a will have the longest wavelength.

7.32. For the first shell, the quantum numbers would have the following allowable values:

$n = 1 \qquad l = 1 \quad m_l = 0, +1, -1$

For the second shell, the quantum numbers would have the following allowable values:

$n = 2 \qquad l = 1 \quad m_l = 0, +1, -1$

$l = 2 \quad m_l = 0, +1, -1, +2, -2$

7.33.

a. The frequency is directly proportional to the energy difference between the two transition levels ($\Delta E = h\nu$). The lowest frequency corresponds with the smallest energy difference. Thus the transition from $n = 3$ to $n = 2$ will emit the lowest-frequency light.

b. The highest frequency corresponds with the largest energy difference. Thus the $n = 3$ to $n = 5$ transition will require (absorb) the highest-frequency light.

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c. Since the frequency is proportional to the energy difference between two transition levels, the energy difference is the same for absorption and transmission, and the color light is the same for both. Thus, green light is absorbed.

7.34.

a. The higher energy would correspond with the larger orbital, which is on the right.

b. Since the orbital on the right is higher in energy than the orbital on the left, the transition of an electron from the orbital on the right to the one on the left would be accompanied by the release of energy.

c. An orbital of the same type that is higher in energy would have the same width but would be taller.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off. Starting with Problem 7.35, the value 2.998×10^8 m/s will be used for the speed of light.

7.35. Solve $c = \lambda\nu$ for λ:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.365 \times 10^6 \text{ /s}} = 219.\underline{6}3 = 219.6 \text{ m}$$

7.36. Solve $c = \lambda\nu$ for λ:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.258 \times 10^{10} \text{ /s}} = 0.023\underline{8}31 = 0.02383 \text{ m} \quad (2.383 \text{ cm})$$

7.37. Solve $c = \lambda\nu$ for ν. Recognize that 478 nm = 478×10^{-9} m, or 4.78×10^{-7} m.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{4.78 \times 10^{-7} \text{ m}} = 6.2\underline{7}1 \times 10^{14} = 6.27 \times 10^{14} \text{ /s}$$

7.38. Solve $c = \lambda\nu$ for ν. Recognize that 656 nm = 656×10^{-9} m = 6.56×10^{-7} m.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{6.56 \times 10^{-7} \text{ m}} = 4.5\underline{7}0 \times 10^{14} = 4.57 \times 10^{14} \text{ /s}$$

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7.39. Radio waves travel at the speed of light, so divide the distance by c:

$$56 \times 10^9 \text{ m} \times \frac{1 \text{ s}}{2.998 \times 10^8 \text{ m}} = 186.7 = 1.9 \times 10^2 \text{ s}$$

7.40. Electromagnetic signals travel at the speed of light, so divide the distance by c:

$$998 \times 10^9 \text{ m} \times \frac{1 \text{ s}}{2.998 \times 10^8 \text{ m}} = 3328.8 = 3.33 \times 10^3 \text{ s} \ (0.925 \text{ hr})$$

7.41. To do the calculation, divide 1 meter by the number of wavelengths in 1 meter to find the wavelength of this transition. Then use the speed of light (with nine digits for significant figures) to calculate the frequency:

$$\lambda = \frac{1 \text{ m}}{1{,}650{,}763.73} = 6.057802106 \times 10^{-7} \text{ m}$$

$$\nu = \frac{c}{\lambda} = \frac{2.99792458 \times 10^8 \text{ m/s}}{6.057802106 \times 10^{-7} \text{ m}} = 4.948865162 \times 10^{14} = 4.94886516 \times 10^{14} \text{ /s}$$

7.42. To find the wavelength, divide the speed of light (with nine digits for significant figures) by the frequency:

$$\lambda = \frac{c}{\nu} = \frac{2.99792458 \times 10^8 \text{ m/s}}{9{,}192{,}631{,}770 \text{ /s}} = 0.032612255772 = 0.0326122557 \text{ m}$$

7.43. Solve for E, using $E = h\nu$, and use four significant figures for h:

$$E = h\nu = (6.626 \times 10^{-34} \text{ J•s}) \times (1.365 \times 10^6 \text{ /s}) = 9.0444 \times 10^{-28}$$
$$= 9.044 \times 10^{-28} \text{ J}$$

7.44. Solve for E, using $E = h\nu$, and use four significant figures for h:

$$E = h\nu = (6.626 \times 10^{-34} \text{ J•s}) \times (1.258 \times 10^{10} \text{ /s}) = 8.33550 \times 10^{-24}$$
$$= 8.336 \times 10^{-24} \text{ J}$$

7.45. Recognize that 535 nm = 535 x 10^{-9} m = 5.35 x 10^{-7} m. Then calculate ν and E.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{5.35 \times 10^{-7} \text{ m}} = 5.6037 \times 10^{14} \text{ /s}$$

$$E = h\nu = (6.626 \times 10^{-34} \text{ J•s}) \times (5.6037 \times 10^{14} \text{/s}) = 3.713 \times 10^{-19} = 3.71 \times 10^{-19} \text{ J}$$

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7.46. Recognize that 451 nm = 451 x 10^{-9} m = 4.51 x 10^{-7} m. Then calculate ν and E.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{4.51 \times 10^{-7}\ \text{m}} = 6.6\underline{4}74 \times 10^{14}\ \text{/s}$$

$$E = h\nu = (6.626 \times 10^{-34}\ \text{J•s}) \times (6.6474 \times 10^{14}\text{/s}) = 4.4\underline{0}4 \times 10^{-19} = 4.40 \times 10^{-19}\ \text{J}$$

7.47. First, calculate the wavelength of this transition from the frequency using the speed of light:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{3.84 \times 10^{14}\ \text{/s}} = 7.8\underline{0}72 \times 10^{-7} = 7.81 \times 10^{-7}\ \text{m}\ (781\ \text{nm})$$

Using Figure 7.5, note that 781 nm is just on the edge of the red end of the spectrum and is barely visible to the eye.

7.48. First, calculate the wavelength of this transition from the frequency using the speed of light:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{5.41 \times 10^{14}\ \text{/s}} = 5.5\underline{4}1 \times 10^{-7} = 5.54 \times 10^{-7}\ \text{m}\ (554\ \text{nm})$$

Using Figure 7.5, note that 554 nm is in the yellow-green region of the spectrum and is visible to the eye.

7.49. Solve the equation $E = -R_H/n^2$ for both E_5 and E_3; equate to $h\nu$, and solve for ν.

$$E = h\nu = = E_5 - E_3 = \frac{-R_H}{5^2} - \frac{-R_H}{3^2} = \frac{-R_H}{25} - \frac{-R_H}{9} = \frac{16R_H}{225}$$

The frequency of the emitted radiation is

$$\nu = \frac{16R_H}{225h} = \frac{16}{225} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J•s}} = 2.3\underline{3}8 \times 10^{14} = 2.34 \times 10^{14}\ \text{/s}$$

7.50. Solve the equation $E = -R_H/n^2$ for both E_4 and E_3; equate to $h\nu$, and solve for ν.

$$E = h\nu = = E_4 - E_3 = \frac{-R_H}{4^2} - \frac{-R_H}{3^2} = \frac{-R_H}{16} - \frac{-R_H}{9} = \frac{7R_H}{144}$$

The frequency of the emitted radiation is

$$\nu = \frac{7R_H}{144h} = \frac{7}{144} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J•s}} = 1.5\underline{9}86 \times 10^{14} = 1.60 \times 10^{14}\ \text{/s}$$

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7.51. Solve the equation $E = -R_H/n^2$ for both E_2 and E_1; solve for ν, and convert to λ.

$$E = h\nu = = E_2 - E_1 = \frac{-R_H}{2^2} - \frac{-R_H}{1^2} = \frac{-R_H}{4} - \frac{-R_H}{1} = \frac{3R_H}{4}$$

The frequency of the emitted radiation is

$$\nu = \frac{3R_H}{4h} = \frac{3}{4} \text{ x } \frac{2.179 \text{ x } 10^{-18} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s}} = 2.466 \text{ x } 10^{15} \text{ /s}$$

The wavelength can now be calculated.

$$\lambda = \frac{c}{\nu} = \frac{2.998 \text{ x } 10^8 \text{ m/s}}{2.466 \text{ x } 10^{15} \text{ /s}} = 1.2155 \text{ x } 10^{-7} = 1.22 \text{ x } 10^{-7} \text{ m (near UV)}$$

7.52. Solve the equation $E = -R_H/n^2$ for both E_5 and E_4; solve for ν, and convert to λ.

$$E = h\nu = = E_5 - E_4 = \frac{-R_H}{5^2} - \frac{-R_H}{4^2} = \frac{-R_H}{25} - \frac{-R_H}{16} = \frac{9R_H}{400}$$

The frequency of the emitted radiation is

$$\nu = \frac{9R_H}{400h} = \frac{9}{400} \text{ x } \frac{2.179 \text{ x } 10^{-18} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s}} = 7.399 \text{ x } 10^{13} \text{ /s}$$

The wavelength can now be calculated.

$$\lambda = \frac{c}{\nu} = \frac{2.998 \text{ x } 10^8 \text{ m/s}}{7.399 \text{ x } 10^{13} \text{ /s}} = 4.0517 \text{ x } 10^{-6} = 4.05 \text{ x } 10^{-6} \text{ m (near IR)}$$

7.53. This is the highest energy transition from the $n = 6$ level, so the electron must undergo a transition to the $n = 1$ level. Solve the Balmer equation using Bohr's approach:

$$E = h\nu = = E_6 - E_1 = \frac{-R_H}{6^2} - \frac{-R_H}{1^2} = \frac{-R_H}{36} - \frac{-R_H}{1} = \frac{35R_H}{36}$$

The frequency of the emitted radiation is

$$\nu = \frac{35R_H}{36h} = \frac{35}{36} \text{ x } \frac{2.179 \text{ x } 10^{-18} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s}} = 3.197 \text{ x } 10^{15} \text{ /s}$$

The wavelength can now be calculated.

$$\lambda = \frac{c}{\nu} = \frac{2.998 \text{ x } 10^8 \text{ m/s}}{3.197 \text{ x } 10^{15} \text{ /s}} = 9.3769 \text{ x } 10^{-8} = 9.38 \text{ x } 10^{-8} \text{ m (93.8 nm)}$$

7.54. This is the lowest energy transition from the $n = 7$ level, so the electron must undergo a transition to the $n = 6$ level. Solve the Balmer equation using Bohr's approach:

$$E = h\nu = = E_7 - E_6 = \frac{-R_H}{7^2} - \frac{-R_H}{6^2} = \frac{-R_H}{49} - \frac{-R_H}{36} = \frac{13R_H}{1764}$$

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The frequency of the emitted radiation is

$$\nu = \frac{13R_H}{1764h} = \frac{13}{1764} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J} \bullet \text{s}} = 2.4235 \times 10^{13}\ /\text{s}$$

The wavelength can now be calculated.

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{2.4235 \times 10^{13}\ /\text{s}} = 1.2370 \times 10^{-5} = 1.237 \times 10^{-5}\ \text{m}\ \ (12.37\ \mu\text{m})$$

7.55. Noting that 422.7 nm = 4.227×10^{-7} m, convert the 422.7 nm to frequency. Then convert the frequency to energy using $E = h\nu$.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{4.227 \times 10^{-7}\ \text{m}} = 7.0925 \times 10^{14}\ /\text{s}$$

$$E = h\nu = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s}) \times 7.0925 \times 10^{14}\ /\text{s}) = 4.6994 \times 10^{-19}$$

$$= 4.699 \times 10^{-19}\ \text{J}$$

7.56. Noting that 285.2 nm = 2.852×10^{-7} m, convert the 285.2-nm wavelength to frequency. Then convert the frequency to energy using $E = h\nu$.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{2.852 \times 10^{-7}\ \text{m}} = 1.0511 \times 10^{15}\ /\text{s}$$

$$E = h\nu = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s}) \times 1.0511 \times 10^{15}\ /\text{s}) = 6.96458 \times 10^{-19}$$

$$= 6.965 \times 10^{-19}\ \text{J}$$

7.57. The mass of a neutron = 1.67493×10^{-27} kg. Its speed or velocity, v, of 4.15 km/s equals 4.15×10^{3} m/s. Substitute these parameters into the de Broglie relation, and solve for λ:

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{1.67493 \times 10^{-27}\ \text{kg} \times 4.15 \times 10^{3}\ \text{m/s}} = 9.532 \times 10^{-11} = 9.53 \times 10^{-11}\ \text{m}$$

A wavelength of 9.53×10^{-11} m (95.3 pm) would be in the x-ray region of the spectrum.

7.58. The mass of a proton = 1.67262×10^{-27}. Its speed or velocity, v, of 6.58 km/s equals 6.58×10^{3} m/s. Substitute these parameters into the de Broglie relation, and solve for λ:

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{1.67262 \times 10^{-27}\ \text{kg} \times 6.58 \times 10^{3}\ \text{m/s}} = 6.020 \times 10^{-11} = 6.02 \times 10^{-11}\ \text{m}$$

A wavelength of 6.02×10^{-11} m (60.2 pm) would be in the x-ray region of the spectrum.

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7.59. The mass of an electron equals 9.109×10^{-31} kg. The wavelength, λ, given as 10.0 pm, is equivalent to 1.00×10^{-11} m. Substitute these parameters into the de Broglie relation, and solve for the frequency, ν:

$$\nu = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{9.109 \times 10^{-31}\ \text{kg} \times 1.00 \times 10^{-11}\ \text{m}} = 7.274 \times 10^{7} = 7.27 \times 10^{7}\ \text{m/s}$$

7.60. The mass of a neutron equals 1.67493×10^{-27} kg. The wavelength, λ, given as 12.0 pm, is equivalent to 1.20×10^{-11} m. Substitute these parameters into the de Broglie relation, and solve for the frequency, ν:

$$\nu = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{1.67493 \times 10^{-27}\ \text{kg} \times 1.20 \times 10^{-11}\ \text{m}} = 3.296 \times 10^{4} = 3.30 \times 10^{4}\ \text{m/s}$$

7.61. Substitute the 1.45×10^{-1} kg mass of the baseball and the 30.0 m/s velocity, v, into the de Broglie relation, and solve for wavelength (recall that 1 pm = 10^{-12} m).

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{1.45 \times 10^{-1}\ \text{kg} \times 30.0\ \text{m/s}} = 1.523 \times 10^{-34} = 1.52 \times 10^{-34}\ \text{m}$$

$$= 1.52 \times 10^{-22}\ \text{pm}$$

Because this is much smaller than 100 pm, the wavelength is much smaller than the diameter of one atom.

7.62. The mass of O_2 to three significant figures is $32.00 \div 6.022 \times 10^{23} = 5.313 \times 10^{-23}$ g = 5.313×10^{-26} kg. Substitute this mass and the 521 m/s velocity, v, into the de Broglie relation, and solve for wavelength (recall that 1 pm = 10^{-12} m).

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg} \bullet \text{m}^2/\text{s}}{5.313 \times 10^{-26}\ \text{kg} \times 521\ \text{m/s}} = 2.3937 \times 10^{-11} = 2.39 \times 10^{-11}\ \text{m}$$

$$= 23.9\ \text{pm}$$

Because this is on the order of 100 pm, the wavelength is on the order of an atomic diameter.

7.63. The possible values of l range from zero to $(n - 1)$, so l may be 0, 1, 2, or 3. The possible values of m_l range from $-l$ to $+l$, so m_l may be −3, −2, −1, 0, +1, +2, or +3.

7.64. The possible l values are 0, 1, 2, 3, 4, and 5. The possible m_l values are −5, −4, −3, −2, −1, 0, 1, 2, 3, 4, or 5.

7.65. For the M shell, $n = 3$; there are three subshells in this shell ($l = 0$, 1, and 2). An f subshell has $l = 3$; the number of orbitals in this subshell is $2(3) + 1 = 7$ ($m_l = -3, -2, -1, 0, 1, 2$, and 3).

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7.66. For the N shell, $n = 4$; there are four subshells in this shell ($l = 0$, 1, 2, and 3). For a *g* subshell, the value of $l = 4$; the number of orbitals in this subshell is $2(4) + 1 = 9$ ($m_l = -4, -3, -2, -1, 0, 1, 2, 3$, and 4).

7.67.

a. 6*d*

b. 5*g*

c. 4*f*

d. 6*p*

7.68.

a. 3*d*

b. 4*s*

c. 4*p*

d. 5*f*

7.69.

a. Not permissible; m_s can be only +1/2 or −1/2.

b. Not permissible; l can be only as large as $(n - 1)$.

c. Not permissible; m_l cannot exceed +2 in magnitude.

d. Not permissible; n cannot be zero.

e. Not permissible; m_s can be only + 1/2 or −1/2.

7.70.

a. Permissible.

b. Not permissible; l can be only as large as $(n - 1)$.

c. Not permissible; n starts at 1, not at zero.

d. Permissible.

e. Not permissible; m_l cannot exceed l in magnitude.

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■ SOLUTIONS TO GENERAL PROBLEMS

7.71. Use $c = \nu\lambda$ to calculate frequency; then use $E = h\nu$ to calculate energy.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8} \text{ m/s}}{4.61 \times 10^{-7} \text{ m}} = 6.5\underline{0}3 \times 10^{14} = 6.50 \times 10^{14} \text{ /s}$$

$$E = h\nu = (6.626 \times 10^{-34} \text{ J•s}) \times (6.503 \times 10^{14}\text{/s}) = 4.3\underline{0}9 \times 10^{-19} = 4.31 \times 10^{-19} \text{ J}$$

7.72. Use $c = \nu\lambda$ to calculate frequency; then use $E = h\nu$ to calculate energy.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8} \text{ m/s}}{5.54 \times 10^{-7} \text{ m}} = 5.4\underline{1}15 \times 10^{14} = 5.41 \times 10^{14} \text{ /s}$$

$$E = h\nu = (6.626 \times 10^{-34} \text{ J•s}) \times (5.4115 \times 10^{14}\text{/s}) = 3.5\underline{8}56 \times 10^{-19} = 3.59 \times 10^{-19} \text{ J}$$

7.73. Calculate the frequency corresponding to 4.10×10^{-19} J. Then convert that to wavelength.

$$\nu = \frac{E}{h} = \frac{4.10 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \bullet \text{s}} = 6.1\underline{8}7 \times 10^{14} \text{ /s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8} \text{ m/s}}{6.187 \times 10^{14} \text{ /s}} = 4.8\underline{4}5 \times 10^{-7} = 4.85 \times 10^{-7} \text{ m} = 485 \text{ nm (blue)}$$

7.74. Calculate the frequency corresponding to 3.34×10^{-19} J. Then convert that to wavelength.

$$\nu = \frac{E}{h} = \frac{3.34 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \bullet \text{s}} = 5.0\underline{4}07 \times 10^{14} \text{ /s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8} \text{ m/s}}{5.0407 \times 10^{14} \text{ /s}} = 5.9\underline{4}7 \times 10^{-7} = 5.95 \times 10^{-7} \text{ m} = 595 \text{ nm (yellow)}$$

7.75. Solve for frequency using $E = h\nu$.

$$\nu = \frac{E}{h} = \frac{4.34 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \bullet \text{s}} = 6.5\underline{4}9 \times 10^{14} = 6.55 \times 10^{14} \text{ /s}$$

7.76. Solve for frequency using $E = h\nu$.

$$\nu = \frac{E}{h} = \frac{5.90 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \bullet \text{s}} = 8.9\underline{0}4 \times 10^{14} = 8.90 \times 10^{14} \text{ /s}$$

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7.77. First calculate E_p, the energy of the 345-nm photon, noting that it is equivalent to 3.45×10^{-7} m.

$$E_p = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \bullet \text{s})(2.998 \times 10^{8}\ \text{m/s})}{3.45 \times 10^{-7}\ \text{m}} = 5.7\underline{5}78 \times 10^{-19}\ \text{J}$$

Now, subtract the work function of Ca = 4.34×10^{-19} J (Problem 7.75) from E_p:

$$5.7578 \times 10^{-19}\ \text{J} - 4.34 \times 10^{-19}\ \text{J} = 1.4\underline{1}78 \times 10^{-19}\ \text{J}$$

Note that for this situation, $E = 1/2mv^2$. Recall that the mass of the electron is 9.1095×10^{-31} kg. Now calculate speed, v:

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2 \times 1.4178 \times 10^{-19}\ \text{J}}{9.1095 \times 10^{-31}\ \text{kg}}} = 5.5\underline{7}9 \times 10^{5} = 5.58 \times 10^{5}\ \text{m/s}$$

7.78. First calculate E_p, the energy of the 276-nm photon, noting that it is equivalent to 2.76×10^{-7} m.

$$E_p = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \bullet \text{s})(2.998 \times 10^{8}\ \text{m/s})}{2.76 \times 10^{-7}\ \text{m}} = 7.1\underline{9}7 \times 10^{-19}\ \text{J}$$

Now, subtract the work function of Mg = 5.90×10^{-19} J (Problem 7.76) from E_p:

$$7.197 \times 10^{-19}\ \text{J} - 5.90 \times 10^{-19}\ \text{J} = 1.2\underline{9}7 \times 10^{-19}\ \text{J}$$

Note that for this situation, $E = 1/2mv^2$. Recall that the mass of the electron is 9.1095×10^{-31} kg. Now calculate speed, v:

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2 \times 1.297 \times 10^{-19}\ \text{J}}{9.1095 \times 10^{-31}\ \text{kg}}} = 5.3\underline{3}7 \times 10^{5} = 5.34 \times 10^{5}\ \text{m/s}$$

7.79. This is a transition from the $n = 5$ level to the $n = 2$ level. Solve the Balmer equation using Bohr's approach.

$$E = h\nu = = E_5 - E_2 = \frac{-R_H}{5^2} - \frac{-R_H}{2^2} = \frac{-R_H}{25} - \frac{-R_H}{4} = \frac{21R_H}{100}$$

The wavelength can now be calculated.

$$\nu = \frac{21R_H}{100h} = \frac{21}{100} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J} \bullet \text{s}} = 6.9\underline{0}59 \times 10^{14}\ \text{/s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{6.9059 \times 10^{14}\ \text{/s}} = 4.3\underline{4}1 \times 10^{-7} = 4.34 \times 10^{-7}\ \text{m}\ (434\ \text{nm})$$

7.80. This is a transition from the $n = 6$ level to the $n = 2$ level. Solve the Balmer equation using Bohr's approach.

$$E = h\nu = = E_6 - E_2 = \frac{-R_H}{6^2} - \frac{-R_H}{2^2} = \frac{-R_H}{36} - \frac{-R_H}{4} = \frac{32R_H}{144}$$

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The wavelength can now be calculated.

$$\nu = \frac{32R_H}{144h} = \frac{32}{144} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J} \bullet \text{s}} = 7.30\underline{7}9 \times 10^{14}\ /\text{s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{7.3079 \times 10^{14}\ /\text{s}} = 4.10\underline{2}4 \times 10^{-7} = 4.102 \times 10^{-7}\ \text{m}\ (410.2\ \text{nm})$$

7.81. Use 397 nm = 3.97×10^{-7} m, and convert to frequency and then to energy.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{3.97 \times 10^{-7}\ \text{m}} = 7.5\underline{5}1 \times 10^{14}\ /\text{s}$$

$$E = h\nu = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s}) \times (7.551 \times 10^{14}) = 5.0\underline{0}37 \times 10^{-19}\ \text{J}$$

Substitute this energy into the Balmer formula, recalling that the Balmer series is an emission spectrum, so ΔE is negative:

$$E = E_2 - E_i = \frac{-R_H}{2^2} - \frac{-R_H}{n_i^2} = \frac{-R_H}{4} - \frac{-R_H}{n_i^2} = 5.0037 \times 10^{-19}\ \text{J}$$

$$\frac{1}{4} - \frac{1}{n_i^2} = \frac{\Delta E}{-R_H} = \frac{-5.0037 \times 10^{-19}\ \text{J}}{-2.179 \times 10^{-18}\ \text{J}} = 0.22\underline{9}63$$

$$\frac{1}{n_i^2} = \frac{1}{4} - 0.22\underline{9}63 = 0.02\underline{0}36$$

$$n_i = \left[\frac{1}{0.02036}\right]^{1/2} = 7.\underline{0}07 = 7.0\ (= n)$$

7.82. Convert 9.50×10^{-8} m to frequency and then to energy.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{9.50 \times 10^{-8}\ \text{m}} = 3.1\underline{5}57 \times 10^{15}\ /\text{s}$$

$$E = h\nu = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s}) \times (3.1557 \times 10^{15}) = 2.0\underline{9}10 \times 10^{-18}\ \text{J}$$

Substitute this energy into the Balmer formula, recalling that the Lyman series is an emission spectrum, so ΔE is negative, and $n_f = 1$:

$$E = E_1 - E_i = \frac{-R_H}{1^2} - \frac{-R_H}{n_i^2} = \frac{-R_H}{1} - \frac{-R_H}{n_i^2} = 2.0\underline{9}10 \times 10^{-18}\ \text{J}$$

$$1 - \frac{1}{n_i^2} = \frac{\Delta E}{-R_H} = \frac{-2.0910 \times 10^{-18}\ \text{J}}{-2.179 \times 10^{-18}\ \text{J}} = 0.95\underline{9}62$$

$$\frac{1}{n_i^2} = 1 - 0.95962 = 0.04\underline{0}37$$

$$n_i = \left[\frac{1}{0.04037}\right]^{1/2} = 4.\underline{9}76 = 5\ (= n)$$

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7.83. Employ the Balmer formula using $Z = 2$ for the He^+ ion.

$$E = h\nu = E_3 - E_2 = \frac{-(2^2)R_H}{3^2} - \frac{-(2^2)R_H}{2^2} = \frac{-4R_H}{9} - \frac{-4R_H}{4} = \frac{20R_H}{36}$$

The frequency of the radiation is

$$\nu = \frac{20R_H}{36h} = \frac{20}{36} \times \frac{2.179 \times 10^{-18}\ J}{6.626 \times 10^{-34}\ J \bullet s} = 1.82\underline{6}9 \times 10^{15}\ /s$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ m/s}{1.8269 \times 10^{15}\ /s} = 1.64\underline{0}9 \times 10^{-7} = 1.641 \times 10^{-7}\ m \ \ (164.1\ nm;\ near\ UV)$$

7.84. Employ the Balmer formula using $Z = 3$ for the Li^{2+} ion.

$$E = h\nu = E_5 - E_3 = \frac{-(3^2)R_H}{5^2} - \frac{-(3^2)R_H}{3^2} = \frac{-9R_H}{25} - \frac{-9R_H}{9} = \frac{144R_H}{225}$$

$$\nu = \frac{144R_H}{225h} = \frac{144}{225} \times \frac{2.179 \times 10^{-18}\ J}{6.626 \times 10^{-34}\ J \bullet s} = 2.10\underline{4}6 \times 10^{15}\ /s$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ m/s}{2.1046 \times 10^{15}\ /s} = 1.42\underline{4}4 \times 10^{-7} = 1.424 \times 10^{-7}\ m \ \ (142.4\ nm;\ UV)$$

7.85. First, use the wavelength of 10.0 pm (1.00×10^{-11} m) and the mass of 9.1095×10^{-31} kg to calculate the velocity, *v*. Then use the kinetic energy equation to calculate kinetic energy from velocity.

$$v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\ kg \bullet m^2/s}{9.1095 \times 10^{-31}\ kg \times 1.00 \times 10^{-11}\ m} = 7.2\underline{7}37 \times 10^{7}\ m/s$$

$$E = 1/2mv^2 = 1/2 \times (9.1095 \times 10^{-31}\ kg) \times (7.273 \times 10^{7}\ m/s)^2 = 2.4\underline{0}9 \times 10^{-15}\ J$$

$$E_{eV} = 2.409 \times 10^{-15}\ J \times \frac{1\ eV}{1.602 \times 10^{-19}\ J} = 1.5\underline{0}3 \times 10^{4} = 1.50 \times 10^{4}\ eV$$

7.86. First, use the wavelength of 10.0 pm (1.00×10^{-11} m) and the mass of 1.675×10^{-27} kg to calculate the velocity, *v*. Then use the kinetic energy equation to calculate kinetic energy from velocity.

$$v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\ kg \bullet m^2/s}{1.675 \times 10^{-27}\ kg \times 1.00 \times 10^{-11}\ m} = 3.9\underline{5}58 \times 10^{4}\ m/s$$

$$E = 1/2mv^2 = 1/2 \times (1.675 \times 10^{-27}\ kg) \times (3.9558 \times 10^{4}\ m/s)^2 = 1.3\underline{1}05 \times 10^{-18}\ J$$

$$E_{eV} = 1.3105 \times 10^{-18}\ J \times \frac{1\ eV}{1.602 \times 10^{-19}\ J} = 8.1803 = 8.18\ eV$$

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7.87.

a. Five
b. Seven
c. Three
d. One

7.88

a. Nine
b. Seven
c. One
d. Three

7.89. The possible subshells for the $n = 6$ shell are 6*s*, 6*p*, 6*d*, 6*f*, 6*g*, and 6*h*.

7.90. The possible subshells for the $n = 7$ shell are 7*s*, 7*p*, 7*d*, 7*f*, 7*g*, 7*h*, and 7*i*.

7.91. Gamma rays are a form of electromagnetic radiation similar to x rays, but the photons of gamma rays have higher energy. High-energy radiation kills bacteria and molds in foods by breaking up the DNA molecules within their cells.

7.92. The gamma rays come from the radioactive decay of cobalt-60. Food is not made radioactive by irradiating it with gamma rays.

7.93. When a photon of appropriate wavelength is used to flash the laser crystal, it stimulates a transition, and a photon of exactly the same wavelength as the original photon is emitted. In place of just one photon, there are now two photons. The net effect is to increase the intensity of the light at this wavelength.

7.94. Music is encoded on a CD in the form of pits, or indentations, on a spiral track. When the disc is played, a small laser beam scans the track and is reflected back to a detector. Light reflected from an indentation is out of phase with light from the laser and interferes with it, reducing the intensity of the wave. As the disc moves around, light is reflected either from the main surface at full intensity (on) or from a pit at reduced intensity (off). A light-sensitive detector converts this reflected light to a digital signal, and a converter changes the signal to one that speakers can accept.

7.95. Tunneling depends on the probability interpretation of quantum mechanics. The probability of an electron in an atom being at a location far from atom A and near atom B is very small but not zero. This means that an electron that normally belongs to atom A can find itself near atom B without any extra energy having been supplied. The electron is said to have tunneled from one atom to another.

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7.96. If the probe is close enough to the sample, electrons can tunnel from the probe to the sample, which gives rise to a measurable electric current. The magnitude of the current depends on the distance between the probe and the sample. By adjusting this distance, the current can be maintained at a fixed value. As the probe scans the sample, it moves toward or away from the sample to maintain a fixed current, following the contours of the sample.

■ SOLUTIONS TO STRATEGY PROBLEMS

7.97. $\lambda = \dfrac{c}{\nu} = \dfrac{3.00 \times 10^{8}\ \text{m/s}}{7.76 \times 10^{9}\ \text{/s}} = 0.03865\ \text{m} = 0.0387\ \text{m}$

7.98. $E = h\nu = (6.63 \times 10^{-34}\ \text{J•s})(1.69 \times 10^{6}\ \text{/s}) = 1.120 \times 10^{-27} = 1.12 \times 10^{-27}\ \text{J}$

7.99. $\nu = \dfrac{E}{h} = \dfrac{4.60 \times 10^{-19}\ \text{J}}{6.63 \times 10^{-34}\ \text{Js}} = 6.938 \times 10^{14}\ \text{/s}$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\ \text{m/s}}{6.938 \times 10^{14}\ \text{/s}} = 4.323 \times 10^{-7} = 4.32 \times 10^{-7}\ \text{m} = 432\ \text{nm}$$

7.100. The shortest wavelength of visible light is for the $n = 6$ to $n = 2$ transition.

$$E = h\nu = = E_6 - E_2 = \frac{-R_H}{6^2} - \frac{-R_H}{2^2} = \frac{-R_H}{36} - \frac{-R_H}{4} = \frac{32R_H}{144}$$

The wavelength can now be calculated.

$$\nu = \frac{32R_H}{144h} = \frac{32}{144} \times \frac{2.179 \times 10^{-18}\ \text{J}}{6.63 \times 10^{-34}\ \text{J} \bullet \text{s}} = 7.303 \times 10^{14}\ \text{/s}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\ \text{m/s}}{7.303 \times 10^{14}\ \text{/s}} = 4.107 \times 10^{-7} = 4.11 \times 10^{-7}\ \text{m}\ (411\ \text{nm})$$

Figure 7.11 includes all the visible lines in the hydrogen spectrum.

7.101. Light of wavelength 1.03×10^{-7} m (103 nm) is in the ultraviolet region of the spectrum. The frequency and energy of this radiation are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.03 \times 10^{-7}\ \text{m}} = 2.912 \times 10^{15}\ \text{/s}$$

$$E = h\nu = (6.63 \times 10^{-34}\ \text{J•s})(2.912 \times 10^{15}\ \text{/s}) = 1.931 \times 10^{-18}\ \text{J}$$

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Now use the appropriate formula to determine the quantum number of the excited (n_i) level. Remember, ΔE is negative for an emission spectrum.

$$\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_H \left(\frac{1}{1^2} - \frac{1}{n_i^2} \right) = -R_H \left(1 - \frac{1}{n_i^2} \right)$$

$$1 - \frac{1}{n_i^2} = \frac{-\Delta E}{-R_H} = \frac{1.931 \times 10^{-18}\ \text{J}}{2.179 \times 10^{-18}\ \text{J}} = 0.88\underline{6}2$$

$$n_i = \sqrt{\frac{1}{1 - 0.8862}} = 2.9\underline{6}4 = 2.96$$

Thus, the quantum number of the excited level is 3.

7.102. First, determine the energy of one photon.

$$E = \frac{799\ \text{kJ}}{1\ \text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{photons}} = 1.3\underline{2}6 \times 10^{-18}\ \text{J}$$

The wavelength can now be determined.

$$\nu = \frac{E}{h} = \frac{1.326 \times 10^{-18}\ \text{J}}{6.63 \times 10^{-34}\ \text{J} \bullet \text{s}} = 2.0\underline{0}1 \times 10^{15}\ /\text{s}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\ \text{m/s}}{2.001 \times 10^{15}\ /\text{s}} = 1.4\underline{9}9 \times 10^{-7} = 1.50 \times 10^{-7}\ \text{m} \quad (150.\ \text{nm})$$

This corresponds to a photon in the near ultra violet region of the spectrum, which is represented by the Lyman series in hydrogen. The minimum energy for a transition in this region corresponds to the $n = 2$ to $n = 1$ transition.

$$\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_H \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{-3R_H}{4} = \frac{-(3)(2.179 \times 10^{-18}\ \text{J})}{4}$$

$$= -1.63\underline{4}2 \times 10^{-18}\ \text{J}$$

This is more than the energy required per photon to break the bond.

7.103. First, calculate the mass of one oxygen molecule.

$$m = \frac{32.00\ \text{g O}_2}{1\ \text{mol}} \times \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{molec}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 5.3\underline{1}3 \times 10^{-26}\ \text{kg}$$

Now the de Broglie wavelength can be calculated.

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{J} \bullet \text{s}}{(5.313 \times 10^{-26}\ \text{kg})(479\ \text{m/s})} = 2.6\underline{0}3 \times 10^{-11} = 2.60 \times 10^{-11}\ \text{m} \quad (26.0\ \text{pm})$$

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This wavelength can be compared to the length of the molecule (242 pm) as follows.

$$\frac{26.03 \text{ pm}}{242 \text{ pm}} \times 100\% = 10.\underline{7}5\% = 10.8\%$$

Thus, the de Broglie wavelength is 10.8% of the length of the molecule.

7.104. The energy required to heat the water is

$$E = s \times m \times \Delta t = (4.18 \text{ J/mol}\bullet\text{°C})(1.00 \text{ g})(1.00\text{°C}) = 4.18 \text{ J}$$

The microwave radiation has a wavelength of 12.2 cm (0.122 m), so the frequency and energy are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \text{ m/s}}{0.122 \text{ m}} = 2.4\underline{5}9 \times 10^{9} \text{ /s}$$

$$E = h\nu = (6.63 \times 10^{-34} \text{ J}\bullet\text{s})(2.459 \times 10^{9} \text{ /s}) = 1.6\underline{3}0 \times 10^{-24} \text{ J/photon}$$

Therefore, the number of photons needed to heat the water is

$$n = \frac{4.18 \text{ J}}{1.630 \times 10^{-24} \text{ J/photon}} = 2.5\underline{6}3 \times 10^{24} = 2.56 \times 10^{24} \text{ photons}$$

7.105.

a. Change m_l to 0 ($n = 3$, $l = 0$, $m_l = 0$) for a count of 1.

b. Change l to 4 ($n = 5$, $l = 4$, $m_l = 4$) for a count of 2.

c. Change n to 4 ($n = 4$, $l = 3$, $m_l = -3$) for a count of 3.

d. Change l to 4 ($n = 5$, $l = 4$, $m_l = 3$) for a count of 2.

The total count is $1 + 2 + 3 + 2 = 8$.

7.106. For the $n = 5$ level, the sublevels are 5*s*, 5*p*, 5*d*, 5*f*, and 5*g*. The numbers of orbitals for the sublevels are 1, 3, 5, 7, and 9, respectively. The total number of orbitals for the $n = 5$ level is therefore $1 + 3 + 5 + 7 + 9 = 25$.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

7.107. First, use Avogadro's number to calculate the energy for one Cl_2 molecule.

$$\frac{239 \text{ kJ}}{1 \text{ mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 3.9\underline{6}87 \times 10^{-19} \text{ J/molecule}$$

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Then convert energy to frequency and finally to wavelength.

$$\nu = \frac{E}{h} = \frac{3.9687 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{J} \bullet \text{s}} = 5.9\underline{8}97 \times 10^{14}\ /\text{s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{5.9897 \times 10^{14}\ /\text{s}} = 5.0\underline{0}52 \times 10^{-7}\ \text{m}\ \ (501\ \text{nm; visible region})$$

7.108. First, use Avogadro's number to calculate the energy per H_2 molecule.

$$\frac{432\ \text{kJ}}{1\ \text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{molecules}} = 7.1\underline{7}36 \times 10^{-19}\ \text{J/molecule}$$

Then convert energy to frequency and finally to wavelength.

$$\nu = \frac{E}{h} = \frac{7.1736 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{J} \bullet \text{s}} = 1.0\underline{8}26 \times 10^{15}\ /\text{s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m/s}}{1.0826 \times 10^{15}\ /\text{s}} = 2.7\underline{6}91 \times 10^{-7}\ \text{m}\ \ (277\ \text{nm; UV})$$

7.109. First, calculate the energy needed to heat the 0.250 L of water from 20.0°C to 100.0°C.

$$0.250\ \text{L} \times \frac{1000\ \text{g}}{1\ \text{L}} \times \frac{4.184\ \text{J}}{(\text{g} \bullet ^\circ\text{C})} \times (100.0\ ^\circ\text{C} - 20.0^\circ\text{C}) = 8.3\underline{6}8 \times 10^{4}\ \text{J}$$

Then calculate the frequency, the energy of one photon, and the number of photons.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{0.125\ \text{m}} = 2.3\underline{9}8 \times 10^{9}\ /\text{s}$$

$$E \text{ of one photon} = h\nu = (6.626 \times 10^{-34}\ \text{J} \bullet \text{s}) \times (2.398 \times 10^{9}/\text{s}) = 1.5\underline{8}9 \times 10^{-24}\ \text{J}$$

$$n = 8.368 \times 10^{4}\ \text{J} \times \frac{1\ \text{photon}}{1.589 \times 10^{-24}\ \text{J}} = 5.2\underline{6}56 \times 10^{28} = 5.27 \times 10^{28}\ \text{photons}$$

7.110. First, calculate the energy needed to heat the 1.00 L of water from 20.0°C to 30.0°C.

$$1.00\ \text{L} \times \frac{1000\ \text{g}}{1\ \text{L}} \times \frac{4.184\ \text{J}}{(\text{g} \bullet ^\circ\text{C})} \times (30.0\ ^\circ\text{C} - 20.0^\circ\text{C}) = 4.1\underline{8}4 \times 10^{4}\ \text{J}$$

Then calculate the frequency, the energy of one photon, and the number of photons.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{m/s}}{2.80 \times 10^{-6}\ \text{m}} = 1.0\underline{7}07 \times 10^{14}\ /\text{s}$$

$$E \text{ of one photon} = h\nu = (6.626 \times 10^{-34}\ \text{J} \bullet \text{s}) \times (1.0707 \times 10^{14}/\text{s}) = 7.0\underline{9}45 \times 10^{-20}\ \text{J}$$

$$n = 4.184 \times 10^{4}\ \text{J} \times \frac{1\ \text{photon}}{7.0945 \times 10^{-20}\ \text{J}} = 5.8\underline{9}74 \times 10^{23} = 5.90 \times 10^{23}\ \text{photons}$$

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7.111. First, write the following equality for the energy to remove one electron, E_{removal}:

$$E_{\text{removal}} = E_{425\text{ nm}} - E_k \text{ of ejected photon}$$

Use $E = h\nu$ to calculate the energy of the photon. Then recall that E_k, the kinetic energy, is $1/2mv^2$. Use this to calculate E_k.

$$E_{425\text{ nm}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{ J}\cdot\text{s})(2.998 \times 10^{8}\text{ m/s})}{4.25 \times 10^{-7}\text{ m}} = 4.6740 \times 10^{-19}\text{ J}$$

$$E_k = 1/2mv^2 = 1/2 \times (9.1095 \times 10^{-31}\text{ kg}) \times (4.88 \times 10^{5}\text{ m/s})^2 = 1.0846 \times 10^{-19}\text{ J}$$

Subtract to find E_{removal}, and convert it to kJ/mol:

$$E_{\text{removal}} = 4.6740 \times 10^{-19}\text{ J} - (1.0847 \times 10^{-19}\text{ J}) = 3.5893 \times 10^{-19} = 3.59 \times 10^{-19}\text{ J/electron}$$

$$E_{\text{removal}} = \frac{3.5893 \times 10^{-19}\text{ J}}{1\text{ e}^-} \times \frac{6.022 \times 10^{23}\text{ e}^-}{1\text{ mol}} \times \frac{1\text{ kJ}}{1000\text{ J}} = 2.161 \times 10^{2}$$

$$= 2.16 \times 10^{2}\text{ kJ/mol}$$

7.112. First, write the following equality for the energy to remove one electron, E_{removal}:

$$E_{\text{removal}} = E_{405\text{ nm}} - E_k \text{ of ejected electron}$$

Use $E = h\nu$ to calculate the energy of the photon. Then recall that E_k, the kinetic energy, is $1/2mv^2$. Use this to calculate E_k.

$$E_{405\text{ nm}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{ J}\cdot\text{s})(2.998 \times 10^{8}\text{ m/s})}{4.05 \times 10^{-7}\text{ m}} = 4.9048 \times 10^{-19}\text{ J}$$

$$E_k = 1/2mv^2 = 1/2 \times (9.1095 \times 10^{-31}\text{ kg}) \times (3.36 \times 10^{5}\text{ m/s})^2 = 5.142 \times 10^{-20}\text{ J}$$

Subtract to find E_{removal}, and convert it to kJ/mol:

$$E_{\text{removal}} = 4.9048 \times 10^{-19} - 5.142 \times 10^{-20} = 4.3906 \times 10^{-19}$$

$$= 4.39 \times 10^{-19}\text{ J/electron}$$

$$E_{\text{removal}} = \frac{4.3906 \times 10^{-19}\text{ J}}{1\text{ e}^-} \times \frac{6.022 \times 10^{23}\text{ e}^-}{1\text{ mol}} \times \frac{1\text{ kJ}}{1000\text{ J}} = 264.4$$

$$= 264\text{ kJ/mol}$$

7.113. First, calculate the energy, E, in joules, using the product of voltage and charge:

$$E = (4.00 \times 10^{3}\text{ V}) \times (1.602 \times 10^{-19}\text{ C}) = 6.408 \times 10^{-16}\text{ J}$$

Now, use the kinetic energy equation, $E_k = 1/2mv^2$, and solve for velocity:

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2 \times 6.408 \times 10^{-16}\text{ J}}{9.1095 \times 10^{-31}\text{ kg}}} = 3.7508 \times 10^{7}\text{ m/s}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\text{ J}\cdot\text{s}}{(9.1095 \times 10^{-31}\text{ kg}) \times (3.7508 \times 10^{7}\text{ m/s})} = 1.939 \times 10^{-11}$$

$$= 1.94 \times 10^{-11}\text{ m}\ (19.4\text{ pm})$$

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7.114. First, calculate the energy, E, in joules, using the product of voltage and charge:

$$E = (1.00 \times 10^{4}\ \text{V}) \times (1.602 \times 10^{-19}\ \text{C}) = 1.602 \times 10^{-15}\ \text{J}$$

Now, use the kinetic energy equation $E_k = 1/2mv^2$, and solve for velocity:

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2 \times 1.602 \times 10^{-15}\ \text{J}}{9.1095 \times 10^{-31}\ \text{kg}}} = 5.9306 \times 10^{7}\ \text{m/s}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{J} \bullet \text{s}}{(9.1095 \times 10^{-31}\ \text{kg}) \times (5.9306 \times 10^{7}\ \text{m/s})} = 1.226 \times 10^{-11}$$

$$= 1.23 \times 10^{-11}\ \text{m}\ \ (12.3\ \text{pm})$$

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CHAPTER 8

Electron Configurations and Periodicity

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

8.1.

a. Possible orbital diagram.

b. Possible orbital diagram.

c. Impossible orbital diagram; there are two electrons in a 2*p* orbital with the same spin.

d. Possible electron configuration.

e. Impossible electron configuration; only two electrons are allowed in an *s* subshell.

f. Impossible electron configuration; only six electrons are allowed in a *p* subshell.

8.2. Look at the periodic table. Start with hydrogen and go through the periods, writing down the subshells being filled, stopping with manganese ($Z = 25$). You obtain the following order:

Order:	1*s*	2*s*2*p*	3*s*3*p*	4*s*3*d*4*p*
Period:	first	second	third	fourth

Now fill the subshells with electrons, remembering that you have a total of twenty-five electrons to distribute. You obtain

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$, or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

8.3. Arsenic is a main-group element in Period 4, Group VA, of the periodic table. The five outer electrons should occupy the 4*s* and 4*p* subshells; the five valence electrons have the configuration $4s^2 4p^3$.

8.4. Because the sum of the $6s^2$ and $6p^2$ electrons gives four outer (valence) electrons, lead should be in Group IVA, which it is. Looking at the table, you find lead in Period 6. From its position, it would be classified as a main-group element.

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8.5. The electron configuration of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$. The orbital diagram is

8.6. The radius tends to decrease across a row of the periodic table from left to right, and it tends to increase from the top of a column to the bottom. Therefore, in order of increasing radius,

Be < Mg < Na

8.7. It is more likely that answer a, 1000 kJ/mol, is the ionization energy for iodine because ionization energies tend to decrease with atomic number in a group (I is below Cl in Group VIIA).

8.8. Fluorine should have a more negative electron affinity because (1) carbon has only two electrons in the *p* subshell, (2) the −1 fluoride ion has a stable noble-gas configuration, and (3) the electron can approach the fluorine nucleus more closely than the carbon nucleus. This follows the general trend, which is toward more negative electron affinities from left to right in any period.

■ ANSWERS TO CONCEPT CHECKS

8.1. The second-period elements are those in which the 2*s* and 2*p* orbitals fill. Each orbital can hold only one electron, so all four orbitals will be filled after four electrons. Therefore, the second period will have four elements.

8.2. The *s* orbital fills in the first two elements of the period (Groups IA and IIA); then the *p* orbital starts to fill (Group IIIA). Thus, the first element is in Group IIA (Mg), and the next element is in Group IIIA (Al).

8.3. From the information given, the element must be in Group IIA. These elements have positive electron affinities and also have large third ionization energies.

8.4. A metalloid is an element near the staircase line in the periodic table (the green elements in the periodic table on the inside front cover of the text). The formula R_2O_5 suggests a Group VA element. There are two metalloids in Group VA, arsenic and antimony. That this is an acidic oxide indicates this metalloid has considerable nonmetal character. So, of the two metalloids, the one nearer the top of the column, arsenic, seems more likely. This agrees with the text, which notes that arsenic(V) oxide is acidic, whereas antimony(V) oxide is amphoteric.

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■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

8.1. In the original Stern-Gerlach experiment, a beam of silver atoms is directed into the field of a specially designed magnet. (The same can be done with hydrogen atoms.) The beam of atoms is split into two by the magnetic field; half are bent toward one magnetic pole face and the other half toward the other magnetic pole face. This effect shows that the atoms themselves act as magnets with a positive or a negative component, as indicated by the positive or negative spin quantum numbers.

8.2. In effect, the electron acts as though it were a sphere of spinning charge (Figure 8.3). Like any circulating electric charge, it creates a magnetic field with a spin axis that has more than one possible direction relative to a magnetic field. Electron spin is subject to a quantum restriction to one of two directions corresponding to the m_s quantum numbers +1/2 and −1/2.

8.3. The Pauli exclusion principle limits the configurations of an atom by excluding configurations in which two or more electrons have the same four quantum numbers. For example, each electron in the same orbital must have different m_s values. This also implies that only two electrons occupy one orbital.

8.4. According to the principles discussed in Section 7.5, the number of orbitals in the *g* subshell ($l = 4$) is given by $2l + 1$ and is thus equal to 9 Because each orbital can hold a maximum of two electrons, the *g* subshell can hold a maximum of eighteen electrons.

8.5. The orbitals, in order of increasing energy up to and including the 3*p* orbitals (but not including the 3*d* orbitals), are as follows: 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* (Figure 8.7).

8.6. The noble-gas core is an inner-shell configuration corresponding to one of the noble gases. The pseudo-noble-gas core is an inner-shell configuration corresponding to one of the noble gases together with $(n - 1)d^{10}$ electrons. Like the noble-gas core electrons, the d^{10} electrons are not involved in chemical reactions. The valence electron is an electron (of an atom) located outside the noble-gas core or pseudo-noble-gas core. It is an electron primarily involved in chemical reactions.

8.7. The orbital diagram for the $1s^2 2s^2 2p^4$ ground state of oxygen is

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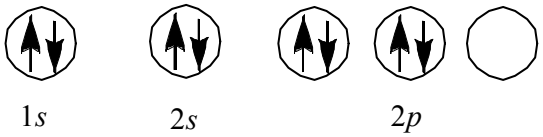
Another possible oxygen orbital diagram, but not a ground state, is



8.8. A diamagnetic substance is a substance that is not attracted by a magnetic field or is very slightly repelled by such a field. This property generally indicates the substance has only paired electrons. A paramagnetic substance is a substance that is weakly attracted by a magnetic field. This property generally indicates the substance has one or more unpaired electrons. Ground-state oxygen has two unpaired 2*p* electrons and is therefore paramagnetic.

8.9. In Groups IA and IIA, the outer *s* subshell is being filled: s^1 for Group IA and s^2 for Group IIA. In Groups IIIA to VIIIA, the outer *p* subshell is being filled: p^1 for IIIA, p^2 for IVA, p^3 for VA, p^4 for VIA, p^5 for VIIA, and p^6 for VIIIA. In the transition elements, the $(n - 1)d$ subshell is being filled from d^1 to d^{10} electrons. In the lanthanides and actinides, the *f* subshell is being filled from f^1 to f^{14} electrons.

8.10. Mendeleev arranged the elements in order of increasing atomic weight, an arrangement that was later changed to atomic numbers. His periodic table was divided into rows (periods) and columns (groups). In his first attempt, he left spaces for what he believed to be undiscovered elements. In his row 5, under aluminum and above indium in Group III, he left a blank space. This Group III element he called eka-aluminum, and he predicted its properties from those of aluminum and indium. Later, the French chemist de Boisbaudran discovered this element and named it gallium.

8.11. In a plot of atomic radii versus atomic number (Figure 8.16), the major trends that emerge are the following: (1) Within each period (horizontal row), the atomic radius tends to decrease with increasing atomic number or nuclear charge. The largest atom in a period is thus the Group 1A atom, and the smallest atom in a period is thus the noble-gas atom. (2) Within each group (vertical column), the atomic radius tends to increase with the period number.

In a plot of ionization energy versus atomic number (Figure 8.18), the major trends are that (1) the ionization energy within a period increases with atomic number, and (2) the ionization energy within a group tends to decrease going down the group.

8.12. The alkaline earth element with the smallest radius is beryllium (Be).

8.13. Group VIIA (halogens) is the main group with the most negative electron affinities. Configurations with filled subshells (ground states of the noble-gas elements) would form unstable negative ions when adding one electron per atom.

8.14. The Na^+ and Mg^{2+} ions are stable because they have the same electronic configuration as the noble gas neon. If Na^{2+} and Mg^{3+} ions were to exist, they would be very unstable because they would not have the same electronic configuration as a noble-gas structure and because of the energy needed to remove an electron from an inner shell.

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8.15. The elements tend to increase in metallic character from right to left in any period. They also tend to increase in metallic character down any column (group) of elements.

8.16. A basic oxide is an oxide that reacts with acids. An example is calcium oxide, CaO. An acidic oxide is an oxide that reacts with bases. An example is carbon dioxide, CO_2.

8.17. Rubidium is the alkali metal atom with a $5s^1$ configuration.

8.18. Atomic number equals 117 (protons in last known element plus those needed to reach Group VIIA).

8.19. The following elements are in Groups IIIA to VIA:

Group IIIA	**Group IVA**	**Group VA**	**Group VIA**
B: metalloid	C: nonmetal	N: nonmetal	O: nonmetal
Al: metal	Si: metalloid	P: nonmetal	S: nonmetal
Ga: metal	Ge: metalloid	As: metalloid	Se: nonmetal
In: metal	Sn: metal	Sb: metalloid	Te: metalloid
Tl: metal	Pb: metal	Bi: metal	Po: metal

Yes, each column displays the expected increasing metallic character.

8.20. The oxides of the following elements are listed as acidic, basic, or amphoteric:

Group IIIA	**Group IVA**	**Group VA**	**Group VIA**
B: acidic	C: acidic	N: acidic	O: amphoteric (H_2O)
Al: amphoteric	Si: acidic	P: acidic	S: acidic
Ga: amphoteric	Ge: acidic	As: acidic	Se: acidic
In: basic	Sn: amphoteric	Sb: amphoteric	Te: amphoteric
Tl: basic	Pb: amphoteric	Bi: basic	Po: amphoteric

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8.21. $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$

8.22. Barium should be a soft, reactive metal. Barium should form the basic oxide, BaO. Barium metal, for example, would be expected to react with water according to the equation

$$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

8.23. The two oxides of carbon are carbon monoxide, CO, and carbon dioxide, CO_2.

8.24.

a. White phosphorus
b. Sulfur
c. Bromine
d. Sodium

8.25. The answer is c, 3.

8.26. The answer is b, $[Ne]3s^2 3p^3$

8.27. The answer is a, First IE 900 kJ/mol, second IE 1750 kJ/mol, third IE 15,000 kJ/mol.

8.28. The answer is b, II only.

■ ANSWERS TO CONCEPT EXPLORATIONS

8.29.

a. Since there is a big jump between the second and the third ionization energies, X be most likely to belong to Group IIA.
b. An ion of element X would be most likely to have a +2 charge.
c. Element Y would not be in the same period as element X. The elements belong in the same group, with Y above X in the group.
d. An atom of Y is smaller than an atom of X. Both elements are in the same group, and Y is above X, so it is smaller.

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8.30.

a. Removing an electron from a −1 ion is the reverse of electron affinity. Since Z has a less negative electron affinity, it will have the smaller energy for the reverse process. Thus, it is easier to remove an electron from Z^-. It would require more energy to remove an electron from a W^- ion.

b. Electron affinity is inversely related to the size of the atom. Since Z has a smaller negative electron affinity, it has the larger atomic radius.

c. The trend for ionization energy parallels the trend for electron affinity. A smaller negative electron affinity (harder to do) means a smaller positive ionization energy (easier to do). Thus, Z has the smaller first ionization energy.

d. The valence electrons in element Z feel a weaker effective nuclear charge than those in element W. The lower negative electron affinity and lower positive ionization energy mean electrons are not attracted as much to the nucleus in an atom of Z compared to an atom of W.

■ ANSWERS TO CONCEPTUAL PROBLEMS

8.31. This statement of the Pauli principle implies there can be two electrons with the same spin in a given orbital. Because an electron can have either one of two spins, any orbital can hold a maximum of four electrons. The first six elements of the periodic table would have the following electron configurations:

(1) $1s^1$

(2) $1s^2$

(3) $1s^3$

(4) $1s^4$

(5) $1s^4 2s^1$

(6) $1s^4 2s^2$

8.32. The first period of the periodic table would have the following allowed quantum numbers: $n = 1$; $l = 1$; $m_l = 0, +1, -1$; $m_s = +1/2, -1/2$. There are six different possible combinations. Therefore, there would be six elements in the first period.

8.33. The elements are in Group IIA (only *s* electrons) and IIIB (*d* electrons). They are also in Period 5. Therefore, the elements are strontium (Sr) and yttrium (Y).

8.34. The elements are in Group IIA. They must also be in Periods 4 (no *d* electrons) and 5 (*d* electrons). Therefore, the elements are calcium (Ca) and strontium (Sr).

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8.35. Keeping in mind that a filled orbital is usually a stable configuration for an atom, an element in this universe with five electrons would probably lose the two electrons in the second orbital and form a cation with a charge of positive two. The other possible option is for the atom to gain seven additional electrons to fill the second orbital. However, this is unlikely given that the nuclear charge would be relatively small, and electron-electron repulsions in such an atom would be large.

8.36. Keep in mind that the ionization energy of an atom provides a measure of how strongly an electron is attracted to that atom. The electron affinity of an atom provides a measure of how strongly attracted an additional electron is to the atom. Both electron affinity and ionization energy provide information about the strength of the attraction between electrons and a particular nucleus. An element that forms an anion easily has an electron affinity much less than zero and a very large first ionization energy. Examples are the elements on the upper right of the periodic table, such as fluorine, with an electron affinity of −328 kJ/mol and a first ionization energy of 1681 kJ/mol.

8.37. The elements that form oxides of the form RO_2 are in Groups IVA and VIA. However, the metalloid oxide in Group VIA is amphoteric. Therefore, the elements are in Group IVA. The metalloid is germanium (Ge), and the metal is tin (Sn). GeO_2 is the acidic oxide, and SnO_2 is the amphoteric oxide.

8.38. Oxides of Groups IIIA and VA have oxides of the form R_2O_3. However, Group VA oxides can also be of the form R_2O_5, so the element is in Group IIIA. It is also acidic. Therefore, it must be boron oxide, B_2O_3.

8.39.

a. Elements of Group IIA and Group VIIIA do not form negative ions; thus they have electron affinities that are greater than zero.

b. The large difference between the second and third ionization energies means this would be a Group IIA element.

c. Luster and conductivity are properties of metals. Group IIA is the only main group that contains just metallic elements.

8.40.

a. These elements would form +2 ions and have oxides with formula AO.

b. $2A + O_2 \rightarrow 2AO$

c. The oxides with formula AO would be basic. The reaction with water would be

$$AO + H_2O \rightarrow A(OH)_2$$

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■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

8.41.

a. Not allowed; the paired electrons in the 2*p* orbital should have opposite spins.

b. Allowed; electron configuration is $1s^2 2s^2 2p^4$.

c. Not allowed; the electrons in the 1*s* orbital must have opposite spins.

d. Not allowed; the 2*s* orbital can hold at most two electrons, with opposite spins.

8.42.

a. Not allowed; the two electrons in the 1*s* orbital must have opposite spins.

b. Allowed; $1s^2 2s^2 2p^4$.

c. Not allowed; the 2*s* orbital can hold at most two electrons, with opposite spins.

d. Not allowed; the unpaired electrons in the 2*p* orbitals should have parallel spins.

8.43.

a. Impossible state; the 2*p* orbitals can hold no more than six electrons.

b. Impossible state; the 3*s* orbital can hold no more than two electrons.

c. Possible state.

d. Possible state; however, the 3*p* and 4*s* orbitals should be filled before the 3*d* orbital.

8.44.

a. Possible state; however, the 2*s* orbital should be filled with two electrons before the 2*p* orbitals are filled completely.

b. Impossible; the 2*p* orbitals can hold no more than six electrons.

c. Impossible; the 2*s* orbital can hold no more than two electrons.

d. Possible state; however, the 3*s* and 3*p* orbitals should be filled before the 3*d* orbital.

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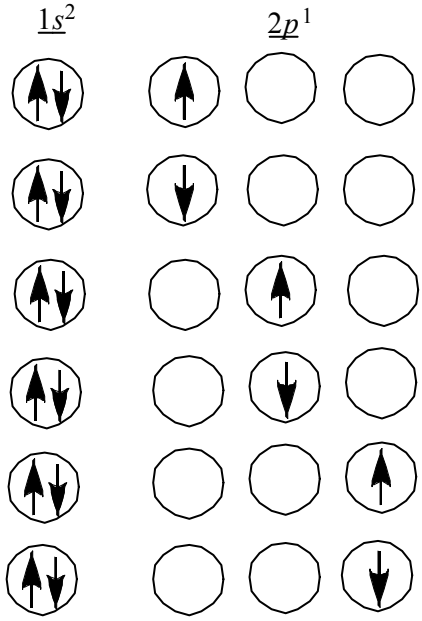
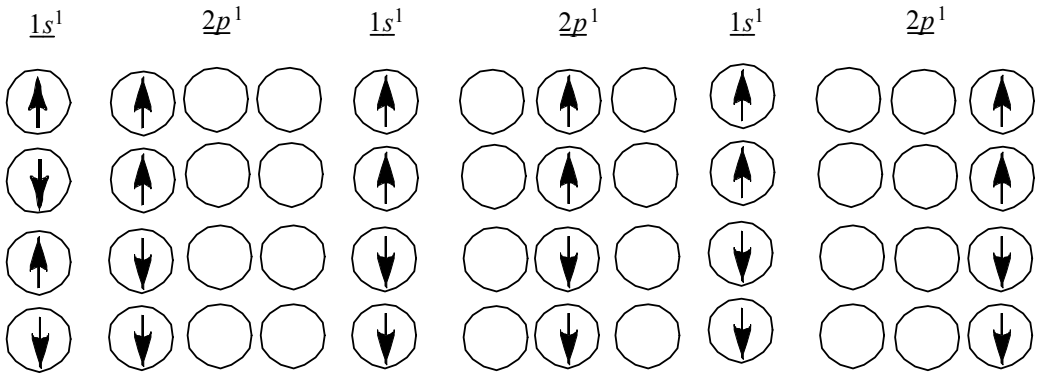
8.45. The six possible orbital diagrams for $1s^2 2p^1$ are



8.46. The twelve possible orbital diagrams for $1s^1 2p^1$ are



8.47. Iodine ($Z = 53$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$

8.48. Phosphorus ($Z = 15$): $1s^2 2s^2 2p^6 3s^2 3p^3$

8.49. Manganese ($Z = 25$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

8.50. Cobalt ($Z = 27$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

8.51. Bromine ($Z = 35$): $4s^2 4p^5$

8.52. Antimony ($Z = 51$): $5s^2 5p^3$

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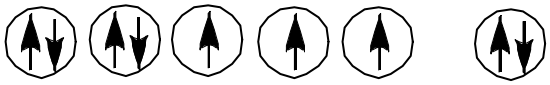
8.53. Zirconium ($Z = 40$): $4d^2 5s^2$

8.54. Titanium ($Z = 22$): $3d^2 4s^2$

8.55. The highest value of n is six, so thallium (Tl) is in the sixth period. The 5*d* subshell is filled, and there is a 6*p* electron, so Tl belongs in an A group. There are three valence electrons, so Tl is in Group IIIA. It is a main-group element.

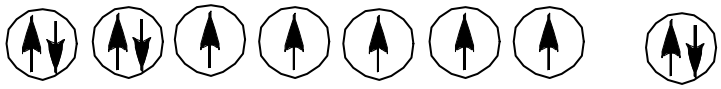
8.56. The highest value of n is six, so iridium (Ir) is in Period 6. The 5*d* subshell is not completely filled, so Ir belongs to a B group. There are nine valence electrons, so Ir is in Group VIIIB. Iridium is a *d*-transition element.

8.57. Cobalt ($Z = 27$): [Ar]



3*d* 4*s*

8.58. Terbium ($Z = 65$): [Xe]



4*f* 6*s*

8.59. Potassium ($Z = 19$): [Ar]

4*s*

All the subshells are filled in the argon core; however, the 4*s* electron is unpaired, causing the ground state of the potassium atom to be a paramagnetic substance.

8.60. Calcium ($Z = 20$): [Ar]

4*s*

All the subshells through the 4*s* subshell are filled, so the ground state of a calcium atom is a diamagnetic substance.

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8.61. Atomic radius increases going down a column (group), from S to Se, and increases going from right to left in a row, from Se to As. Thus, the order by increasing atomic radius is S, Se, As.

8.62. Atomic radius increases going down a column (group), from O to S, and increases going from right to left in a row, from S to P. Thus, the order by increasing atomic radius is O, S, P.

8.63. Ionization energy increases going left to right in a row. Thus, the order by increasing ionization energy is Na, Al, Cl, Ar.

8.64. Ionization energy increases going up a column (group), from Ca to Mg, and increases going left to right in a row, from Mg to S. Thus, the order by increasing ionization energy is Ca, Mg, S.

8.65.

a. In general, the electron affinity becomes more negative going from left to right within a period. Thus, Br has a more negative electron affinity than As.

b. In general, a nonmetal has a more negative electron affinity than a metal. Thus, F has a more negative electron affinity than Li.

8.66.

a. In general, the electron affinity becomes more negative going from left to right within a period. Thus, Cl has a more negative electron affinity than S.

b. In general, the electron affinity of a nonmetal is more negative than that of a metal. Thus, Se has a more negative electron affinity than K.

8.67. Chlorine forms the ClO_3^- ion, so bromine should form the BrO_3^- ion, and potassium forms the K^+ ion, so lithium should be Li^+. Thus, the expected formula of lithium bromate is $LiBrO_3$.

8.68. The expected positive oxidation states of selenium are +4 and +6. The corresponding oxides have the simplest formulas of SeO_2 and SeO_3.

■ SOLUTIONS TO GENERAL PROBLEMS

8.69. Strontium: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$

8.70. Tin: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$

8.71. Polonium: $6s^2 6p^4$

8.72. Thallium: $6s^2 6p^1$

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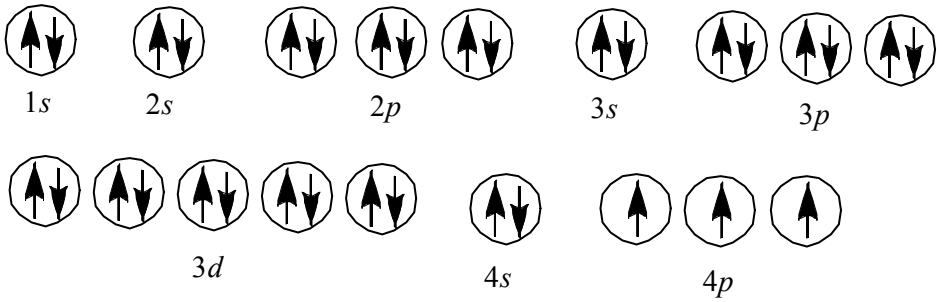
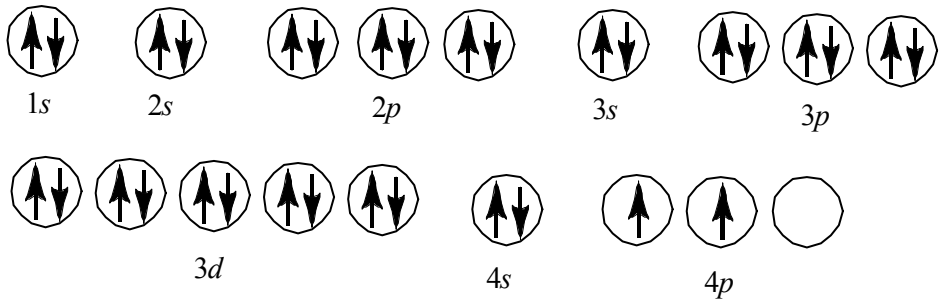
8.73. The orbital diagram for arsenic is



8.74. The orbital diagram for germanium is



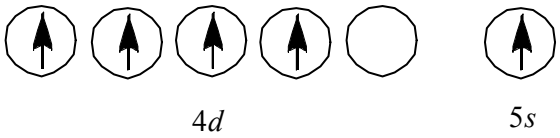
8.75. For eka-lead: [Rn] $5f^{14}6d^{10}7s^{2}7p^{2}$. It is a metal; the oxide is eka-PbO or eka-PbO_2.

8.76. For eka-bismuth: [Rn] $5f^{14}6d^{10}7s^{2}7p^{3}$. It is a metal; the oxide is eka-Bi_2O_3 or eka-Bi_2O_5.

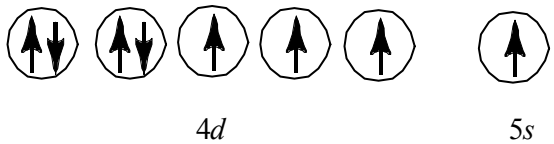
8.77. The ionization energy of Fr is ~370 kJ/mol (slightly less than that of Cs).

8.78. The ionization energy of At is ~900 kJ/mol (between the ionization energy of Po and Rn).

8.79. Niobium: [Kr]



8.80. Ruthenium: [Kr]



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8.81.

a. Cl_2

b. Na

c. Sb

d. Ar

8.82.

a. F_2

b. Ba

c. Ga

d. O_2

8.83. Element with $Z = 23$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$. The element is in Group VB (three of the five valence electrons are *d* electrons) and in Period 4 (largest *n* is 4). It is a *d*-block transition element.

8.84. Element with $Z = 33$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$. The element is in Group VA (five valence electrons, none of them *d* electrons) and in Period 4 (largest *n* is 4). It is a main-group element.

8.85. Nuclear magnetic resonance depends upon the property of nuclear spin. NMR uses the frequency range 300 MHz to 900 MHz.

8.86. Chemical shift depends on the chemical environment of the proton, so the external magnetic field needed to bring a proton into resonance with the radiation varies with the chemical (bonding) environment.

8.87. When an electron in the cathode ray hits a metal atom in the target, it can (if it has sufficient energy) knock an electron from an inner shell of the atom. This produces a metal ion with an electron missing from an inner orbital. This electron configuration is unstable, so an electron from an orbital of higher energy drops into the half-filled orbital, and a photon is emitted. The photon corresponds to electromagnetic radiation in the x-ray region.

8.88. Instead of irradiating a sample with an electron beam and analyzing the frequencies of emitted x rays, you irradiate a sample with x rays and analyze the kinetic energies of ejected electrons. When you scan the various kinetic energies of ejected electrons, you see a spectrum with peaks corresponding to the different occupied orbitals. These ionization energies are approximately equal to the positive values of the orbital energies, so this spectrum provides direct experimental verification of the discrete energy levels associated with the electrons of the atom.

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8.89. When you place a diamagnetic material in an external magnetic field, its electrons move so as to induce, or generate, a smaller magnetic field that is opposite in direction to the external field. This results in a repulsive force between the diamagnetic material and the external field. This repulsive force can be made upward to balance the downward force of gravity so the diamagnetic material can be levitated by a magnetic field.

8.90. A frog was used.

■ SOLUTIONS TO STRATEGY PROBLEMS

8.91. The element is in Group IA, so it is rubidium. The ground-state electron configuration is [Kr]$5s^1$.

8.92. The element is in Group VA, so it is phosphorus. The ground-state valence-shell configuration is $3s^2 3p^3$.

8.93. The element is in Group VIA, so it is tellurium. The valence-shell configuration is $5s^2 5p^4$.

8.94. The element is in the sixth period and is the tenth element from the left, which is platinum. Its symbol is Pt.

8.95. The element is in Period 5, so it is tellurium. Its symbol is Te. The value of *b* must be 4.

8.96. The main-group element in Period 5 with five valence electrons is antimony. Its symbol is Sb. The oxide with the most oxygens is Sb_2O_5.

8.97. The main-group atom in Period 5 with the smallest radius is xenon. The trend in atomic radius is to decrease as you go from left to right across a period. This is because electrons are being added to the same valence shell, but the charge on the nucleus is increasing. The net effect is to pull the valence electrons closer to the nucleus. The orbital diagram for xenon is

5*s* 5*p*

8.98. Hydrogen is the smallest atom. All of the other atoms are in the fourth period. The trend is the atomic radius increases from right to left in a period. Thus, K (potassium), which is in Group IA, has the largest radius.

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8.99. The element in Period 6 that forms the ion R^{+2} and forms the oxides RO and RO_2 is lead (Group IVA). The element that immediately follows lead is bismuth ($Z = 83$) and is in Group VA. The orbital diagram for the ground-state valence-shell electrons is

6*s* 6*p*

8.100. In order of increasing ionization energy, Se < Br < Cl.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

8.101. The equation is

$$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

Using the equation, calculate the moles of H_2; then use the ideal gas law to convert to volume.

$$\text{mol } H_2 = 2.50 \text{ g Ba} \times \frac{1 \text{ mol Ba}}{137.33 \text{ g Ba}} \times \frac{1 \text{ mol } H_2}{1 \text{ mol Ba}} = 0.018\underline{2}04 \text{ mol}$$

$$V = \frac{nRT}{P} = \frac{(0.018204 \text{ mol})(0.082057 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(294.2 \text{ K})}{(748/760) \text{ atm}}$$

$$= 0.44\underline{6}51 \text{ L} \quad (447 \text{ mL})$$

8.102. The equation is

$$2Cs(s) + 2H_2O(l) \rightarrow 2CsOH(aq) + H_2(g)$$

Use the ideal gas law to calculate moles of H_2 from 48.1 mL (0.0481 L). Then use the equation to convert moles of H_2 to moles and mass of Cs.

$$n = \frac{PV}{RT} = \frac{[(768/760) \text{ atm}](0.0481 \text{ L})}{(0.082057 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(292.2 \text{ K})} = 0.002\underline{0}27 \text{ mol } H_2$$

$$\text{mol Cs} = 0.002027 \text{ mol } H_2 \times \frac{2 \text{ mol Cs}}{1 \text{ mol } H_2} = 0.004\underline{0}54 \text{ mol Cs}$$

$$\text{mass Cs} = 0.004054 \text{ mol Cs} \times \frac{132.9 \text{ g Cs}}{1 \text{ mol Cs}} = 0.53\underline{8}7 = 0.539 \text{ g Cs}$$

8.103. Radium is in Group IIA; hence, the radium cation is Ra^{2+}, and its oxide is RaO. Use the atomic weights to calculate the percentage of Ra in RaO.

$$\text{Percent Ra} = \frac{226 \text{ amu Ra}}{226 \text{ amu Ra} + 16.00 \text{ amu O}} \times 100\% = 93.\underline{3}8 = 93.4\% \text{ Ra}$$

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8.104. Tellurium is in Group VIA; hence, its anion is Te^{2-}, and its hydrogen compound is H_2Te. Use the atomic weights to calculate the percentage of Te in H_2Te.

$$\text{Percent Te} = \frac{127.60 \text{ amu Te}}{127.60 \text{ amu Te} + (2)(1.00794 \text{ amu H})} \times 100\% = 98.44\underline{4}7$$

$$= 98.445\% \text{ Te}$$

8.105. Convert 5.00 mg (0.00500 g) Na to moles of Na; then convert to energy using the first ionization energy of 496 kJ/mol Na.

$$\text{mol Na} = 0.00500 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 2.1\underline{7}4 \times 10^{-4} \text{ mol Na}$$

$$2.1\underline{7}4 \times 10^{-4} \text{ mol Na} \times \frac{496 \text{ kJ}}{1 \text{ mol Na}} = 0.10\underline{7}8 = 0.108 \text{ kJ} = 108 \text{ J}$$

8.106. Convert 2.65 mg (0.00265 g) Cl atoms to moles of Cl(*g*); then convert to energy using the electron affinity of 349 kJ/mol Cl(*g*).

$$\text{mol Cl} = 0.00265 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 7.4\underline{7}53 \times 10^{-5} \text{ mol Cl}$$

$$7.4\underline{7}53 \times 10^{-5} \text{ mol Cl} \times \frac{-349 \text{ kJ}}{1 \text{ mol Cl}} = -2.6\underline{0}8 \times 10^{-2} = -2.61 \times 10^{-2} \text{ kJ}$$

8.107. Use the Bohr formula, where $n_f = \infty$ and $n_i = 1$.

$$\Delta E = -R_H \left[\frac{1}{\infty^2} - \frac{1}{1^2} \right] = -R_H[-1] = R_H = \frac{2.179 \times 10^{-18} \text{ J}}{1 \text{ H atom}}$$

$$I.E. = \frac{2.179 \times 10^{-18} \text{ J}}{1 \text{ H atom}} \times \frac{6.022 \times 10^{23} \text{ H atoms}}{1 \text{ mol H}} = \frac{1.31\underline{2}19 \times 10^{6} \text{ J}}{1 \text{ mol H}}$$

$$= 1.312 \times 10^{3} \text{ kJ/mol H}$$

8.108. Use the Bohr formula, where $n_f = \infty$, $n_i = 1$, and $Z = 2$.

$$\Delta E = -R_H \left[\frac{2^2}{\infty^2} - \frac{2^2}{1^2} \right] = -R_H[-4] = 4R_H = \frac{4 \times 2.179 \times 10^{-18} \text{ J}}{1 \text{ He}^+ \text{ ion}}$$

$$I.E. = \frac{4 \times 2.179 \times 10^{-18} \text{ J}}{1 \text{ He}^+ \text{ ion}} \times \frac{6.022 \times 10^{23} \text{ He}^+ \text{ ions}}{1 \text{ mol He}^+} = \frac{5.2\underline{4}87 \times 10^{6} \text{ J}}{1 \text{ mol He}^+}$$

$$= 5.25 \times 10^{3} \text{ kJ/mol He}^+$$

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8.109. Add the three equations after reversing the equation for the lattice energy and its ΔH:

$Na(g)$			$\rightarrow$	$Na^+(g)$	+	e^-	$\Delta H = +496$ kJ/mol
$Cl(g)$	+	e^-	$\rightarrow$	$Cl^-(g)$			$\Delta H = -349$ kJ/mol
$Na^+(g)$	+	$Cl^-(g)$	$\rightarrow$	$NaCl(s)$			$-1(\Delta H = 786$ kJ/mol)
$Na(g)$	+	$Cl(g)$	$\rightarrow$	$NaCl(s)$			$\Delta H = -639$ kJ/mol

8.110. Add the three equations after reversing the equation for the lattice energy and its ΔH:

$K(g)$			$\rightarrow$	$K^+(g)$	+	e^-	$\Delta H = +419$ kJ/mol
$Br(g)$	+	e^-	$\rightarrow$	$Br^-(g)$			$\Delta H = -325$ kJ/mol
$K^+(g)$	+	$Br^-(g)$	$\rightarrow$	$KBr(s)$			$-1(\Delta H = 689$ kJ/mol)
$K(g)$	+	$Br(g)$	$\rightarrow$	$KBr(s)$			$\Delta H = -595$ kJ/mol

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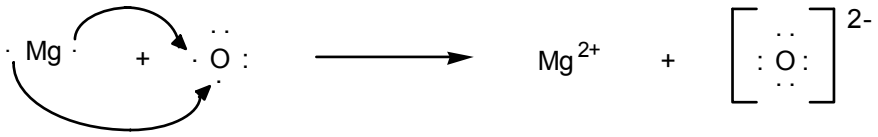
CHAPTER 9

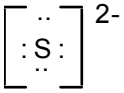
Ionic and Covalent Bonding

■ SOLUTIONS TO EXERCISES

9.1. The Lewis symbol for oxygen is $:\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}\cdot$ and the Lewis symbol for magnesium is $\cdot$ Mg $\cdot$. The magnesium atom loses two electrons, and the oxygen atom accepts two electrons. You can represent this electron transfer as follows:



9.2. The electron configuration of the Ca atom is [Ar]$4s^2$. By losing two electrons, the atom assumes a 2+ charge and the argon configuration, [Ar]. The Lewis symbol is Ca^{2+}. The S atom has the configuration [Ne]$3s^2 3p^4$. By gaining two electrons, the atom assumes a 2− charge and the argon configuration [Ne]$3s^2 3p^6$ and is the same as [Ar]. The Lewis symbol is



9.3. The electron configuration of lead (Pb) is [Xe]$4f^{14}5d^{10}6s^2 6p^2$. The electron configuration of Pb^{2+} is [Xe]$4f^{14}5d^{10}6s^2$.

9.4. The electron configuration of manganese ($Z = 25$) is [Ar]$3d^5 4s^2$. To find the ion configuration, remove first the 4*s* electrons, then the 3*d* electrons. In this case, only two electrons need to be removed. The electron configuration of Mn^{2+} is [Ar]$3d^5$.

9.5. S^{2-} has a larger radius than S. The anion has more electrons than the atom. The electron-electron repulsion is greater; hence, the valence orbitals expand. The anion radius is larger than the atomic radius.

9.6. The ionic radii increase down any column because of the addition of electron shells. All of these ions are from the Group IIA family; therefore, $Mg^{2+} < Ca^{2+} < Sr^{2+}$.

9.7. Cl^-, Ca^{2+}, and P^{3-} are isoelectronic with an electron configuration equivalent to [Ar]. In an isoelectronic sequence, the ionic radius decreases with increasing nuclear charge. Therefore, in order of increasing ionic radius, we have Ca^{2+}, Cl^-, and P^{3-}.

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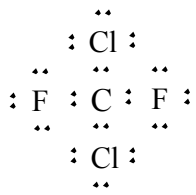
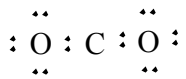
9.8. The absolute values of the electronegativity differences are C–O, 1.0; C–S, 0.0; and H–Br, 0.7. Therefore, C–O is the most polar bond.

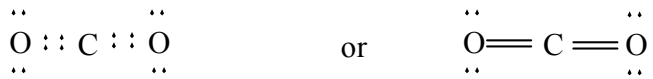
9.9. First, calculate the total number of valence electrons. C has four, Cl has seven, and F has seven. The total number is 4 + (2 x 7) + (2 x 7) = 32. The expected skeleton consists of a carbon atom surrounded by Cl and F atoms. Distribute the electron pairs to the surrounding atoms to satisfy the octet rule. All 32 electrons (16 pairs) are accounted for.



9.10. The total number of electrons in CO_2 is 4 + (2 x 6) = 16. Because carbon is more electropositive than oxygen, it is expected to be the central atom. Distribute the electrons to the surrounding atoms to satisfy the octet rule.

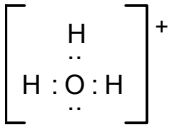


All sixteen electrons have been used, but note that there are only four electrons on carbon. This is four electrons short of a complete octet, which suggests the existence of double bonds. Move a pair of electrons from each oxygen to the carbon-oxygen bonds.



9.11.

a. There are (3 x 1) + 6 = 9 valence electrons in H_3O. The H_3O^+ ion has one less electron than is provided by the neutral atoms because the charge on the ion is 1+. Hence, there are eight valence electrons in H_3O^+. The electron-dot formula is



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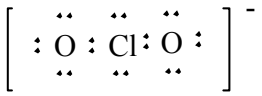
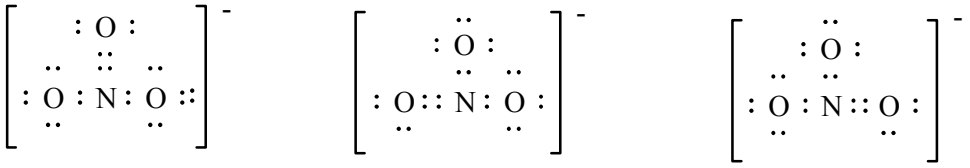
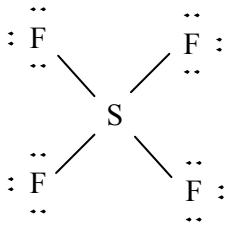
b. Cl has seven valence electrons, and O has six valence electrons. The total number of valence electrons from the neutral atoms is 7 + (2 x 6) = 19. The charge on the ClO_2^- is −1, which provides one more electron than the neutral atoms. This makes a total of 20 valence electrons. The electron-dot formula for ClO_2^- is



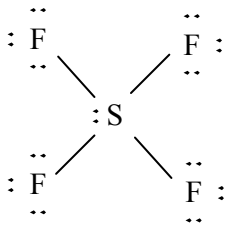
9.12. The resonance formulas for NO_3^- are



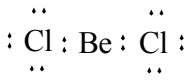
9.13. The number of valence electrons in SF_4 is 6 + (4 x 7) = 34. The skeleton structure is a sulfur atom surrounded by fluorine atoms. After the electron pairs are placed on the F atoms to satisfy the octet rule, two electrons remain.



These additional two electrons are put on the sulfur atom because it had *d* orbitals and, therefore, can expand its octet.



9.14. Be has two valence electrons, and Cl has seven valence electrons. The total number of valence electrons is 2 + (2 x 7) = 16 in the $BeCl_2$ molecule. Be, a Group IIA element, can have fewer than eight electrons around it. The electron-dot formula of $BeCl_2$ is



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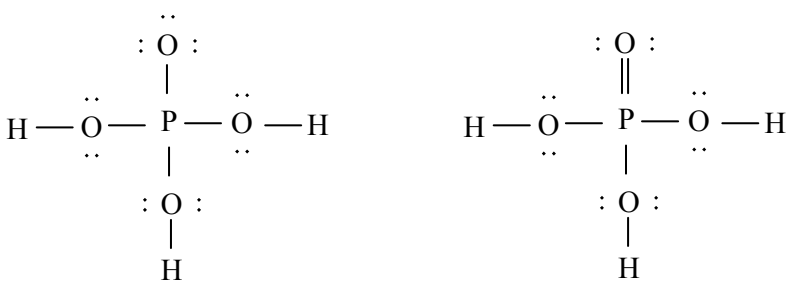
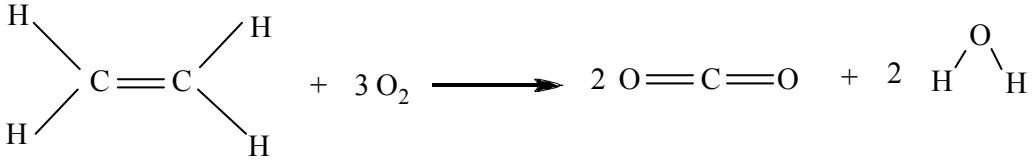
9.15. The total number of electrons in H_3PO_4 is 3 + 5 + 24 = 32. Assume a skeleton structure in which the phosphorus atom is surrounded by the more electronegative four oxygen atoms. The hydrogen atoms are then attached to the oxygen atoms. Distribute the electron pairs to the surrounding atoms to satisfy the octet rule. If you assume all single bonds (structure on the left), the formal charge on the phosphorus is 1+ and the formal charge on the top oxygen is 1−. Using the principle of forming a double bond with a pair of electrons on the atom with the negative formal charge, you obtain the structure on the right. The formal charge on all oxygens in this structure is zero; the formal charge on phosphorus is 5 − 5 = 0. This is the better structure.



9.16. The bond length can be predicted by adding the covalent radii of the two atoms. For O–H, we have 66 pm + 37 pm = 103 pm.

9.17. As the bond order increases, the bond length decreases. Since the C=O is a double bond, we would expect it to be the shorter one, 123 pm.

9.18.



One C=C bond, four C–H bonds, and three O_2 bonds are broken. There are four C=O bonds and four O–H bonds formed.

$$\Delta H = \{[602 + (4 \times 411) + (3 \times 494)] - [(4 \times 799) + (4 \times 459)]\} \text{ kJ} = -1304 \text{ kJ}$$

■ ANSWERS TO CONCEPT CHECKS

9.1.

a. The +2 ions are common in transition elements, but it is the outer *s* electrons that are lost to form these ions in compounds. Iron, whose configuration is $[Ar]3d^6 4s^2$, would be expected to lose two 4*s* electrons to give the configuration $[Ar]3d^6$ for the Fe^{2+} ion in compounds. The configuration given in the problem is for an excited state; you would not expect to see it in compounds.

b. Nitrogen, whose ground-state atomic configuration is $[He]2s^2 2p^3$, would be expected to form an anion with a noble-gas configuration by gaining three electrons. This would give the anion N^{3-} with the configuration $[He]2s^2 2p^6$. You would not expect to see the anion N^{2-} in compounds.

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c. The zinc atom has the ground-state configuration [Ar]$3d^{10}4s^2$. The element is often considered to be a transition element. In any case, you would expect the atom to form compounds by losing its 4*s* electrons to give Zn^{2+} with the pseudo-noble-gas configuration [Ar]$3d^{10}$. This is the ion configuration given in the problem.

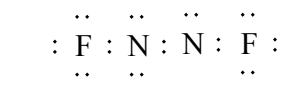
d. The configuration of the ground-state sodium atom is [He]$2s^22p^63s^1$. You would expect the atom to lose one electron to give the Na^+ ion with the noble-gas configuration [He]$2s^22p^6$. You would not expect to see compounds with the Na^{2+} ion.

e. The ground state of the calcium atom is [Ne]$3s^23p^64s^2$. You would expect the atom to lose its two outer electrons to give Ca^{2+} with the noble-gas configuration [Ne]$3s^23p^6$, which is the configuration given in the problem.

9.2.

a. There are two basic points to consider in assessing the validity of each of the formulas given in the problem. One is whether the formula has the correct skeleton structure. You expect the F atoms to be bonded to the central N atoms because the F atoms are more electronegative. The second point is the number of dots in the formula. This should equal the total number of electrons in the valence shell of the atoms (five for each nitrogen atom and seven for each fluorine atom), which is (2 x 5) + (2 x 7) = 24, or twelve pairs. The number showing in the formula here is thirteen, which is incorrect.

b. This formula has the correct skeleton structure and the correct number of dots. All of the atoms have octets, so the formula would appear to be correct. As a final check, however, you might try drawing the formula beginning with the skeleton structure. In drawing an electron-dot formula, after connecting atoms by single bonds (a single electron pair), you would place electron pairs around the outer atoms (the F atoms in this formula) to give octets. After doing that, you would have used up nine electron pairs (three for the single bonds and three for each F atom to fill out its octet). This leaves three pairs, which you might distribute as follows:



One of the nitrogen atoms (the one on the right) does not have an octet. The lack of an octet on this atom suggests trying for a double bond. This suggests that you move one of the lone pairs on the left N atom into one of the adjacent bonding regions. Moving this lone pair into the N–N region would give a symmetrical result, whereas moving the lone pair into the F–N region would not. The text notes that the atoms often showing multiple bonds are C, N, O, and S. The formula given here with a nitrogen-nitrogen double bond appears quite reasonable.

c. This formula is similar to the previous one, b, but the double bond is between the F and N atoms. Multiple bonds to F are less likely than those between two N atoms, so this is not the preferred formula. You could also apply the rules of formal charge in this case, and you would come to the same conclusion. The formula here gives a 1− charge to the left F atom and a 1+ charge to the right N atom, whereas each of the atoms in the b formula has zero formal charge. Rule A says that whenever you can write several Lewis formulas for a molecule, you should choose the formula having the lowest magnitudes of formal charges. In this case, this is the formula b. Strictly speaking, both b and c could be regarded as resonance formulas, but b would have much more importance than c in describing the electronic structure of the molecule.

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d. This formula is similar to the one you drew earlier in describing how you would get to the formula in b. The left N atom does not have an octet, which suggests you move a lone pair on the other N atom into the N–N bond region to give a double bond.

e. This formula does not have the correct skeleton structure.

f. This formula has the correct skeleton structure and the correct total number of electron dots, but neither N atom has an octet. In fact, there is no bond between the two N atoms.

9.3.

a. This model and corresponding Lewis structure, H:C:::N:, has the expected skeleton structure. (H must be an exterior atom, but either C or N might be in the center; however, you expect the more electropositive, or less electronegative, atom, C, to be in this position). This formula also has the correct number of electron dots (1 + 4 + 5 = 10, or 5 pairs). Finally, the formal charge of each atom is zero. Therefore, this model should be an accurate representation of the HCN molecule.

b. This structure has the more electronegative atom, N, in the central position; you don't expect this to be the correct structure. You can also look at this from the point of view of formal charges. This formula has a 1+ charge on the N atom and a 1− charge on the C atom. You would not expect the more electronegative atom to have the positive formal charge. Moreover, the previous formula, a, has zero charges for each atom, which would be preferred.

c. If you draw the Lewis structure, you will see that each atom has an octet, but the formula has too many electron pairs (seven instead of five). You can remove two pairs and still retain octets if you move two lone pairs into the bonding region, to give a triple bond.

d. If you draw the Lewis structure, you will see that each atom has an octet, but the formula has too many electron pairs (six instead of five). You would arrive at the same conclusion using formal charges. The formal charges are 2− for H, 1+ for C, and 1+ for N. Since you already know that formula a has zero formal charge for each atom, such high formal charges for the atoms in formula d mean it is not a very good representation of the molecule.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

9.1. As an Na atom approaches a Cl atom, the outer electron of the Na atom is transferred to the Cl atom. The result is an Na^+ and a Cl^- ion. Positively charged ions attract negatively charged ions, so, finally, the NaCl crystal consists of Na^+ ions surrounded by six Cl^- ions surrounded by six Na^+ ions.

9.2. Ions tend to attract as many ions of opposite charge about them as possible. The result is that ions tend to form crystalline solids rather than molecular substances.

9.3. The energy terms involved in the formation of an ionic solid from atoms are the ionization energy of the metal atom, the electron affinity of the nonmetal atom, and the energy of the attraction of the ions forming the ionic solid. The energy of the solid will be low if the ionization energy of the metal is low, the electron affinity of the nonmetal is high, and the energy of the attraction of the ions is large.

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9.4. The lattice energy for potassium bromide is the change in energy that occurs when KBr(*s*) is separated into isolated $K^+(g)$ and $Br^-(g)$ ions in the gas phase.

$$KBr(s) \rightarrow K^+(g) + Br^-(g)$$

9.5. A monatomic cation with a charge equal to the group number corresponds to the loss of all valence electrons. This loss of electrons would give a noble-gas configuration, which is especially stable. A monatomic anion with a charge equal to the group number minus eight would have a noble-gas configuration.

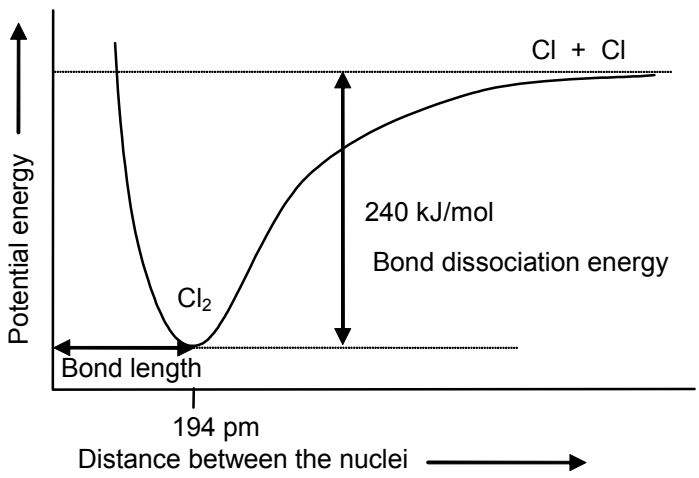
9.6. Most of the transition elements have configurations in which the outer *s* subshell is doubly occupied. These electrons will be lost first, and we might expect each to be lost with almost equal ease, resulting in +2 ions.

9.7. If we assume the ions are spheres that are just touching, the distances between centers of the spheres will be related to the radii of the spheres. For example, in LiI, we assume that the −1 ions are large spheres that are touching. The distance between centers of the I^- ions equals two times the radius of the I^- ion.

9.8. In going across a period, the cations decrease in radius. When we reach the anions, there is an abrupt increase in radius, and then the radii again decrease. Ionic radii increase going down any column of the periodic table.

9.9. As the H atoms approach one another, their 1*s* orbitals begin to overlap. Each electron can then occupy the space around both atoms; that is, the two electrons are shared by the atoms.

9.10.



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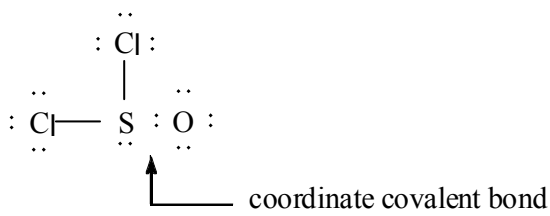
9.11. An example is thionyl chloride, $SOCl_2$:



Note that the O atom has eight electrons around it; that is, it has two more electrons than the neutral atom. These two electrons must have come from the S atom. Thus, this bond is a coordinate covalent bond.

9.12. In many atoms of the main-group elements, bonding uses an *s* orbital and the three *p* orbitals of the valence shell. These four orbitals are filled with eight electrons, thus accounting for the octet rule.

9.13. Electronegativity increases from left to right (with the exception of the noble gases) and decreases from top to bottom in the periodic table.

9.14. The absolute difference in the electronegativities of the two atoms in a bond gives a rough measure of the polarity of the bond.

9.15. Resonance is used to describe the electron structure of a molecule in which bonding electrons are delocalized. In a resonance description, the molecule is described in terms of two or more Lewis formulas. If we want to retain Lewis formulas, resonance is required because each Lewis formula assumes that a bonding pair of electrons occupies the region between two atoms. We must imagine that the actual electron structure of the molecule is a composite of all resonance formulas.

9.16. Molecules having an odd number of electrons do not obey the octet rule. An example is nitrogen monoxide, NO. The other exceptions fall into two groups. In one group are molecules with an atom having fewer than eight valence electrons around it. An example is borane, BH_3. In the other group are molecules with an atom having more than eight valence electrons around it. An example is sulfur hexafluoride, SF_6.

9.17. As the bond order increases, the bond length decreases. For example, the average carbon-carbon single-bond length is 154 pm, whereas the carbon-carbon double-bond length is 134 pm, and the carbon-carbon triple-bond length is 120 pm.

9.18. Bond energy is the average enthalpy change for the breaking of a bond in a molecule. The enthalpy of a reaction for gaseous reactions can be determined by summing the bond energies of all the bonds that are broken and subtracting the sum of the bond energies of all the bonds that are formed.

9.19. The answer is a, $BaCO_3$.

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9.20. The answer is e, $S^- > S > S^+$.

9.21. The answer is d, $1s^2 2s^2 2p^5$.

9.22. The answer is a, sulfur.

■ ANSWERS TO CONCEPT EXPLORATIONS

9.23.

a. Since a cation is smaller than the neutral atom, the smallest sphere (far right) is the correct representation of M^+.

b. Since an anion is larger than the neutral atom, the largest sphere is the correct representation of X^-.

c. The chemical equation for the reaction is

$$M(s) + X(g) \rightarrow MX(s)$$

d. The product of the reaction is an ionic compound. The M atom readily forms the M^+ ion, and the X atom readily forms the X^- ion. This is characteristic of an electron-transfer reaction, in which ionic compounds are formed.

e. Since MX is an ionic compound, the best representation of its structure is the crystal.

9.24.

a. The formation of a bond is an energy-releasing process and is exothermic.

b. Bond energy is the energy required to break a bond. It is the reverse process from part a, so it is an endothermic process and a positive quantity.

c. $\Delta H_{rxn} \cong BE(\text{reactants}) - BE(\text{products}) = 0 - BE(\text{X–X})$

$BE(\text{X–X}) = -\Delta H_{rxn} = -(-500 \text{ kJ/mol}) = 500 \text{ kJ/mol}$

d. $\Delta H_{rxn} \cong BE(\text{reactants}) - BE(\text{products}) = BE(\text{X–X}) + BE(\text{Y–Y}) - 2BE(\text{X–Y})$

$\cong 500 \text{ kJ/mol} + 750 \text{ kJ/mol} - 2(1500 \text{ kJ/mol}) = -1750 \text{ kJ/mol}$

e. The approach here is to use the Born-Haber cycle to calculate ΔH for the reaction. The reactions and energies are as follows.

$A(g) \rightarrow A^+(g) + e^-$	$\Delta H_1 = I_1 = 400 \text{ kJ}$
$1/2X_2(g) \rightarrow X(g)$	$\Delta H_2 = 1/2BE = 1/2(500 \text{ kJ}) = 250 \text{ kJ}$
$X(g) + e^- \rightarrow X^-(g)$	$\Delta H_3 = EA = -525 \text{ kJ}$
$A^+(g) + X^-(g) \rightarrow AX(s)$	$\Delta H_4 = -U = -(100 \text{ kJ}) = -100 \text{ kJ}$
$A(g) + 1/2X_2(g) \rightarrow AX(s)$	$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

$\Delta H_{rxn} = 400 \text{ kJ} + 250 \text{ kJ} + -525 \text{ kJ} + -100 \text{ kJ} = 25 \text{ kJ}$

Since the reaction is endothermic, it is not likely that AX will be formed in the reaction.

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f. You would predict that the formation of AX(*s*) would be likely if the reaction were exothermic, so ΔH_{rxn} must be negative. Therefore, the minimum amount of AX(*s*) lattice energy required would be 100 kJ + 25 kJ = 125 kJ.

■ ANSWERS TO CONCEPTUAL PROBLEMS

9.25. Because the compound that forms is a combination of a metal and a nonmetal, we would expect it to be ionic. If we assume that metal atoms tend to lose electrons to obtain filled shells, then the metal atom X would lose three electrons from the $n = 2$ level, forming the X^{3+} cation. We can expect the nonmetal atom Y to gain electrons to obtain a filled shell, so it requires an additional electron to fill the $n = 1$ level, forming the Y^- anion. To produce an ionic compound with an overall charge of zero, the compound formed from these two elements would be XY_3.

9.26. Elements in higher periods in Group IIIA tend to form ions either by losing the outer *p* electron to form +1 ions or by losing the outer *s* and *p* electrons to form +3 ions. In the case of thallium, these ions have the configurations in d and b, respectively. The +2 ion given in configuration a represents a loss of the two outer *s* electrons, leaving the outer *p* electrons of higher energy. This configuration would represent an excited state of the +2 ion. You would not expect a +2 ion in thallium compounds, and an excited configuration is even less likely. The +4 ion given in c is formed by loss of the outer *s* and *p* electrons plus a *d* electron from the closed *d* subshell. This would be an unlikely ion for thallium compounds.

9.27. The smaller atom on the left (yellow) becomes a larger ion on the right, while the larger atom on the left (blue) becomes the smaller ion on the right. Since cations are smaller than their parent atom, and anions are larger than their parent atom, the cation on the right is the smaller ion (blue), and the anion is the larger ion (yellow). Finally, since metals tend to form cations, and nonmetals form anions, the metal on the left is the larger atom (blue), and the nonmetal is the smaller atom (yellow).

9.28. Element 117 would fall in Group VII A, the halogens. The monatomic ion for this element would probably be like the other halogens, an anion with a 1− charge. Since anions are larger than the parent atom, the larger sphere (on the right) would be the ion, and the smaller sphere (on the left) would be the atom.

9.29.

a. Incorrect. The atoms in this formula do not obey the octet rule. The formula has the correct number of valence electrons, so this suggests a multiple bond between the N atoms.

b. Correct. The central atom is surrounded by more electronegative atoms, as you would expect, and each atom obeys the octet rule.

c. Incorrect. The skeleton structure is acceptable (the central atom is surrounded by more electronegative atoms), but you would expect the double bond to be between C and O rather than between C and F (C, N, O, and S form multiple bonds). You would come to this same conclusion using rules of formal charge. (The formula has a formal charge of 1+ on F and 1− on O, whereas you would expect these formal charges to be interchanged, with the negative charge on the F atom, which is more electronegative.)

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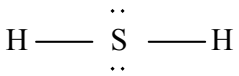
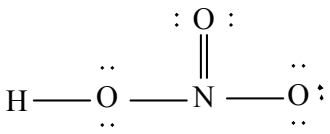
d. Incorrect. The skeleton structure is OK, but the carbon atom has ten valence electrons about it. This suggests that you replace the two carbon-oxygen double bonds by one carbon-oxygen double bond (because there is one extra pair of electrons on the C atom). The most symmetrical location of the double bond uses the oxygen atom not bonded to an H atom. Also, only this formula has zero formal charges on all atoms.

9.30.

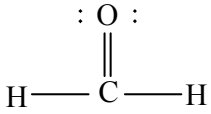
a.



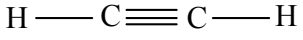
b.



c.

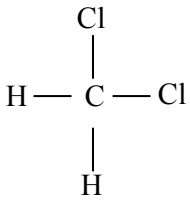


d.

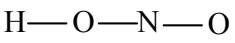


9.31.

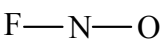
a. To arrive at a skeleton structure, you decide which is the central atom. (It cannot be H). The C atom is less electronegative than the Cl atom, so you place it as the central atom and surround it by the other atoms.



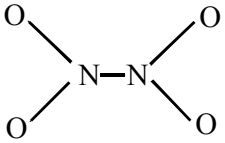
b. HNO_2 is an oxyacid in which O atoms bond to the central atom with the H bonded to O. The central atom must be N (the only other atom), so the skeletal structure is



c. You place the least electronegative atom (N) as the central atom and bond it to the other atoms.



d. N is less electronegative than O. The most symmetrical structure would be the two N atoms in the center with two O atoms bonded to each N atom.



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9.32. The ranking is a, c, b (best) for the following reasons:

a. This formula has a 2− formal charge on the outer N and 1+ charges on the other two atoms. This formula has a larger magnitude of formal charges than either of the other two formulas, so it ranks last as a representation of the electron structure of the N_2O molecule.

b. This formula has a 1− formal charge on O and a 1+ formal charge on the central N. This places the negative formal charge on the more electronegative atom, O, making this the best representation of the electron structure of the molecule.

c. This formula has a 1− formal charge on the outer N atom and a 1+ formal charge on the central N atom. This is better than resonance formula a, but not as good as b.

9.33.

a. In order to be a neutral ionic compound, element X must have a charge of 3−. In an ionic compound, calcium forms the Ca^{2+} cation. The combination of Ca^{2+} and X^{3-} would form the ionic compound with the formula Ca_3X_2.

b. Since element X formed an ionic compound with sodium metal, it is probably a nonmetal with a high electron affinity. When a nonmetal with a high electron affinity combines with a metal such as calcium, an ionic compound is formed.

9.34.

a. In general, the enthalpy of a reaction is (approximately) equal to the sum of the bond energies for the bonds broken minus the sum of the bond energies for the bonds formed. Therefore, the bond energy (*BE*) for each of the reactions can be calculated by the following relationships:

$$\Delta H = BE(\text{X–X}) + BE(\text{O=O}) - 2 \times BE(\text{X–O}) - BE(\text{O–O})$$

$$\Delta H = BE(\text{Y–Y}) + BE(\text{O=O}) - 2 \times BE(\text{Y–O}) - BE(\text{O–O})$$

$$\Delta H = BE(\text{Z–Z}) + BE(\text{O=O}) - 2 \times BE(\text{Z–O}) - BE(\text{O–O})$$

Because the bond energies of X–O, Y–O, and Z–O are all equal, the difference in the values of ΔH for each reaction is solely a function of the X–X, Y–Y, or Z–Z bonds. Therefore, the compound with the most positive value of ΔH has the strongest bonds. The ranking of strongest to weakest bond is Y–Y > Z–Z > X–X.

b. Since the bond strengths of all the products are equal, the same amount of energy would be required to dissociate each of the products into atoms.

c. In this case, less energy would be required to break the bonds, so the ΔH for each reaction would decrease.

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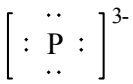
■ SOLUTIONS TO PRACTICE PROBLEMS

9.35.

a. P has the electron configuration [Ne]$3s^2 3p^3$. It has five electrons in its valence shell. The Lewis formula is

b. P^{3-} has three more valence electrons than P. It now has eight electrons in its valence shell. The Lewis formula is



c. Ga has the electron configuration [Ar]$3d^{10}4s^2 4p^1$. It has three electrons in its valence shell. The Lewis formula is

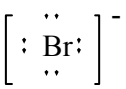
d. Ga^{3+} has three fewer valence electrons than Ga. It now has zero electrons in its valence shell. The Lewis formula is

Ga^{3+}

9.36.

a. Br has the valence configuration [Ar]$3d^{10}4s^2 4p^5$. It has seven electrons in its valence shell. The Lewis formula is

b. Br^- has one more electron than Br. It now has eight electrons in its valence shell. The Lewis formula is



c. Strontium has the electron configuration [Kr]$5s^2$. It has two valence electrons in its valence shell. The Lewis formula is

d. Sr^{2+} has two fewer electrons than Sr. It now has zero electrons in its valence shell. The Lewis formula is

Sr^{2+}

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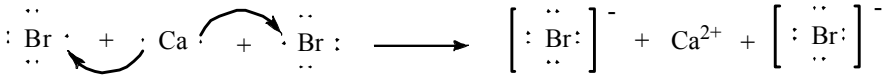
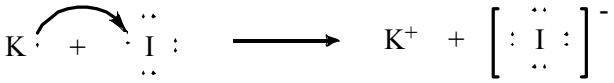
9.37.

a. If the calcium atom loses two electrons, and the bromine atoms gain one electron each, all three atoms will assume noble-gas configurations. This can be represented as follows.

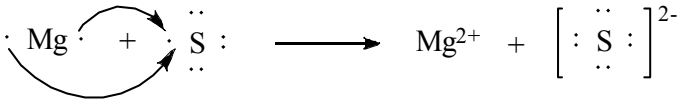


b. If the potassium atom loses one electron, and the iodine atom gains one electron, both atoms will assume a noble-gas configuration. This can be represented as follows.



9.38.

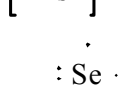
a. If the magnesium atom loses two electrons, and the sulfur atom gains two electrons, both atoms will assume a noble-gas configuration. This can be represented as follows:



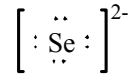
b. If the barium atom loses two electrons, and both iodine atoms gain one electron, all three atoms will have noble-gas configurations. This can be represented as follows.

9.39.

a. As: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$

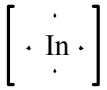
b. As^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ 

c. Se: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

d. Se^{2-}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ 

9.40.

a. In: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^1$

b. In^-: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ 

c. K^+: $1s^2 2s^2 2p^6 3s^2 3p^6$ K^+

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d. I^-: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

9.41.

a. Bi: $[Xe]4f^{14}5d^{10}6s^2 6p^3$

b.

Bi^{3+}: The three $6p$ electrons are lost from the valence shell.
$[Xe]4f^{14}5d^{10}6s^2$

9.42.

a. Sn: $[Kr]4d^{10}5s^2 5p^2$

b.

Sn^{2+}: The two $5p$ electrons are lost from the valence shell.
$[Kr]4d^{10}5s^2$

9.43. The +2 ion is formed by the loss of electrons from the 4*s* subshell.

Ni^{2+}: $[Ar]3d^8$

The +3 ion is formed by the loss of electrons from the 4*s* and 3*d* subshells.

Ni^{3+}: $[Ar]3d^7$

9.44. The +1 ion is formed by the loss of the one electron in the 4*s* subshell.

Cu^+: $[Ar]3d^{10}$

The +2 ion is formed by the loss of a 4*s* and a 3*d* electron.

Cu^{2+}: $[Ar]3d^9$

9.45.

a. $Sr^{2+} < Sr$

The cation is smaller than the neutral atom because it has lost all its valence electrons; hence, it has one less shell of electrons. The electron-electron repulsion is reduced, so the orbitals shrink because of the increased attraction of the electrons to the nucleus.

b. $Br < Br^-$

The anion is larger than the neutral atom because it has more electrons. The electron-electron repulsion is greater, so the valence orbitals expand to give a larger radius.

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9.46.

a. $Te < Te^{2-}$

The anion is larger than the neutral atom because it has more electrons. The electron-electron repulsion is greater, so the valence orbitals expand to give a larger radius.

b. $Al^{3+} < Al$

The cation is smaller than the neutral atom because it has lost all its valence electrons; hence, it has one less shell of electrons. The electron-electron repulsion is reduced, so the orbitals shrink because of the increased attraction of the electrons to the nucleus.

9.47. $S^{2-} < Se^{2-} < Te^{2-}$

All have the same number of electrons in the valence shell. The radius increases with the increasing number of filled shells.

9.48. P^{3-} is larger. It has the same number of valence electrons as N^{3-}, but the valence shell has $n = 3$ for P^{3-} and $n = 2$ for N^{3-}. The radius increases with the increasing number of filled shells.

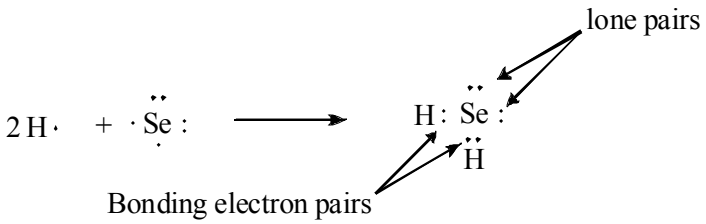
9.49. Smallest Na^+ ($Z = 11$), F^- ($Z = 9$), N^{3-} ($Z = 7$) Largest

These ions are isoelectronic. The atomic radius increases with the decreasing nuclear charge (Z).

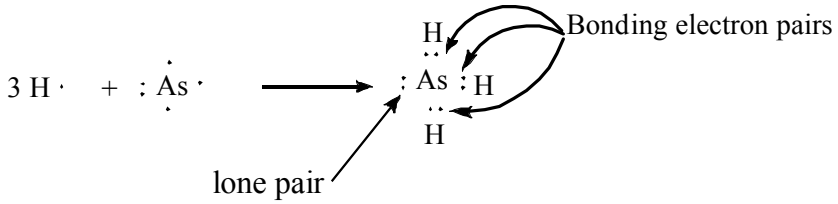
9.50. Smallest Na^+ ($Z = 11$), Cl^- ($Z = 17$), S^{2-} ($Z = 16$) Largest

These ions are all from elements in the third row of the periodic table. The atomic radius increases with increasing negative charge.

9.51.



9.52.



9.53. Arsenic is in Group VA on the periodic table and has five valence electrons. Bromine is in Group VIIA and has seven valence electrons. Arsenic forms three covalent bonds, and bromine forms one covalent bond. Therefore, the simplest compound would be $AsBr_3$.

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9.54. Silicon is in Group IVA on the periodic table and has four valence electrons. Chlorine is in Group VIIA and has seven valence electrons. Silicon forms four covalent bonds, and chlorine forms one covalent bond. Therefore, the simplest compound would be $SiCl_4$.

9.55.

a. P, N, O

Electronegativity increases from left to right and from bottom to top in the periodic table.

b. Na, Mg, Al

Electronegativity increases from left to right within a period.

c. Al, Si, C

Electronegativity increases from left to right and from bottom to top in the periodic table.

9.56.

a. Rb, Sr, Ca

Electronegativity increases from left to right and from bottom to top in the periodic table.

b. Ca, Ga, Ge

Electronegativity increases from left to right within a period.

c. Sb, As, Se

Electronegativity increases from left to right and from bottom to top in the periodic table.

9.57. $X_O - X_P = 3.5 - 2.1 = 1.4$

$X_{Cl} - X_C = 3.0 - 2.5 = 0.5$

$X_{Br} - X_{As} = 2.8 - 2.0 = 0.8$

The bonds arranged by increasing difference in electronegativity are C–Cl, As–Br, P–O.

9.58. $X_N - X_H = 3.0 - 2.1 = 0.9$

$X_{Br} - X_{Si} = 2.8 - 1.8 = 1.0$

$X_{Cl} - X_N = 3.0 - 3.0 = 0.0$

The difference in electronegativity is smallest for the N–Cl bond; hence, it is the least polar.

9.59.

a. P–O

$\delta+ \quad \delta-$

b. C–Cl

$\delta+ \quad \delta-$

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c. As–Br

δ+ δ−

9.60. The atom with the greater electronegativity has the partial negative charge.

a. H–N

δ+ δ−

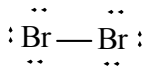
b. Si–Br

δ+ δ−

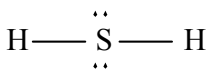
c. Nonpolar

9.61.

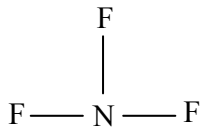
a. Total number of valence electrons = 7 + 7 = 14. Br–Br is the skeleton. Distribute the remaining 12 electrons.



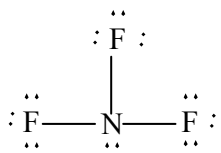
b. Total valence electrons = (2 x 1) + 6 = 8. The skeleton is H–Se–H. Distribute the remaining 4 electrons.



c. Total valence electrons = (3 x 7) + 5 = 26. The skeleton is

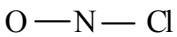


Distribute the remaining 20 electrons.

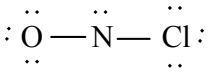


9.62.

a. Total valence electrons = 7 + 5 + 6 = 18. The skeleton is



Distribute the remaining 14 electrons so that the O and Cl atoms have an octet.



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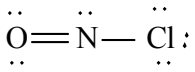
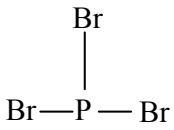
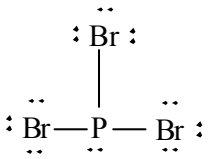
Draw a nitrogen-oxygen double bond to achieve an N octet.



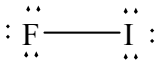
b. Total valence electrons = 5 + (3 x 7) = 26. The skeleton is



Distribute the remaining 20 electrons.

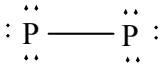


c. Total valence electrons = 7 + 7 = 14. F–I is the skeleton. Distribute the remaining 12 electrons.

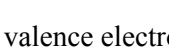


9.63.

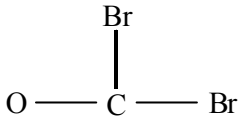
a. Total valence electrons = 2 x 5 = 10. The skeleton is P–P. Distribute the remaining electrons symmetrically:



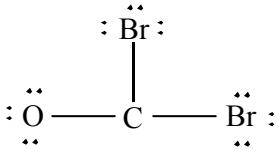
Neither P atom has an octet. There are 4 fewer electrons than needed. This suggests the presence of a triple bond. Make one lone pair from each P a bonding pair.



b. Total valence electrons = 4 + 6 + (2 x 7) = 24. The skeleton is



Distribute the remaining 18 electrons.



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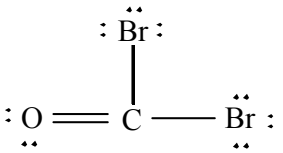
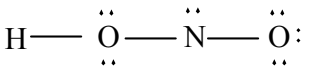
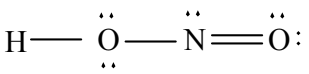
Note that carbon is two electrons short of an octet. This suggests the presence of a double bond. The most likely double bond is between C and O.



c. Total valence electrons = 1 + 5 + (2 x 6) = 18. The skeleton is most likely H–O–N–O. Distribute the remaining 12 electrons:

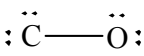


Note that the N atom does not have an octet. It is two electrons short. The most likely double bond is between N and O.



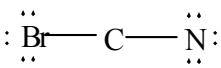
9.64.

a. Total valence electrons = 4 + 6 = 10. The skeleton is C–O. Distribute the remaining 8 electrons:

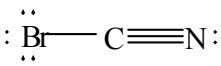


Neither atom has an octet. There are 4 fewer electrons than needed. This suggests a triple bond.

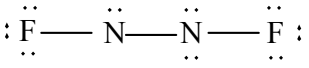
b. Total valence electrons = 7 + 4 + 5 = 16. The skeleton is Br–C–N. Distribute the remaining 12 electrons:



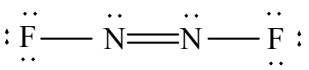
Note that the carbon atom is four electrons short of an octet. Make a triple bond between C and N from the four nonbonding electrons on nitrogen.



c. Total valence electrons = (2 x 5) + (2 x 7) = 24. The skeleton is F–N–N–F. Distribute the remaining 18 electrons.



Note that one of the nitrogens is two electrons short of an octet. This suggests the presence of a double bond. The most likely double bond is between the nitrogens.



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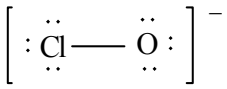
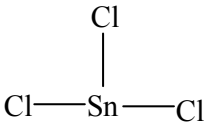
9.65.

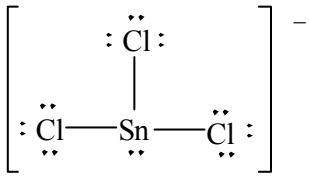
a. Total valence electrons = 7 + 6 + 1 = 14. The skeleton is Cl–O. Distribute the remaining 12 electrons.



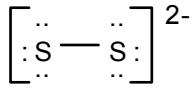
b. Total valence electrons = 4 + (3 x 7) + 1 = 26. The skeleton is



Distribute the remaining 20 electrons so that each atom has an octet.

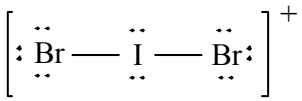


c. Total valence electrons = (2 x 6) + 2 = 14. The skeleton is S–S. Distribute the remaining 12 electrons.

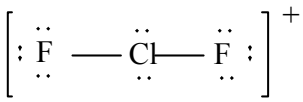


9.66.

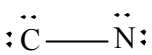
a. Valence electrons = 7 + (2 x 7) − 1 = 20. The skeleton is Br–I–Br. Distribute the remaining 16 electrons.



b. Total valence electrons = 7 + (2 x 7) − 1 = 20. The skeleton is F–Cl–F. Distribute the remaining 16 electrons.



c. Total valence electrons = 4 + 5 + 1 = 10. The skeleton is C–N. Distribute the remaining 8 electrons.



Note that neither atom has an octet. There are four fewer electrons than needed, suggesting a triple bond:

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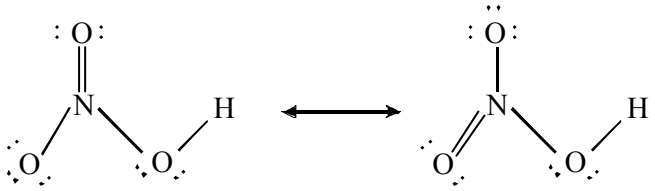
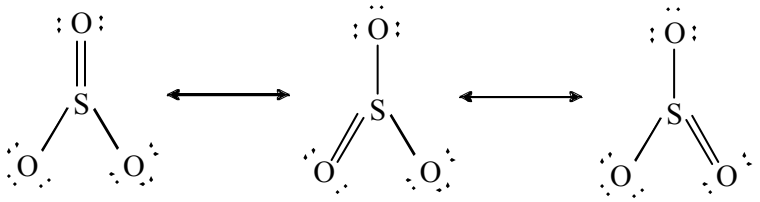
9.67.

a. There are two possible resonance structures for HNO_3.



One electron pair is delocalized over the nitrogen atom and the two oxygen atoms.

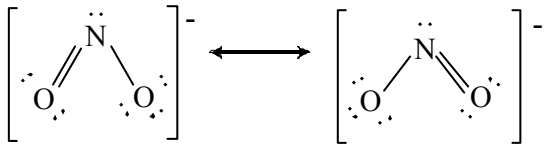
b. There are three possible resonance structures for SO_3.



One pair of electrons is delocalized over the region of the three sulfur-oxygen bonds.

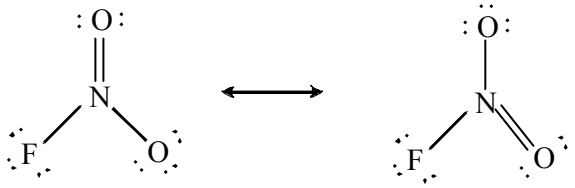
9.68.

a. There are two resonance forms for NO_2^-.



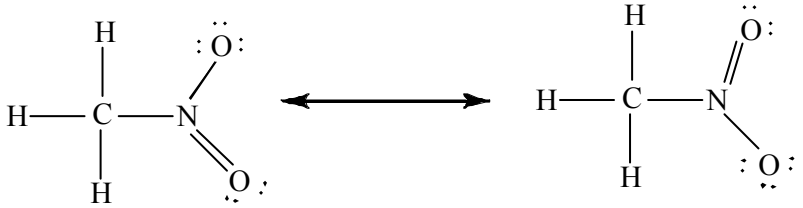
One pair of electrons is delocalized over the region of both nitrogen-oxygen bonds.

b. There are two possible resonance structures for FNO_2.



One electron pair is delocalized over the nitrogen atom and the two oxygen atoms.

9.69.



One pair of electrons is delocalized over the O–N–O bonds.

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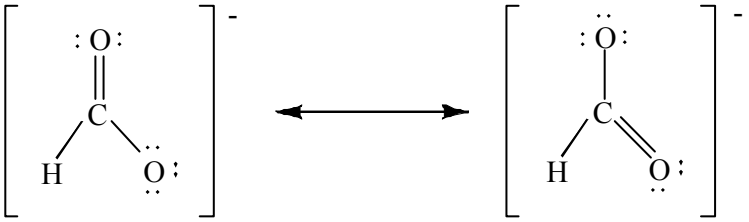
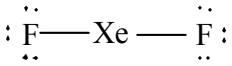
9.70.



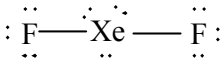
The two carbon-oxygen bonds are expected to be the same. This means one pair of electrons is delocalized over the region of the O–C–O bonds.

9.71.

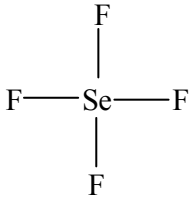
a. Total valence electrons = 8 + (2 x 7) = 22. The skeleton is F–Xe–F. Place six electrons around each fluorine atom to satisfy its octet.



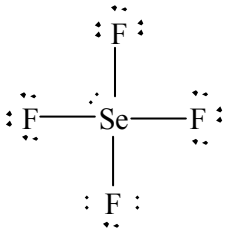
There are three electron pairs remaining. Place them on the xenon atom.



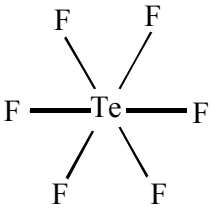
b. Total valence electrons = 6 + (4 x 7) = 34. The skeleton is



Distribute 24 of the remaining 26 electrons on the fluorine atoms. The remaining pair of electrons is placed on the selenium atom.



c. Total valence electrons = 6 + (6 x 7) = 48. The skeleton is



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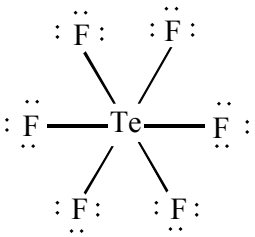
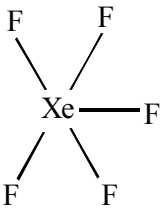
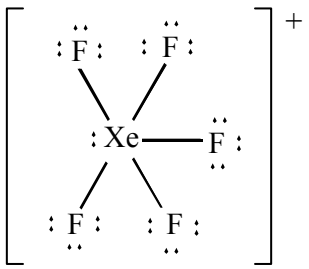
Distribute the remaining 36 electrons on the fluorine atoms.



d. Total valence electrons = 8 + (5 x 7) − 1 = 42. The skeleton is

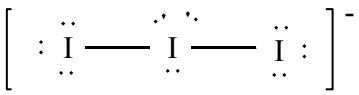


Use 30 of the remaining 32 electrons on the fluorine atoms to complete their octets. The remaining 2 electrons form a lone pair on the xenon atom.

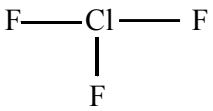


9.72.

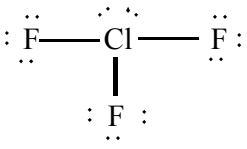
a. Total valence electrons = (3 x 7) + 1 = 22. The skeleton is I–I–I. Distribute the remaining 18 electrons. The central iodine atom may expand its octet.



b. Total valence electrons = 7 + (3 x 7) = 28. The skeleton is



Distribute 18 of the remaining 22 electrons to complete the octets of the fluorine atoms. The four remaining electrons form two sets of lone pairs on the chlorine atom.



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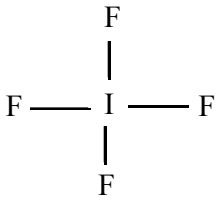
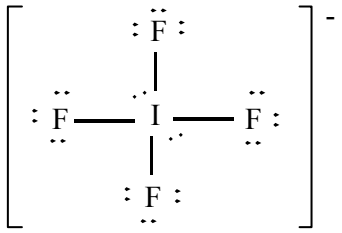
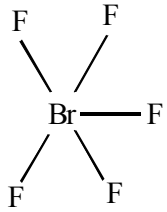
c. Total valence electrons = 7 + (4 x 7) + 1 = 36. The skeleton is



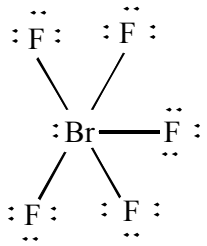
Distribute 24 of the 28 remaining electrons to complete the octets of the fluorine atoms. The 4 electrons remaining form two sets of lone pairs on the iodine atom.



d. Total valence electrons = 7 + (5 x 7) = 42. The skeleton is

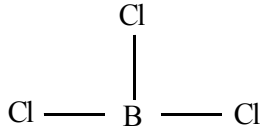


Use 30 of the remaining 32 electrons to complete the octets of the fluorine atoms. The 2 electrons remaining form a lone pair on the bromine atom.



9.73.

a. Total valence electrons = 3 + (3 x 7) = 24. The skeleton is



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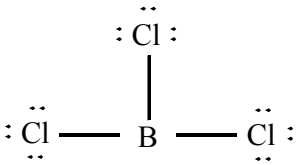
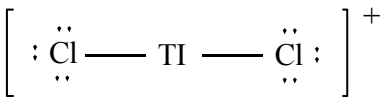
Distribute the remaining 18 electrons.



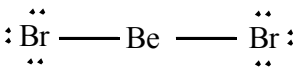
Although boron has only 6 electrons, it has the normal number of covalent bonds.

b. Total valence electrons = 3 + (2 x 7) − 1 = 16. The skeleton is Cl–Tl–Cl. Distribute the remaining 12 electrons.



Tl has only 4 electrons around it.

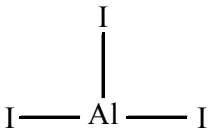
c. Total valence electrons = 2 + (2 x 7) = 16. The skeleton is Br–Be–Br. Distribute the remaining 12 electrons.



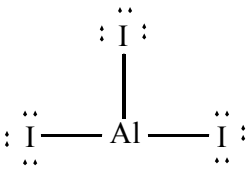
In covalent compounds, beryllium frequently has two bonds, even though it does not have an octet.

9.74.

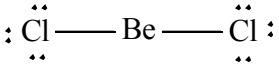
a. Total valence electrons = 3 + (3 x 7) = 24. The skeleton is



Distribute the remaining 18 electrons to the iodine atoms.



b. Total valence electrons = 2 + (2 x 7) = 16. The skeleton is Cl–Be–Cl. Distribute the remaining 12 electrons.



In covalent compounds, beryllium commonly has two bonds, even though it does not have an octet.

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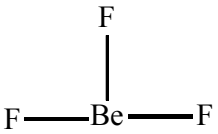
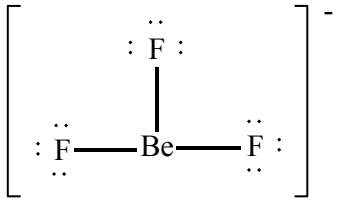
c. Total valence electrons = 2 + (3 x 7) + 1 = 24. The skeleton is



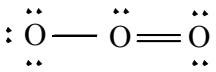
Distribute the remaining 18 electrons on the fluorine atoms.



This ion is isoelectronic with BF_3, and the beryllium, like boron, has only 6 electrons around it.

9.75.

a. The total number of electrons in O_3 is 3 x 6 = 18. Assume a skeleton structure in which one oxygen atom is singly bonded to the other two oxygen atoms. This requires four electrons for the two single bonds, leaving fourteen electrons to be used. Distribute three electron pairs to each of the outer oxygen atoms to complete their octets. This requires twelve more electrons, leaving two electrons to distribute. Since this is two electrons short of an octet, move a pair of electrons from one of the outer oxygen atoms to give an oxygen-oxygen double bond. One of the possible resonance structures is shown below; the other structure would have the double bond written between the left and central oxygen atoms.



Starting with the left oxygen, the formal charge of this oxygen is 6 − 1 − 6 = −1. The formal charge of just the central oxygen is 6 − 3 − 2 = +1. The formal charge of the right oxygen is 6 − 2 − 4 = 0. The sum of all three is 0.

b. The total number of electrons in CO is 4 + 6 = 10. Assume a skeleton structure in which the oxygen atom is singly bonded to the carbon atom. This requires two electrons for the single bond and leaves eight electrons. Distribute these remaining electrons around the atoms. Since four more electrons are needed to complete octets on both atoms, move two electron pairs to give a carbon-oxygen triple bond.

The structure is

The formal charge of the carbon is 4 − 3 − 2 = −1. The formal charge of the oxygen is 6 − 3 − 2 = +1. The sum of both is 0.

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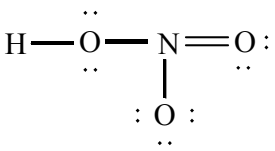
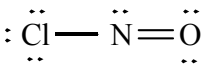
c. The total number of electrons in HNO_3 is 1 + 5 + 18 = 24. Assume a skeleton structure in which the nitrogen atom is singly bonded to two oxygen atoms and doubly bonded to one oxygen. This requires two electrons for the O–H single bond and leaves eight electrons to be used for the N bonds.



The formal charge of the nitrogen is 5 − 4 − 0 = +1. The formal charge of the hydrogen is 1 − 1 − 0 = 0. The formal charge of the oxygen bonded to the hydrogen is 6 − 2 − 4 = 0. The formal charge of the other singly bonded oxygen is 6 − 1 − 6 = −1. The formal charge of the doubly bonded oxygen is 6 − 2 − 4 = 0.

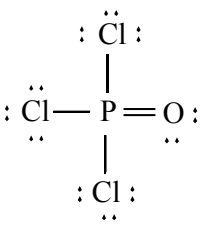
9.76.

a. The total number of electrons in ClNO is 7 + 5 + 6 = 18. Assume a skeleton structure in which one chlorine atom is singly bonded to the nitrogen atom. If a N–O single bond is assumed, twenty electrons are needed to fill the outer octets. Hence, a N=O double bond must be used, the structure being



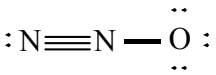
The formal charge of the chlorine is 7 – 1 – 6 = 0. The formal charge of the nitrogen is 5 – 3 – 2 = 0. The formal charge of the oxygen is 6 – 2 – 4 = 0.

b. The total number of electrons in $POCl_3$ is 5 + 6 + 21 = 32. Assume a skeleton structure in which the phosphorus atom is singly bonded to each of the three chlorines and doubly bonded to the oxygen. This structure has a lower formal charge than one with a single P–O bond.



The formal charge of phosphorus is 5 – 5 – 0 = 0. The formal charge on each chlorine is 7 – 1 – 6 = 0. The formal charge of oxygen is 6 – 2 – 4 = 0.

c. The total number of electrons in N_2O is 2 x 5 + 6 = 16. Assume a skeleton structure in which the two nitrogen atoms are double bonded to each other. The oxygen atom can be singly bonded or doubly bonded to the central nitrogen. Using a N–O single bond gives the lowest formal charge.



The formal charge of the end nitrogen is 5 − 2 − 3 = 0. The formal charge of the nitrogen between the end nitrogen and oxygen is 5 − 4 = +1. The formal charge of the oxygen is 6 − 6 − 1 = −1.

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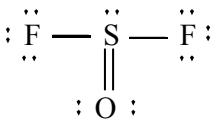
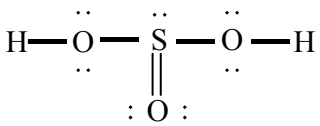
9.77.

a. The total number of electrons in SOF_2 is 6 + 6 + 14 = 26. Assume a skeleton structure in which the sulfur atom is singly bonded to the two fluorine atoms. If a S–O single bond is assumed, 26 electrons are needed. However, there would be formal charges of +1 on the sulfur and −1 on the oxygen. Using a S=O double bond requires only 26 electrons and results in zero formal charge.



The formal charge on each of the two fluorine atoms is 7 − 1 − 6 = 0. The formal charge on the oxygen is 6 − 2 − 4 = 0. The formal charge on the sulfur is 6 − 4 − 2 = 0.

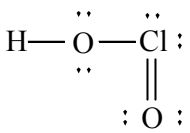
b. The total number of electrons in H_2SO_3 is 2 + 6 + 18 = 26. Assume a skeleton structure in which the sulfur atom is singly bonded to the three oxygen atoms. Then form single bonds from the two hydrogen atoms to each of two oxygen atoms. If a S–O single bond is assumed, 26 electrons are needed. However, there would be formal charges of +1 on the sulfur and −1 on the oxygen. A S=O double bond also requires 26 electrons but results in zero formal charge on all atoms.



The formal charge of each hydrogen is 1 − 1 = 0. The formal charge of each oxygen bonded to a hydrogen is 6 − 2 − 4 = 0. The formal charge of the oxygen doubly bonded to the sulfur is 6 − 2 − 4 = 0. The formal charge of the sulfur is 6 − 4 − 2 = 0.

c. The total number of electrons in $HClO_2$ is 1 + 7 + 12 = 20. Assume a skeleton structure in which the chlorine atom is singly bonded to the two oxygen atoms, and the hydrogen is singly bonded to one of the oxygen atoms. If all Cl–O single bonds are assumed, 20 electrons are needed, but the chlorine exhibits a formal charge of +1 and one oxygen exhibits a formal charge of −1.

Hence, a pair of electrons on the oxygen without the hydrogen is used to form a Cl=O double bond.



The formal charge of hydrogen is 1 − 1 = 0. The formal charge of the oxygen bonded to hydrogen is 6 − 2 − 4 = 0. The formal charge of the oxygen that is not bonded to the hydrogen is 6 − 2 − 4 = 0. The formal charge of the chlorine is 7 − 3 − 4 = 0.

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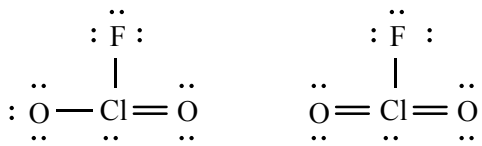
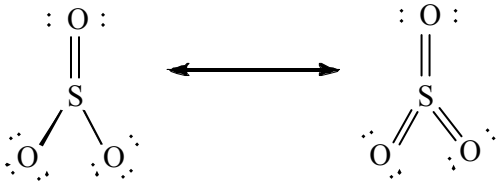
9.78.

a. The total number of electrons in ClO_2F is 7 + 12 + 7 = 26. Assume a skeleton structure in which the chlorine atom is singly bonded to the two oxygen atoms and the fluorine atom. If all single bonds are assumed, the chlorine has a formal charge of +2, and each oxygen has a formal charge of −1. The general principle to be followed whenever two atoms on a bond have opposite charges is to move an electron pair on the atom with the negative charge into the bond and form a double bond. Doing this once gives the structure on the left below. In this structure, the chlorine now has a formal charge of +1, and the oxygen on the left has a formal charge of −1. Following the general principle again results in the formation of a second double bond, as shown in the structure on the right.



In the structure on the right, the formal charge of each oxygen is 6 − 2 − 4 = 0. The formal charge of the fluorine is 7 − 1 − 6 = 0. The formal charge of the chlorine is 7 − 5 − 2 = 0.

b. The total number of electrons in SO_3 is 6 + 18 = 24. Assume a skeleton structure in which the sulfur atom is singly bonded to the three oxygen atoms. If all single bonds are assumed, the sulfur atom has a formal charge of +3, and each of the oxygen atoms has a formal charge of −1. As in part a, the general principle to be followed whenever two atoms on a bond have opposite charges is to move an electron pair on the atom with the negative charge into the bond and form a double bond. Doing this once gives the structure on the left below. In this structure, the sulfur now has a formal charge of +2, and the other oxygen atoms have a formal charge of −1. Following the general principle again two more times results in the formation of two more double bonds, as shown in the structure on the right.



The formal charge of the oxygen atoms in the structure on the right is 6 − 2 − 4 = 0. The formal charge of the sulfur is 6 − 6 = 0.

c. The total number of electrons in BrO_3^-, including the charge, is 26. Assume a skeleton structure in which the bromine atom is singly bonded to the three oxygen atoms. If all single bonds are assumed, the bromine atom has a formal charge of +2, and each of the oxygen atoms has a formal charge of −1. As in part a, the general principle to be followed whenever two atoms on a bond have opposite charges is to move an electron pair on the atom with the negative charge into the bond and form a double bond. Doing this once gives the structure on the left below. In this structure, the bromine now has a formal charge of +1, and the two oxygen atoms have a formal charge of −1.

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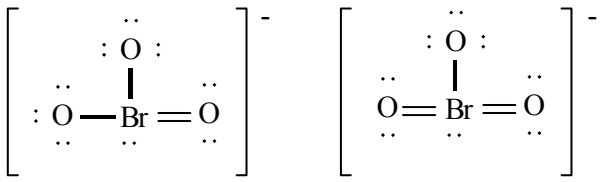
Following the general principle again results in the formation of a second double bond, as shown in the structure on the right.



In the right-hand structure, the formal charge of the two doubly bonded oxygen atoms is $6 - 2 - 4 = 0$. The formal charge of the singly bonded oxygen is $6 - 1 - 6 = -1$. The formal charge of the bromine is $7 - 5 - 2 = 0$.

9.79. $r_F = 64$ pm

$r_P = 110$ pm

$d_{P-F} = r_F + r_P = 64 \text{ pm} + 110 \text{ pm} = 174 \text{ pm}$

9.80. $r_B = 88$ pm

$r_F = 64$ pm

$d_{B-F} = r_B + r_F = 88 \text{ pm} + 64 \text{ pm} = 152 \text{ pm}$

9.81.

a. $d_{C-H} = r_C + r_H = 77 \text{ pm} + 37 \text{ pm} = 114 \text{ pm}$

b. $d_{S-Cl} = r_S + r_{Cl} = 104 \text{ pm} + 99 \text{ pm} = 203 \text{ pm}$

c. $d_{Br-Cl} = r_{Br} + r_{Cl} = 114 \text{ pm} + 99 \text{ pm} = 213 \text{ pm}$

d. $d_{Si-O} = r_{Si} + r_O = 117 \text{ pm} + 66 \text{ pm} = 183 \text{ pm}$

9.82. $d_{C-H} = r_C + r_H = 77 \text{ pm} + 37 \text{ pm} = 114 \text{ pm}$ $\quad d_{exp} = 107$ pm

$d_{C-Cl} = r_C + r_{Cl} = 77 \text{ pm} + 99 \text{ pm} = 176 \text{ pm}$ $\quad d_{exp} = 177$ pm

The calculated bond distances agree very well with the experimental values.

9.83.

Methylamine	147pm	Single C–N bond is longer.
Acetonitrile	116pm	Triple C–N bond is shorter.

9.84. Formaldehyde has a shorter carbon-oxygen bond than methanol. In methanol, the carbon-oxygen bond is a single bond, and in formaldehyde it is a double bond.

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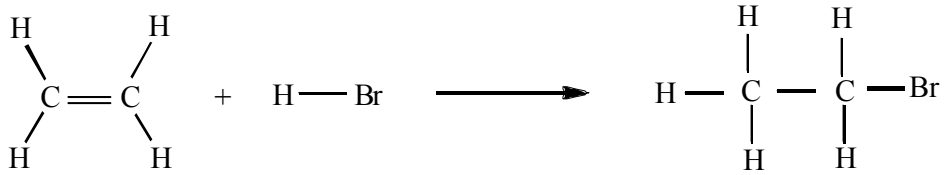
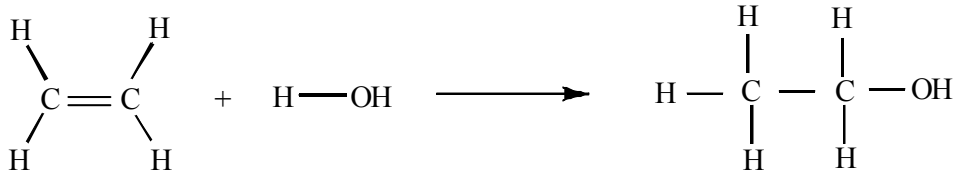
9.85. 

In the reaction, a C=C double bond is converted to a C–C single bond. An H–Br bond is broken, and one C–H bond and one C–Br bond are formed.

$$\Delta H \cong BE(\text{C=C}) + BE(\text{H–Br}) - BE(\text{C–C}) - BE(\text{C–H}) - BE(\text{C–Br})$$
$$= (602 + 362 - 346 - 411 - 285)\ \text{kJ} = -78\ \text{kJ}$$

9.86. 

In the reaction, a C=C bond and an O–H bond are converted to a C–C single bond, a C–O bond, and a C–H bond.

$$\Delta H \cong [BE(\text{C=C}) + BE(\text{O–H})] - [BE(\text{C–C}) + BE(\text{C–O}) + BE(\text{C–H})]$$
$$= [(602 + 459) - (346 + 358 + 411)]\ \text{kJ} = -54\ \text{kJ}$$

■ SOLUTIONS TO GENERAL PROBLEMS

9.87.

a. Strontium is a metal, and oxygen is a nonmetal. The binary compound is likely to be ionic. Strontium, in Group IIA, forms Sr^{2+} ions; oxygen, from Group VIA, forms O^{2-} ions. The binary compound has the formula SrO and is named strontium oxide.

b. Carbon and bromine are both nonmetals; hence, the binary compound is likely to be covalent. Carbon usually forms four bonds, and bromine usually forms one bond. The formula for the binary compound is CBr_4. It is called carbon tetrabromide.

c. Gallium is a metal, and fluorine is a nonmetal. The binary compound is likely to be ionic. Gallium is in Group IIIA and forms Ga^{3+} ions. Fluorine is in Group VIIA and forms F^- ions. The binary compound is GaF_3 and is named gallium(III) fluoride.

d. Nitrogen and bromine are both nonmetals; hence, the binary compound is likely to be covalent. Nitrogen usually forms three bonds, and bromine usually forms one bond. The formula for the binary compound is NBr_3. It is called nitrogen tribromide.

9.88.

a. Sodium is a metal, and sulfur is a nonmetal. The binary compound is likely to be ionic. Sodium, in Group IA, forms Na^+ ions. Sulfur, in Group VIA, forms S^{2-} ions. The binary compound is Na_2S. It is named sodium sulfide.

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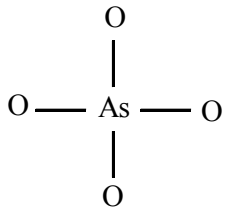
b. Aluminum is a metal, and fluorine is a nonmetal. The binary compound is likely to be ionic. Aluminum, in Group IIIA, forms Al^{3+} ions. Fluorine, in Group VIIA, forms F^- ions. The binary compound is AlF_3. It is named aluminum fluoride.

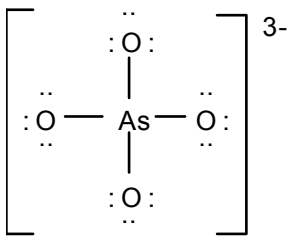
c. Calcium is a metal, and chlorine is a nonmetal. The binary compound is likely to be ionic. Calcium, in Group IIA, forms Ca^{2+} ions. Chlorine, in Group VIIA, forms Cl^- ions. The binary compound is $CaCl_2$. It is named calcium chloride.

d. Silicon and bromine are both nonmetals; hence, the binary compound is likely to be covalent. Silicon usually forms four bonds, and bromine usually forms one bond. The formula for the binary compound is $SiBr_4$. It is called silicon tetrabromide.

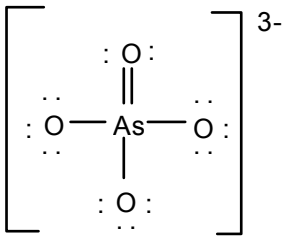
9.89. Total valence electrons = 5 + (4 x 6) + 3 = 32. The skeleton is



Distribute the remaining 24 electrons to complete the octets around the oxygen atoms.

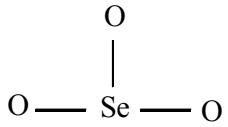


or

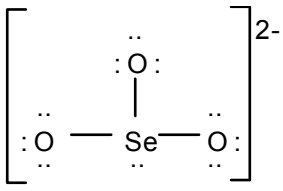


The formula for lead(II) arsenate is $Pb_3(AsO_4)_2$.

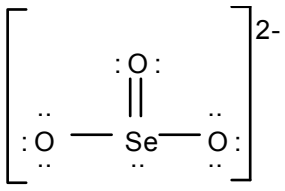
9.90. Total valence electrons = 6 + (3 x 6) + 2 = 26. The skeleton is



Distribute the remaining 20 electrons to complete the octets of oxygen and selenium atoms.



or



The formula for aluminum selenite is $Al_2(SeO_3)_3$.

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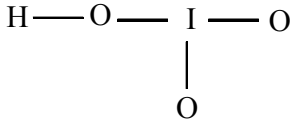
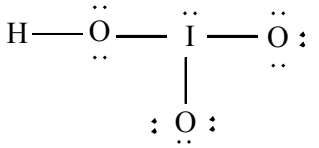
9.91. Total valence electrons = 1 + 7 + (3 x 6) = 26. The skeleton is



Distribute the remaining 18 electrons to satisfy the octet rule. The structure on the right has no formal charge.



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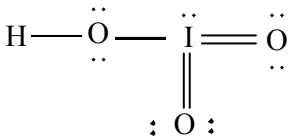
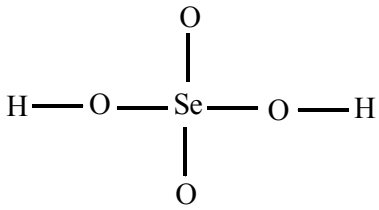
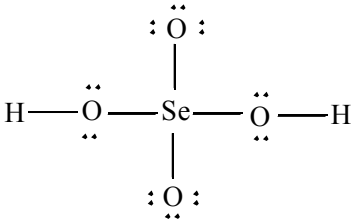


9.92. Total valence electrons = (2 x 1) + 6 + (4 x 6) = 32. The skeleton is



Distribute the remaining 20 electrons to satisfy the octet rule. The structure on the right has no formal charge.



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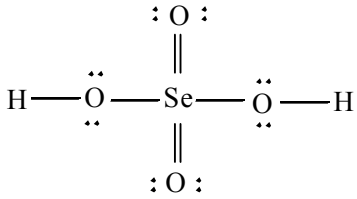
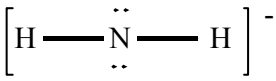
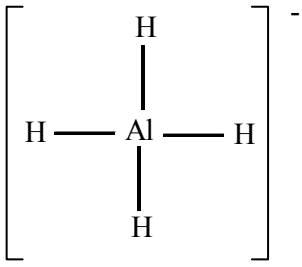


9.93. Total valence electrons = 5 + (2 x 1) + 1 = 8. The skeleton is H–N–H. Distribute the remaining 4 electrons to complete the octet of the nitrogen atom.



9.94. Total valence electrons = 3 + (4 x 1) + 1 = 8. The skeleton structure will use all the electrons. Because there are no electrons left, the Lewis structure is



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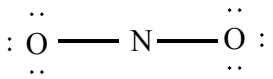
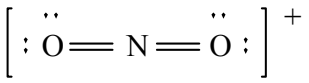
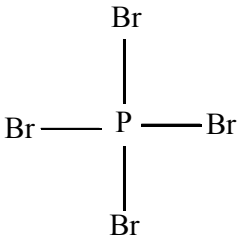
9.95. Total valence electrons = 5 + (2 x 6) − 1 = 16. The skeleton is O–N–O. Distribute the remaining electrons on the oxygen atoms.



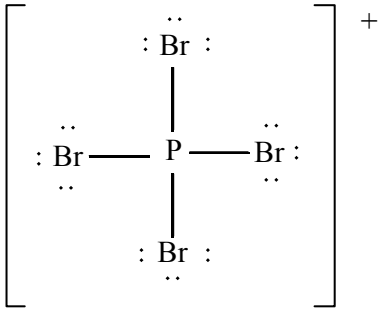
The nitrogen atom is short four electrons. Use two double bonds, one with each oxygen.



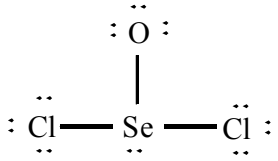
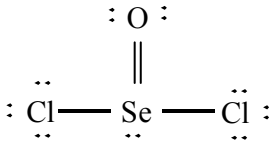
9.96. Total valence electrons = 5 + (4 x 7) − 1 = 32. The skeleton is

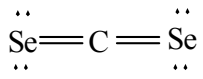


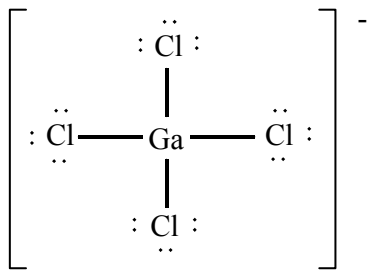
Distribute the 24 remaining electrons to complete the octets on the bromine atoms.



9.97.

a.  or 

b. 

c. 

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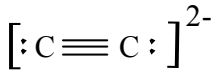
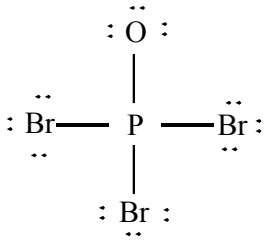
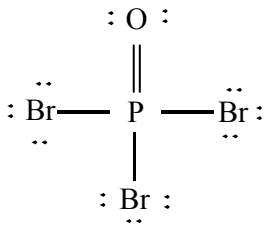
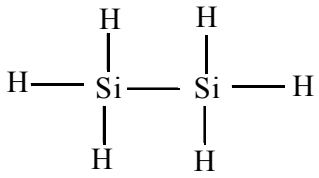
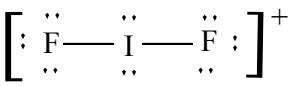
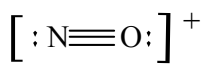
d. 

9.98.

a.  or 

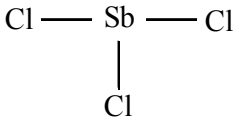
b. 

c. 

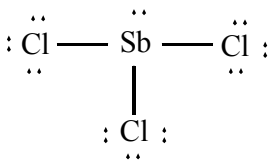
d. 

9.99.

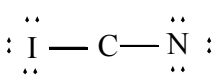
a. Total valence electrons = 5 + (3 x 7) = 26. The skeleton is



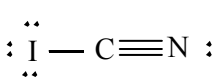
Distribute the remaining 20 electrons to the chlorine atoms and the antimony atom to complete their octets.



b. Total valence electrons = 7 + 4 + 5 = 16. The skeleton is I–C–N. Distribute the remaining 12 electrons.



Notice the carbon atom is four electrons short of an octet. Make a triple bond between C and N from the four nonbonding electrons on the nitrogen.



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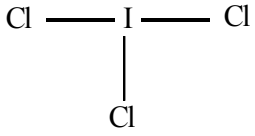
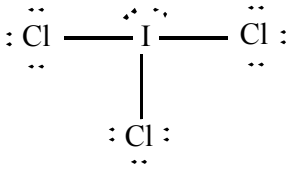
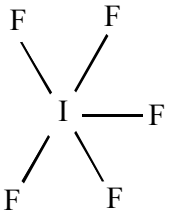
c. Total valence electrons = 7 + (3 x 7) = 28. The skeleton is



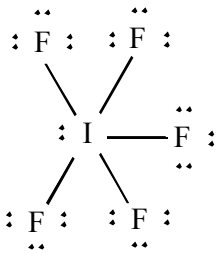
Distribute 18 of the remaining 22 electrons to complete the octets of the chlorine atoms. The 4 remaining electrons form two sets of lone pairs on the iodine atom.



d. Total valence electrons = 7 + (5 x 7) = 42. The skeleton is

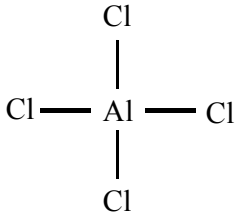


Use 30 of the remaining 32 electrons to complete the octets of the fluorine atoms. The 2 electrons remaining form a lone pair on the iodine atom:



9.100.

a. Total valence electrons = 3 + (4 x 7) + 1 = 32. The skeleton is



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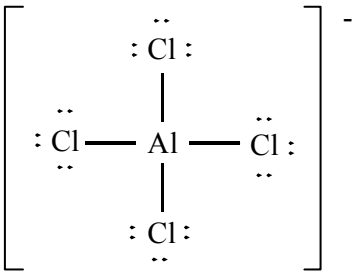
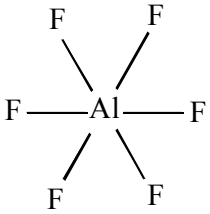
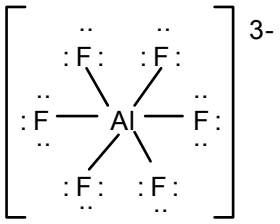
Distribute the remaining 24 electrons to complete the octets of the Cl atoms.



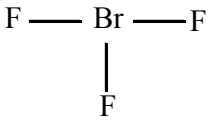
b. Total valence electrons = 3 + (6 x 7) + 3 = 48. The skeleton is



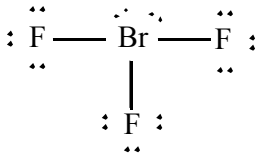
Distribute the remaining 36 electrons to complete the octets of the F atoms.



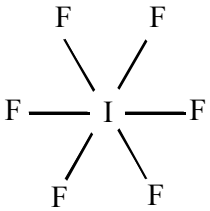
c. Total valence electrons = 7 + (3 x 7) = 28. The skeleton is



Distribute 18 of the remaining 22 electrons to complete the octets of the fluorine atoms. The 4 remaining electrons form two sets of lone pairs on the bromine atom.



d. Total valence electrons = 7 + (6 x 7) − 1 = 48. The skeleton is



Distribute the remaining 36 electrons to complete the octets of the fluorine atoms.

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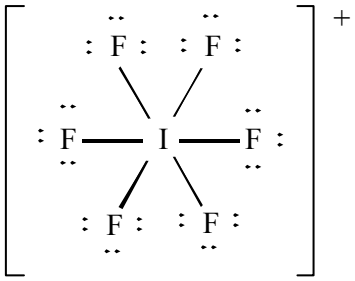
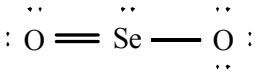
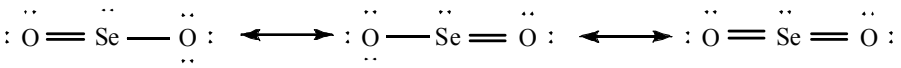


9.101.

a. One possible electron-dot structure is

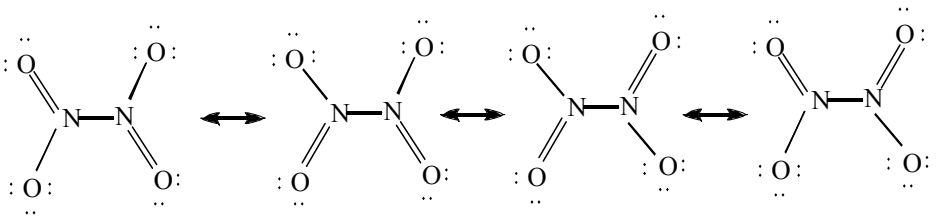


Because the selenium-oxygen bonds are expected to be equivalent, the structure must be described in resonance terms.



The electrons are delocalized over the selenium atom and the two oxygen atoms.

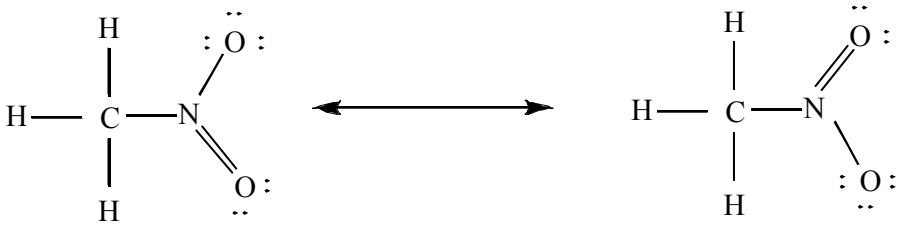
b. The possible electron-dot structures are



At each end of the molecule, a pair of electrons is delocalized over the region of the nitrogen atom and the two oxygen atoms.

9.102.

a.



One pair of electrons is delocalized over the O–N–O bonds.

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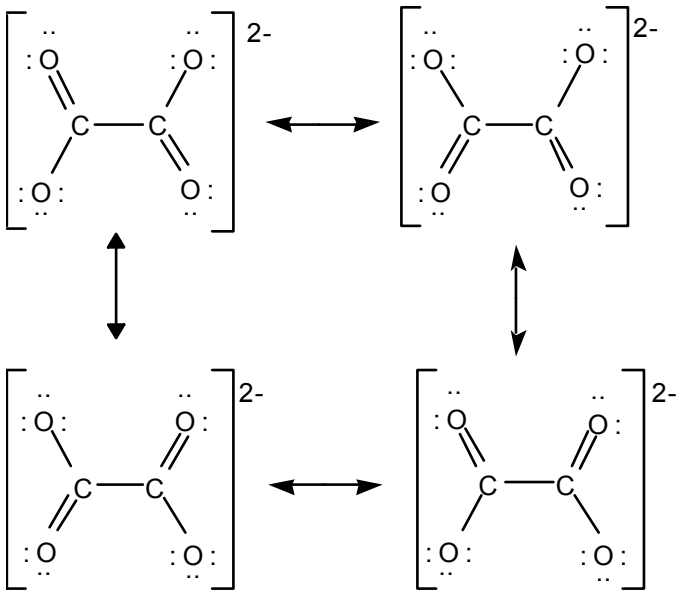
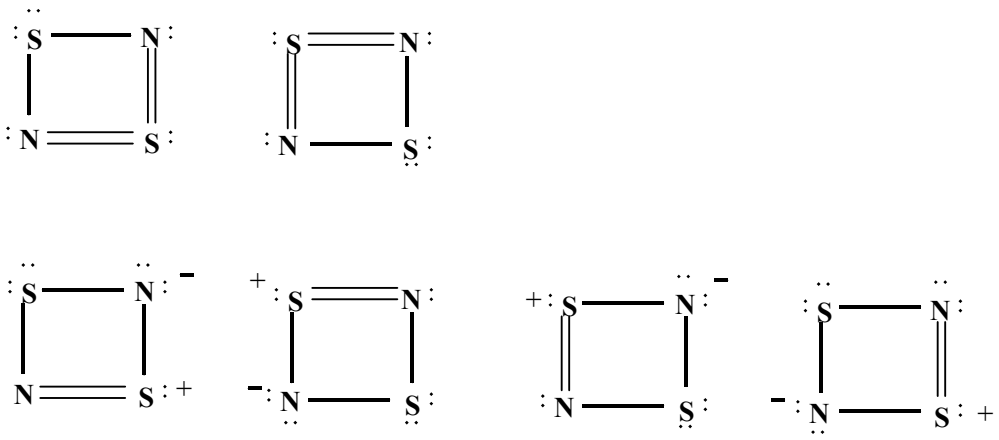
b. The possible electron-dot structures are



At each end of the molecule, a pair of electrons is delocalized over the region of the two carbon-oxygen bonds.

9.103. The compound S_2N_2 will have a four-membered ring structure. Calculate the total number of valence electrons of sulfur and nitrogen, which will be 6 + 6 + 5 + 5 = 22. Writing the skeleton of the four-membered ring with single S–N bonds will use up eight electrons, leaving fourteen electrons for electron pairs. After writing an electron pair on each atom, there will be six electrons left for three electron pairs. No matter where these electrons are written, either a nitrogen or a sulfur will be left with less than eight electrons. This suggests one or more double bonds are needed. If only one S=N double bond is written, writing the remaining twelve electrons as six electron pairs will give the sulfur in the S=N double bond a formal charge of 1+ (see second line of formulas on next page). Writing two S=N double bonds using the same sulfur for both double bonds will give a formal charge of zero for all four atoms (see first line of formulas). The first two resonance formulas below have a zero formal charge on all atoms. However, one of the sulfur atoms does not obey the octet rule.



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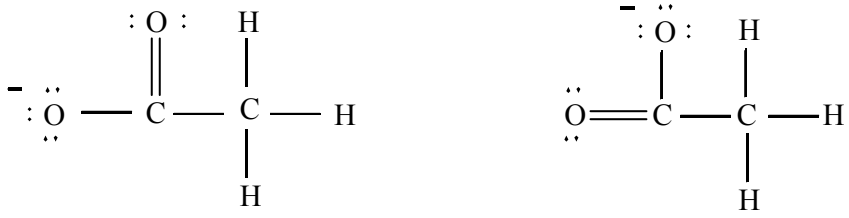
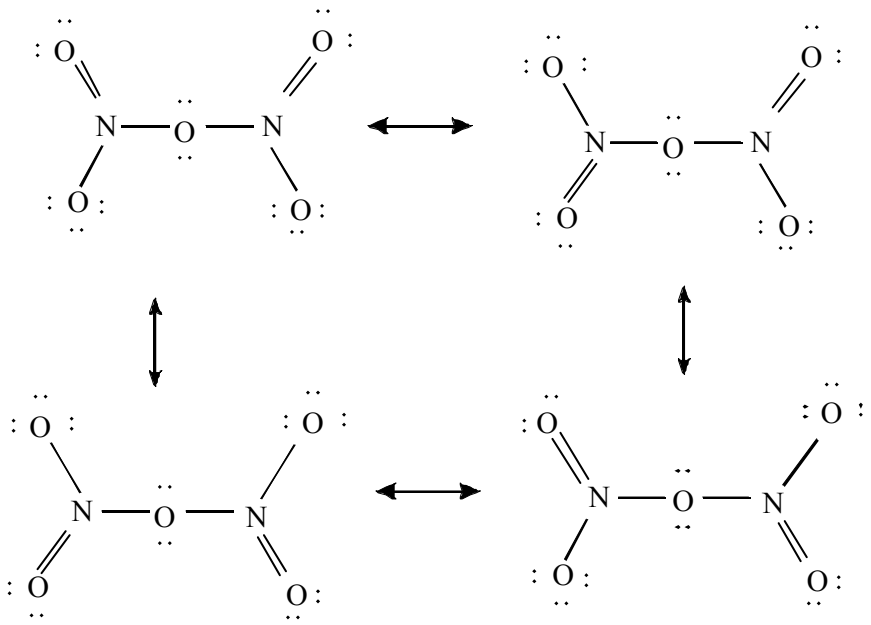
In the four resonance formulas at the bottom of the previous page, all of the atoms obey the octet rule, but there is a positive formal charge on one sulfur atom and a negative formal charge on one nitrogen atom.

9.104. If you try to write an electron-dot formula for the acetate ion, you will find you can write two formulas.



According to theory, the C=O double bond is delocalized; that is, a bonding pair of electrons is spread over the carbon atom and the two oxygen atoms, rather than localized between a carbon and one oxygen. This results in both bonds being of identical length.

9.105. The possible electron-dot structures are



Because double bonds are shorter, the terminal N–O bonds are 118 pm, and the central N–O bonds are 136 pm.

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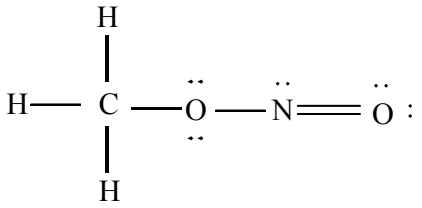
9.106. The best possible electron-dot structure is



Because double bonds are shorter, the terminal N=O bond is 122 pm, and the inner N–O bond is 137 pm.

9.107. $\Delta H = BE(\text{H–H}) + BE(\text{O=O}) - 2BE(\text{H–O}) - BE(\text{O–O})$

$= (432 + 494 - 2 \times 459 - 142)\ \text{kJ} = -134\ \text{kJ}$

9.108. $\Delta H = 2BE(\text{H–H}) + BE(\text{N}\equiv\text{N}) - BE(\text{N–N}) - 4BE(\text{N–H})$

$= (2 \times 432 + 942 - 167 - 4 \times 386)\ \text{kJ} = +95\ \text{kJ}$

9.109. $\Delta H = BE(\text{N=N}) + BE(\text{F–F}) - BE(\text{N–N}) - 2BE(\text{N–F})$

$= (418 + 155 - 167 - 2 \times 283)\ \text{kJ} = -1.60 \times 10^2\ \text{kJ}$

9.110. $\Delta H = BE(\text{C}\equiv\text{N}) + 2BE(\text{H–H}) - BE(\text{C–N}) - 2BE(\text{C–H}) - 2BE(\text{N–H})$

$= (887 + 2 \times 432 - 305 - 2 \times 411 - 2 \times 386)\ \text{kJ} = -148\ \text{kJ}$

9.111. Ionic materials like NaCl are solids at room temperature, with high melting points. The molten liquid, which is clear, is very corrosive. Ionic materials consist of small, spherical ions that pack closely together. Thus, the ions interact strongly, giving a solid with a high melting point. Room-temperature ionic liquids, which are also clear, consist of large, nonspherical cations with various anions. The large, bulky cation keeps the ions from packing closely, yielding a substance with weak interactions and a low melting point.

9.112. Organic solvents are volatile liquids that evaporate easily into the surrounding air, where they can contribute to air pollution. Organic solvents are often flammable. Ionic liquids are neither volatile nor flammable. Also, the proper choice of ionic liquid may improve the yield and lower the costs of a chemical process.

9.113. The decomposition of nitroglycerin is given by

$$4C_3H_5(ONO_2)_3(l) \rightarrow 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)$$

The stability of the products results from their strong bonds, which are much stronger than those in nitroglycerin. Nitrogen has a strong nitrogen-nitrogen triple bond, and carbon dioxide has two strong carbon-oxygen double bonds.

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9.114. Nobel discovered that nitroglycerin behaved better when absorbed on diatomaceous earth, a crumbly rock, giving an explosive mixture called dynamite.

9.115. A chemical bond acts like a stiff spring connecting nuclei. As a result, the nuclei in a molecule vibrate relative to each other. The vibration of molecules is revealed in their absorption of infrared radiation. The frequency of radiation absorbed equals the frequencies of nuclear vibrations.

9.116. The IR spectrum can act as a compound's fingerprint. It can also yield structural information. Certain structural features of molecules appear as absorption peaks in definite regions of the infrared spectrum. Knowledge of where various bands absorb provide clues to the structure of the molecule.

■ SOLUTIONS TO STRATEGY PROBLEMS

9.117. Structure a is incorrect. Al^{3+} ion has zero valence electrons. The rest are valid Lewis structures.

9.118. Both structure a (Ar) and structure d (Cl^-) are isoelectronic with the potassium ion, K^+. The electron configuration is $[Ne]3s^2 3p^6$.

9.119. The ion is Ti^{2+} ($Z = 22$) and the atom is Ca ($Z = 20$).

9.120.

a. Cl^-

b. Ca^+

c. Ni^{2+}

d. Ge^{2+}

e. Br^-

9.121. Both structure c ($COCl_2$) and structure d (C_2H_4) possess a double bond. CN^- has an atom with a nonzero formal charge.

9.122. Only structure b (CO_2) contains only double bonds.

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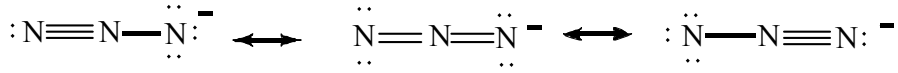
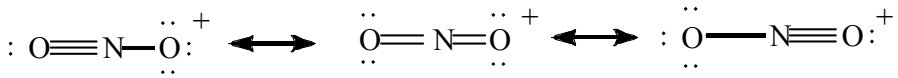
9.123. The resonance structures for the azide ion are



In the structure on the left, the nitrogen on the right has a formal charge of 2− and the central nitrogen has a formal charge of 1+. In the center structure, the nitrogen atoms on each end have formal charges of 1−, and the central nitrogen has a formal charge of 1+. In the structure on the right, the nitrogen on the left has a formal charge of 2− and the central nitrogen has a formal charge of 1+. The center structure is the most likely because it has smaller formal charges.

The resonance structures for the nitronium ion are



In the structure on the left, the oxygen on the right has a formal charge of 1−, the nitrogen has a formal charge of 1+, and the oxygen on the left has a formal charge of 1+. In the center structure, the oxygen atoms on each end have formal charges of zero, and the nitrogen has a formal charge of 1+. In the structure on the right, the oxygen on the left has a formal charge of 1−, the nitrogen has a formal charge of 1+, and the oxygen on the right has a formal charge of 1+. The center structure is the most likely because it has smaller formal charges.

9.124. If M is Fe, then the electron configuration of X is $[Ar]3d^{10}4s^24p^4$. If M is Co, the electron configuration of X is exactly the same as for iron.

9.125. The reaction is $X_2 + Y_2 \rightarrow 2XY$. The enthalpy of the reaction is

$$\Delta H°_{rxn} = 2\Delta H°_f[XY] - \Delta H°_f[X_2] - \Delta H°_f[Y_2] = 2\Delta H°_f[XY] - 0 - 0 = 2\Delta H°_f[XY]$$

$$\cong BE[X–X] + BE[Y–Y] - 2BE[X–Y] \cong BE[X–X] + BE[Y–Y] - 2BE[X–Y]$$

Combining the two expressions gives

$$2\Delta H°_f[XY] = BE[X–X] + BE[Y–Y] - 2BE[X–Y]$$

$$BE[X–Y] = \frac{BE[X\text{-}X] + BE[Y\text{-}Y] - 2\Delta H°_f[XY]}{2 \text{ mol}} = \frac{414 \text{ kJ} + 159 \text{ kJ} - 2(-336 \text{ kJ})}{2 \text{ mol}}$$

$$= 622.5 = 623 \text{ kJ/mol} = 622.5 = 623 \text{ kJ/mol}$$

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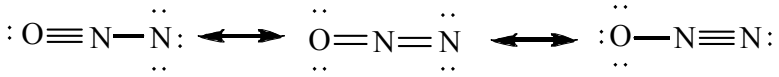
9.126. The resonance formulas for nitrous oxide are



In the structure on the left, the oxygen has a formal charge of 1+, the nitrogen in the center has a formal charge of 1+, and the nitrogen on the left has a formal charge of 2−. In the center structure, the oxygen has a formal charge of zero, the nitrogen in the center has a formal charge of 1+, and the nitrogen on the right has a formal charge of 1−. In the structure on the right, the oxygen has a formal charge of 1−, the nitrogen in the center has a formal charge of 1+, and the nitrogen on the right has a formal charge of zero. The structure on the right is the most likely because it has smaller formal charges, and the negative formal charge is on the oxygen atom. The structure in the middle also has smaller formal charges, but here, nitrogen has the negative formal charge, which is less favorable than to have it on the oxygen atom. The structure on the left is the least likely structure. Thus, the NN bond length should be between the triple-bond length, which is 109 pm, and the double-bond length, which is 122 pm. Since the most likely structure places a triple-bond between the nitrogen atoms, the value should be closer to the triple bond value of 109 pm.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

Note on significant figures: The final answer to each cumulative-skills problem is given first with one nonsignificant figure (the rightmost significant figure is underlined) and then is rounded to the correct number of figures. Intermediate answers usually also have at least one nonsignificant figure. Atomic weights, except for that of hydrogen, are rounded to two decimal places.

9.127. The electronegativity differences and bond polarities are

P–H	0.0	nonpolar
O–H	1.4	polar (acidic)

$$H_3PO_3(aq) + 2NaOH(aq) \rightarrow Na_2HPO_3(aq) + 2H_2O(l)$$

$$\frac{0.1250 \text{ mol NaOH}}{1 \text{ L}} \times 0.02250 \text{ L} \times \frac{1}{0.2000 \text{ L } H_3PO_3} \times \frac{1 \text{ mol } H_3PO_3}{2 \text{ mol NaOH}}$$

$$= 0.007031\underline{2} = 0.007031 \text{ M } H_3PO_3$$

9.128. The electronegativity differences and bond polarities are

P–H	0.0	nonpolar
O–H	1.4	polar (acidic)

$$H_3PO_2(aq) + NaOH(aq) \rightarrow NaH_2PO_2(aq) + H_2O(l)$$

$$\frac{0.1250 \text{ mol NaOH}}{1 \text{ L}} \times 0.02250 \text{ L} \times \frac{1}{0.2000 \text{ L } H_3PO_2} \times \frac{1 \text{ mol } H_3PO_2}{1 \text{ mol NaOH}}$$

$$= 0.014062 = 0.01406 \text{ M } H_3PO_2$$

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9.129. After assuming a 100.0-g sample, convert to moles:

$$10.9 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.3 \text{ g Mg}} = 0.44\underline{8}5 \text{ mol Mg}$$

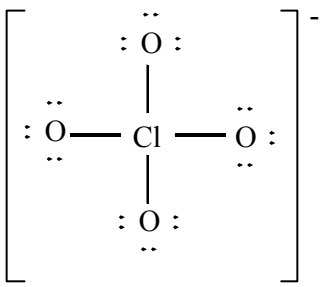
$$31.8 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.453 \text{ g Cl}} = 0.89\underline{6}96 \text{ mol Cl}$$

$$57.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.5\underline{8}1 \text{ mol O}$$

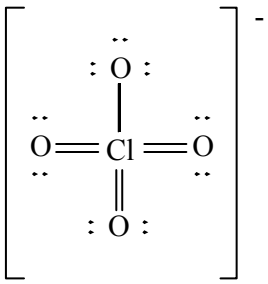
Divide by 0.4485:

$$\text{Mg: } \frac{0.4485}{0.4485} = 1; \text{ Cl: } \frac{0.89696}{0.4485} = 2.00; \text{ O: } \frac{3.581}{0.4485} = 7.98$$

The simplest formula is $MgCl_2O_8$. However, since $Cl_2O_8^{2-}$ is not a well-known ion, write the simplest formula as $Mg(ClO_4)_2$, magnesium perchlorate. The Lewis formulas are Mg^{2+} and



or



9.130. After assuming a 100.0-g sample, convert to moles:

$$30.3 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} = 0.75\underline{5}9 \text{ mol Ca}$$

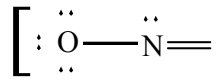
$$21.2 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.5\underline{1}3 \text{ mol N}$$

$$48.5 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.0\underline{3}1 \text{ mol O}$$

Divide by 0.7559:

$$\text{Ca: } \frac{0.7559}{0.7559} = 1; \text{ N: } \frac{1.513}{0.7559} = 2.00; \text{ O: } \frac{3.031}{0.7559} = 4.01$$

The simplest formula is CaN_2O_4. However, since $N_2O_4^{2-}$ is not a well-known ion, write the simplest formula as $Ca(NO_2)_2$, calcium nitrite. The Lewis formulas are Ca^{2+} and



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9.131. After assuming a 100.0-g sample, convert to moles:

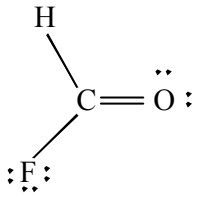
$$25.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.0\underline{8}1 \text{ mol C}$$

$$2.1 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 2.\underline{0}8 \text{ mol H}$$

$$39.6 \text{ g F} \times \frac{1 \text{ mol F}}{18.99 \text{ g F}} = 2.0\underline{8}5 \text{ mol F}$$

$$33.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.0\underline{8}1 \text{ mol O}$$

The simplest formula is CHOF. Because the molecular mass of 48.0 divided by the formula mass of 48.0 is one, the molecular formula is also CHOF. The Lewis formula is



9.132. After assuming a 100.0-g sample, convert to moles:

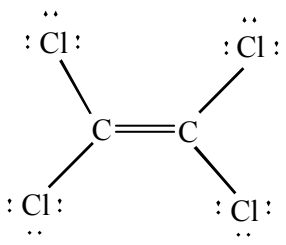
$$14.5 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 1.2\underline{0}7 \text{ mol C}$$

$$85.5 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.453 \text{ g Cl}} = 2.4\underline{1}16 \text{ mol Cl}$$

Divide by 1.207:Divide by 1.207:

$$\text{C: } \frac{1.207}{1.207} = 1; \quad \text{Cl: } \frac{2.4116}{1.207} = 1.998$$

The simplest formula is CCl_2. Dividing the molecular mass by the formula mass gives 166 amu ÷ 82.92 amu = 2.0. The molecular formula is C_2Cl_4. The Lewis formula is



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9.133. First, calculate the number of moles in one liter:

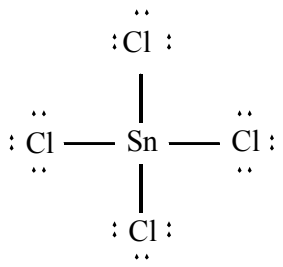
$$n = \frac{PV}{RT} = \frac{1.00 \text{ atm x } 1.00 \text{ L}}{0.0821 \text{ L} \bullet \text{atm/ (K} \bullet \text{mol) x } 424 \text{ K}} = 0.028727 \text{ mol}$$

$$MW = \frac{\text{g}}{\text{mol}} = \frac{7.49 \text{ g}}{0.028727 \text{ mol}} = 260.7 \text{ g/mol}$$

$$MW = 260.7 \text{ amu} = 118.69 \text{ amu Sn} + n \text{ x } (35.453 \text{ amu Cl})$$

$$n = \frac{260.7 - 118.69}{35.453} = 4.0055$$

The formula is $SnCl_4$. It is molecular because the electronegativity difference is 1.2, and because it is a liquid, and is volatile at 151°C. The Lewis formula is



9.134. First, calculate the number of moles present:

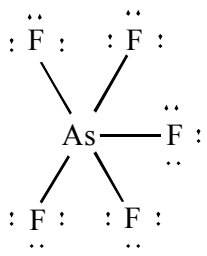
$$n = \frac{PV}{RT} = \frac{(765/760) \text{ atm x } 0.0142 \text{ L}}{0.0821 \text{ L} \bullet \text{atm/ (K} \bullet \text{mol) x } 296 \text{ K}} = 5.8816 \text{ x } 10^{-4} \text{ mol}$$

$$MW = \frac{\text{g}}{\text{mol}} = \frac{0.100 \text{ g}}{5.8816 \text{ x } 10^{-4} \text{ mol}} = 170.02 \text{ g/mol}$$

$MW = 170.02$ amu $= 74.92$ amu As $+ n$ x (18.998 amu F)

$$n = \frac{170.02 - 74.92}{18.998} = 5.0057$$

The formula is AsF_5. The Lewis formula is



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9.135.

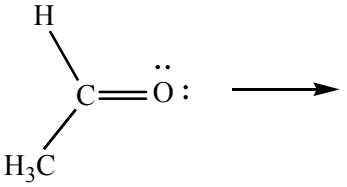
$$\underset{(135.1}{HCN(g)} \rightarrow \underset{218.0}{H(g)} + \underset{716.7}{C(g)} + \underset{472.7)}{N(g)} \quad \Delta H_f\text{(kJ/mol)}$$

ΔH_{rxn} = 1272.3 kJ/mol

$BE(C\equiv N)$ = ΔH_{rxn} − BE(C–H) = [1272.3 − 411] kJ/mol

= 86<u>1</u>.3 kJ/mol (Table 9.5 has 887 kJ/mol.)

9.136.



$$\underset{(-166.1}{\text{}} \quad \underset{4 \times 218}{\text{}} \quad \underset{2 \times 716.7}{\text{}} \quad \underset{249.2)}{\text{}} \quad \Delta H_f\text{(kJ/mol)}$$

ΔH_{rxn} = 2720.7 kJ/mol

BE(C=O) = ΔH_{rxn} − [4 x BE(C–H)] − BE(C–C)

= [2720.7 − (4 x 411) − 346] kJ/mol

= 73<u>0</u>.7 kJ/mol (Table 9.5 has 745 kJ/mol.)

9.137. Use the O–H bond and its bond energy of 459 kJ/mol to calculate X_O.

BE(O–H) = 1/2[BE(H−) + BE(O−)] + k$(X_O - X_H)^2$

459 kJ/mol = 1/2(432 kJ/mol + 142 kJ/mol) + 98.6 kJ $(X_O - X_H)^2$

Collecting the terms gives

$$\frac{459 - 287}{98.6} = (X_O - X_H)^2$$

Taking the square root of both sides gives

1.32<u>0</u>7 = 1.32 = $(X_O - X_H)$

Because X_H = 2.1, X_O = 2.1 + 1.32 = 3.42 = 3.4.

9.138. BE(N–I) = 1/2[BE(N–N) + BE(I–I)] + k x $(X_N - X_I)^2$

BE(N–I) = 1/2(167 + 149) + (98.6)$(3.0 - 2.5)^2$

BE(N–I) = 158 + 24.65 = 18<u>2</u>.65 = 183 kJ/mol

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9.139. $X = \frac{\text{I.E. - E.A.}}{2} = \frac{[1250 - (-349)]\ \text{kJ/mol}}{2} = 799.5\ \text{kJ/mol}$

$$\frac{799.5\ \text{kJ/mol}}{230\ \text{kJ/mol}} = 3.47\ (\text{Pauling's } X = 3.0)$$

9.140. $X = \frac{\text{I.E. - E.A.}}{2} = \frac{[1314 - (-141)]\ \text{kJ/mol}}{2} = 727.5\ \text{kJ/mol}$

$$\frac{727.5\ \text{kJ/mol}}{230\ \text{kJ/mol}} = 3.16\ (\text{Pauling's } X = 3.5)$$

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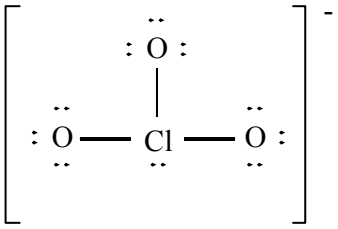
CHAPTER 10

Molecular Geometry and Chemical Bonding Theory

■ SOLUTIONS TO EXERCISES

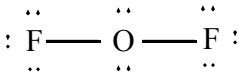
10.1.

a. A Lewis structure of ClO_3^- is



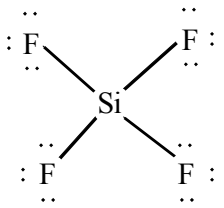
There are four electron pairs in a tetrahedral arrangement about the central atom. Three pairs are bonding, and one pair is nonbonding. The expected geometry is trigonal pyramidal.

b. The Lewis structure of OF_2 is



There are four electron pairs in a tetrahedral arrangement about the central atom. Two pairs are bonding, and two pairs are nonbonding. The expected geometry is bent.

c. The Lewis structure of SiF_4 is



There are four bonding electron pairs in a tetrahedral arrangement around the central atom. The expected geometry is tetrahedral.

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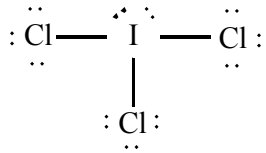
10.2. First, distribute the valence electrons to the bonds and the chlorine atoms. Then distribute the remaining electrons to iodine.

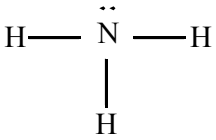


The five electron pairs around iodine should have a trigonal bipyramidal arrangement with two lone pairs occupying equatorial positions. The molecule is T-shaped.

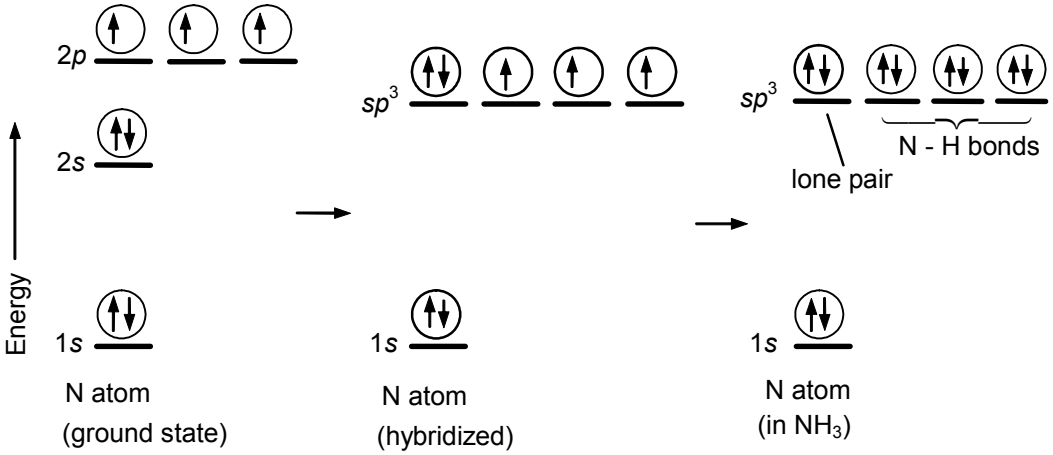
10.3. Both trigonal pyramidal (b) and T-shaped (c) geometries are consistent with a nonzero dipole moment. In trigonal planar geometry, the Br–F contributions to the dipole moment would cancel.

10.4. On the basis of symmetry, SiF_4 (b) would be expected to have a dipole moment of zero. The bonds are all symmetrical about the central atom.

10.5. The Lewis structure for ammonia, NH_3, is



There are four pairs of electrons around the nitrogen atom. According to the VSEPR model, these are arranged tetrahedrally around the nitrogen atom, and you should use sp^3 hybrid orbitals. Each N–H bond is formed by the overlap of a 1*s* orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the nitrogen atom. This gives the following bonding description for NH_3:



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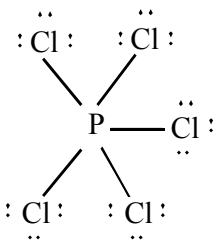
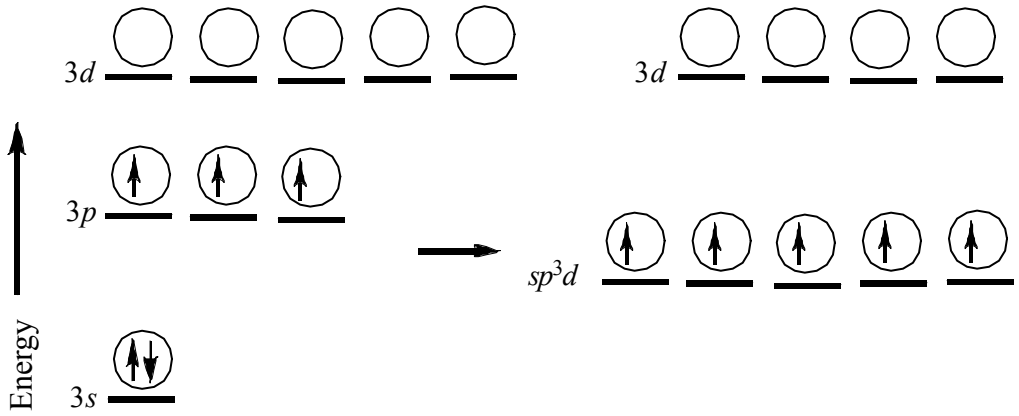
10.6. The Lewis structure for PCl_5 is



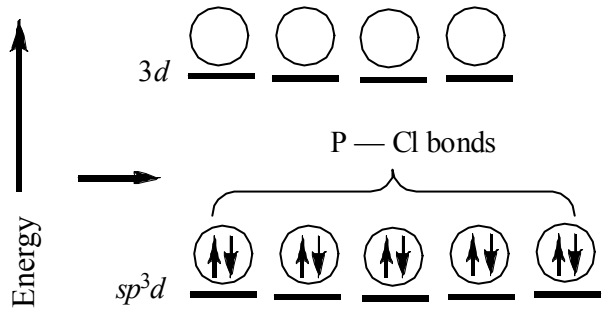
The phosphorus atom has five single bonds and no lone pairs around it. This suggests that you use sp^3d hybrid orbitals on phosphorus. Each chlorine atom (valence-shell configuration $3s^2 3p^5$) has one singly occupied $3p$ orbital. The P–Cl bonds are formed by the overlap of a phosphorus sp^3d hybrid orbital with a singly occupied chlorine $3p$ orbital. The hybridization of phosphorus can be represented as follows:



P atom
(ground state)

P atom
(hybridized)

The bonding description of phosphorus in PCl_5 is



P atom
(in PCl_5)

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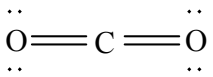
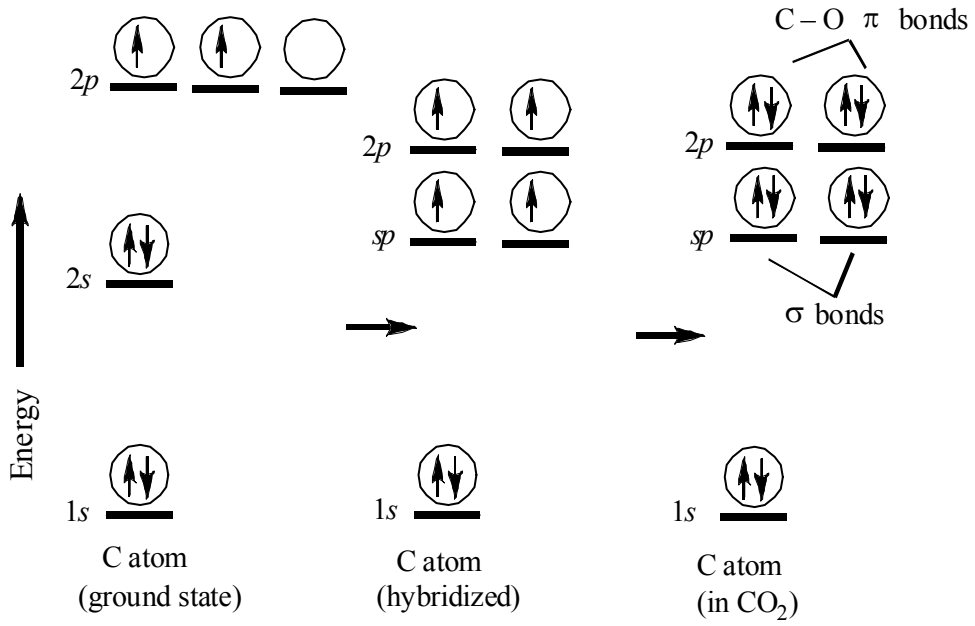
10.7. The Lewis structure of CO_2 is

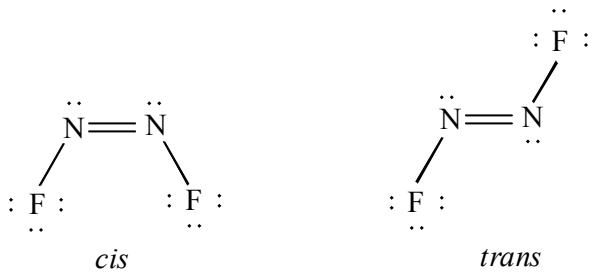


The double bonds are each a π bond plus a σ bond. Hybrid orbitals are needed to describe the two σ bonds. This suggests *sp* hybridization. Each *sp* hybrid orbital on the carbon atom overlaps with a 2*p* orbital on one of the oxygen atoms to form a σ bond.

The π bonds are formed by the overlap of a 2*p* orbital on the carbon atom with a 2*p* orbital on one of the oxygen atoms. Hybridization and bonding of the carbon atom are shown as follows:



10.8. The structural formulas for the isomers are as follows:



These compounds exist as separate isomers with different properties. For these to interconvert, one end of the molecule would have to rotate with respect to the other end. This would require breaking the π bond and expending considerable energy.

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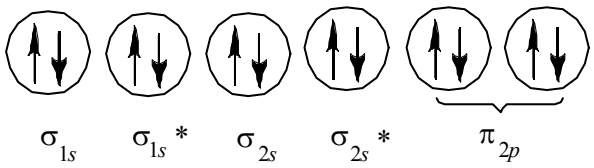
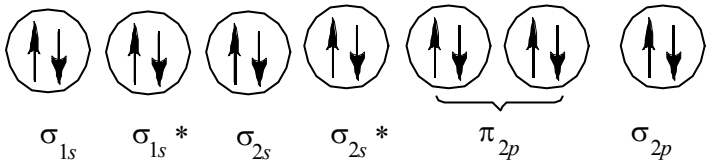
10.9. There are 2 x 6 = 12 electrons in C_2. They occupy the orbitals as shown below.



The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$. There are no unpaired electrons; therefore, C_2 is diamagnetic. There are eight bonding and four antibonding electrons. The bond order is 1/2 (8 − 4) = 2.

10.10. There are 6 + 8 = 14 electrons in CO. The orbital diagram is



The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$. There are ten bonding and four antibonding electrons. The bond order is 1/2(10 − 4) = 3. There are no unpaired electrons; hence, CO is diamagnetic.

■ ANSWERS TO CONCEPT CHECKS

10.1. The VSEPR model predicts that four electron pairs about any atom in a molecule will distribute themselves to give a tetrahedral arrangement. Any three of these electron pairs would have a trigonal pyramidal arrangement. The geometry of a molecule having a central atom with three atoms bonded to it would be trigonal pyramidal.

10.2. A molecule, AX_3, could have one of three geometries: it could be trigonal planar, trigonal pyramidal, or T-shaped. Assuming the three groups attached to the central atom are alike, as indicated by the formula, the planar geometry should be symmetrical, so even if the A–X bonds are polar, their polarities would cancel to give a nonpolar molecule (dipole moment of zero). This would not be the case in the trigonal pyramidal geometry. In that situation, the bonds all point to one side of the molecule. It is possible for such a molecule to have a lone pair that points away from the bonds and whose polarity might fortuitously cancel the bond polarities, but an exact cancellation is not likely. In general, you should expect the trigonal pyramidal molecule to have a nonzero dipole moment, but a zero dipole is possible. The argument for the T-shaped geometry is similar to that for the trigonal pyramidal geometry. The bonds point in a plane, but toward one side of the molecule. Unless the sum of the bond polarities was fortuitously canceled by the polarities from the lone pairs, this geometry would have a nonzero dipole moment. This means that molecule Y is likely to be trigonal planar, but trigonal pyramidal or T-shaped geometries are possible. Molecule Z cannot have a trigonal planar geometry; it must be either trigonal pyramidal or T-shaped.

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10.3. Assuming there are no lone pairs, the atom has four electron pairs and, therefore, an octet of electrons about it. The single bond and the triple bond each require a sigma bond orbital for a total of two such orbitals. This suggests *sp* hybrids on the central atom.

ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

10.1. The VSEPR model is used to predict the geometry of molecules. The electron pairs around an atom are assumed to arrange themselves to reduce electron repulsion. The molecular geometry is determined by the positions of the bonding electron pairs.

10.2. The arrangements are linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral.

10.3. A lone pair is "larger" than a bonding pair; therefore, it will occupy an equatorial position, where it encounters less repulsion than if it were in an axial position.

10.4. The bonds could be polar, but if they are arranged symmetrically, the molecule will be nonpolar. The bond dipoles will cancel.

10.5. Nitrogen trifluoride has three N–F bonds arranged to form a trigonal pyramid. These bonds are polar and would give a polar molecule with partial negative charges on the fluorine atoms and a partial positive charge on the nitrogen atom. However, there is also a lone pair of electrons on nitrogen that is directed away from the bonds. The result is that the lone pair nearly cancels the polarity of the bonds and gives a molecule with a very small dipole moment.

10.6. Certain orbitals, such as *p* orbitals and hybrid orbitals, have lobes in given directions. Bonding to these orbitals is directional; that is, the bonding is in preferred directions. This explains why the bonding gives a particular molecular geometry.

10.7. The angle is 109.5°.

10.8. A sigma bond has a cylindrical shape about the bond axis. A *pi* bond has a distribution of electrons above and below the bond axis.

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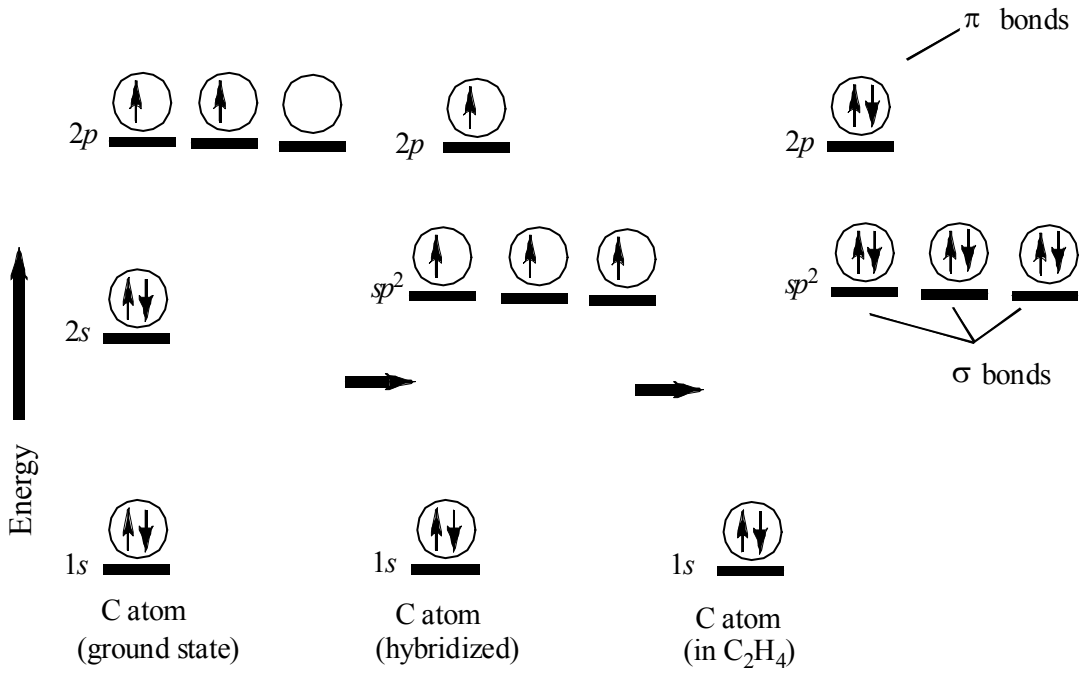
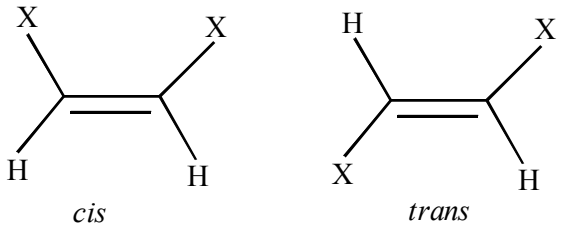
10.9. In ethylene, C_2H_4, the changes on a given carbon atom may be described as follows:



An sp^2 hybrid orbital on one carbon atom overlaps a similar hybrid orbital on the other carbon atom to form a σ bond. The remaining hybrid orbitals on the two carbon atoms overlap 1*s* orbitals from the hydrogen atoms to form four C–H bonds. The unhybridized 2*p* orbital on one carbon atom overlaps the unhybridized 2*p* orbital on the other carbon atom to form a π bond. The σ and π bonds together constitute a double bond.

10.10. Both of the unhybridized 2*p* orbitals, one from each carbon atom, are perpendicular to their CH_2 planes. When these orbitals overlap each other, they fix both planes in the same plane. The two ends of the molecule cannot twist around without breaking the π bond, which requires considerable energy.

Therefore, it is possible to have stable molecules with the following structures:



Because these have the same molecular formulas, they are isomers. In this case, they are called *cis*-*trans* isomers, or geometrical isomers.

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10.11. In a bonding orbital, the probability of finding electrons between the two nuclei is high. For this reason, the energy of the bonding orbital is lower than that of the separate atomic orbitals. In an antibonding orbital, the probability of finding electrons between the two nuclei is low. For this reason, the energy of the antibonding orbital is higher than that of the separate atomic orbitals.

10.12. The factors determining the strength of interaction of two atomic orbitals are (1) the energy difference between the interacting orbitals and (2) the magnitude of their overlap.

10.13. When two 2*s* orbitals overlap, they interact to form a bonding orbital, σ_{2s}, and an antibonding orbital, σ_{2s}*. The bonding orbital is at lower energy than the antibonding orbital.

10.14. When two 2*p* orbitals overlap along their axes, they interact to form one σ_{2p} bonding orbital and one σ_{2p}* antibonding orbital. When they overlap sideways, they form π_{2p} and π_{2p}* molecular orbitals.

10.15. A σ bonding orbital is formed by the overlap of the 1*s* orbital on the H atom with the 2*p* orbital on the F atom. This H–F orbital is made up primarily of the fluorine orbital.

10.16. The O_3 molecule consists of a framework of localized orbitals and of delocalized *pi* molecular orbitals. The localized framework is formed from sp^2 hybrid orbitals on each atom. Thus, an O–O bond is formed by the overlap of a hybrid orbital on the left O atom with a hybrid orbital on the center O atom. Another O–O bond is formed by the overlap of another hybrid orbital on the right O atom with a hybrid orbital on the center O atom. The remaining hybrid orbitals are occupied by lone pairs of electrons. Also, there is one unhybridized *p* orbital on each of the atoms. These *p* orbitals are perpendicular to the plane of the molecule and overlap sidewise to give three pi molecular orbitals that are delocalized. The two orbitals of lowest energy are occupied by pairs of electrons.

10.17. The answer is e, a little less than 109.5°.

10.18. The answer is d, square pyramidal.

10.19. The answer is b, H_2S.

10.20. The answer is e, 5/2.

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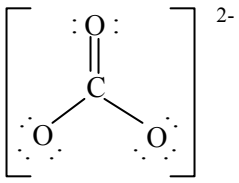
■ ANSWERS TO CONCEPT EXPLORATIONS

10.21.

a. The Lewis structure does not obey the octet rule. There are ten electrons around the carbon atom. The carbon has a formal charge of 1−, and the single-bonded oxygen has a formal charge of 1−. It is difficult to describe the bonding in VB terms, since carbon cannot hybridize to form three σ bonds and two π bonds. Three σ bonds requires sp^2 hybridization, leaving only one unhybridized 2*p* orbital. This is available to form only one π bond with the oxygen atoms, not two as required.

b. The Lewis structure given is not the best. The following structure is a better one.

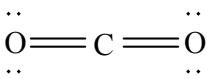


This structure is better because all atoms obey the octet rule. Also, the formal charges are 1− on both the single-bonded oxygen atoms.

c. Yes, the description is incorrect. The left formula predicts a bent geometry, with angles around 120°. The right formula predicts a linear geometry, with angles around 180°.

d. Both formulas are incorrect. Neither one is better than the other. They represent resonance structures of each other. The left structure will have a larger dipole moment than that of the right structure.

e. A Lewis formula that gives a better description of CO_2 is given below.



All atoms obey the octet rule, and there are no formal charges.

10.22.

a. The second structure from the left is the best description of SeO_2. There is a double bond between the selenium atom and one of the oxygen atoms, sharing four electrons. The other oxygen atom is singly bonded to the selenium atom, sharing two electrons. There is also a lone pair on selenium, completing its octet.

b. The selenium atom is sp^2 hybridized, forming two σ bonds by overlap with the oxygen atom's 2*p* orbitals. The third sp^2 hybrid orbital holds the lone pair of electrons. The unhybridized 2*p* orbital overlaps with a 2*p* orbital on the oxygen atom, forming a double bond.

c. The arrangement of electron pairs around the selenium atom is trigonal planar. The molecule has a bent geometry.

d. The O–Se–O angle is slightly less than 120°. The lone pair of electrons are bulky, so the angle will be decreased.

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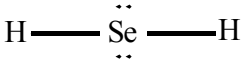
e. The molecular geometry of H_2Se is bent, the same as water. The selenium atom is sp^3 hybridized.



f. The H–Se–H angle is less than the tetrahedral (sp^3) angle of 109°, whereas the O–Se–O angle is less than the trigonal planar (sp^2) angle of 120°. Therefore, the H–Se–H angle is smaller.

g. Both molecules have dipole moments because they lack the proper molecular symmetry for the polar bonds to cancel each other.

■ ANSWERS TO CONCEPTUAL PROBLEMS

10.23. In order to solve this problem, draw the Lewis structure for each of the listed molecules. In each case, use your Lewis structure to determine the geometry, and match this geometry with the correct model.

a. SeO_2 is angular and has an AX_2 geometry. This is represented by model (ii).

b. $BeCl_2$ is linear and has an AX_2 geometry. This goes with model (i).

c. PBr_3 is trigonal pyramidal and has an AX_3 geometry. This goes with model (iv).

d. BCl_3 is trigonal planar and has an AX_3 geometry. This is represented by model (iii).

10.24. First, determine the geometry about the central atom, carbon. There is a total of 16 valence electrons for the molecule. For each atom to obey the octet rule, eight electrons must be shared in bonds. This would require four bonding pairs, a single bond (one pair) between C and Cl, and a triple bond (three pairs) between C and N. The geometry about the central atom is AX_2, which is linear. This is represented by model (a), on the left.

10.25. In a CH_3CH_3 molecule, each C atom has four electron pairs arranged tetrahedrally. Within this molecule, each CH_3 considered as a separate group has a trigonal pyramidal geometry (with three C–H bonding pairs and a fourth pair from the C–C bond around the C atom). The $:CH_3$ molecule retains this trigonal pyramidal geometry, having three bonding pairs and one lone pair around the C atom. The CH_3 molecule, however, has only three electron pairs around the C atom. Initially, as the CH_3 molecule breaks away from the ethane molecule, it has the trigonal pyramidal geometry it had in the ethane molecule. However, the repulsions of the bonding electron pairs on the CH_3 molecule are no longer balanced by the fourth pair (from the C–C bond), so the molecule flattens out to form a trigonal planar geometry.

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10.26. The BF_3 molecule starts out in a trigonal planar geometry with three bonding pairs of electrons distributed about the B atom in a plane and 120° apart. After the bond between B and N is formed, the geometry about the B atom is tetrahedral, with 109° bond angles. As the bond begins to form, the lone pair on N approaches the plane of the BF_3 molecule and begins to interact with the bonding pairs. The repulsion between the electron pairs causes the bonding pairs to be pushed downward, forcing them closer together.

10.27. First, determine the geometry of each molecule using VSEPR theory. Then compare to the orbital pictures for the correct number of bonding and nonbonding orbitals.

a. BeF_2 is an AX_2 molecule, which has linear geometry. This is depicted by orbital drawing (i).

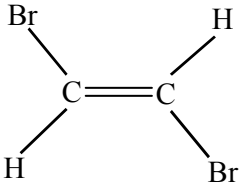
b. SiF_4 is an AX_4 molecule, which has tetrahedral geometry. This is depicted by orbital drawing (iii).

c. SeF_4 is an AX_4 molecule, which has seesaw geometry. This is depicted by orbital drawing (iv).

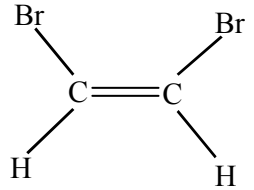
d. RnF_4 is an AX_4 molecule, which has square planar geometry. This is depicted by orbital drawing (v).

10.28. The arrangement of electron pairs about this atom suggested by the two bonds and one lone pair is trigonal planar. You would expect sp^2 hybrid orbitals for this atom (a total of three hybrid orbitals). Two of these hybrid orbitals would be used to form the two bonds; the third hybrid orbital would be used for the lone pair.

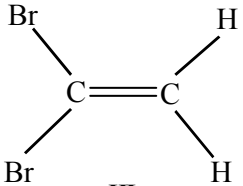
10.29. The reaction with Br_2 indicates that $C_2H_2Br_2$ has a double bond. There are three possible isomers of $C_2H_2Br_2$ having double bonds:



I

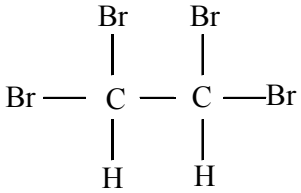


II

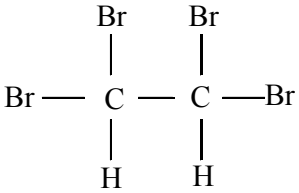


III

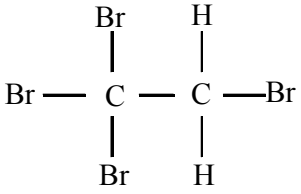
Compounds II and III have dipole moments. The addition of Br_2, with one Br going to each C atom, yields the following products:



IA



IIA



IIIA

Products IA and IIA are identical and arise from compounds I and II. Thus, the original two compounds, one not having a dipole moment, the other having a dipole moment, but both reacting with bromine to give the same product, are compounds I and II, respectively.

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10.30. A neutral molecule of the form XF_4 could have four, five, or six electron pairs around X. With four bonding pairs and no lone pairs, the geometry would be tetrahedral. The molecule would be symmetrical and nonpolar. Similarly, with four bonding pairs and two lone pairs, the geometry would be square planar; the molecule would again be symmetrical and nonpolar.

However, with four bonding pairs and one lone pair, the geometry would be seesaw; the molecule would be nonsymmetrical in shape and could be polar. This fits the description of a compound with dipole moment 0.63 D. To identify X, let's look at the total number of valence electrons in XF_4. Each F atom, with its bonding electrons, has an octet (8) of electrons. In addition, there is a lone pair, or two electrons. Thus, the total number of valence electrons is 4 x 8 + 2 = 34. Of these, 4 x 7 = 28 are from the F atoms, leaving 34 − 28 = 6 valence electrons coming from X. So X is a Group VIA element. X cannot be oxygen because a seesaw geometry would require sp^3d hybrid orbitals, and oxygen does not have *d* orbitals to hybridize. Thus, X must be sulfur (S), selenium (Se), or tellurium (Te).

10.31. First, determine the geometry about atoms a, b, and c using VSEPR theory. Then compare to the geometry in each drawing.

a. The geometry about atom a (carbon) is AX_4, which is tetrahedral geometry. This is depicted by drawing (ii).

b. The geometry about atom b (carbon) is AX_3, which is trigonal planar geometry. This is depicted by drawing (iv).

c. The geometry about atom c (oxygen) is AX_2, which is bent geometry. This is depicted by drawing (i).

10.32. The formate ion, HCO_2^-, is expected to have trigonal planar geometry by the VSEPR model. (Each resonance formula has one C=O bond, one C–O bond, and one C–H bond, giving a total of three groups about the C atom.) The VSEPR model predicts bond angles of 120°. However, a bond between the carbon atom and the oxygen atom has a bond order of 3/2 (resonance between a single and a double bond) and requires more room than a pure single bond. The repulsion between the two C–O bonds would be greater than the repulsion between a C–O bond and the C–H bond. Thus, you would predict that the O–C–O angle is slightly greater than 120°, whereas the O–C–H angle is slightly less than 120°.

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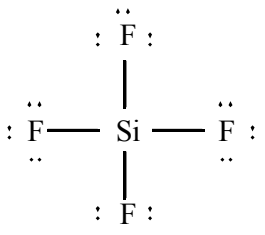
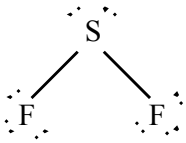
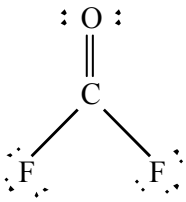
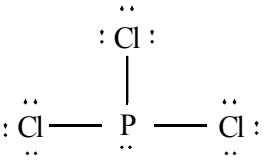
■ SOLUTIONS TO PRACTICE PROBLEMS

10.33. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	4	0	Tetrahedral
	4	2	Bent
	3	0	Trigonal planar
	4	1	Trigonal pyramidal

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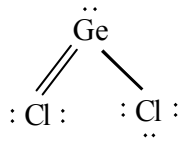
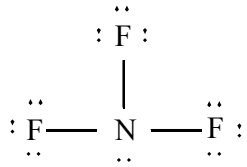
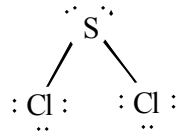
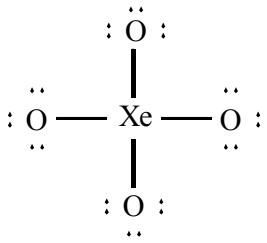
10.34. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	3	1	Bent (angular)
	4	1	Trigonal pyramidal
	3	0	Bent (angular)
	4	0	Tetrahedral

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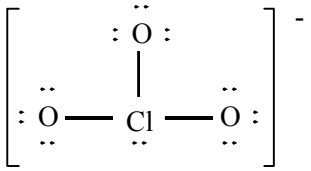
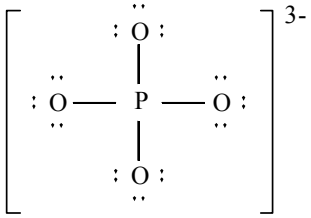
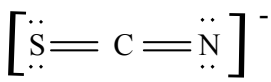
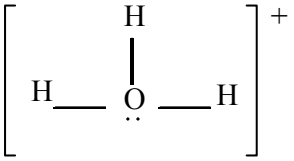
10.35. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	4	1	
	4	0	Tetrahedral
	2	0	Linear
	4	1	Trigonal pyramidal

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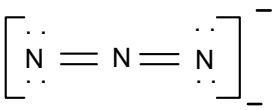
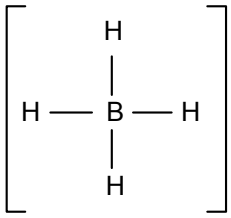
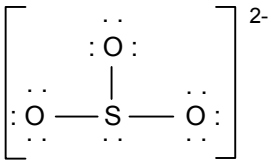
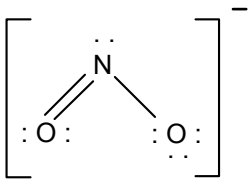
10.36. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	2	0	Linear
	4	0	Tetrahedral
	4	1	Trigonal pyramidal
	3	1	Bent (angular)

10.37.

a. CCl_4 is tetrahedral, VSEPR predicts that the bond angles will be 109°, and you would expect them to be this angle.

b. SCl_2 is bent, and VSEPR theory predicts bond angles of 109°, but you would expect the Cl–S–Cl bond angle to be less.

c. $COCl_2$ is trigonal planar. VSEPR theory predicts 120° bond angles. The C–O bond is a double bond, so you would expect the Cl–C–O bond to be more than 120° and the Cl–C–Cl bond to be less than 120°.

d. AsH_3 is trigonal pyramidal, and VSEPR theory predicts bond angles of 109°, but you would expect the H–As–H bond angle to be less.

10.38.

a. NCl_3 is trigonal pyramidal, and VSEPR theory predicts bond angles of 109°, but you would expect the Cl–N–Cl bond angle to be less.

b. Both carbon atoms are trigonal planar. VSEPR theory predicts 120° bond angles. The C–C bond is a double bond, so you would expect the F–C–C bond to be more than 120° and the F–C–F bond to be less than 120°.

c. SiF_4 is tetrahedral, VSEPR predicts that the bond angles will be 109°, and you would expect them to be this angle.

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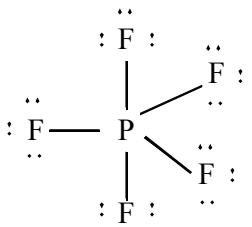
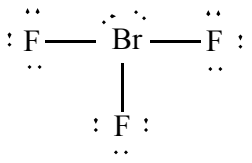
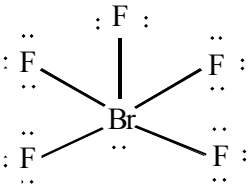
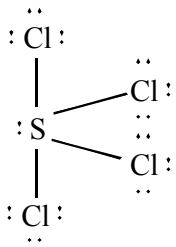
d. OF_2 is angular, and VSEPR theory predicts bond angles of 109°, but you would expect the F–O–F bond angle to be less.

10.39. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	5	0	Trigonal bipyramidal
	5	2	T-shaped
	6	1	Square pyramidal
	5	1	Seesaw

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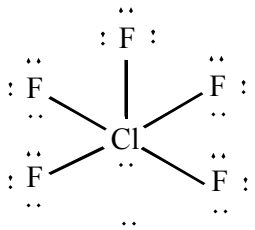
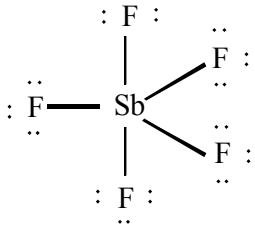
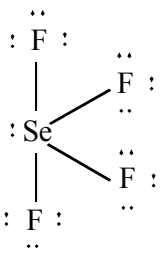
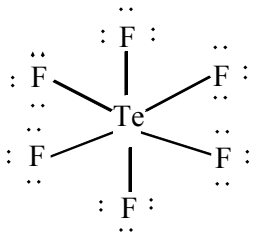
10.40. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	6	1	Square pyramidal
	5	0	Trigonal bipyramidal
	5	1	Seesaw
	6	0	Octahedral

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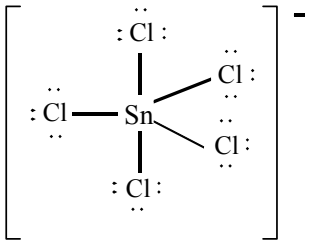
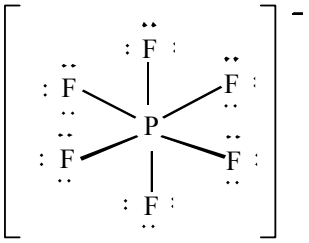
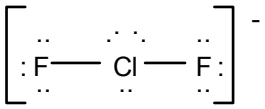
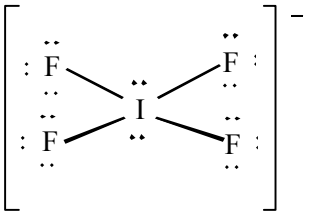
10.41. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	5	0	Trigonal bipyramidal
	6	0	Octahedral
	5	3	Linear
	6	2	Square planar

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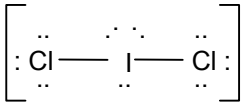
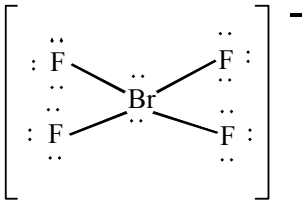
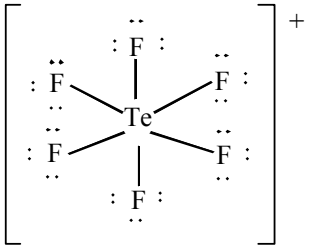
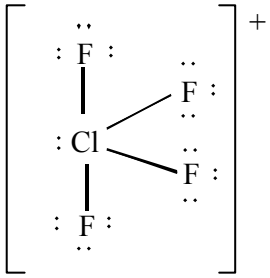
10.42. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	5	3	Linear
	6	2	Square planar
	6	0	Octahedral
	5	1	Seesaw

10.43.

a. Trigonal pyramidal and T-shaped. Trigonal planar would have a dipole moment of zero.

b. Bent. Linear would have a dipole moment of zero.

10.44.

a. Trigonal pyramidal and T-shaped. Trigonal planar would have a dipole moment of zero.

b. Seesaw. Square planar and tetrahedral would have dipole moments of zero.

10.45.

a. CS_2 has a linear geometry and has no dipole moment.

b. TeF_2 has a bent geometry and has a dipole moment.

c. $SeCl_4$ has a seesaw geometry and has a dipole moment.

d. XeF_4 has a square planar geometry and has no dipole moment.

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10.46.

a. SeF_2 has a bent, or angular, geometry and has a dipole moment.

b. BeI_2 has a linear geometry and has no dipole moment.

c. TeF_6 has an octahedral geometry and has no dipole moment.

d. TeF_4 has a seesaw geometry and has a dipole moment.

10.47.

a. SF_2 is an angular model. The sulfur atom is sp^3 hybridized.

b. ClO_3^- is a trigonal pyramidal molecule. The chlorine atom is sp^3 hybridized.

10.48.

a. $AlCl_3$ is a trigonal planar molecule. The aluminum atom is sp^2 hybridized.

b. BF_4^- is a tetrahedral ion. The boron atom is sp^3 hybridized.

10.49.

a. $SeCl_2$ is a bent molecule. The Se atom is sp^3 hybridized.

b. NO_2^- is a bent ion. The N atom is sp^2 hybridized.

c. CO_2 is a linear molecule. The C atom is sp hybridized.

d. COF_2 is a trigonal planar molecule. The C atom is sp^2 hybridized.

10.50.

a. $GeCl_4$ is a tetrahedral molecule. The Ge atom is sp^3 hybridized.

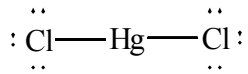
b. PBr_3 is a trigonal pyramidal molecule. The P atom is sp^3 hybridized.

c. BeF_2 is a linear molecule. The Be atom is sp hybridized.

d. SO_2 is a bent molecule. The S atom is sp^2 hybridized.

10.51.

a. The Lewis structure is



The presence of two single bonds and no lone pairs suggests sp hybridization. Thus, an Hg atom with the configuration $[Xe]4f^{14}5d^{10}6s^2$ is promoted to $[Xe]4f^{14}5d^{10}6s^16p^1$, then hybridized. An Hg–Cl bond is formed by overlapping an Hg hybrid orbital with a $3p$ orbital of Cl.

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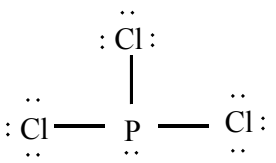
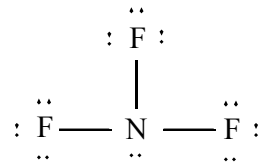
b. The Lewis structure is



The presence of three single bonds and one lone pair suggests sp^3 hybridization of the P atom. Three hybrid orbitals each overlap a 3*p* orbital of a Cl atom to form a P–Cl bond. The fourth hybrid orbital contains the lone pair.

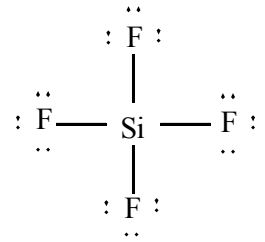
10.52.

a. The Lewis structure is



The presence of three single bonds and one lone pair suggests sp^3 hybridization of the N atom. Three hybrid orbitals each overlap a 2*p* orbital of an F atom to form an N–F bond. The fourth hybrid orbital contains the lone pair.

b. The Lewis structure is



The presence of four single bonds and no lone pairs suggests sp^3 hybridization of the Si atom. Each hybrid orbital overlaps a 2*p* orbital of an F atom to form an Si–F bond.

10.53.

a. Xenon has eight valence electrons. Each F atom donates one electron to give a total of ten electrons, or five electron pairs, around the Xe atom. The hybridization is sp^3d.

b. Bromine has seven valence electrons. Each F atom donates one electron to give a total of twelve electrons, or six electron pairs, around the Br atom. The hybridization is sp^3d^2.

c. Phosphorus has five valence electrons. The Cl atoms each donate one electron to give a total of ten electrons, or five electron pairs, around the P atom. The hybridization is sp^3d.

d. Chlorine has seven valence electrons, to which may be added one electron from each F atom minus one electron for the charge on the ion. This gives a total of ten electrons, or five electron pairs, around chlorine. The hybridization is sp^3d.

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10.54.

a. Bromine has seven valence electrons, and each fluorine has seven valence electrons for a total of 28 valence electrons for the molecule. The bromine atom has a total of five electron pairs around it, giving sp^3d hybridization.

b. Tellurium has six valence electrons. The F atoms each have seven electron to give a total of 34 electrons for the molecule. The tellurium atom has five electron pairs around it, giving sp^3d hybridization.

c. Xenon has eight valence electrons. Each F atom has seven valence electrons to give a total of 36 electrons for the molecule. The xenon atom has six electron pairs around it, and the hybridization is sp^3d^2.

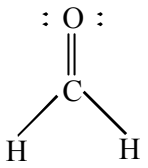
d. Iodine has seven valence electrons, each F atom has seven valence electrons, and one electron to account for the charge on the ion gives 36 electrons for the ion. This gives a total of six electron pairs around the I atom. The hybridization is sp^3d^2.

10.55. The P atom in PCl_6^- has six single bonds around it and no lone pairs. This suggests sp^3d^2 hybridization. Each bond in this ion is a σ bond formed by overlap of an sp^3d^2 hybrid orbital on P with a 3*p* orbital on Cl.

10.56. The central I atom in I_3^- has two single bonds and three lone pairs around it. This suggests sp^3d hybridization. Each I–I bond is formed by the overlap of an sp^3d hybrid orbital on the central I with a 5*p* orbital from a terminal I.

10.57.

a. The structural formula of formaldehyde is



Because the C is bonded to three other atoms, it is assumed to be sp^2 hybridized. One 2*p* orbital remains unhybridized. The carbon–hydrogen bonds are σ bonds formed by the overlap of an sp^2 hybrid orbital on C with a 1*s* orbital on H. The remaining sp^2 hybrid orbital on C overlaps with a 2*p* orbital on O to form a σ bond. The unhybridized 2*p* orbital on C overlaps with a parallel 2*p* orbital on O to form a π bond. Together, the σ and π bonds constitute a double bond.

b. The nitrogen atoms are *sp* hybridized. A σ bond is formed by the overlap of an *sp* hybrid orbital from each N. The remaining *sp* hybrid orbitals contain lone pairs of electrons. The two unhybridized 2*p* orbitals on one N overlap with the parallel unhybridized 2*p* orbitals on the other N to form two π bonds.

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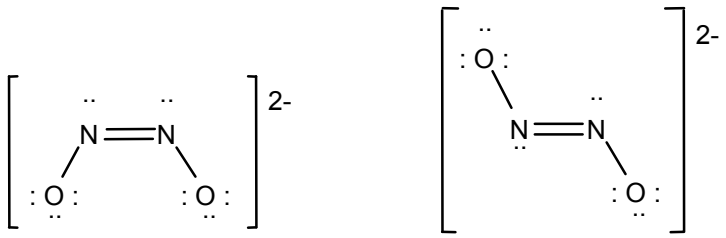
10.58.

a. Each nitrogen atom is bonded to two other atoms and also has a lone pair of electrons in its valence shell. Therefore, the nitrogen atoms are expected to be sp^2 hybridized. The N–H bonds are σ bonds formed by the overlap of an sp^2 hybrid orbital of an N atom with a 1*s* orbital on an H atom. Each N also contains a lone pair of electrons in an sp^2 hybrid orbital. The remaining sp^2 hybrid orbitals, one on each N, overlap with each other to form a σ bond. The two 2*p* orbitals, one on each N, are oriented parallel to each other so that they may overlap to form a π bond.

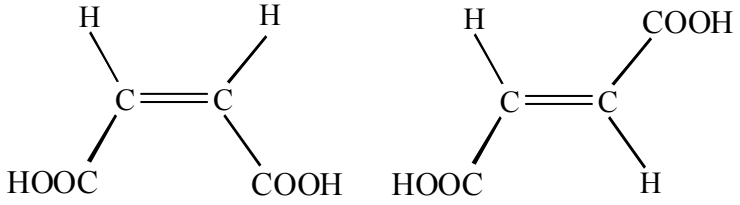
b. The carbon atom is bonded to two atoms and has no lone pairs; hence, it is expected to be *sp* hybridized. The C–H bond is a σ bond formed by the overlap of an *sp* hybrid orbital on carbon with a 1*s* orbital on hydrogen. The other *sp* hybrid orbital overlaps with an *sp* orbital on the nitrogen atom to form a σ bond. The remaining *sp* hybrid orbital on N contains a lone pair. There remain two unhybridized 2*p* orbitals on the carbon and two 2*p* orbitals on the nitrogen atom. One 2*p* orbital from the C and a parallel 2*p* orbital on the N overlap to form a π bond. The remaining two 2*p* orbitals overlap to form a second π bond between the carbon and nitrogen.

10.59. Each of the N atoms has a lone pair of electrons and is bonded to two atoms. The N atoms are sp^2 hybridized. The two possible arrangements of the O atoms relative to one another are shown below. Because the π bond between the N atoms must be broken to interconvert these two forms, it is to be expected that the hyponitrite ion will exhibit *cis–trans* isomerism.



cis *trans*

10.60. The C=C bond consists of a σ bond and a π bond. The π bond depends on the parallel orientation of the two *p* orbitals that overlap to form the bond. In order to interconvert the *cis* and *trans* forms, one end of the molecule would have to be rotated relative to the other end, thus changing the orientation of the *p* orbitals and breaking the bond. Because this requires considerable energy, the *cis* and *trans* forms are stable relative to interconversion.



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10.61.

a. Total electrons = 2 x 5 = 10.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$.

Bond order = 1/2 ($n_b - n_a$) = 1/2 (6 − 4) = 1

The B_2 molecule is stable. It is paramagnetic because the two electrons in the π_{2p} subshell occupy separate orbitals.

b. Total electrons = (2 x 5) − 1 = 9.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^1$.

Bond order = 1/2 ($n_b - n_a$) = 1/2 (5 − 4) = 1/2

The B_2^+ molecule should be stable and is paramagnetic because there is one unpaired electron in the π_{2p} subshell.

c. Total electrons = (2 x 8) + 1 = 17.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^3$.

Bond order = 1/2 ($n_b - n_a$) = 1/2 (10 − 7) = 3/2

The O_2^- molecule should be stable and is paramagnetic because there is one unpaired electron in the π_{2p}^* subshell.

10.62.

a. Total electrons = (2 x 4) − 1 = 7.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^1$.

Bond order = 1/2 ($n_b - n_a$) = 1/2 (4 − 3) = 1/2

The Be_2^+ molecule is expected to be stable and paramagnetic.

b. Total electrons = 2 x 10 = 20.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$.

Bond order = 1/2 ($n_b - n_a$) = 1/2 (10 − 10) = 0

The Ne_2 molecule is expected to be unstable and diamagnetic.

c. Total electrons = (2 x 5) + 1 = 11.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^3$.

Bond order = 1/2 ($n_b - n_a$) = 1/2 (7 − 4) = 3/2

The B_2^- molecule is expected to be stable. It is paramagnetic because there is one unpaired electron in the π_{2p} subshell.

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10.63. Total electrons = 6 + 7 + 1 = 14.

The electron configuration is KK$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$.

Bond order = 1/2 $(n_b - n_a)$ = 1/2 (10 − 4) = 3

The CN^- ion is diamagnetic.

10.64. Total electrons = 5 + 7 = 12.

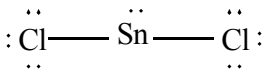
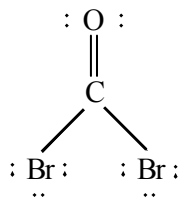
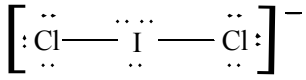
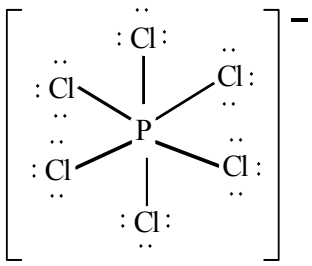
The electron configuration is KK$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$.

Bond order = 1/2 $(n_b - n_a)$ = 1/2 (8 − 4) = 2

The BN molecule is diamagnetic.

■ SOLUTIONS TO GENERAL PROBLEMS

10.65. The number of electron pairs, number of lone pairs, and geometry are for the central atom.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	2	1	Bent
	3	0	Trigonal planar
	5	3	Linear
	6	0	Octahedral

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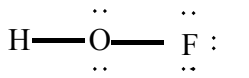
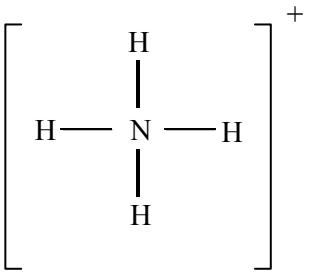
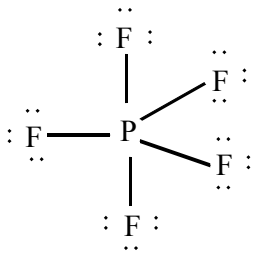
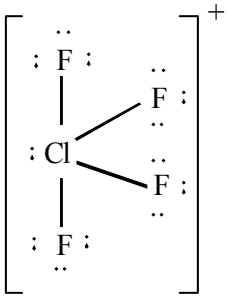
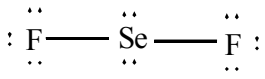
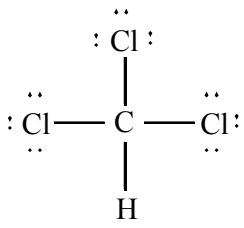
10.66.

Electron-Dot Structure	Number of Electron Pairs	Number of Lone Pairs	Geometry
	4	2	Bent, or angular
	4	0	Tetrahedral
	5	0	Trigonal bypyramidal
	5	1	Seesaw

10.67.

a.  Bent

b.  Tetrahedral

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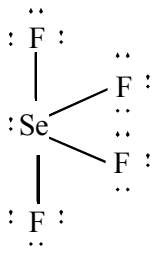
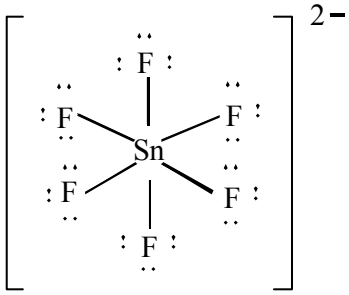
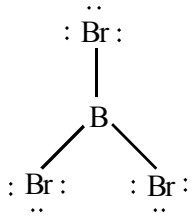
c. 

Seesaw

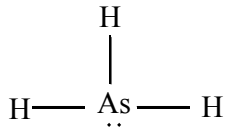
d. 

Octahedral

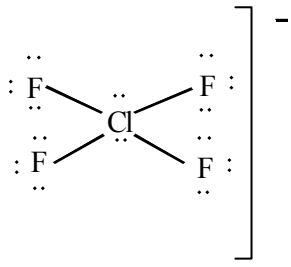
10.68.

a. 

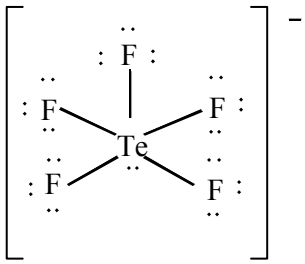
Trigonal planar

b. 

Trigonal pyramidal

c. 

Square planar

d. 

Square pyramidal

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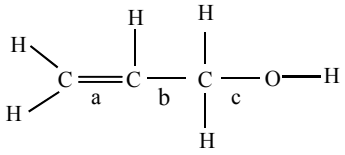
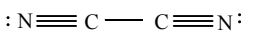
10.69.

a. 

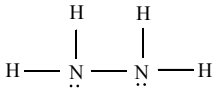
C_a and C_b: Three electron pairs around them. They are sp^2hybridized.

C_c: Four electron pairs around it. It is sp^3 hybridized.

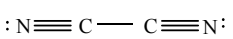
b. 

Both C atoms are bonded to two other atoms and have no lone pairs of electrons. They are *sp* hybridized.

10.70.

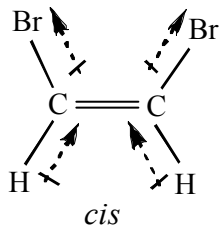
a. 

Each N has three atoms and one lone pair of electrons. They are sp^3 hybridized.

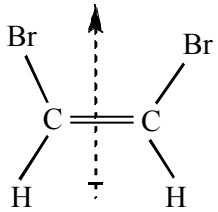
b. 

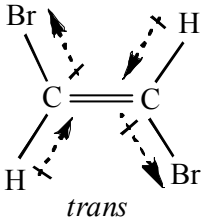
Each N has a σ bond to one atom and a lone pair of electrons. They are sp hybridized.

10.71.



cis

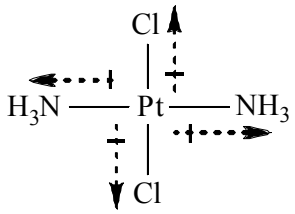
has a net dipole 



trans

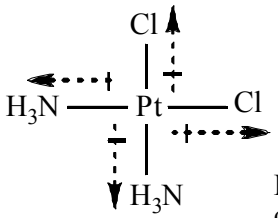
has no net dipole. The two C–Br bond dipoles cancel and the two C–H bond dipoles cancel.

10.72.



zero

Identical bond dipoles cancel each other.



nonzero

Bond dipoles cannot cancel. Dissimilar across from each other.

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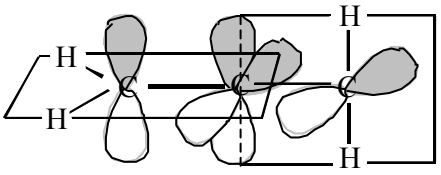
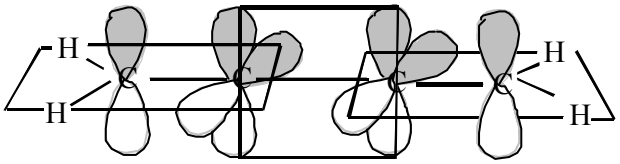
10.73. All four hydrogen atoms of $H_2C=C=CH_2$ cannot lie in the same plane because the second C=C bond forms perpendicular to the plane of the first C=C bond. By looking at Figure 10.26, you can see how this is so. The second C=C bond forms in the plane of the C–H bonds. Thus, the plane of the C–H bonds on the right side will be perpendicular to the plane of the C–H bonds on the left side. This is shown below using the π orbitals of the two C=C double bonds.



10.74. All four hydrogen atoms of $H_2C=C=C=CH_2$ lie in the same plane because the second C=C bond forms perpendicular to the plane of the first C=C bond, and the third C=C bond forms perpendicular to the plane of the second C=C bond. Thus, the right-hand CH_2 is in the same plane as the left-hand H_2C group.



10.75. Total electrons = 2 + 1 − 1 = 2.

The electron configuration is $(\sigma_{1s})^2$.

Bond order = 1/2 $(n_b - n_a)$ = 1/2 (2) = 1

The HeH^+ ion is expected to be stable.

10.76. Total electrons = (2 x 2) − 1 = 3.

The electron configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$.

Bond order = 1/2 $(n_b - n_a)$ = 1/2 (2 − 1) = 1/2

The He_2^+ ion is expected to be stable.

10.77. Total electrons = (2 x 6) + 2 = 14.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$.

Bond order = 1/2 $(n_b - n_a)$ = 1/2 (10 − 4) = 3

10.78. Total electrons = (2 x 8) + 2 = 18.

The electron configuration is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^4$.

Bond order = 1/2 $(n_b - n_a)$ = 1/2 (10 − 8) = 1

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10.79. The molecular orbital configuration of O_2 is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$. O_2^+ has one electron less than O_2. The difference is in the number of electrons in the π_{2p}^* antibonding orbital. This means that the bond order is larger for O_2^+ than for O_2.

O_2: Bond order $= 1/2\,(n_b - n_a) = 1/2\,(10 - 6) = 2$

O_2^+: Bond order $= 1/2\,(n_b - n_a) = 1/2\,(10 - 5) = 5/2$

It is expected that the species with the higher bond order, O_2^+, has the shorter bond length. In O_2^-, there is one more electron than in O_2. This additional electron occupies a π_{2p}^* orbital. Increasing the number of electrons in antibonding orbitals decreases the bond order; hence, O_2^- should have a longer bond length than O_2.

10.80. The molecular orbital configuration of N_2 is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$. N_2^+ has one electron less than N_2. The difference is in the number of electrons in the σ_{2p} bonding orbital. Because N_2^+ has fewer electrons in bonding orbitals than N_2 and the same number in antibonding orbitals, N_2^+ has a lower bond order and a longer bond distance. In N_2^-, there is one more electron than in N_2. This additional electron occupies a π_{2p}^* antibonding orbital. Because N_2^- has more electrons in antibonding orbitals and the same number in bonding orbitals, the bond order is lower; hence, N_2^- has a longer bond length than N_2.

10.81. As shown in Figure 10.34, the occupation of molecular orbitals by the N_2 valence electrons is

$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^0$

To form the first excited state of N_2, a σ_{2p} electron is promoted to the π_{2p}^* orbital, giving

$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1(\pi_{2p}^*)^1$

The differences in properties are as follows:

Magnetic character: The ground state is diamagnetic (all electrons paired), and the excited state is paramagnetic.

Bond order: ground state order $= 1/2\,(8 - 2) = 3$

excited state order $= 1/2\,(7 - 3) = 2$

Bond dissociation energy: ground-state energy = 942 kJ; excited-state energy is less than 942 kJ (excited state does not possess a stable triple bond like the ground state)

Bond length: ground-state length = 110 pm; excited-state length is more than 110 pm.

10.82. For N_2, refer to Figure 10.34. Note that the energy of the highest occupied orbital of atomic nitrogen is greater than the energy of the highest occupied orbital of N_2. Thus the outer electrons of atomic nitrogen are farther from the nucleus and have a smaller ionization energy than that of N_2.

The occupation of the molecular orbitals of O_2 are almost the same as shown in Figure 10.34; the electron configuration for O_2 given in Example 10.7 is below along with the electron configuration of atomic oxygen:

O_2: $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$

O: $1s^2 2s^2 2p^4$

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Referring again to Figure 10.34 (after inserting two π_{2p}* electrons for O_2), we see that the energy of the highest occupied orbital of O_2 is greater than the energy of the highest occupied orbital of atomic oxygen. Thus, the outer electrons of O_2 are farther from the nucleus and have a smaller ionization energy than that of atomic oxygen.

10.83. A person's two hands are similar but not identical. A person's left hand is a mirror image of the other hand, yet the two hands are nonsuperimposible. The presence of handedness in molecules depends on the fact that atoms in the molecules occupy specific places in three-dimensional space.

10.84. The chemical substance responsible for the flavor of spearmint is *L*-carvone. The substance responsible for the flavor of caraway seeds is *D*-carvone. These are two substances whose molecules differ only in being mirror images of one another. Nevertheless, they have strikingly different flavors: one is minty, the other a pungent aromatic.

10.85. Color vision is possible because three types of cone cells exist: one type absorbs light in the red region of the spectrum, another absorbs in the green region, and a third absorbs in the blue region. The chemical substance primarily responsible for human vision is 11-*cis*-retinal. In each of the different cone cells, 11-*cis*-retinal is attached to a different protein molecule, which affects the region of light that is absorbed by retinal.

10.86. When a photon of light in the ultraviolet region (near 180 nm) is absorbed by *cis*-1,2-dichloroethene, an electron in the π orbital undergoes a transition to the π* orbital. As a result, the double bond becomes a single bond, and rotation about the bond is now possible. The *cis* isomer tends to rotate into the *trans* isomer, which is more stable. The electron in the π* orbital undergoes a transition back to the π orbital; the single bond becomes a double bond again. The net result is the conversion of the *cis* isomer to the *trans* isomer.

10.87. Ozone in the stratosphere absorbs ultraviolet radiation between 200 and 300 nm, which is vitally important to life on earth. Radiation from the sum contains ultraviolet rays that are harmful to the DNA of biological organisms. Oxygen, O_2, absorbs the most energetic of these ultraviolet rays in the earth's upper atmosphere, but only ozone in the stratosphere absorbs the remaining ultraviolet radiation that is destructive to life on earth.

10.88. In 1974, Mario J. Molina and F. Sherwood Rowland expressed concern that chlorofluorocarbons (CFC's), such as $CClF_3$, and CCl_2F_2, would be a source of chlorine atoms that could catalyze the decomposition of ozone in the stratosphere, so that the ozone would be destroyed faster than it could be produced. The chlorofluorocarbons are relatively inert compounds used as refrigerants, spray-can propellants, and blowing agents (substances used to produce plastic foams). As a result of their inertness, however, CFC's concentrate in the atmosphere, where they steadily rise into the stratosphere. Once they are in the stratosphere, ultraviolet light decomposes them to form chlorine atoms, which react with ozone to form ClO and O_2. The ClO molecules react with oxygen atoms in the stratosphere to regenerate Cl atoms.

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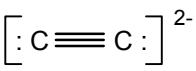
$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$$
$$\underline{ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)}$$
$$O_3(g) + O(g) \rightarrow 2O_2(g)$$

The net result is the decomposition of ozone to dioxygen. Chlorine atoms are consumed in the first step but regenerated in the second. Thus, chlorine atoms are not used up, so they function as a catalyst.

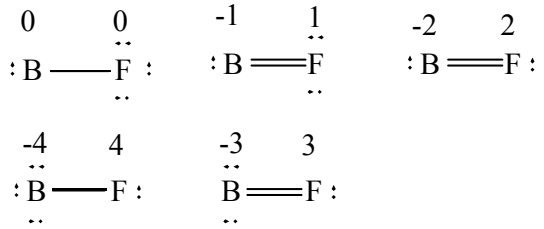
■ SOLUTIONS TO STRATEGY PROBLEMS

10.89. The electron dot formula for C_2^{2-} is



The valence bond description of the bonding is a triple bond, involving a σ bond formed by the overlap of a *sp* hybrid orbital on each carbon, and two π bonds formed by the overlap of the two unhybridized 2*p* orbitals on each carbon. Each atom obeys the octet rule, and there is a formal charge of −1 on each carbon. The molecular orbital description is based on a total of 14 electrons for the ion, with a configuration of $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$. The bond order is 1/2(8 – 2) = 3. This agrees with the valence bond description.

10.90. The Lewis structures and formal charges are as follows.



The formula that best fits the molecule is in the upper-right corner. The boron atom is singly bonded to the fluorine atom, and there is no formal charge on either atom. Also, the fluorine atom obeys the octet rule, but the boron atom does not, but this is not unusual. The valence bond description is a σ bond formed by the overlap of an *sp* hybrid orbital on boron with an sp^3 orbital on fluorine.

10.91. In BF_3NH_3, both the boron atom and the nitrogen atom are in a tetrahedral geometry, with sp^3 hybrid orbitals. In terms of valence bond theory, the bond between boron and fluorine is a σ bond, formed by the overlap of an sp^3 orbital on boron with an sp^3 orbital on nitrogen. For the reactant molecules, BF_3 is trigonal planar with sp^2 hybrid orbitals, and NH_3 is trigonal pyramidal with sp^3 hybrid orbitals.

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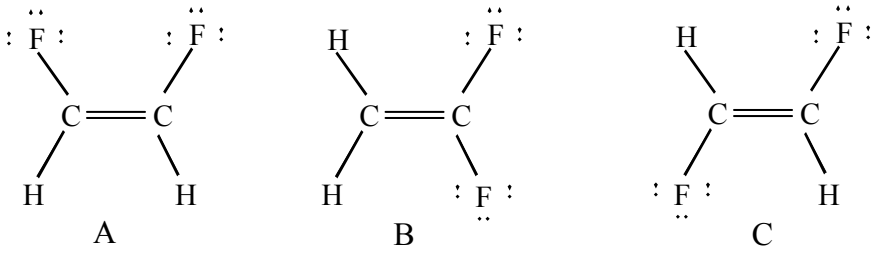
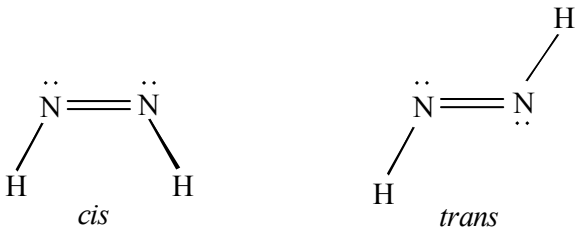
10.92. The bonding about the carbon atom is trigonal planar geometry, with the carbon having sp^2 hybrid orbitals. The carbon–oxygen double bond is a σ bond, formed by the overlap of an sp^2 orbital on carbon with a 2*p* orbital on oxygen, and a π bond, formed by the overlap of an unhybridized 2*p* orbital on carbon with another 2*p* orbital on oxygen. Another sp^2 hybrid orbital on carbon overlaps with an sp^2 orbital of the carbon in the ring. The third σ bond is another sp^2 orbital on carbon overlapping with an sp^3 orbital of the oxygen atom in the single bond.

10.93. In the molecule XF_6, X must have six valence electrons. Therefore, XF_4 has a total of 34 valence electrons. This gives four X–F single bonds and one lone pair around the X atom. The XF_6 molecule has an octahedral geometry, with sp^3d^2 hybrid orbitals. The XF_4 molecule has seesaw geometry, with sp^3d hybrid orbitals. Molecules with seesaw geometries are polar, so the observed dipole moment of 0.632 D for XF_4 is not unexpected. Some possibilities for X are sulfur (S), selenium (Se), and tellurium (Te).

10.94. The structures for the compounds are



10.95. The Lewis formulas for the two isomers of N_2H_2 are



The bonding descriptions for both structures are the same. All of the nitrogen–hydrogen bonds are σ bonds formed by the overlap of an sp^2 orbital on nitrogen with a 1*s* orbital on hydrogen. The nitrogen–nitrogen double bond is a σ bond, formed by the overlap of an sp^2 orbital on one nitrogen with an sp^2 orbital on the other nitrogen, and a π bond, formed by the overlap of an unhybridized 2*p* orbital on one nitrogen with a 2*p* orbital on the other nitrogen. The double bond requires a lot of energy to break, allowing free rotation, so it doesn't happen at normal temperatures. Thus, both isomers are stable.

10.96. The molecular orbital description of an O_2 molecule is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$. In the π_{2p}^* orbital, both electrons must be in the same orbital for all electrons to be paired. The ground state would have one electron in each of the two π_{2p}^* orbitals. In both cases, the bond order is 2, but the excited state is diamagnetic, whereas the ground state is paramagnetic.

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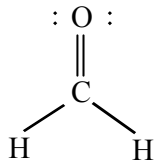
10.97. If you construct molecular orbitals similar to oxygen, you get the following configuration for S_2: [core]$(\sigma_{3s})^2(\sigma_{3s}^*)^2(\pi_{3p})^4(\sigma_{3p})^2(\pi_{3p}^*)^2(\sigma_{3p}^*)^0$. This would predict a bond order of 2. If two electrons were added to give S_2^{2-}, they would go into the π_{3p}^* orbital, and the bond order would be reduced to 1. Thus, the bond length should increase in this case. If two electrons were taken away to give S_2^{2+}, they would be removed from the π_{3p}^* orbital, and the bond order would increase to 3. Thus, the bond length would decrease in this case.

10.98. The Lewis formula for formaldehyde is



Because the C is bonded to three other atoms, it is assumed to be sp^2 hybridized. One 2*p* orbital remains unhybridized. The carbon–hydrogen bonds are σ bonds formed by the overlap of an sp^2 hybrid orbital on C with a 1*s* orbital on H. The remaining sp^2 hybrid orbital on C overlaps with a 2*p* orbital on O to form a σ bond. The unhybridized 2*p* orbital on C overlaps with a parallel 2*p* orbital on O to form the π bond.

In molecular orbital theory, the carbon–oxygen double bond has a σ and a π molecular orbital that are occupied by electrons. There is also a π^* orbital that is unoccupied in the ground state. The transition at 270 nm (UV region) is due to an electron moving from the occupied π orbital to the unoccupied π^* orbital to give an excited state.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

10.99. After assuming a 100.0-g sample, convert to moles:

$$60.4 \text{ g Xe} \times \frac{1 \text{ mol Xe}}{131.29 \text{ g Xe}} = 0.460\underline{0}5 \text{ mol Xe}$$

$$22.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.3\underline{8}1 \text{ mol O}$$

$$17.5 \text{ g F} \times \frac{1 \text{ mol F}}{18.99 \text{ g F}} = 0.92\underline{1}5 \text{ mol F}$$

Divide by 0.460 :

$$\text{Xe: } \frac{0.460}{0.460} = 1; \quad \text{O: } \frac{1.381}{0.460} = 3.00; \quad \text{F: } \frac{0.9215}{0.460} = 2.00$$

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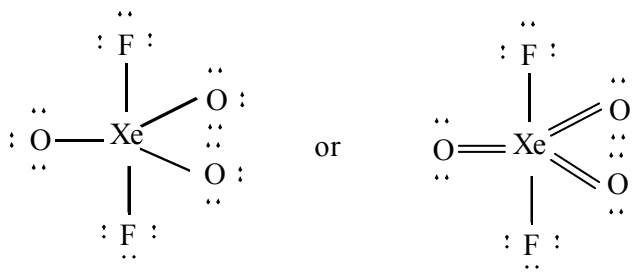
The simplest formula is XeO_3F_2. This is also the molecular formula. The Lewis formula is



Number of electron pairs = 5, number of lone pairs = 0; hence, the geometry is trigonal bipyramidal. Because xenon has five single bonds, it will require five orbitals to describe the bonding. This suggests sp^3d hybridization.

10.100. After assuming a 100.0-g sample, convert to moles:

$$58.8 \text{ g Xe} \times \frac{1 \text{ mol Xe}}{131.29 \text{ g Xe}} = 0.4478 \text{ mol Xe}$$

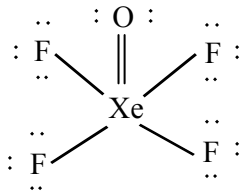
$$7.2 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.4500 \text{ mol O}$$

$$34.0 \text{ g F} \times \frac{1 \text{ mol F}}{18.99 \text{ g F}} = 1.7904 \text{ mol F}$$

Divide by 0.4478 :

$$\text{Xe: } \frac{0.4478}{0.4478} = 1; \text{ O: } \frac{0.450}{0.4478} = 1.00; \text{ F: } \frac{1.7904}{0.4478} = 4.00$$

The simplest formula is $XeOF_4$. This is also the molecular formula. The Lewis formula is



Number of electron pairs = 6, number of lone pairs = 1; hence, the geometry is square pyramidal. Because xenon has six electron pairs, it will require six orbitals to describe the bonding. This suggests sp^3d^2 hybridization.

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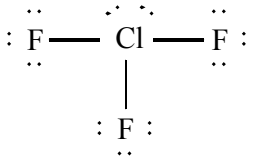
10.101. $U(s) + ClF_n \rightarrow UF_6 + ClF(g)$

$$\text{mol } UF_6 = 3.53 \text{ g } UF_6 \times \frac{1 \text{ mol } UF_6}{352.07 \text{ g } UF_6} = 0.010\underline{0}3 \text{ mol } UF_6$$

$$\text{mol ClF} = n = \frac{PV}{RT} = \frac{2.50 \text{ atm} \times 0.343 \text{ L}}{0.082057 \text{ L} \bullet \text{atm/ (K} \bullet \text{mol)} \times 348 \text{ K}} = 0.30\underline{0}2 \text{ mol ClF}$$

0.010 mol UF_6 = 0.060 mol F, and 0.030 mol ClF = 0.030 mol F; therefore, the total moles of F from ClF_n = 0.090 mol F. Because mol ClF_n must equal mol ClF, mol ClF_n = 0.030 mol and n = 0.090 mol F ÷ 0.030 mol ClF_n = 3. The Lewis formula is



Number of electron pairs = 5, number of lone pairs = 2; hence, the geometry is T-shaped. Because chlorine has five electron pairs, it will require five orbitals to describe the bonding. This suggests sp^3d hybridization.

10.102. $Br_2 + \text{excess } F_2 \rightarrow 2BrF_n$

$$\text{mol } Br_2 = n = \frac{PV}{RT} = \frac{(748/760) \text{ atm} \times 0.423 \text{ L}}{0.082057 \text{ L} \bullet \text{atm/(K} \bullet \text{mol)} \times 423 \text{ K}} = 0.011\underline{9}9 = 0.0120 \text{ mol } Br_2$$

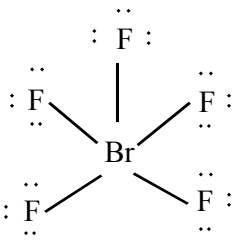
From the equation, 0.0120 mol Br_2 must produce 0.0240 mol BrF_n.

$$\text{Formula mass } BrF_n = \frac{4.20 \text{ g}}{0.0240 \text{ mol}} = 175 \text{ g/mol}$$

$$175 \text{ g/mol} = 79.9 \text{ g Br/mol} + 19.00 \times n \text{ g F/mol}$$

$$n = \frac{175 - 79.9}{19.00} = 5.00$$

The Lewis formula is



Number of electron pairs = 6, number of lone pairs = 1; hence, the geometry is square pyramidal. Because bromine has six electron pairs, it will require six orbitals to describe the bonding. This suggests sp^3d^2 hybridization.

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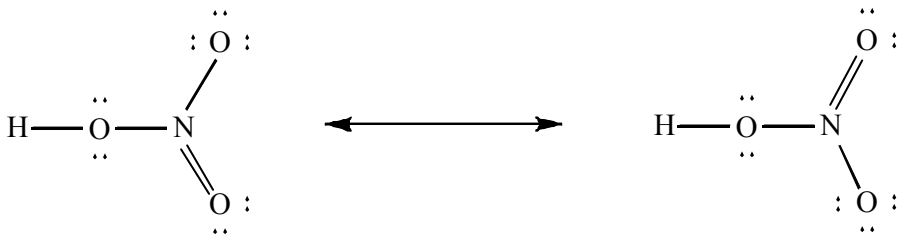
10.103. N_2: Triple bond; bond length = 110 pm. Geometry is linear; *sp* hybrid orbitals are needed for one lone pair and one σ bond.

N_2F_2: Double bond; bond length = 122 pm. Geometry is trigonal planar; sp^2 hybrid orbitals are needed for one lone pair and two σ bonds.

N_2H_4: Single bond; bond length = 145 pm. Geometry is tetrahedral; sp^3 hybrid orbitals are needed for one lone pair and three σ bonds.

10.104. The bond length of C_2 is close to that of C_2H_4, suggesting the same bond order for C_2 as for C_2H_4, which has a C=C bond. Total electrons for C_2 = 2 x 6 = 12. The molecular orbital configuration for C_2 is $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^0$. Bond order = 1/2(8 − 4) = 2. This agrees with the bond-length prediction.

10.105. HNO_3 resonance formulas:



The geometry around the nitrogen is trigonal planar; therefore, the hybridization is sp^2.

Formation reaction: $H_2(g) + 3O_2(g) + N_2(g) \rightarrow 2HNO_3(g)$

$2 \times \Delta H_f^\circ = [BE(\text{H–H}) + 3BE(O_2) + BE(N_2)] - [2BE(\text{H–O}) + 4BE(\text{N–O}) + 2BE(\text{N=O})]$

$= [(432 + 3 \times 494 + 942) - (2 \times 459 + 4 \times 201 + 2 \times 607)\ \text{kJ/2 mol}]$

$\Delta H_f^\circ = -80\ \text{kJ/2 mol} = -40\ \text{kJ/mol}$

Resonance energy = −40 kJ − (−135 kJ) = 95 kJ

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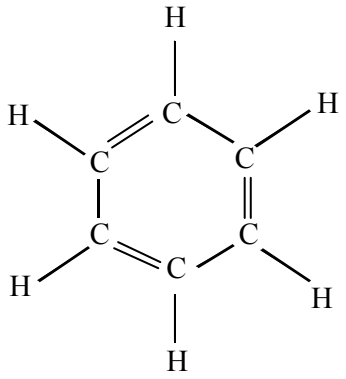
10.106. This is the other resonance formula of benzene.



Geometry is trigonal planar; therefore, the hybridization is sp^2.

Formation reaction: $3H_2(g) + 6C(\text{graphite}) \rightarrow C_6H_6(g)$ $[+ C(\text{graphite}) \rightarrow C(g)]$

$\Delta H_f^\circ = [3BE(\text{H–H}) + 6 \times \Delta H\, C(g)] - [6BE(\text{C–H}) + 3BE(\text{C–C}) + 3BE(\text{C=C})]$

$= [(3 \times 432 + 6 \times 715) - (6 \times 411 + 3 \times 346 + 3 \times 602)\ \text{kJ/mol}]$

$= +276\ \text{kJ/mol}$

Resonance energy $= +276\ \text{kJ} - (-83\ \text{kJ}) = 359\ \text{kJ}$

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CHAPTER 11

States of Matter; Liquids and Solids

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

11.1. First, calculate the heat required to vaporize 1.00 kg of ammonia:

$$1.00\ \text{kg NH}_3 \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol NH}_3}{17.03\ \text{g NH}_3} \times \frac{23.4\ \text{kJ}}{1\ \text{mol}} = 13\underline{7}4.04\ \text{kJ}$$

The amount of water at 0°C that can be frozen to ice at 0°C with this heat is

$$13\underline{7}4.04\ \text{kJ} \times \frac{1\ \text{mol H}_2\text{O}}{6.01\ \text{kJ}} \times \frac{18.01\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}} = 41\underline{1}7.54\text{g} = 4.12\ \text{kg H}_2\text{O}$$

11.2. Use the two-point form of the Clausius-Clapeyron equation to calculate P_2:

$$\ln \frac{P_2}{760\ \text{mmHg}} = \frac{26.8 \times 10^3\ \text{J/mol}}{8.31\ \text{J/(K}\bullet\text{mol)}} \left[\frac{1}{319\ \text{K}} - \frac{1}{308\ \text{K}} \right]$$

$$= 3225\ \text{K} \left[\frac{-1.12 \times 10^{-4}}{\text{K}} \right] = -0.36\underline{1}06$$

Converting to antilogs gives

$$\frac{P_2}{760\ \text{mmHg}} = \text{antilog}(-0.36106) = e^{-0.36106} = 0.69\underline{6}93$$

$$P_2 = 0.69693 \times 760\ \text{mmHg} = 529.6 = 5.30 \times 10^2\ \text{mmHg}$$

11.3. Use the two-point form of the Clausius-Clapeyron equation to solve for ΔH_{vap}:

$$\ln \frac{757\ \text{mmHg}}{522\ \text{mmHg}} = \frac{\Delta H_{vap}}{8.31\ \text{J/(K}\bullet\text{mol)}} \left[\frac{1}{368\ \text{K}} - \frac{1}{378\ \text{K}} \right]$$

$$0.37\underline{1}69 = \frac{\Delta H_{vap}}{8.31\ \text{J/(K}\bullet\text{mol)}} \left[\frac{7.188 \times 10^{-5}}{\text{K}} \right]$$

$$\Delta H_{vap} = 4.2\underline{9}6 \times 10^4\ \text{J/mol}\ \ (43.0\ \text{kJ/mol})$$

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11.4.

a. Liquefy methyl chloride by a sufficient increase in pressure below 144°C.

b. Liquefy oxygen by compressing to 50 atm below −119°C.

11.5.

a. Propanol has a hydrogen atom bonded to an oxygen atom. Therefore, hydrogen bonding is expected. Because propanol is polar (from the O–H bond), we also expect dipole-dipole forces. Weak London forces exist, too, because such forces exist between all molecules.

b. Linear carbon dioxide is not polar, so only London forces exist among CO_2 molecules.

c. Bent sulfur dioxide is polar, so we expect dipole-dipole forces; we also expect the usual London forces.

11.6. The order of increasing vapor pressure is butane (C_4H_{10}), propane (C_3H_8), and ethane (C_2H_6). Because London forces tend to increase with increasing molecular mass, we would expect the molecule with the highest molecular mass to have the lowest vapor pressure.

11.7. Because ethanol has an H atom bonded to an O atom, strong hydrogen bonding exists in ethanol but not in methyl chloride. Hydrogen bonding explains the lower vapor pressure of ethanol compared to methyl chloride.

11.8.

a. Zinc, a metal, is a metallic solid.

b. Sodium iodide, an ionic substance, exists as an ionic solid.

c. Silicon carbide, a compound in which carbon and silicon might be expected to form covalent bonds to other carbon and silicon atoms, exists as a covalent network solid.

d. Methane, at room temperature a gaseous molecular compound with covalent bonds, freezes as a molecular solid.

11.9. Only $MgSO_4$ is an ionic solid; C_2H_5OH, CH_4, and CH_3Cl form molecular solids; thus $MgSO_4$ should have the highest melting point. Of the molecular solids, CH_4 has the lowest molecular mass (16.0 amu) and would be expected to have the lowest melting point. Both C_2H_5OH and CH_3Cl have approximately the same molecular masses (46.0 amu vs. 50.5 amu), but C_2H_5OH exhibits strong hydrogen bonding and, therefore, would be expected to have the higher melting point. The order of increasing melting points is CH_4, CH_3Cl, C_2H_5OH, and $MgSO_4$.

11.10. Each of the four corners of the cell contains one atom, which is shared by a total of four unit cells. Therefore, the corners contribute one whole atom.

$$\frac{\text{Atoms}}{\text{Unit cell}} = 4 \text{ corners} \times \frac{1/4 \text{ atom}}{1 \text{ corner}} = 1 \text{ atom}$$

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11.11. Use the edge length to calculate the volume of the unit cell. Then, use the density to determine the mass of one atom. Divide the molar mass by the mass of one atom.

$$V = (3.509 \times 10^{-10}\ \text{m})^3 = 4.321 \times 10^{-29}\ \text{m}^3$$

$$d = \frac{0.534\ \text{g}}{1\ \text{cm}^3} \times \left[\frac{100\ \text{cm}}{1\ \text{m}}\right]^3 = 5.34 \times 10^5\ \text{g/m}^3$$

Mass of 1 unit $= d \times V$

$= (5.34 \times 10^5\ \text{g/m}^3) \times (4.321 \times 10^{-29}\ \text{m}^3) = 2.3074 \times 10^{-23}\ \text{g}$

There are two atoms in a body-centered cubic unit cell; thus, the mass of one lithium atom is

$$1/2 \times 2.3074 \times 10^{-23}\ \text{g} = 1.1537 \times 10^{-23}\ \text{g}$$

The known atomic mass of lithium is 6.941 amu, so Avogadro's number is

$$N_A = \frac{6.941\ \text{g/mol}}{1.1537 \times 10^{-23}\ \text{g/atom}} = 6.016 \times 10^{23} = 6.02 \times 10^{23}\ \text{atoms/mol}$$

11.12. Use Avogadro's number to convert the molar mass of potassium to the mass per one atom.

$$\frac{39.0983\ \text{g K}}{1\ \text{mol K}} \times \frac{1\ \text{mol K}}{6.022 \times 10^{23}\ \text{atoms}} = \frac{6.4925 \times 10^{-23}\ \text{g K}}{1\ \text{atom}}$$

There are two K atoms per unit cell; therefore, the mass per unit cell is

$$\frac{6.4925 \times 10^{-23}\ \text{g K}}{1\ \text{atom}} \times \frac{2\ \text{atoms}}{1\ \text{unit cell}} = \frac{1.2985 \times 10^{-22}\ \text{g}}{1\ \text{unit cell}}$$

The density of 0.856 g/cm^3 is equal to the mass of one unit cell divided by its unknown volume, V. After solving for V, determine the edge length from the cube root of the volume.

$$0.856\ \text{g/cm}^3 = \frac{1.2985 \times 10^{-22}\ \text{g}}{V}$$

$$V = \frac{1.2985 \times 10^{-22}\ \text{g}}{0.856\ \text{g/cm}^3} = 1.517 \times 10^{-22}\ \text{cm}^3\ (1.517 \times 10^{-28}\ \text{m}^3)$$

$$\text{Edge length} = \sqrt[3]{1.517 \times 10^{-28}\ \text{m}^3} = 5.333 \times 10^{-10} = 5.33 \times 10^{-10}\ \text{m}\ (533\ \text{pm})$$

■ ANSWERS TO CONCEPT CHECKS

11.1.

a.

(1) At $t = 0$, since the system is not at equilibrium and there are no H_2O molecules in the gaseous state, you would expect the rate of evaporation to exceed the rate of condensation. At $t = 1$, since evaporation has proceeded at a greater rate than condensation, there must now be fewer molecules in the liquid state, resulting in a lower level of $H_2O(l)$.

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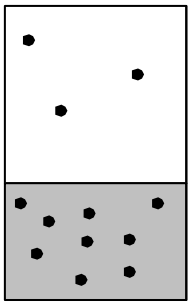
(2) At $t = 1$, since some of the H_2O has gone into the vapor state, the vapor pressure must be higher.

(3) At $t = 1$, since evaporation has occurred, there must be more molecules in the vapor state.

(4) At $t = 0$, since the system is not at equilibrium, and there are no H_2O molecules in the gaseous state, you would expect the rate of evaporation to exceed the rate of condensation.

(5)



$t = 1$

b.

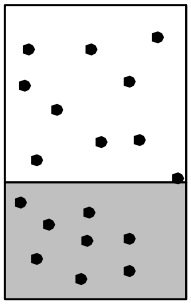
(1) Between $t = 1$ and $t = 2$, the system has still not reached equilibrium. Therefore, because the rate of evaporation continues to exceed the rate of condensation, you would expect the water level to be lower.

(2) Prior to reaching equilibrium at $t = 2$, you would continue to observe a rate of evaporation greater than the rate of condensation, resulting in a higher vapor pressure than $t = 1$.

(3) Since evaporation has been occurring at a greater rate than condensation between points $t = 1$ and $t = 2$, you would expect more molecules in the vapor state at $t = 2$.

(4) When the system has reached equilibrium at $t = 2$, the rate of evaporation equals the rate of condensation.

(5)



$t = 2$

11.2. You would have to cook the egg for a longer time. The reason is that, since the temperature is lower, it would take longer for the egg to become hard, a chemical process (which slows down at lower temperature).

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11.3.

a. If the first reaction occurred, the mixture of hydrogen and oxygen that resulted would form an explosive mixture. At 100°C, 2 moles of water make 61.2 L of gaseous water. In the incorrect reaction, 2 moles of water produce 91.8 L of gaseous products.

b. Since you would be breaking strong chemical bonds and forming relatively weak bonds, the enthalpy for the first reaction (the wrong reaction) would be many times greater (more positive) than for the second reaction.

c. Apply Hess's law. The enthalpy for the wrong reaction would be equal to two times the negative of ΔH_f^o for $H_2O(l)$ plus the heat required to raise the temperature of 2 moles of water from 25°C to 100°C.

11.4.

a. First, consider the B balls (small). There are four atoms, each completely inside the cell. Thus, there are four B atoms per cell. Next, there are fourteen A atoms (large). Of these, eight are in corners, and contribute 1/8 to the cell. Six atoms are in faces, and contribute 1/2 to the cell. Thus, there are 8 x (1/8) + 6 x (1/2) = 4 A atoms per cell. The ratio of A atoms to B atoms is 4 to 4, or 1 to 1. Thus, the formula of the compound is AB.

b. Since all of the B atoms are completely within the cell, the shape of the cell is determined by the A atoms only. It is a face-centered cubic unit cell.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

11.1. The six different phase transitions, with examples in parentheses, are melting (snow melting), sublimation (dry ice subliming directly to carbon dioxide gas), freezing (water freezing), vaporization (water evaporating), condensation (dew forming on the ground), and gas-solid condensation or deposition (frost forming on the ground).

11.2. Iodine can be purified by heating it in a beaker covered with a dish containing ice or ice water. Only pure iodine should sublime, crystallizing on the cold bottom surface of the dish above the iodine. The common impurities in iodine do not sublime nor do they vaporize significantly.

11.3. The vapor pressure of a liquid is the partial pressure of the vapor over the liquid, measured at equilibrium. In molecular terms, vapor pressure involves molecules of a liquid vaporizing from the liquid phase, colliding with any surface above the liquid, and exerting pressure on it. The equilibrium is a dynamic one because molecules of the liquid are continually leaving the liquid phase and returning to it from the vapor phase.

11.4. Steam at 100°C will melt more ice than the same weight of water at 100°C because it contains much more energy in the form of its heat of vaporization. It will transfer this energy to the ice and condense in doing so. The condensed steam and the water will both transfer heat to the ice as the temperature then drops.

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11.5. The heat of fusion is smaller than the heat of vaporization because melting requires only enough energy for molecules to escape from their sites in the crystal lattice, leaving other molecular attractions intact. In vaporization, sufficient energy must be added to break almost all molecular attractions and also to do the work of pushing back the atmosphere.

11.6. Evaporation leads to cooling of a liquid because the gaseous molecules require heat to evaporate; as they leave the other liquid molecules, they remove the heat energy required to vaporize them. This leaves less energy in the liquid, the temperature of which then drops.

11.7. As the temperature increases for a liquid and its vapor in the closed vessel, the two, which are separated by a meniscus, gradually become identical. The meniscus first becomes fuzzy and then disappears altogether as the temperature reaches the critical temperature. Above this temperature, only the vapor exists.

11.8. A permanent gas can be liquefied only by lowering the temperature below its critical temperature while compressing the gas.

11.9. The pressure in the cylinder of nitrogen at room temperature (above its critical temperature of −147°C) decreases continuously as gas is released because the number of molecules in the vapor phase, which governs the pressure, decreases continuously. The pressure in the cylinder of propane at room temperature (below its critical temperature) is constant because liquid propane and gaseous propane exist at equilibrium in the cylinder. The pressure will remain constant at the vapor pressure of propane until only gaseous propane remains. At that point, the pressure will decrease until all of the propane is gone.

11.10. The vapor pressure of a liquid depends on the intermolecular forces in the liquid phase since the ease with which a molecule leaves the liquid phase depends on how strongly it is attracted to the other molecules. If such molecules attract each other strongly, the vapor pressure will be relatively low; if they attract each other weakly, the vapor pressure will be relatively high.

11.11. Surface tension makes a liquid act as though it had a skin, because for an object to break through the surface, the surface area must increase. This requires energy, so there is some resistance to the object breaking through the surface.

11.12. London forces, also known as dispersion forces, originate between any two molecules that are weakly attracted to each other by means of small instantaneous dipoles that occur as a result of the varying positions of the electrons during their movement about their nuclei.

11.13. Hydrogen bonding is a weak to moderate attractive force that exists between a hydrogen atom covalently bonded to a very electronegative atom, X (N, O, or F), and a lone pair of electrons on another small, electronegative atom, Y. (X and Y may be the same or different elements.) Hydrogen bonding in water involves a hydrogen atom of one water molecule bonding to a lone pair of electrons on the oxygen atom of another water molecule.

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11.14. Molecular substances have relatively low melting points because the forces broken by melting are weak intermolecular attractions in the solid state, not strong bonding attractions.

11.15. A crystalline solid has a well-defined, orderly structure; an amorphous solid has a random arrangement of structural units.

11.16. In a face-centered cubic cell, there are atoms at the center of each face of the unit cell in addition to those at the corners.

11.17. The structure of thallium(I) iodide is a simple cubic lattice for both the metal ions and the anions. Thus, the structure consists of two interpenetrating cubic lattices of cation and anion.

11.18. The coordination number of Cs^+ in CsCl is 8; the coordination number of Na^+ in NaCl is 6; and the coordination number of Zn^{2+} in ZnS is 4.

11.19. Starting with the edge length of a cubic crystal, we can calculate the volume of a unit cell by cubing the edge length. Next, knowing the density of the crystalline solid, we can calculate the mass of the atoms in the unit cell. Then, the mass of the atoms in the unit cell is divided by the number of atoms in the unit cell, to give the mass of one atom. Dividing the mass of one mole of the crystal by the mass of one atom yields a value for Avogadro's number.

11.20. X rays can strike a crystal and be reflected at various angles; at most angles, the reflected waves will be out of phase and will interfere destructively. At certain angles, however, the reflected waves will be in phase and will interfere constructively, giving rise to a diffraction pattern.

11.21. The answer is e, cooling the H_2O sample from 105°C to 84°C.

11.22. The answer is d, sublime.

11.23. The answer is c, London (dispersion) forces.

11.24. The answer is b, 6.40×10^7 pm^3.

■ ANSWERS TO CONCEPT EXPLORATIONS

11.25.

a. In the container, A is in solid form, B is in liquid form, and C is in gaseous form.

b. The greatest intermolecular attractions are in the solid (A), second is for the liquid (B), and the least intermolecular attractions are for the gas (C).

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c. Since each of these substances is a monatomic nonmetal, the only forces present are London (dispersion) forces.

d. The greatest atomic mass will be for the strongest intermolecular forces, which is A.

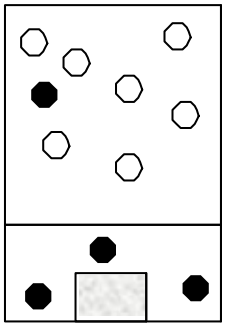
e. The element with the normal boiling point of 2 K is the gas, C. A gas is a substance whose boiling point is below ambient temperature.

f. The substance with a melting point of 50 K is A. Since it is a solid, its melting point must be above ambient temperature.

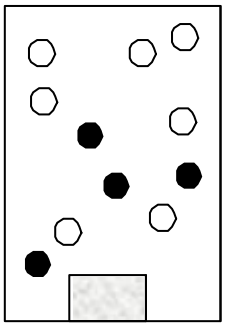
g. The substance with a normal boiling point of 25 K is B. It cannot have a freezing point of 7 K, or it would be in solid form. In order for a substance to be a liquid, the freezing point must be below ambient temperature.

h. As you began to heat the container to 20 K, the gas would expand and the piston would move up.

i. There would not be much difference in the container and its contents at 20 K. The gas (C) would have expanded its volume in accordance with Charles's law, and the new volume would be five times the volume at 4 K. The solid component (A) would appear unchanged. Since the temperature is nearing the boiling point of the liquid component (B), which is 25 K, some of B should appear in the vapor phase. In the drawing below, The gray is A, the black B, and the white C.



j. At 30 K, the temperature is now above the boiling point of B, which is 25 K, so both B and C are now gases. A remains in the solid state.



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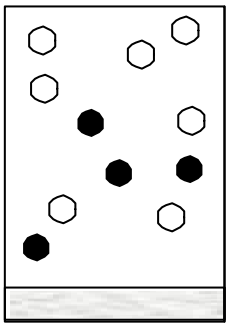
k. When the temperature of the container reaches 60 K, component A has now melted and is in the liquid state. The gases (B and C) continue to expand according to Charles's law.



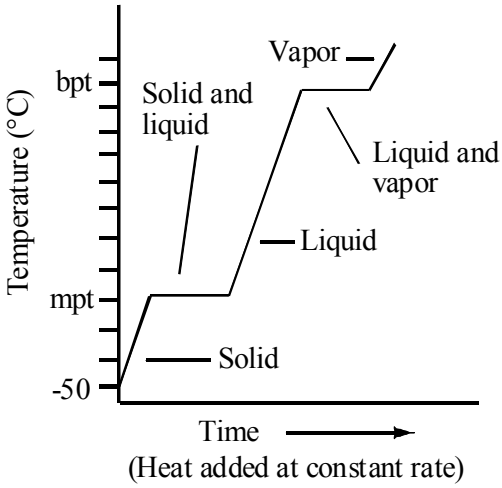
11.26. **Part 1**

a. Yes, it is possible to add heat to a pure substance and not observe a temperature change. This occurs during phase changes: melting (freezing) or boiling (condensing).

b. On a molecular level, when heat is first added to a solid substance, it causes the particles that make up the substance to begin vibrating in their locus sites. This causes the temperature of the substance to increase, until the melting point is reached. At this point, enough energy has been added to the substance to overcome the intermolecular forces of attraction, and particles begin to escape into the liquid phase. This occurs at a constant temperature, until the entire sample has melted.

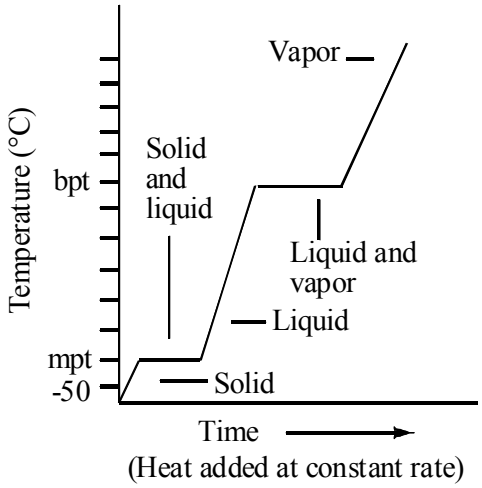
Part 2

Heating curve for substance A



(Heat added at constant rate)

Heating curve for substance B



(Heat added at constant rate)

a. No, substance B melted first. Since the melting point of substance B is lower, it requires less heat to reach the melting point. The curves for the solid region of each graph have about the same slope, so both solids warm at the same rate. Since it takes less heat, it also takes less time to reach the melting point for substance B, and it melts first.

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b. The boiling points are not the same. The boiling point for substance B is lower than for substance A. Since the curves in the liquid portion of the graphs for both substances have the same slope, the boiling point for substance B is proportionately lower.

c. Substance B reached the boiling point first. It requires less total heat to reach the boiling point, and thus less time.

d. No, melting and vaporizing are not the same process, and they involve different forces. It takes more energy to transform a liquid to a vapor than to melt a solid, so the heat required to convert all of substance A to a gas at its boiling point is greater than the heat required to melt it. On the graphs, the horizontal line for liquid-vapor equilibrium is longer than the horizontal line for solid-liquid equilibrium.

■ ANSWERS TO CONCEPTUAL PROBLEMS

11.27.

a. The molecules of A would have the majority of molecules in the gas phase because at this temperature, liquid A has the higher fraction of molecules that have sufficient kinetic energy and can vaporize.

b. The molecules with the strongest intermolecular attractions will have the fewest molecules in the gas phase because a higher kinetic energy is needed to overcome the attractions. Since molecules of C have the smallest fraction of molecules with sufficient kinetic energy, they have the strongest intermolecular attractions.

c. The molecules with the strongest intermolecular attractions will have the lowest vapor pressure. Thus, molecules of C would have the lowest vapor pressure.

11.28. You will need to compare the heats of fusion and vaporization of substance X (ΔH_{fus} = 9.0 kJ/mol and ΔH_{vap} = 20.3 kJ/mol) with the values for water, which are ΔH_{fus} = 6.01 kJ/mol and ΔH_{vap} = 40.7 kJ/mol. Comparing values shows that ΔH_{fus} is 1.5 times larger for substance X and that ΔH_{vap} is 2.0 times larger for H_2O.

Heating the substance, or water, from −10°C to the boiling point is a three-step process. Step 1 is to heat the solid from −10°C to 0°C, the freezing point. The heat required for this step is equal to mass x specific heat capacity x temperature change. Step 2 is to melt the solid to liquid at 0°C. The heat required for this step is equal to moles x ΔH_{fus}. Step 3 is to heat the liquid from 0°C to 100°C. The heat required for this step is equal to mass x specific heat capacity x temperature change.

a. Since the masses, heat capacities, and temperature changes for water and for substance X are all equal, the heat required for Step 1 and Step 3 are the same for both. Since ΔH_{fus} is larger for substance X (per mole), Step 2 will require more heat for substance X and thus take longer. Therefore, H_2O will reach the boiling point first.

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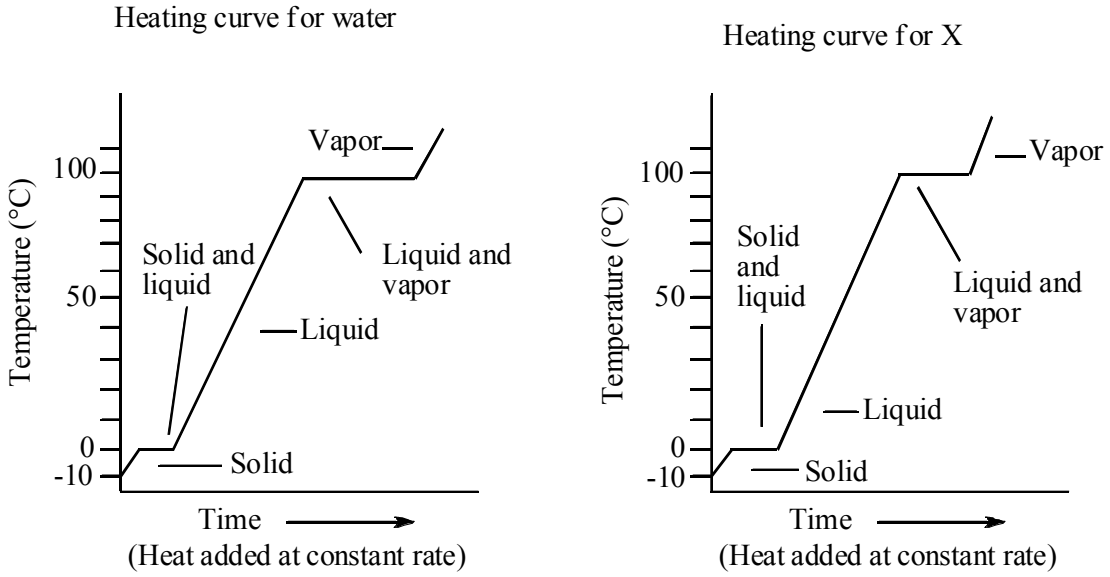
b. To completely boil away the substance, an additional step is required. Step 4 is to boil the liquid to vapor at 100°C. The heat required for this step is equal to moles x ΔH_{vap}. Since the ΔH_{vap} values are much larger than the ΔH_{fus} values, Step 4 will require much more heat than Step 2 for both substance X and H_2O. Since ΔH_{vap} is smaller for substance X (per mole), Step 4 will require less heat for substance X and thus take less time. The total heat required for the four steps is directly proportional to the time it would take to completely boil away the substance. Steps 1 and 3 are the same for both. Step 2 takes 1.5 times as long for substance X, but Step 4 takes 2.0 times as long for water. Since Step 4 requires the most heat, water will require more time to complete this step, so substance X will boil away first.

c. The heating curves for substance X and for water are shown below.



11.29. The water the farmers spray above and on their fruit is warmer than the temperature of the fruit on the trees. Therefore, as the temperature of the air drops, it absorbs heat from the water, converting it into ice, before absorbing any heat from the fruit. The heat released when the liquid-to-solid phase change occurs prevents the fruit from freezing.

11.30.

a. Bottle A is probably mislabeled. If it is an ionic compound, the boiling point should be higher than 35°C. Most ionic compounds are solids with high melting points.

b. The substance with the highest boiling point will have the strongest intermolecular attractions. Thus, the compound in bottle C has the strongest intermolecular attractions.

c. The substance with the lowest boiling point will have the highest vapor pressure. Thus, the substance in bottle B will have the highest vapor pressure.

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11.31.

a. Considering the A atoms, there are nine A atoms per cell. Of these, eight are in corners and contribute 1/8 per cell, and one is completely inside the cell. Thus there are 8 x (1/8) + 1 x (1) = 2 A atoms per cell. Next, considering the B atoms, there are six per cell. Of these, four are in faces and contribute 1/2 per cell, and two are completely inside the cell. Thus, there are 4 x (1/2) + 2 x (1) = 4 B atoms per unit cell. The ratio of A atoms to B atoms is 2 to 4, or 1 to 2. Thus, the formula of the compound is AB_2.

b. The A atoms are in the arrangement of a body-centered cell.

11.32. Consulting the phase diagram for water (Figure 11.11), you see that by increasing the pressure on solid ice at constant temperature, you will convert solid ice into liquid water. As the weights continue to exert pressure on the ice through the wire, the ice below the wire continues to melt. Above the wire, the pressure is released, and the water refreezes, re-forming the ice. Thus the wire passed through the block but the block was not cut in half.

11.33. As the water evaporates, molecules with higher kinetic energy escape the liquid and leave behind molecules with lower energy. The result is a drop in temperature of the liquid. Since the cup is well insulated, the energy lost with the evaporated molecules is not rapidly replaced.

11.34. The heat released when the vapor of a substance condenses to liquid is equal to the negative (opposite) of the heat of vaporization for the substance. As a consequence of its strong intermolecular attractions, water has a larger heat of vaporization, so it releases more heat when condensing on the skin, causing a more severe burn.

11.35. This question can be answered by looking at the packing efficiencies of the three types of crystals: simple cubic, 52.4% body-centered cubic, 68% and face-centered cubic, 74%.

a. The highest density would correspond to the type of crystal with the highest packing efficiency. Of the three types of crystals, the face-centered cubic has the highest packing efficiency (74%) and thus has the highest density.

b. The most empty space corresponds to the type of crystal with the lowest packing efficiency. Of the three types of crystals, the simple cubic has the lowest packing efficiency (52.4%) and therefore the most empty space.

11.36. Since the liquids have comparable molar masses, differences in properties can be attributed to differences in intermolecular forces. The flask on the left has more molecules in the vapor phase than the flask on the right, and therefore, the substance in this flask has a higher vapor pressure. Since vapor pressure decreases as intermolecular forces increase, the intermolecular forces for the substance in the flask on the right are stronger than for the substance in the flask on the left.

a. Substance A has hydrogen bonding, whereas substance B does not. Hydrogen bonding is a stronger intermolecular force than a dipole-dipole force. This implies that substance A, with the lower vapor pressure, is in the flask on the right.

b. The amount of vapor present at 35°C (an increase of 15°C) would be greater in both flasks compared to the amount present at 20°C, but since the intermolecular forces of substance B are weaker, substance B will experience a larger increase.

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■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

11.37.

a. Vaporization

b. Freezing of eggs and sublimation of ice

c. Condensation

d. Gas-solid condensation, deposition

e. Freezing

11.38.

a. Sublimation

b. Vaporization

c. Sublimation of the filament and gas-solid condensation of the vapor

d. Freezing

e. Melting, fusion

11.39. Dropping a line from the intersection of a 350-mmHg line with the diethyl ether curve in Figure 11.7 intersects the temperature axis at about 10°C.

11.40. Dropping a line from the intersection of a 250-mmHg line with the carbon tetrachloride curve in Figure 11.7 intersects the temperature axis at about 40°C.

11.41. The total amount of energy provided by the heater in 4.54 min is

$$4.54 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{3.48 \text{ J}}{\text{s}} = 94\underline{7}.95 \text{ J} \ (0.94\underline{7}95 \text{ kJ})$$

The heat of fusion per mole of I_2 is

$$\frac{0.9479 \text{ kJ}}{15.5 \text{ g } I_2} \times \frac{2 \times 126.9 \text{ g } I_2}{\text{mol } I_2} = 15.\underline{5}2 = \frac{15.5 \text{ kJ}}{\text{mol } I_2}$$

11.42. The total amount of energy provided by the heater in 6.92 min is

$$6.92 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{4.66 \text{ J}}{1 \text{ s}} = 19\underline{3}4.8 \text{ J} \ (1.9\underline{3}48 \text{ kJ})$$

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The heat of fusion per mole of Cd is

$$\frac{1.9348\ \text{kJ}}{15.5\ \text{g Cd}} \times \frac{112.4\ \text{g Cd}}{\text{mol Cd}} = 6.0\underline{7}4 = \frac{6.07\ \text{kJ}}{\text{mol Cd}}$$

11.43. The heat absorbed per 2.25 g of isopropyl alcohol, C_3H_8O, is

$$2.25\ \text{g } C_3H_8O \times \frac{1\ \text{mol } C_3H_8O}{60.09\ \text{g } C_3H_8O} \times \frac{42.1\ \text{kJ}}{1\ \text{mol } C_3H_8O} = 1.5\underline{7}6 = 1.58\ \text{kJ}$$

11.44. For 39.3 g of butane, C_4H_{10}, the heat needed is

$$39.3\ \text{g } C_4H_{10} \times \frac{1\ \text{mol } C_4H_{10}}{58.12\ \text{g } C_4H_{10}} \times \frac{21.3\ \text{kJ}}{1\ \text{mol } C_4H_{10}} = 14.\underline{4}0 = 14.4\ \text{kJ}$$

11.45. Because all the heat released by freezing the water is used to evaporate the remaining water, you must first calculate the amount of heat released in the freezing:

$$9.31\ \text{g } H_2O \times \frac{\text{mol } H_2O}{18.02\ \text{g } H_2O} \times \frac{6.01\ \text{kJ}}{\text{mol } H_2O} = 3.1\underline{0}505\ \text{kJ}$$

Finally, calculate the mass of H_2O that was vaporized by the 3.10505 kJ of heat:

$$3.10505\ \text{kJ} \times \frac{18.02\ \text{g } H_2O}{1\ \text{mol } H_2O} \times \frac{1\ \text{mol } H_2O}{44.9\ \text{kJ}} = 1.2\underline{4}6 = 1.25\ \text{g } H_2O$$

11.46. Enough ice must have been added so that the heat consumed in melting the ice is equal to the heat released in cooling the water from 21.0°C to 0.0°C.

$$\text{Heat released by cooling} = [(33.6\ \text{g})(0.0°\text{C} - 21.0°\text{C})(4.18\ \text{J/g}\bullet°\text{C})]$$
$$= -2.9\underline{4}94 \times 10^3\ \text{J} = -2.9\underline{4}94\ \text{kJ}$$

Convert this heat (2.9494 kJ) to the mass of ice melted:

$$2.9494\ \text{kJ} \times \frac{1\ \text{mol } H_2O}{6.01\ \text{kJ}} \times \frac{18.02\ \text{g } H_2O}{1\ \text{mol } H_2O} = 8.8\underline{4}33 = 8.84\ \text{g } H_2O$$

11.47. Calculate how much heat is released by cooling 64.3 g of H_2O from 55°C to 15°C.

$$\text{Heat released} = (64.3\ \text{g})(15°\text{C} - 55°\text{C})\left(\frac{4.18\ \text{J}}{1\ \text{g}\bullet°\text{C}}\right) = -1.\underline{0}7509 \times 10^4\ \text{J} = -1\underline{0}.7509\ \text{kJ}$$

The heat released is used first to melt the ice and then to warm the liquid from 0°C to 15°C. Let the mass of ice equal *y* grams. Then, for fusion, and for warming, we have

$$\text{Fusion: } (y\ \text{g } H_2O) \times \frac{1\ \text{mol } H_2O}{18.02\ \text{g } H_2O} \times \frac{6.01\ \text{kJ}}{1\ \text{mol } H_2O} = 0.33\underline{3}5\ y\ \text{kJ}$$

$$\text{Warming: } (y\ \text{g } H_2O)(15°\text{C} - 0°\text{C})\left(\frac{4.18\ \text{J}}{1\ \text{g}\bullet°\text{C}}\right) = 6\underline{2}.70\ y\ \text{J}\ \ (0.06\underline{2}70\ y\ \text{kJ})$$

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Because the total heat required for melting and warming must equal the heat released by cooling, equate the two, and solve for y.

$$10.7509 \text{ kJ} = 0.3335y \text{ kJ} + 0.0627y \text{ kJ} = y(0.3335 + 0.0627) \text{ kJ}$$

$$y = 10.7509 \text{ kJ} \div 0.3962 \text{ kJ} = 27.13 \text{ (grams)}$$

Thus, 27 g of ice was added.

11.48. If all the steam condensed, the quantity of heat used to warm the water in the flask must equal the heat released by condensation and cooling of the steam. Thus, first find the quantity of heat used to warm the water in the flask.

$$\text{Heat required} = (275 \text{ g})(83°\text{C} - 21°\text{C})(4.18 \text{ J/(g}\bullet°\text{C)}) = 71.26 \times 10^3 \text{ J} \ (71.26 \text{ kJ})$$

Now let y = the mass of the steam. Then find the quantity of heat released by condensation:

$$y \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{-40.7 \text{ kJ}}{1 \text{ mol } H_2O} = -2.259 \, y \text{ kJ}$$

Now find the quantity of heat released by cooling y grams of H_2O from 100°C to 83°C:

$$\text{Heat released.} = y \, (83°\text{C} - 100°\text{C}) \, (4.18 \text{ J/(g}\bullet°\text{C)}) = -71.06y \text{ J} \ (-0.07106y \text{ kJ})$$

The total quantity of heat released in condensing and cooling the steam is equal in magnitude, but opposite in sign, to the quantity of heat required to warm the water in the flask:

$$-71.26 \text{ kJ} = -2.259y \text{ kJ} + (-0.07106y) \text{ kJ}$$

$$y \text{ g steam} = \frac{71.26 \text{ kJ}}{(2.259 + 0.07106) \text{ kJ}} = 30.58 = 31 \text{ g}$$

Thus, 31 g of steam condensed.

11.49. At the normal boiling point, the vapor pressure of a liquid is 760.0 mmHg. Use the Clausius-Clapeyron equation to find P_2 when P_1 = 760.0 mmHg, T_1 = 334.85 K (61.7°C), and T_2 = 309.35 K (36.2°C). Also use ΔH_{vap} = 31.4 x 10^3 J/mol.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{P_2}{760 \text{ mmHg}} = \frac{31.4 \times 10^3 \text{ J/mol}}{8.31 \text{ J/K} \bullet \text{mol}}\left(\frac{1}{334.85 \text{ K}} - \frac{1}{309.35 \text{ K}}\right) = -0.93018$$

Taking antilogs of both sides gives

$$\frac{P_2}{760 \text{ mmHg}} = e^{-0.93018} = 0.3944$$

$$P_2 = 0.3944 \times 760 \text{ mmHg} = 299.8 = 3.00 \times 10^2 \text{ mmHg (300. mmHg)}$$

11.50. At methanol's normal boiling point, its vapor pressure is 760.0 mmHg. Use the Clausius-Clapeyron equation to calculate P_2 when P_1 = 760 mmHg, T_1 = 338.2 K, and T_2 = 295.2 K. Also use ΔH_{vap} = 37.4 x 10^3 J/mol.

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$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{P_2}{760 \text{ mmHg}} = \frac{37.4 \times 10^3 \text{ J/mol}}{8.31 \text{ J/K} \bullet \text{mol}}\left(\frac{1}{338.2 \text{ K}} - \frac{1}{295.2 \text{ K}}\right) = -1.9\underline{3}84$$

Taking antilogs of both sides gives

$$\frac{P_2}{760 \text{ mmHg}} = e^{-1.9384} = 0.14\underline{3}93$$

$$P_2 = 0.14393 \times 760 \text{ mmHg} = 10\underline{9}.38 = 109 \text{ mmHg}$$

11.51. From the Clausius-Clapeyron equation,

$$\Delta H_{vap} = R\left(\frac{T_2\ T_1}{T_2 - T_1}\right)\left[\ln \frac{P_2}{P_1}\right] = [8.31 \text{ J/(K•mol)}]\left[\frac{(553.2 \text{ K})(524.2 \text{ K})}{(553.2 - 524.2) \text{ K}}\right]\left[\ln \frac{760.0 \text{ mmHg}}{400.0 \text{ mmHg}}\right]$$

$$= 5.3\underline{3}36 \times 10^4 \text{ J/ mol} = 53.3 \text{ kJ/ mol}$$

11.52. From the Clausius-Clapeyron equation,

$$\Delta H_{vap} = R\left(\frac{T_2\ T_1}{T_2 - T_1}\right)\left[\ln \frac{P_2}{P_1}\right] = [8.31 \text{ J/(K•mol)}]\left[\frac{(319.7 \text{ K})(301.2 \text{ K})}{(319.7 - 301.2) \text{ K}}\right]\left[\ln \frac{760.0 \text{ mmHg}}{400.0 \text{ mmHg}}\right]$$

$$= 2.7\underline{7}62 \times 10^4 \text{ J/ mol} = 27.8 \text{ kJ/ mol}$$

11.53.

a. At point A, the substance will be a gas.

b. The substance will be a gas.

c. The substance will be a liquid.

d. No

11.54.

a. At point A, the substance will be a gas.

b. The substance will be a solid.

c. The substance will be a gas.

d. No

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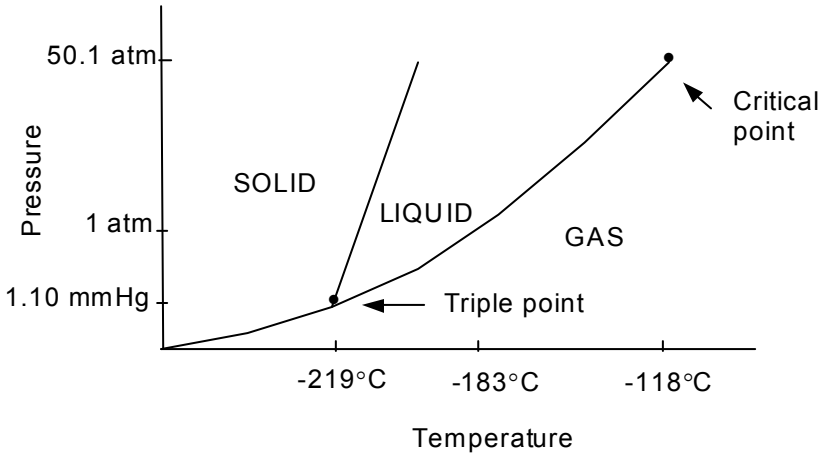
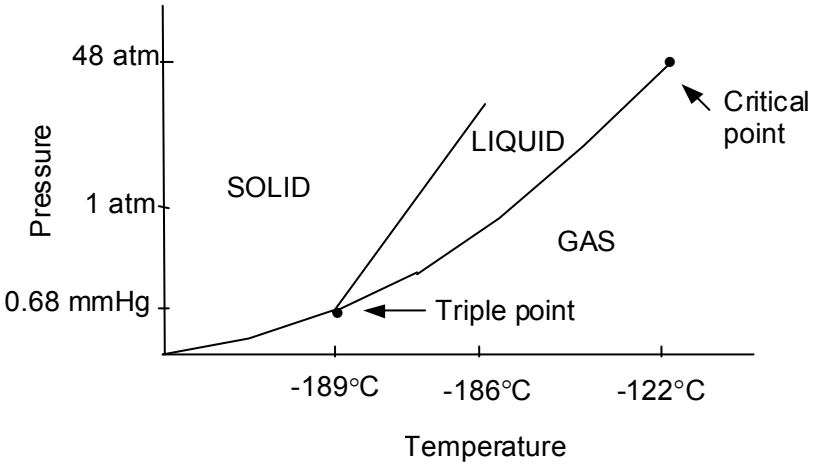
11.55. The phase diagram for oxygen is shown below. It is plotted from these points: triple point = −219°C, boiling point = −183°C, and critical point = −118°C. The graph is not drawn to scale.



11.56. The phase diagram for argon below is plotted from these points: triple point = −189°C, boiling point = −186°C, and critical point = −122°C. The graph is not drawn to scale.



11.57. Liquefied at 25°C: SO_2 and C_2H_2. To liquefy CH_4, lower its temperature below −82°C, and then compress it. To liquefy CO, lower its temperature below −140°C, and then compress it.

11.58.

a. If CF_4 is in the tank, it's not in liquid form because the liquid phase cannot exist above −46°C.

b. If C_4H_{10} is in the tank, it's not in liquid form because 21°C is above its boiling point (1.0 atm).

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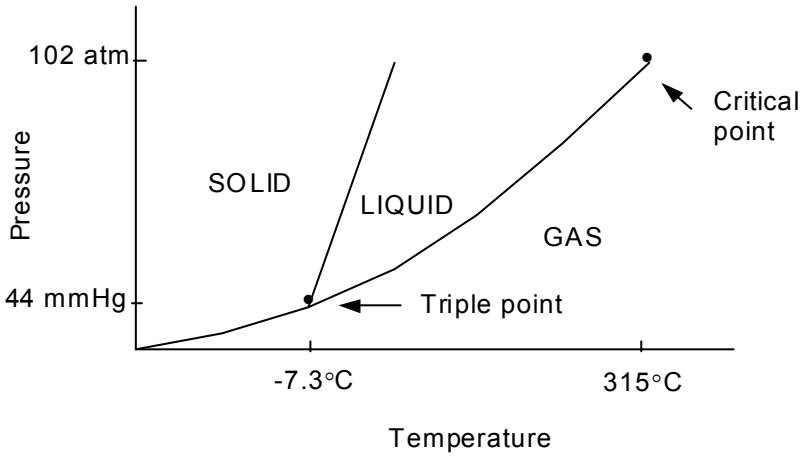
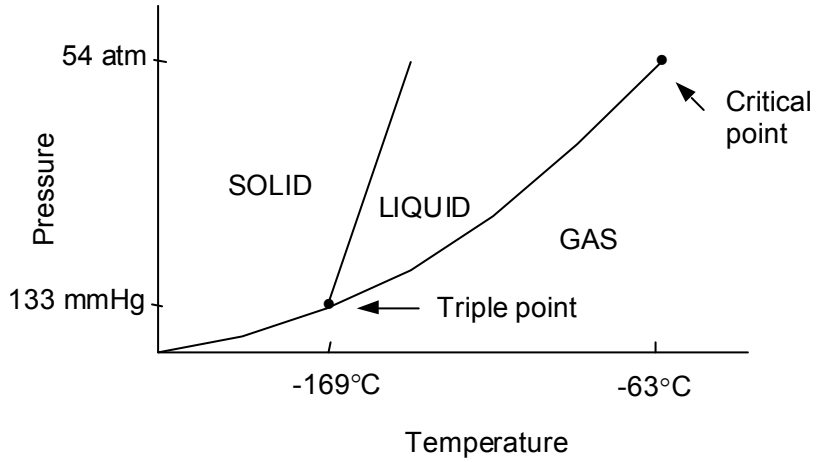
11.59. Br_2 phase diagram:



a. Circle "solid." The pressure of 40 mmHg is lower than the pressure at the triple point, so the liquid phase cannot exist.

b. Circle "liquid." The pressure of 400 mmHg is above the triple point, so the gas will condense to a liquid.

11.60. Kr phase diagram:



a. Circle "sublimes." The pressure of 130 mmHg is lower than the pressure at the triple point, so the liquid phase cannot exist.

b. Circle "melts." The pressure of 760 mmHg is higher than the pressure at the triple point, so the solid melts to the liquid phase.

11.61. Yes, the heats of vaporization of 0.9, 5.6, and 20.4 kJ/mol (for H_2, N_2, and Cl_2, respectively) increase in the order of the respective molecular masses of 2.016, 28.02, and 71.0. (London forces increase in order of increasing molecular mass.)

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11.62. The heats of vaporization of 1.8 kJ/mol for Ne and 6.8 kJ/mol for O_2 increase in the order of the respective molecular masses of 20.1 and 32.0 because only London forces are involved. The heat of vaporization of 34.5 kJ/mol for methanol (molecular mass = 32.0) is higher than that of oxygen because of strong hydrogen bonding between H and O.

11.63.

a. London forces

b. London and dipole-dipole forces, hydrogen bonding

c. London and dipole-dipole forces

d. London forces

11.64. Both c and d exhibit only London forces. Compound a is an ionic species. Thus, it has other forces present in addition to London forces. The substance depicted in b has a dipole moment as well as London forces.

11.65. The order is $CCl_4 < SiCl_4 < GeCl_4$ (in order of increasing molecular mass).

11.66. The order is Ne < Kr < Xe (in order of increasing atomic mass).

11.67. CCl_4 has the lowest vapor pressure because it has the largest molecular mass and the greatest London forces even though $HCCl_3$ and H_3CCl have dipole-dipole interactions.

11.68. ClF has the smallest molecular mass and hence the smallest intermolecular forces and the highest vapor pressure. Thus, it should have the lowest boiling point.

11.69. The order of increasing vapor pressure is $HOCH_2CH_2OH$, FCH_2CH_2OH, FCH_2CH_2F. There is no hydrogen bonding in the third molecule; the second molecule can hydrogen-bond at only one end; and the first molecule can hydrogen-bond at both ends for the strongest interaction.

11.70. The order is $HOCH_2CH_2CH_2OH < CH_3CH_2CH_2CH_2OH < CH_3CH_2OCH_2CH_3$. There is no hydrogen bonding in the third molecule; the second molecule can hydrogen-bond at only one end; and the first molecule can hydrogen-bond at both ends for the strongest interaction and lowest vapor pressure.

11.71. The order is $CH_4 < C_2H_6 < CH_3OH < CH_2OHCH_2OH$. The weakest forces are the London forces in CH_4 and C_2H_6, which increase with molecular mass. The next-strongest interaction is in CH_3OH, which can hydrogen-bond at only one end of the molecule. The strongest interaction is in the last molecule, which can hydrogen-bond at both ends.

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11.72. The order is $C_2H_6 < C_3H_8 < (CH_3)_3N < C_4H_9OH$. The weakest forces are the London forces in C_2H_6, C_3H_8, and $(CH_3)_3N$, which increase with molecular mass. The strongest interaction is in C_4H_9OH, which can hydrogen-bond from oxygen to hydrogen, a stronger force than in the other three molecules.

11.73.

a. Metallic
b. Metallic
c. Covalent network
d. Molecular
e. Ionic

11.74.

a. Ionic
b. Ionic
c. Molecular
d. Molecular
e. Molecular

11.75.

a. Metallic
b. Covalent network (like diamond)
c. Molecular
d. Molecular

11.76.

a. Molecular
b. Not molecular (ionic)
c. Not molecular (metallic)
d. Molecular

11.77. The order is $(C_2H_5)_2O < C_4H_9OH < KCl < CaO$. Melting points increase in the order of attraction between molecules or ions in the solid state. Hydrogen bonding in C_4H_9OH causes it to melt at a higher temperature than $(C_2H_5)_2O$. Both KCl and CaO are ionic solids with much stronger attraction than the organic molecules. In CaO, the higher charges cause the lattice energy to be higher than in KCl.

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11.78. The order is $C_2H_6 < CH_3OH < NaCl < Si$. Melting points increase in the order of attraction between molecules or atoms. Hydrogen bonding in CH_3OH causes it to melt at a higher temperature than C_2H_6. Because NaCl is an ionic solid, it melts at a higher temperature than either of the previous two. Silicon is a covalent network solid with the highest melting point.

11.79.

a. Low-melting and brittle

b. High-melting, hard, and brittle

c. Malleable and electrically conducting

d. Hard and high-melting

11.80.

a. Metallic (from conductivity and luster)

b. Covalent network (from high-melting, hard, and nonconducting liquid)

c. Ionic (from high melting point and conducting liquid)

d. Molecular (from low melting point and odor or vapor pressure at room temperature)

11.81.

a. LiCl

b. SiC

c. CHI_3

d. Co

11.82.

a. Pb

b. $CaCl_2$

c. P_4S_3

d. BN

11.83. In a simple cubic lattice with one atom at each lattice point, there are atoms only at the corners of unit cells. Each corner is shared by eight unit cells, and there are eight corners per unit cell. Therefore, there is one atom per unit cell.

11.84. There are two atoms per unit cell, one from the corners and one atom at the center of the unit cell.

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11.85. Calculate the volume of the unit cell, change density to g/m^3, and then convert volume to mass, using density:

$$\text{Volume} = (2.866 \times 10^{-10}\ \text{m})^3 = 2.354 \times 20^{-29}\ \text{m}^3$$

$$\frac{7.87\ \text{g}}{1\ \text{cm}^3} \times \left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^3 = 7.87 \times 10^6\ \text{g/m}^3$$

$$\text{Mass of one cell} = (7.87 \times 10^6\ \text{g/m}^3) \times (2.354 \times 10^{-29}\ \text{m}^3) = 1.8\underline{5}26 \times 10^{-22}\ \text{g}$$

Because Fe is a body-centered cubic cell, there are two Fe atoms in the cell, and

$$\text{Mass of one Fe atom} = (1.8526 \times 10^{-22}\ \text{g}) \div 2 = 9.2\underline{6}3 \times 10^{-23}\ \text{g}$$

Using the molar mass to calculate the mass of one Fe atom, you find the agreement is good:

$$\frac{55.85\ \text{g Fe}}{1\ \text{mol Fe}} \times \frac{1\ \text{mol Fe}}{6.022 \times 10^{23}\ \text{Fe atoms}} = 9.27\underline{4}3 \times 10^{-23}\ \text{g/Fe atom}$$

11.86. Calculate the volume of the unit cell, change density to g/m^3, and then convert volume to mass, using density:

$$\text{Volume} = (3.524 \times 10^{-10}\ \text{m})^3 = 4.376 \times 20^{-29}\ \text{m}^3$$

$$\frac{8.91\ \text{g}}{1\ \text{cm}^3} \times \left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^3 = 8.91 \times 10^6\ \text{g/m}^3$$

$$\text{Mass of one cell} = (8.91 \times 10^6\ \text{g/m}^3) \times (4.376 \times 10^{-29}\ \text{m}^3) = 3.8\underline{9}9 \times 10^{-22}\ \text{g}$$

Because Ni is a face-centered unit cell, there are four Ni atoms per cell, and

$$\text{Mass of one Ni atom} = (3.899 \times 10^{-22}\ \text{g}) \div 4 = 9.7\underline{4}7 \times 20^{-23}\ \text{g}$$

Using the molar mass to calculate Avogadro's number, you obtain

$$\frac{58.70\ \text{g Ni}}{1\ \text{mol Ni}} \times \frac{1\ \text{atom Ni}}{9.747 \times 10^{-23}\ \text{g Ni}} = 6.0\underline{2}2 \times 10^{23}\ \text{atoms/mol}$$

11.87. There are four Cu atoms in the face-centered cubic structure, so the mass of one cell is

$$4\ \text{Cu atoms} \times \frac{1\ \text{mol Cu}}{6.022 \times 10^{23}\ \text{Cu atoms}} \times \frac{63.5\ \text{g Cu}}{1\ \text{mol Cu}} = 4.2\underline{1}8 \times 10^{-22}\ \text{g}$$

$$\text{Cell volume} = \frac{4.218 \times 10^{-22}\ \text{g}}{8.93\ \text{g/cm}^3} = 4.7\underline{2}3 \times 10^{-23}\ \text{cm}^3$$

All edges are the same length in a cubic cell, so the edge length, l, is

$$l = \sqrt[3]{V} = \sqrt[3]{4.723 \times 10^{-23}\ \text{cm}^3} = 3.6\underline{1}4 \times 10^{-8}$$

$$= 3.61 \times 10^{-8}\ \text{cm} \quad (361\ \text{pm})$$

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11.88. There are two Ba atoms in the face-centered cubic structure, so the mass of one cell is

$$2 \text{ Ba atoms} \times \frac{1 \text{ mol Ba}}{6.022 \times 10^{23} \text{ Ba atoms}} \times \frac{137.33 \text{ g Ba}}{1 \text{ mol Ba}} = 4.561 \times 10^{-22} \text{ g}$$

$$\text{Cell volume} = \frac{4.561 \times 10^{-22} \text{ g}}{3.51 \text{ g/cm}^3} = 1.2994 \times 10^{-22} \text{ cm}^3$$

All edges are the same length in a cubic cell, so the edge length, *l*, is

$$l = \sqrt[3]{V} = \sqrt[3]{1.2994 \times 10^{-22} \text{ cm}^3} = 5.0651 \times 10^{-8}$$

$$= 5.07 \times 10^{-8} \text{ cm} \quad (507 \text{ pm})$$

11.89. Calculate the volume from the edge length of 407.9 pm (4.079×10^{-8} cm), and then use it to calculate the mass of the unit cell:

$$\text{Cell volume} = (4.079 \times 10^{-8} \text{ cm}^3 = 6.7869 \times 10^{-23} \text{ cm}^3$$

$$\text{Cell mass} = (19.3 \text{ g/cm}^3)(6.7869 \times 20^{-23} \text{ cm}^3) = 1.3098 \times 10^{-21} \text{ g}$$

Calculate the mass of one gold atom:

$$1 \text{ Au atom} \times \frac{1 \text{ mol Au}}{6.022 \times 10^{23} \text{ Au atoms}} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} = 3.2708 \times 10^{-22} \text{ g}$$

$$\frac{1.3098 \times 10^{-21} \text{ g}}{1 \text{ unit cell}} \times \frac{1 \text{ Au atom}}{3.2708 \times 10^{-22} \text{ g Au}} = \frac{4.004 \text{ Au atoms}}{\text{unit cell}}$$

Since there are four atoms per unit cell, it is a face-centered cubic.

11.90. Calculate the volume from the edge (288.5 pm = 2.885×10^{-8} cm). Use it to calculate the mass:

$$\text{Cell volume} = (2.885 \times 10^{-8} \text{ cm})^3 = 2.401 \times 10^{-23} \text{ cm}^3$$

$$\text{Cell mass} = (7.20 \text{ g/cm}^3)(2.401 \times 10^{-23} \text{ cm}^3) = 1.729 \times 10^{-22} \text{ g}$$

Calculate the mass of one chromium atom:

$$1 \text{ Cr atom} \times \frac{1 \text{ mol Cr}}{6.022 \times 10^{23} \text{ Au atoms}} \times \frac{51.996 \text{ g Cr}}{1 \text{ mol Cr}} = 8.634 \times 10^{-23} \text{ g Cr}$$

$$\frac{1.729 \times 10^{-22} \text{ g}}{1 \text{ unit cell}} \times \frac{1 \text{ Cr atom}}{8.634 \times 10^{-23} \text{ g Cr}} = \frac{2.002 \text{ Cr atoms}}{1 \text{ unit cell}}$$

Since there are two atoms per unit cell, it is a body-centered cubic.

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11.91. Calculate the volume from the edge (316.5 pm = 3.165 x 10^{-8} cm). Use it to calculate the mass:

Cell volume = $(3.165 \times 10^{-8}\ \text{cm})^3 = 3.170\underline{5} \times 10^{-23}\ \text{cm}^3$

For a body-centered cubic lattice, there are two atoms per cell, so their mass is

$$2\ \text{W atoms} \times \frac{1\ \text{mol W}}{6.022 \times 10^{23}\ \text{W atoms}} \times \frac{183.8\ \text{g W}}{1\ \text{mol W}} = 6.104\underline{3} \times 10^{-22}\ \text{g W}$$

$$\text{Density} = \frac{6.1043 \times 10^{-22}\ \text{g W}}{3.1705 \times 10^{-23}\ \text{cm}^3} = 19.25\underline{3} = 19.25\ \text{g/cm}^3$$

11.92. Calculate the volume from the edge (495.0 pm = 4.950 x 10^{-8} cm). Use it to calculate the mass:

Cell volume = $(4.950 \times 10^{-8}\ \text{cm})^3 = 1.212\underline{9} \times 10^{-22}\ \text{cm}^3$

For a face-centered cubic lattice, there are four atoms per cell, so their mass is

$$4\ \text{Pb atoms} \times \frac{1\ \text{mol Pb}}{6.022 \times 10^{23}\ \text{Pb atoms}} \times \frac{207.2\ \text{g Pb}}{1\ \text{mol Pb}} = 1.3763 \times 10^{-21}\ \text{g Pb}$$

$$\text{Density} = \frac{1.3763 \times 10^{-21}\ \text{g Pb}}{1.2129 \times 10^{-22}\ \text{cm}^3} = 11.34\underline{7} = 11.35\ \text{g/cm}^3$$

11.93. Use Avogadro's number to calculate the number of atoms in 1.74 g (= d x 1.000 cm^3):

$$1.74\ \text{g Mg} \times \frac{1\ \text{mol Mg}}{24.305\ \text{g Mg}} \times \frac{6.022 \times 10^{23}\ \text{Mg atoms}}{1\ \text{mol Mg}}$$

$$= 4.311 \times 10^{22}\ \text{Mg atoms}$$

Because the space occupied by the Mg atoms = 0.741 cm^3, each atom's volume is

$$\text{Volume 1 Mg atom} = \frac{0.741\ \text{cm}^3}{4.311 \times 10^{22}\ \text{Mg atoms}} = 1.71\underline{9} \times 10^{-23}\ \text{cm}^3$$

$$\text{Volume} = \frac{4\pi r^3}{3}$$

so

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3}{4\pi}(1.719 \times 10^{-23}\ \text{cm}^3)} = 1.60\underline{1} \times 10^{-8} = 1.60 \times 10^{-8}\ \text{cm}$$

$$= 1.60 \times 10^{2}\ \text{pm}$$

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11.94. Use Avogadro's number to calculate the number of atoms in 3.51 g (= d x 1.000 cm^3):

$$3.51 \text{ g Ba} \times \frac{1 \text{ mol Ba}}{137.33 \text{ g Ba}} \times \frac{6.022 \times 10^{23} \text{ Ba atoms}}{1 \text{ mol Ba}}$$

$$= 1.539 \times 10^{22} \text{ Ba atoms}$$

Because the space occupied by the Ba atoms = 0.680 cm^3, each atom's volume is

$$\text{Volume one Ba atom} = \frac{0.680 \text{ cm}^3}{1.539 \times 10^{22} \text{ Ba atoms}} = 4.4\underline{1}8 \times 10^{-23} \text{ cm}^3$$

$$\text{Volume} = \frac{4\pi r^3}{3}$$

so

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3}{4\pi}(4.418 \times 10^{-23} \text{ cm}^3)} = 2.1\underline{9}3 \times 10^{-8} = 2.19 \times 10^{-8} \text{ cm} = 219 \text{ pm}$$

■ SOLUTIONS TO GENERAL PROBLEMS

11.95. Water vapor deposits directly to solid water (frost) without forming liquid water. After heating, most of the frost melted to liquid water, which then vaporized to water vapor. Some of the frost may have sublimed directly to water vapor.

11.96. Water vapor condenses directly to solid water (snow) in the upper atmosphere. After falling through the warm air mass, the snow melts to liquid water (rain). After falling on a sunny spot, the rain is vaporized to water vapor.

11.97. From Table 5.6, the vapor pressures are 18.7 mmHg at 21°C and 12.8 mmHg at 15°C. If the moisture did not begin to condense until the air had been cooled to 15°C, then the partial pressure of water in the air at 21°C must have been 12.8 mmHg. The relative humidity is

$$\text{Percent relative humidity} = \frac{12.8 \text{ mmHg}}{18.7 \text{ mmHg}} \times 100\% = 68.\underline{4}4 = 68.4 \text{ percent}$$

11.98. The vapor pressure of water at 21°C is 18.7 mmHg (Table 5.6). Therefore,

$$\text{Percent relative humidity} = 58 \text{ percent} = \frac{x \text{ mmHg}}{18.7 \text{ mmHg}} \times 100\%;$$

$$x = 1\underline{0}.8 \text{ mmHg}$$

The partial pressure of water in the air at 21°C is thus 10.8 mmHg. The water will begin to condense when the temperature drops to the temperature at which the vapor pressure of water is 10.8 mmHg. This temperature is between 12°C and 13°C (Table 5.5).

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11.99. After labeling the problem data as shown below, use the Clausius-Clapeyron equation to obtain ΔH_{vap}, which can then be used to calculate the boiling point.

At T_1 = 299.3 K, P_1 = 100.0 mmHg; at T_2 = 333.8 K, P_2 = 400.0 mmHg

$$\ln \frac{400.0 \text{ mmHg}}{100.0 \text{ mmHg}} = \frac{\Delta H_{vap}}{8.31 \text{ J/(K • mol)}} \left[\frac{333.8 \text{ K} - 299.3 \text{ K}}{333.8 \text{ K} \times 299.3 \text{ K}} \right]$$

$$1.3862 = \Delta H_{vap} (4.1535 \times 10^{-5} \text{ mol/J})$$

$$\Delta H_{vap} = 33.37 \times 10^3 \text{ J/mol (33.4 kJ/mol)}$$

Now, use this value of ΔH_{vap} and the following data to calculate the boiling point:

At T_1 = 299.3 K, P_1 = 100.0 mmHg; at T_2 (boiling pt.), P_2 = 760 mmHg

$$\ln \frac{760.0 \text{ mmHg}}{100.0 \text{ mmHg}} = \frac{33.4 \times 10^3 \text{ J/mol}}{8.314 \text{ J/(K • mol)}} \left[\frac{1}{299.3 \text{ K}} - \frac{1}{T_2} \right]$$

$$2.0281 = 4.0144 \times 10^3 \text{ K} \left[\frac{1}{299.3 \text{ K}} - \frac{1}{T_2} \right]$$

$$\frac{1}{T_2} = \frac{1}{299.3 \text{ K}} - \frac{2.0281}{4.0144 \times 10^3 \text{ K}} = 2.8359 \times 10^{-3}/\text{K}$$

$$T_2 = 352.6 = 353 \text{ K (80°C)}$$

11.100. After labeling the problem data as shown below, use the Clausius-Clapeyron equation to obtain ΔH_{vap}, which can then be used to calculate the boiling point.

At T_1 = 293.2 K, P_1 = 17.5 mmHg; at T_2 = 353.2 K, P_2 = 355.1 mmHg

$$\ln \frac{355.1 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{\Delta H_{vap}}{8.31 \text{ J/(K • mol)}} \left[\frac{353.2 \text{ K} - 293.2 \text{ K}}{353.2 \text{ K} \times 293.2 \text{ K}} \right]$$

$$3.0101 = \Delta H_{vap} (6.9687 \times 10^{-5} \text{ mol/J})$$

$$\Delta H_{vap} = 43.19 \times 10^3 \text{ J/mol (43.2 kJ/mol)}$$

Now, use this value of ΔH_{vap} and the following data to calculate the boiling point:

At T_1 = 293.32 K, P_1 = 17.5 mmHg; at T_2 (boiling pt.), P_2 = 760 mmHg

$$\ln \frac{760.0 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{43.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/(K • mol)}} \left[\frac{1}{293.2 \text{ K}} - \frac{1}{T_2} \right]$$

$$3.7711 = 5.1955 \times 10^3 \text{ K} \left[\frac{1}{293.2 \text{ K}} - \frac{1}{T_2} \right]$$

$$\frac{1}{T_2} = \frac{1}{293.2 \text{ K}} - \frac{3.7711}{5.1955 \times 10^3 \text{ K}} = 2.6848 \times 10^{-3}/\text{K}$$

$$T_2 = 372.46 = 372 \text{ K (99°C)}$$

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11.101.

a. As this gas is compressed at 20°C, it will condense into a liquid because 20°C is above the triple point but below the critical point.

b. As this gas is compressed at −70°C, it will condense directly to the solid phase because the temperature of −70°C is below the triple point.

c. As this gas is compressed at 40°C, it will not condense because 40°C is above the critical point.

11.102.

a. As I_2 vapor is cooled at 120 atm, no change to a distinct liquid will be observed, but the I_2 will condense to a solid phase at some definite temperature.

b. As I_2 vapor is cooled at 1 atm, the vapor will condense to a liquid and then freeze to the solid phase.

c. As I_2 vapor is cooled at 50 mmHg (below the triple point), the vapor will condense directly to the solid phase without going through the liquid phase.

11.103. In propanol, hydrogen bonding exists between the hydrogen of the OH group and the lone pair of electrons of oxygen of the OH group of an adjacent propanol molecule. For two adjacent propanol molecules, the hydrogen bond may be represented as follows:

C_3H_7 –O–H•••O(H)C_3H_7

11.104. In hydrogen peroxide, hydrogen bonding exists between any hydrogen and the lone pair of electrons of oxygen of an adjacent hydrogen peroxide. For two adjacent hydrogen peroxide molecules, the hydrogen bond may be represented as follows:

HO–O–H•••O(H)–OH

11.105. Ethylene glycol molecules are capable of hydrogen bonding to each other, whereas pentane molecules are not. The greater intermolecular forces in ethylene glycol are reflected in greater resistance to flow (viscosity) and high boiling point.

11.106. Pentylamine molecules are capable of hydrogen bonding to each other, but triethylamine molecules are not. The greater intermolecular forces in pentylamine cause a higher boiling point and greater resistance to flow.

11.107. Aluminum (Group IIIA) forms a metallic solid. Silicon (Group IVA) forms a covalent network solid. Phosphorus (Group VA) forms a molecular solid. Sulfur (Group VIA) forms a molecular (amorphous) solid.

11.108. AlF_3 forms an ionic solid. SiF_4, PF_3, and SF_4 form molecular solids.

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11.109.

a. Lower: KCl. The lattice energy should be lower for ions with a lower charge. A lower lattice energy implies a lower melting point.

b. Lower: CCl_4. Both are molecular solids, so the compound with the lower molecular mass should have weaker London forces and, therefore, the lower melting point.

c. Lower: Zn. Melting points for Group IIB metals are lower than for metals near the middle of the transition-metal series.

d. Lower: C_2H_5Cl. Ethyl chloride cannot hydrogen-bond, but acetic acid can. The compound with the weaker intermolecular forces has the lower melting point.

11.110.

a. Lower: C_6H_{14}. A molecular solid has a lower melting point than an ionic solid.

b. Lower: 1-propanol. The 1-propanol can hydrogen-bond at only one end; ethylene glycol can hydrogen-bond at both ends, so its intermolecular forces are stronger.

c. Lower: Na. Sodium is a metallic solid, but Si is a covalent network solid (high melting point).

d. Lower: CH_4. Both form molecular solids, but CH_4 has a lower molecular mass with weaker London forces and, therefore, the lower melting point.

11.111. The face-centered cubic structure means one atom is at each lattice point. All edges are the same length in such a structure, so the volume is

$$\text{Volume} = l^3 = (3.839 \times 10^{-8}\ \text{cm})^3 = 5.65\underline{7}9 \times 10^{-23}\ \text{cm}^3$$

$$\text{Mass of unit cell} = dV = (22.42\ \text{g/cm}^3)(5.6579 \times 10^{-23}\ \text{cm}^3) = 1.26\underline{8}5 \times 10^{-21}\ \text{g}$$

There are four atoms in a face-centered cubic cell, so

$$\text{Mass of one Ir atom} = \text{mass of unit cell} \div 4 = (1.2685 \times 10^{-21}\ \text{g}) \div 4$$

$$= 3.17\underline{1}2 \times 10^{-22}\ \text{g}$$

$$\text{Molar mass of Ir} = (3.1712 \times 10^{-22}\ \text{g/Ir atom}) \times (6.022 \times 10^{23}\ \text{Ir atoms/mol})$$

$$= 190.96 = 191.0\ \text{g/mol}\ \ (\text{The atomic mass} = 191.0\ \text{amu.})$$

11.112. The body-centered cubic structure means that one atom is at each lattice point. All edges are the same length in such a structure, so the volume is

$$\text{Volume} = l^3 = (3.306 \times 10^{-8}\ \text{cm})^3 = 3.61\underline{3}3 \times 10^{-23}\ \text{cm}^3$$

$$\text{Mass of unit cell} = dV = (16.69\ \text{g/cm}^3)(3.6133 \times 10^{-23}\ \text{cm}^3) = (6.03\underline{0}6 \times 10^{-22}\ \text{g})$$

There are two atoms in a body-centered cubic cell, so

$$\text{Mass of one Ta atom} = \text{mass of unit cell} \div 2 = (6.0306 \times 10^{-22}\ \text{g}) \div 2$$

$$= 3.01\underline{5}3 \times 10^{-22}\ \text{g}$$

$$\text{Molar mass of Ta} = (3.0153 \times 10^{-22}\ \text{g/Ta atom}) \times (6.022 \times 10^{23}\ \text{Ta atoms/ mol})$$

$$= 181.\underline{5}8 = 181.6\ \text{g/mol}\ \ (\text{The atomic mass} = 181.6\ \text{amu.})$$

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11.113. From Problem 11.87, the cell edge length (l) is 361.4 pm. There are four copper atom radii along the diagonal of a unit-cell face. Because the diagonal square = $l^2 + l^2$ (Pythagorean theorem),

$$4r = \sqrt{2\,l^2} = \sqrt{2}\,l, \text{ or } r = \frac{\sqrt{2}}{4}(361.4 \text{ pm}) = 127.7 = 128 \text{ pm}$$

11.114. A body-centered cubic cell has two atoms per cell. The mass of the unit cell is

$$2 \text{ Rb atoms} \times \frac{1 \text{ mol Rb}}{6.022 \times 10^{23} \text{ Rb atoms}} \times \frac{85.468 \text{ g Rb}}{1 \text{ mol Rb}} = 2.8385 \times 10^{-22} \text{ g}$$

The volume of the unit cell is

$$\text{Volume} = \frac{2.8385 \times 10^{-22} \text{ g}}{1.532 \text{ g/cm}^3} = 1.8528 \times 10^{-22} \text{ cm}^3$$

$$l = \sqrt[3]{\text{Volume}} = \sqrt[3]{1.8528 \times 10^{-22} \text{ cm}^3} = 5.7009 \times 10^{-8} \text{ cm}$$

Because the corner spheres touch the body-centered sphere, the length of the body diagonal (diagonal passing through the center of the cell) must be four times the radius of the Rb atom. Also, from the geometry of a cube and the Pythagorean theorem, the square of the body diagonal equals $l^2 + d^2$ (l is the unit-cell edge length, and d is the diagonal along a face of the unit cell).

Because $d^2 = l^2 + l^2$, or $d = \sqrt{2}\,l$, you can write

$$(\text{Body diagonal})^2 = l^2 + d^2 = l^2 + 2l^2 = 3l^2$$

$$\text{Body diagonal} = \sqrt{3}\,l = \sqrt{3}\,(5.7009 \times 10^{-8} \text{ cm}) = 9.8742 \times 10^{-8} \text{ cm}$$

$$\text{Radius of Rb atom} = (9.8742 \times 10^{-8} \text{ cm}) \div 4 = 2.4686 \times 10^{-8} \text{ cm (246.9 pm)}$$

11.115. The body diagonal (diagonal passing through the center of the cell) is four times the radius, r, of a sphere. Also, from the geometry of a cube and the Pythagorean theorem, the body diagonal equals $\sqrt{3}\,l$, where l is the edge length of the unit cell. Thus

$$4r = \sqrt{3}\,l$$

or

$$l = \frac{4r}{\sqrt{3}}$$

Because the unit cell contains two spheres, the volume occupied by the spheres is

$$V_{\text{spheres}} = 2 \times \frac{4}{3}\pi r^3$$

and

$$V_{\text{cell}} = l^3 = \left[\frac{4r}{\sqrt{3}}\right]^3 = \frac{64r^3}{3\sqrt{3}}$$

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Finally, to obtain the percent volume of the cell occupied, divide $V_{spheres}$ by V_{cell}:

$$\text{Percent } V = \frac{V_{spheres}}{V_{cell}} \times 100\% = \frac{2\left[\frac{4\pi r^3}{3}\right]}{\frac{64r^3}{3\sqrt{3}}} \times 100\% = \frac{\pi\sqrt{3}}{8} \times 100\%$$

$$= 68.01 = 68.0\%$$

11.116. Because the spheres touch along the diagonal of a face, d, the radius, r, of the spheres is

$$r = d/4 = l(\sqrt{2})/4$$

or

$$l = \frac{4r}{\sqrt{2}}$$

$$V_{cell} = l^3 = \left[\frac{4r}{\sqrt{2}}\right]^3$$

For a face-centered cubic structure, there are four spheres per cell, so the volume, $V_{spheres}$, occupied by the spheres is

$$V_{spheres} = 4\left[\frac{4\pi r^3}{3}\right]$$

$$\text{Percent } V = \frac{V_{spheres}}{V_{cell}} \times 100\% = \frac{4\left[\frac{4\pi r^3}{3}\right]}{\left[\frac{4r}{\sqrt{2}}\right]^3} \times 100\% = \frac{\pi\sqrt{2}}{6} \times 100\%$$

$$= 74.04 = 74 \text{ percent}$$

11.117.

a. The boiling point increases as the size (number of electrons in the atom or molecule) increases. The London forces or dispersion forces increase.

b. Hydrogen bonding occurs between the H–F molecules and is much stronger than the London forces.

c. In addition to the dispersion forces, the hydrogen halides are polar (have dipole moments), so there are dipole-dipole interactions.

11.118.

a. The boiling point increases as the size (number of electrons in the molecule) increases. The London forces or dispersion forces increase.

b. Hydrogen bonding occurs among the NH_3 molecules.

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c. The nitrogen family compounds consist of polar molecules, whereas the carbon family molecules are nonpolar. Thus the nitrogen family has dipole-dipole interactions as well as the contributions from the dispersion forces.

11.119.

a. Diamond and silicon carbide are covalent network solids with strong covalent bonds between all the atoms. Graphite is a layered structure, and the forces holding the layers together are weak dispersion forces.

b. Silicon dioxide is a giant molecule with an infinite array of O–S–O bonds. Each silicon is bonded to four oxygen atoms in a covalent network solid. Carbon dioxide is a discrete, nonpolar molecule.

11.120. The first member atoms are very small and highly electronegative. Oxygen readily forms double bonds, whereas the larger atoms have difficulty getting close enough together to form multiple bonds. Hence, we have O_2 vs. S_8.

Because oxygen has a higher attraction for hydrogen, the dipole moment is so large that it is possible to have hydrogen bonding in H_2O, but there is no hydrogen bonding in H_2S.

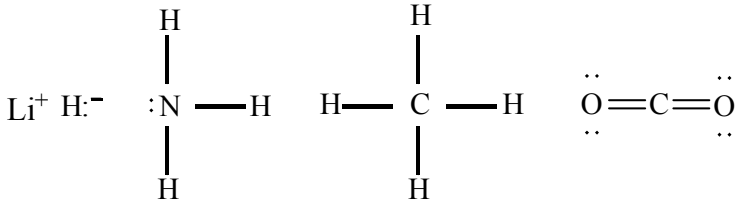
11.121.

a. CO_2 consists of discrete nonpolar molecules that are held together in the solid by weak dispersion forces. SiO_2 is a covalent network solid with all the atoms held together by strong covalent bonds.

b. HF(l) has extensive hydrogen bonding among the molecules. HCl(l) boils much lower because it doesn't have hydrogen bonding.

c. SiF_4 is a larger molecule (it has more electrons than CF_4), so it has stronger dispersion forces and a higher boiling point than CF_4. Both molecules are tetrahadrally symmetrical and, therefore, nonpolar.

11.122.

a. 

b. LiH has the highest boiling point because of the ionic bonding and crystalline lattice of LiH.

c. CH_4 has the lowest boiling point because it is a small, nonpolar molecule. The only intermolecular forces are dispersion forces.

d. NH_3 is a polar molecule that also has hydrogen bonding between the molecules.

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11.123. In a tank of carbon dioxide under pressure (for example, in a CO_2 fire extinguisher), the substance normally exists as the liquid in equilibrium with its gas phase. At 35°C (above 31°C), the two phases, gas and liquid, are replaced by a single fluid phase. Thus the carbon dioxide in the tank is above its critical temperature and pressure and exists as the supercritical fluid.

11.124. Under normal conditions, carbon dioxide is not a very good solvent for organic substances, but supercritical carbon dioxide readily dissolves many of these substances, including caffeine. It is nontoxic and nonflammable. It also has no effect on the stratospheric ozone layer, whereas methylene chloride does. Carbon dioxide does contribute to the greenhouse effect, but the gas once used can be recirculated for solvent use and not vented to the atmosphere.

11.125. Van der Waals forces exist between any two surfaces but are extremely weak unless relatively large areas of the two surfaces come quite close together. The toe of a gecko is covered with fine hairs, each hair having a thousand or so split ends. As the gecko walks across a surface, it presses these stalks of hairs against the surface. The intimate contact of a billion or so split ends of hairs with the surface results in a large attractive force, holding the gecko fast. This is not true for your finger, where the contact between the surfaces is much less.

11.126. As the gecko walks, its foot naturally bends in such a way that the hairs at the back edge of its toes disengage, row after row, until the toe is free. It is the mechanics of the gecko's walk that allow it to connect to, and disengage easily from, a surface.

11.127. The nematic liquid crystals consist of rodlike, polar molecules in a phase that is intermediate in order between that of a liquid and that of a crystalline solid. The molecules tend to align or orient themselves in the same direction along their long axes, like matches in a matchbox, but they occupy random positions within the substance. Thus, nematic liquid crystals have orientation order but no position order.

11.128. The molecular order in a nematic liquid crystal, which results from weak intermolecular forces, is easily disrupted. And because these molecules are polar, they can be reoriented by the application of an electric field. A liquid-crystal display (LCD) uses this ease of molecular reorientation by an electric field to change small areas, or pixels, of the display from light to dark. An image is formed by turning various screen pixels on and others off by means of software.

11.129. The Bragg equation, $n\lambda = 2d \sin \theta$, relates the wavelength of x rays, λ, to the distance between atomic planes, d, and the angle of reflection, θ. Note that reflections occur at several angles, corresponding to different values of n ($n = 1, 2, 3, \ldots$).

11.130. A molecular crystal has many different atomic planes, so it reflects an x-ray beam in many different directions. By analyzing the intensities and angular directions of the reflected beams, you can determine the exact positions of all the atoms in the unit cell of the crystal and therefore obtain the structure of the molecule.

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11.131. Water has several unusual properties that set it apart from other substances. For example, its solid phase, ice, is less dense than liquid water, whereas for most substances the solid phase is more dense than the liquid. In addition, water has an unusually large heat capacity. The unusual properties of water are largely linked to its ability to form hydrogen bonds. For example, ice is less dense than liquid water because ice has an open, hydrogen-bonded structure. Each oxygen atom in the structure of ice is surrounded tetrahedrally by four hydrogen atoms: two that are close and covalently bonded to give the H_2O molecule, and two others that are farther away and held by hydrogen bonds. The tetrahedral angles give rise to a three-dimensional structure that contains open space. The solvent properties of water are also unusual. Water is both a polar substance and a hydrogen-bonding molecule. As a result, water dissolves many substances, including ionic and polar compounds. These properties make water the premier solvent, biologically and industrially.

11.132. The fact that ice is less dense than water means that it forms on top of the liquid when freezing occurs. This has far-reaching effects, both for weather and for aquatic animals. When ice forms on a body of water, it insulates the underlying water from the cold air and limits further freezing. Fish depend on this for winter survival. Consider what would happen to a lake if ice were more dense than water. The ice would freeze from the bottom of the lake upward. Without the insulating effect at the surface, the lake could well freeze solid, killing the fish. Spring thaw would be prolonged, because the insulating effect of the surface water would make it take much longer for the ice at the bottom of a lake to melt.

■ SOLUTIONS TO STRATEGY PROBLEMS

11.133.

a. $$n = \frac{PV}{RT} = \frac{(750.0/760 \text{ atm})(20.00 \text{ L})}{(0.082058 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(293.15 \text{ K})} = 0.820\underline{4}77 = 0.8205 \text{ mol } N_2$$

b. $$353.6 \times 10^{-3} \text{ g} \times \frac{1 \text{ mol } H_2O}{18.0153 \text{ g}} = 0.0196\underline{2}77 = 0.01963 \text{ mol } H_2O$$

The water evaporated and was pushed out of the flask by the nitrogen.

c. During the experiment, the total number of moles of gas that exited the flask is

$$n_{tot} = 0.820477 \text{ mol } N_2 + 0.0196277 \text{ mol } H_2O = 0.840\underline{1}0 \text{ mol}$$

The partial pressure of nitrogen is

$$P_{N_2} = X_{N_2} P_{tot} = \frac{0.820477 \text{ mol } N_2}{0.84010 \text{ mol}} \times 750\ 0 \text{ mmHg} = 732.\underline{4}7 = 732.5 \text{ mmHg}$$

d. The vapor pressure of water is

$$P_{H_2O} = P_{tot} - P_{N_2} = 750.0 \text{ mmHg} - 732.5 \text{ mmHg} = 17.5 \text{ mmHg.}$$

The appendix lists the vapor pressure of water at 20°C as 17.5 mmHg, so the calculated value agrees with this value.

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11.134. At 30.0°C, the vapor pressure of water is 31.8 mmHg. With a relative humidity of 80.0%, the number of moles of water vapor in a 1.00-L flask of this air is

$$n = \frac{PV}{RT} = \frac{(0.80)(31.8/760 \text{ atm})(1.00 \text{ L})}{(0.082058 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(303.15 \text{ K})} = 0.0013\underline{4}56 \text{ mol}$$

The mass of this water is

$$\text{Mass} = 0.0013456 \text{ mol} \times \frac{18.0153 \text{ g}}{1 \text{ mol } H_2O} = 0.024\underline{2}4 \text{ g } H_2O$$

At 5°C, the vapor pressure of water is 6.5 mmHg. The mass of water that still exists in the gas phase at this temperature is

$$\text{Mass} = \frac{(6.5/760 \text{ atm})(1.00 \text{ L})}{(0.082058 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(278.15 \text{ K})} \times \frac{18.0153 \text{ g}}{1 \text{ mol } H_2O} = 0.006\underline{7}50 \text{ g } H_2O$$

The mass of liquid water that condensed out is

$$\text{Mass} = 0.02424 \text{ g} - 0.006750 \text{ g} = 0.017\underline{4}9 = 0.0175 \text{ g}$$

11.135. There are three triple points in the phase diagram for sulfur. The triple point at 95°C and 1×10^{-5} atm has the phases rhombic solid, monoclinic solid, and vapor in equilibrium. At 119°C and 6×10^{-5} atm, the phases present are monoclinic solid, liquid, and vapor. The triple point at 151°C and 1290 atm has the phases rhombic solid, monoclinic solid, and liquid in equilibrium. If you cooled liquid sulfur, the solid phase that would freeze out would be monoclinic. It is not the normal phase of solid sulfur, which is rhombic. The rhombic form of solid sulfur cannot form from the liquid except at very high pressures. Only the triple point at 151°C and 1290 atm has the two phases in equilibrium with each other.

11.136. Even though the liquid state is the stable state of water below 100°C, water vapor is present at all temperatures between the triple point and the critical point. At 20°C, liquid water will evaporate until the vapor pressure is reached. In an open container, the vapor pressure is never reached, so the water evaporates completely. The statement at the beginning of this problem is inaccurate because it describes a system undergoing change and not a system in a closed container at equilibrium.

11.137.

a. At room temperature, carbon dioxide is below its critical temperature, so it would be present in two different phases: liquid and gas. Thus, inside the tank you would expect to see a liquid phase separated from a gaseous phase by a meniscus.

b. The pressure of carbon dioxide would remain constant at the vapor pressure at 20°C for the gas. It would remain the same as long as liquid carbon dioxide was present. As soon as all of the liquid carbon dioxide disappeared, the pressure of the gas would begin to drop, eventually reaching a gauge pressure of zero.

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11.138.

a. In 1-pentanol, the intermolecular forces present are London forces, dipole-dipole forces, and hydrogen bonding. In hexane, only London forces are present.

b. Since boiling point increases with increasing intermolecular forces, 1-pentanol would be expected to have the higher boiling point. Thus the boiling point of hexane would be 69°C, the lower value.

c. Viscosity increases with increasing intermolecular forces. Since 1-pentanol has the greater intermolecular forces, its viscosity should be 2.987 g/(cm·s), and hexane, with the weaker intermolecular forces, should have a viscosity of 0.313 g/(cm·s).

d. The compound $CH_3CH_2CH_2CH_2CH_2Cl$ has London forces and dipole-dipole forces, so its boiling point should be intermediate between those of hexane and 1-pentanol.

11.139.

a. CH_3CHO is a polar molecule, so it has London forces and dipole-dipole forces present. $CH_3CH_2CH_3$ is a nonpolar molecule and has only London forces present. CH_3CH_2OH is a polar molecule with London forces, dipole-dipole forces, and hydrogen bonding.

b. The heat of vaporization increases with increasing intermolecular forces. Since CH_3CHO has stronger intermolecular forces than $CH_3CH_2CH_3$ and weaker intermolecular forces than CH_3CH_2OH, you would expect it to have a heat of vaporization of 25.8 kJ/mol.

c. Use the Clapeyron equation to find the vapor pressure at 15°C.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{P_2}{760 \text{ mmHg}} = \frac{25.8 \times 10^3 \text{ J/mol}}{8.31 \text{ J/K} \cdot \text{mol}}\left(\frac{1}{294 \text{ K}} - \frac{1}{288 \text{ K}}\right) = -0.21\underline{9}8$$

Taking antilogs of both sides gives

$$\frac{P_2}{760 \text{ mmHg}} = e^{-0.2198} = 0.80\underline{2}60$$

$$P_2 = 0.80260 \times 760 \text{ mmHg} = 60\underline{9}.97 = 610. \text{ mmHg}$$

11.140. Use the Clapeyron equation to find the vapor pressure at 15°C.

$$\ln \frac{P_2}{760 \text{ mmHg}} = \frac{32 \times 10^3 \text{ J/mol}}{8.31 \text{ J/K} \cdot \text{mol}}\left(\frac{1}{354 \text{ K}} - \frac{1}{288 \text{ K}}\right) = -2.\underline{4}928$$

Taking antilogs of both sides gives

$$\frac{P_2}{760 \text{ mmHg}} = e^{-2.4928} = 0.08\underline{2}673$$

$$P_2 = 0.082673 \times 760 \text{ mmHg} = 6\underline{2}.9 = 63 \text{ mmHg}$$

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11.141.

a. The rhenium atoms (smaller spheres) are occupying each corner in the unit cell, each atom contributing 1/8 rhenium atom to the unit cell. This gives 1/8(8), or one, rhenium atom per unit cell. The oxygen atoms (larger spheres) are occupying each edge in the unit cell. There are twelve edges in the cell, and each atom on an edge contributes 1/4 oxygen atom to the unit cell. This gives 1/4(12), or three, oxygen atoms per unit cell.

b. Each unit cell has one rhenium atom and three oxygen atoms for a formula unit of ReO_3, which is red.

11.142.

a. Since metal cations are smaller than nonmetal anions, the red spheres represent the metal ions.

b. The red spheres occupy each corner and each face of the unit cell. This gives 1/8(8) + 1/2(6) = 4 metal atoms per unit cell. Each of the green spheres is internal and is totally within the unit cell. This gives 8 nonmetal atoms per unit cell.

c. Since the unit cell has four metal atoms and eight nonmetal atoms, the simplest formula is MX_2. The formula of the cation is M^{2+} and the formula of the anion is X^-.

d. An example of a compound with this formula is CaF_2. It has the proper mole ratio and is an ionic compound. The red spheres would represent Ca^{2+}.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

11.143. Use the ideal gas law to calculate n, the number of moles of N_2:

$$N_2: n = \frac{PV}{RT} = \frac{(745/760 \text{ atm})(5.40 \text{ L})}{(0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(293 \text{ K})} = 0.2201 \text{ mol}$$

$$C_3H_8O: n = 0.6149 \text{ g } C_3H_8O \times \frac{1 \text{ mol } C_3H_8O}{60.094 \text{ g } C_3H_8O} = 0.010232 \text{ mol}$$

$$X_{C_3H_8O} = \frac{0.010232 \text{ mol } C_3H_8O}{(0.010232 \text{ mol} + 0.2201 \text{ mol})} = 0.04442 \text{ mole fraction}$$

Partial P = 0.04442 x 745 mmHg = 33.093 mmHg = 33.1 mmHg

Vapor pressure of C_3H_8O = 33.1 mmHg

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11.144. Use the ideal gas law to calculate n, the number of moles of N_2:

$$N_2: n = \frac{PV}{RT} = \frac{(768/760 \text{ atm})(6.35 \text{ L})}{(0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.26\underline{2}4 \text{ mol}$$

$$C_3H_6O: n = 6.550 \text{ g } C_3H_6O \times \frac{1 \text{ mol } C_3H_6O}{58.05 \text{ g } C_3H_6O} = 0.112\underline{8}3 \text{ mol}$$

$$X_{C_3H_6O} = \frac{0.11283 \text{ mol } C_3H_6O}{(0.11283 \text{ mol} + 0.2624 \text{ mol})} = 0.30\underline{0}7 \text{ mole fraction}$$

Partial P = 0.3007 x 768 mmHg = 23$\underline{0}$.9 mmHg = 231 mmHg

Vapor pressure of C_3H_6O = 231 mmHg

11.145. Calculate the moles of HCN in 10.0 mL of the solution (density = 0.687 g HCN/mL HCN):

$$10.0 \text{ mL HCN} \times \frac{0.687 \text{ g HCN}}{1 \text{ mL HCN}} \times \frac{1 \text{ mol HCN}}{27.03 \text{ g HCN}} = 0.25\underline{4}1 \text{ mol HCN}$$

0.2541 mol HCN(l) $\rightarrow$ 0.2541 mol HCN(g)

(ΔH_f° = 108.9 kJ/mol) (ΔH_f° = 135 kJ/mol)

ΔH° = 0.2541 mol x [135 kJ/mol − 108.9 kJ/mol] = 6.$\underline{6}$33 = 6.6 kJ

11.146. Calculate moles of CH_3OH in the 20.0-mL solution (density = 0.787 g CH_3OH/mL CH_3OH):

$$20.0 \text{ mL } CH_3OH \times \frac{0.787 \text{ g } CH_3OH}{1 \text{ mL } CH_3OH} \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} = 0.49\underline{1}26 \text{ mol } CH_3OH$$

0.49126 mol $CH_3OH(l)$ $\rightarrow$ 0.49126 mol $CH_3OH(g)$

(ΔH_f° = −238.7 kJ/mol) (ΔH_f° = −200.7 kJ/mol)

ΔH° = 0.49126 mol x [−200.7 kJ/mol − (−238.7 kJ/mol)] = 18.$\underline{6}$6 = 18.7 kJ

11.147. First, convert the mass to moles; then multiply by the standard heat of formation to obtain the heat absorbed in vaporizing this mass:

$$12.5 \text{ g } P_4 \times \frac{1 \text{ mol } P_4}{123.88 \text{ g } P_4} = 0.10\underline{0}9 \text{ mol } P_4$$

$$0.1009 \text{ mol } P_4 \times \frac{95.4 \text{ J}}{^\circ\text{C} \cdot \text{mol } P_4} \times (44.1^\circ\text{C} - 25.0^\circ\text{C}) = 18\underline{3}.86 \text{ J} = 0.18\underline{3}86 \text{ kJ}$$

2.63 kJ/mol P_4 x 0.1009 mol P_4 = 0.26$\underline{5}$37 kJ

Total heat = 0.26537 kJ + 0.18386 kJ = 0.44$\underline{9}$23 = 0.449 kJ = 449 J

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11.148. First, convert the mass to moles; then multiply by the standard heat of formation to obtain the heat absorbed in vaporizing this mass:

$$25.0 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 1.0\underline{8}74 \text{ mol Na}$$

$$1.0874 \text{ mol Na} \times \frac{28.2 \text{ J}}{°\text{C} \bullet \text{mol Na}} \times (97.8°\text{C} - 25.0°\text{C}) = 22\underline{3}2 \text{ J} \ (2232 \text{ kJ})$$

$$2.60 \text{ kJ/mol Na} \times 1.0874 \text{ mol Na} = 2.8\underline{2}73 \text{ kJ}$$

$$\text{Total heat} = 2.8273 \text{ kJ} + 2.232 \text{ kJ} = 5.0\underline{5}97 = 5.06 \text{ kJ}$$

11.149. Use the ideal gas law to calculate the total number of moles of monomer and dimer:

$$n = \frac{PV}{RT} = \frac{(436/760)\text{atm} \times 1.000 \text{ L}}{[0.082057 \text{ L} \bullet \text{atm}/(\text{K} \bullet \text{mol})] \times 373.75 \text{ K}}$$

$$= 0.018\underline{7}057 \text{ mol monomer + dimer}$$

$$(0.018\underline{7}057 \text{ mol monomer + dimer}) \times \frac{0.630 \text{ mol dimer}}{1 \text{ mol dimer + monomer}} = 0.011\underline{7}8 \text{ mol dimer}$$

$$0.0187057 \text{ mol both} - 0.01178 \text{ mol dimer} = 0.006\underline{9}2 \text{ mol monomer}$$

$$\text{Mass dimer} = 0.011\underline{7}8 \text{ mol dimer} \times \frac{120.1 \text{ g dimer}}{1 \text{ mol dimer}} = 1.4\underline{1}4 \text{ g dimer}$$

$$\text{Mass monomer} = 0.00692 \text{ mol monomer} \times \frac{60.05 \text{ g monomer}}{1 \text{ mol monomer}} = 0.4\underline{1}55 \text{ g monomer}$$

$$\text{Density} = \frac{1.414 \text{ g} + 0.4155 \text{ g}}{1.000 \text{ L}} = 1.8\underline{2}9 = 1.83 \text{ g/L vapor}$$

11.150. Use the ideal gas law to calculate the total number of moles of monomer and dimer:

$$n = \frac{PV}{RT} = \frac{(146/760)\text{atm} \times 1.000 \text{ L}}{[0.082057 \text{ L} \bullet \text{atm}/(\text{K} \bullet \text{mol})] \times 344.45 \text{ K}} = 0.006\underline{7}96 \text{ mol monomer + dimer}$$

Let X_d = mole fraction of dimer; then write one equation in one unknown based on 1.000 L of gas:

$$0.702 \text{ g both} = 0.006796 \text{ mol } X_d \ (120.1 \text{ g/mol}) + 0.006796 \ (1 - X_d) \ (60.05 \text{ g/mol})$$

$$0.702 \text{ g} = 0.8162 \ X_d + 0.4081 - 0.4081 X_d$$

$$X_d = \frac{(0.702 - 0.4081)}{0.4081} = 0.72\underline{0}1 = 0.720$$

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CHAPTER 12

Solutions

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

12.1. An example of a solid solution prepared from a liquid and a solid is a dental filling made of liquid mercury and solid silver.

12.2. The C_4H_9OH molecules will be more soluble in water because their –OH ends can form hydrogen bonds with water.

12.3. The Na^+ ion has a larger energy of hydration because its ionic radius is smaller, giving Na^+ a more concentrated electric field than K^+.

12.4. Write Henry's law ($S = k_H P$) for 159 mmHg (P_2), and divide it by Henry's law for 1 atm, or 760 mmHg (P_1). Then substitute the experimental values of P_1, P_2, and S_1 to solve for S_2.

$$\frac{S_2}{S_1} = \frac{k_H P_2}{k_H P_1} = \frac{P_2}{P_1}$$

Solving for S_2 gives

$$S_2 = \frac{P_2 S_1}{P_1} = \frac{(159 \text{ mmHg})(0.0404 \text{ g } O_2/\text{L})}{760 \text{ mmHg}} = 8.4\underline{5}2 \times 10^{-3} = 8.45 \times 10^{-3} \text{ g } O_2/\text{L}$$

12.5. The mass of HCl in 20.2% HCl (0.202 = fraction of HCl) is

$$0.202 \times 35.0 \text{ g} = 7.0\underline{7}0 = 7.07 \text{ g HCl}$$

The mass of H_2O in 20.2% HCl is

$$35.0 \text{ g solution} - 7.07 \text{ g HCl} = 27.\underline{9}3 = 27.9 \text{ g } H_2O$$

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12.6. Calculate the moles of toluene using its molar mass of 92.14 g/mol:

$$35.6 \text{ g toluene} \times \frac{1 \text{ mol toluene}}{92.14 \text{ g toluene}} = 0.3863 \text{ mol toluene}$$

To calculate molality, divide the moles of toluene by the mass in kg of the solvent (C_6H_6):

$$\text{Molality} \times \frac{0.3863 \text{ mol toluene}}{0.125 \text{ kg solvent}} = 3.0904 = 3.09 \textit{ m} \text{ toluene}$$

12.7. The number of moles of toluene = 0.3863 (previous exercise); the number of moles of benzene is

$$125 \text{ g benzene} \times \frac{1 \text{ mol benzene}}{78.11 \text{ g benzene}} = 1.6003 \text{ mol benzene}$$

The total number of moles is 1.6003 + 0.3863 = 1.9866, and the mole fractions are

$$\text{Mole fraction benzene} \times \frac{1.6003 \text{ mol benzene}}{1.9866 \text{ mol}} = 0.80554 = 0.806$$

$$\text{Mole fraction toluene} \times \frac{0.3863 \text{ mol toluene}}{1.9866 \text{ mol}} = 0.1944 = 0.194$$

The sum of the mole fractions = 1.000.

12.8. This solution contains 0.120 moles of methanol dissolved in 1.00 kg of ethanol. The number of moles in 1.00 kg of ethanol is

$$1.00 \times 10^3 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 21.706 \text{ mol } C_2H_5OH$$

The total number of moles is 21.706 + 0.120 = 21.826, and the mole fractions are

$$\text{Mole fraction } C_2H_5OH = \frac{21.706 \text{ mol } C_2H_5OH}{21.826 \text{ mol}} = 0.994501 = 0.995$$

$$\text{Mole fraction } CH_3OH = \frac{0.120 \text{ mol } CH_3OH}{21.826 \text{ mol}} = 0.005498 = 0.00550$$

The sum of the mole fractions is 1.000.

12.9. One mole of solution contains 0.250 mol methanol and 0.750 mol ethanol. The mass of this amount of ethanol, the solvent, is

$$0.750 \text{ mol } C_2H_5OH \times \frac{46.07 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH} = 34.55 \text{ g } C_2H_5OH \text{ (0.03455 kg)}$$

The molality of methanol in the ethanol solvent is

$$\frac{0.250 \text{ mol } CH_3OH}{0.03455 \text{ kg } C_2H_5OH} = 7.2358 = 7.24 \text{ m } CH_3OH$$

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12.10. Assume an amount of solution contains 1 kg of water. The mass of urea in this mass is

$$3.42 \text{ mol urea} \times \frac{60.05 \text{ g urea}}{1 \text{ mol urea}} = 205.4 \text{ g urea}$$

The total mass of solution is 205.4 + 1000.0 g = 1205.4 g. The volume and molarity are

$$\text{Volume of solution} = 1205.4 \text{ g} \times \frac{1 \text{ mL}}{1.045 \text{ g}} = 1153.49 \text{ mL} = 1.15349 \text{ L}$$

$$\text{Molarity} = \frac{3.42 \text{ mol urea}}{1.15349 \text{ L solution}} = 2.9649 \text{ mol/L} = 2.96 \, M$$

12.11. Assume a volume equal to 1.000 L of solution. Then

$$\text{Mass of solution} = 1.029 \text{ g/mL} \times (1.000 \times 10^3 \text{ mL}) = 1029 \text{ g}$$

$$\text{Mass of urea} = 2.00 \text{ mol urea} \times \frac{60.05 \text{ g urea}}{1 \text{ mol urea}} = 120.1 \text{ g urea}$$

$$\text{Mass of water} = (1029 - 120.1) \text{ g} = 908.9 \text{ g water } (0.9089 \text{ kg})$$

$$\text{Molality} = \frac{2.00 \text{ mol urea}}{0.9089 \text{ kg solvent}} = 2.2004 = 2.20 \, m \text{ urea}$$

12.12. Calculate the moles of naphthalene and the moles of chloroform:

$$0.515 \text{ g } C_{10}H_8 \times \frac{1 \text{ mol } C_{10}H_8}{128.17 \text{ g } C_{10}H_8} = 0.004018 \text{ mol } C_{10}H_8$$

$$60.8 \text{ g } CHCl_3 \times \frac{1 \text{ mol } CHCl_3}{119.38 \text{ g } CHCl_3} = 0.50929 \text{ mol } CHCl_3$$

The total number of moles is 0.004018 + 0.50929 = 0.5133 mol, and the mole fraction of chloroform is

$$\text{Mole fraction } CHCl_3 = \frac{0.50929 \text{ mol } CHCl_3}{0.5133 \text{ mol}} = 0.9921$$

$$\text{Mole fraction } C_{10}H_8 = \frac{0.004018 \text{ mol } C_{10}H_8}{0.5133 \text{ mol}} = 0.007828$$

The vapor-pressure lowering is

$$\Delta P = P^\circ X_{C_{10}H_8} = (156 \text{ mmHg})(0.007828) = 1.221 = 1.22 \text{ mmHg}$$

Use Raoult's law to calculate the vapor pressure of chloroform:

$$P = P^\circ X_{CHCl_3} = (156 \text{ mmHg})(0.9921) = 154.7 = 155 \text{ mmHg}$$

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12.13. Solve for c_m in the freezing-point-depression equation ($\Delta T = K_f c_m$; K_f in Table 12.3):

$$c_m = \frac{\Delta T}{K_f} = \frac{0.150°C}{1.858°C/m} = 0.807\underline{3}\ m$$

Use the molal concentration to solve for the mass of ethylene glycol:

$$\frac{0.08073 \text{ mol glycol}}{1 \text{ kg solvent}} \text{ x } 0.0378 \text{ kg solvent} = 0.003051 \text{ mol glycol}$$

$$0.003051 \text{ mol glycol} \text{ x } \frac{62.1 \text{ g glycol}}{1 \text{ mol glycol}} = 1.89\underline{4} \text{ x } 10^{-1} = 1.89 \text{ x } 10^{-1} \text{ g glycol}$$

12.14. Calculate the moles of ascorbic acid (vitamin C) from the molality, and then divide the mass of 0.930 g by the number of moles to obtain the molar mass:

$$\frac{0.0555 \text{ mol vit. C}}{1 \text{ kg } H_2O} \text{ x } 0.0950 \text{ kg } H_2O = 0.005272 \text{ mol vit C}$$

$$\frac{0.930 \text{ g vit. C}}{0.005272 \text{ mol vit. C}} = 176.4 = 176 \text{ g/mol}$$

The molecular mass of ascorbic acid, or vitamin C, is 176 amu.

12.15. The molal concentration of white phosphorus is

$$c_m = \frac{\Delta T}{K_b} = \frac{0.159°C}{2.40°C/m} = 0.0662\underline{5}\ m$$

The number of moles of white phosphorus (P_x) present in this solution is

$$\frac{0.06625 \text{ mol } P_x}{1 \text{ kg } CS_2} \text{ x } 0.0250 \text{ kg } CS_2 = 0.001656 \text{ mol } P_x$$

The molar mass of white phosphorus equals the mass divided by moles:

$$0.205 \text{ g} \div 0.001656 \text{ mol} = 123.77 = 124 \text{ g/mol}$$

Thus, the molecular mass of P_x is 124 amu. The number of P atoms in the molecule of white phosphorus is obtained by dividing the molecular mass by the atomic mass of P:

$$\frac{123.77 \text{ amu } P_x}{30.97 \text{ amu P}} = 3.996\underline{5} = 4.00$$

Hence, the molecular formula is P_4 ($x = 4$).

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12.16. The number of moles of sucrose is

$$5.0 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} = 0.01\underline{4}6 \text{ mol sucrose}$$

The molarity of the solution is

$$\frac{0.0146 \text{ mol sucrose}}{0.100 \text{ L}} = 0.1\underline{4}6 \ M \text{ sucrose}$$

The osmotic pressure, π, is equal to MRT and is calculated as follows:

$$\frac{0.146 \text{ mol sucrose}}{1 \text{ L}} \times \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 293 \text{ K} = 3.\underline{5}1 = 3.5 \text{ atm}$$

12.17. The number of ions from each formula unit is i. Here,

$$i = 1 + 2 = 3$$

The boiling-point elevation is

$$\Delta T_b = K_b c_m = 3 \times \frac{0.512°\text{C}}{m} \times 0.050 \ m = 0.07\underline{6}81 = 0.077°\text{C}$$

The boiling point of aqueous $MgCl_2$ is 100.077°C.

12.18. $AlCl_3$ would be most effective in coagulating colloidal sulfur because of the greater magnitude of charge on the Al ion (3+).

■ ANSWERS TO CONCEPT CHECKS

12.1. In each case, the component present in the greatest amount is the solvent.

a. Mo is the solute, and Cr is the solvent.

b. $MgCl_2$ is the solute, and water is the solvent.

c. N_2 and O_2 are the solutes, and Ar is the solvent.

12.2. The two main factors to consider when trying to determine the solubility of an ionic compound in water are ionic size and lattice energy. In this case, the lattice energy for the two compounds is the same; you can discount its effects. Since a smaller cation will have a more concentrated electric field leading to a larger energy of hydration, you would expect that if AB_2 has a smaller cation, then AB_2 will have a greater energy of hydration and AB_2 will be the more soluble compound.

12.3. As the altitude increases, the atmospheric pressure decreases, and thus the partial pressure of oxygen decreases. Above 3500 m, the partial pressure of oxygen in air has decreased to the point that not enough will dissolve in the water to sustain the fish.

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12.4. In order to boil at a lower temperature than water, the vapor pressure of the solution (water + liquid) must be greater than that of water. To make this solution, you must add a liquid that is both soluble in water and chemically similar to water. It must have a higher vapor pressure than water and a boiling point lower than 100°C. One possible liquid is ethanol, with a boiling point of 78.3°C (Table 12.3).

12.5. By the principle of osmosis, in a brine solution, water will flow out of the pickle (lower concentration of ions) into the brine (higher concentration of ions). If the pickles were stored in a water solution, the water (lower concentration of ions) would flow into the pickle (higher concentration of ions) and cause it to swell up and probably burst.

12.6. These are water solutions of identical volume (normal boiling point 100°C) containing different numbers of moles of solute. The boiling point of a solution can be determined by the formula $\Delta T_b = iK_b m$. The solution with the largest ΔT_b will have the highest boiling point. Since K_b is a constant, this will be the compound with the largest factor of $i \bullet m$. Also, since the volume is constant, the factor reduces to $i \bullet$ moles. Ideally, all of the compounds will dissolve completely, so NaCl and KBr have $i = 2$, and Na_2SO_4 and $MgCl_2$ have $i = 3$.

This gives

For NaCl, $i \bullet$ moles $= 2 \times 1.5 = 3.0$

For Na_2SO_4, $i \bullet$ moles $= 3 \times 1.3 = 3.9$

For $MgCl_2$, $i \bullet$ moles $= 3 \times 2.0 = 6.0$

For KBr, $i \bullet$ moles $= 2 \times 2.0 = 4.0$

The result is given from highest boiling point to lowest boiling point:

$MgCl_2 > KBr > Na_2SO_4 > NaCl$

12.7. Iron(III) hydroxide is a hydrophobic colloid. As the colloid forms in water, an excess of iron(III) ion (Fe^{3+}) is present on the surface, giving each crystal an excess positive charge. These positively charged crystals repel one another, so aggregation to larger particles of iron(III) hydroxide is prevented. When the electrodes are dipped into the colloidal solution, iron(III) hydroxide precipitates because electrons from the negative electrode neutralize the excess positive charge on the iron(III) hydroxide, allowing larger particles to form (precipitate).

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

12.1. An example of a gaseous solution is air, in which nitrogen (78%) acts as a solvent for a gas such as oxygen (21%). Recall that the solvent is the component that is present in greater amount. An example of a liquid solution containing a gas is any carbonated beverage in which water acts as the solvent for carbon dioxide gas. Ethanol in water is an example of a liquid-liquid solution. An example of a solid solution is any gold-silver alloy.

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12.2. The two factors that explain differences in solubilities are (1) the natural tendency of substances to mix together, or the natural tendency of substances to become disordered, and (2) the relative forces of attraction between solute species (or solvent species) compared to that between the solute and solvent species. The strongest interactions are always achieved.

12.3. This is not a case of "like dissolves like." There are strong hydrogen-bonding forces between the water molecules. For the octane to mix with water, hydrogen bonds must be broken and replaced by the much weaker London forces between water and octane. Thus, octane does not dissolve in water, because the maximum forces of attraction among molecules are obtained if it does not dissolve.

12.4. In most cases, the wide differences in solubility can be explained in terms of the different energies of attraction between ions in the crystal and between ions and water. Hydration energy is used to measure the attraction of ions for water molecules, and lattice energy is used to measure the attraction of positive ions for negative ions in the crystal lattice. An ionic substance is soluble when the hydration energy is much larger than the lattice energy. An ionic substance is insoluble when the lattice energy is much larger than the hydration energy.

12.5. A sodium chloride crystal dissolves in water because of two factors. The positive Na^+ ion is strongly attracted to the oxygen (negative end of the water dipole) and dissolves as $Na^+(aq)$. The negative Cl^- ion is strongly attracted to the hydrogens (positive end of the water dipole) and dissolves as $Cl^-(aq)$.

12.6. When the temperature (energy of a solution) is increased, the solubility of an ionic compound usually increases. A number of salts are exceptions to this rule, particularly a number of calcium salts such as calcium acetate, calcium sulfate, and calcium hydroxide (although the solubilities of calcium bromide, calcium chloride, calcium fluoride, and calcium iodide all increase with temperature).

12.7. Calcium chloride is an example of a salt that releases heat when it dissolves (exothermic heat of solution). Ammonium nitrate is an example of a salt that absorbs heat when it dissolves (endothermic heat of solution).

12.8. As the temperature of the solution was increased by heating, the concentration of the dissolved gas would decrease.

12.9. A carbonated beverage must be stored in a closed container because carbonated beverages must contain more carbon dioxide than is soluble in water at atmospheric pressure. It is possible to add carbon dioxide under pressure to a closed container before it is sealed and increase the solubility of carbon dioxide. This is an illustration of Le Châtelier's principle, which states that the equilibrium between gaseous and dissolved carbon dioxide is shifted in favor of the dissolved carbon dioxide by an increase in pressure.

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12.10. According to Le Châtelier's principle, a gas is more soluble in a liquid at higher pressures because, when the gas dissolves in the liquid, the system decreases in volume, tending to decrease the applied pressure. However, when a solid dissolves in a liquid, there is very little volume change. Thus, pressure has very little effect on the solubility of a solid in a liquid.

12.11. The four ways to express the concentration of a solute in a solution are (1) molarity, which is moles per liter; (2) mass percentage of solute, which is the percentage by mass of solute contained in a given mass of solution; (3) molality, which is the moles of solute per kilogram of solvent; and (4) mole fraction, which is the moles of the component substance divided by the total moles of solution.

12.12. The vapor pressure of the solvent of the dilute solution is larger than the vapor pressure of the solvent of the more concentrated solution (Raoult's law). Thus, the more dilute solution loses solvent and becomes more concentrated while the solvent molecules in the vapor state condense into the concentrated solution, making it more dilute. After sufficient time has passed, the vapor pressure of the solvent in the closed container will reach a steady value (equilibrium), at which time the concentration of solute will be the same in the two solutions.

12.13. In fractional distillation, the vapor that first appears over a solution will have a greater mole fraction of the more volatile component. If a portion of this is vaporized and condensed, the liquid will be still richer in the more volatile component. After successive distillation stages, eventually the more volatile component will be obtained in pure form (Figure 12.20).

12.14. The boiling point of the solution is higher because the nonvolatile solute lowers the vapor pressure of the solvent. Thus, the temperature must be increased to a value greater than the boiling point of the pure solvent to achieve a vapor pressure equal to atmospheric pressure.

12.15. One application is the use of ethylene glycol in automobile radiators as antifreeze; the glycol-water mixture usually has a freezing point well below the average low temperature during the winter. A second application is spreading sodium chloride on icy roads in the winter to melt the ice. The ice usually melts, because at equilibrium, a concentrated solution of NaCl usually freezes at a temperature below that of the roads.

12.16. If a pressure greater than the osmotic pressure of the ocean water is applied, the natural osmotic flow can be reversed. Then, the water solvent flows from the ocean water through a membrane to a more dilute solution or to pure water, leaving behind the salt and other ionic compounds from the ocean in a more concentrated solution.

12.17. Part of the light from the sun is scattered in the direction of an observer by fine particles in the clouds (Tyndall effect) rather than being completely absorbed by the clouds. The scattered light becomes visible against the darker background of dense clouds.

12.18. Fog is an aerosol, whipped cream is a foam, mayonnaise is an emulsion, solid silver chloride dispersed in water is a sol, and fruit jelly is a gel.

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12.19. The polar –OH group on glycerol allows it to interact (hydrogen-bond) with the polar water molecules, which means it is like water and, therefore, will dissolve in water. Benzene is a nonpolar molecule, which indicates that it is not "like" water and, therefore, will not dissolve in water.

12.20. Soap removes oil from a fabric by absorbing the oil into the hydrophobic centers of the soap micelles and off the surface of the fabric. Rinsing removes the micelles from contact with the fabric and leaves only water on the fabric, which can then be dried.

12.21. The answer is a, 6.50×10^{-2} mol.

12.22. The answer is c, 8.66 *m*.

12.23. The answer is e, 25.3 g/mol.

12.24. The answer is a, the solution would freeze at a lower temperature than pure water.

■ ANSWERS TO CONCEPT EXPLORATIONS

12.25.

a. The lower boiling point will be for the solution with the smaller ΔT_b and hence the lower particle concentration. For solutions with equal concentrations, the solution with the smallest *i* factor will have the lowest particle concentration. Substance AB breaks into ions and has an *i* factor of 2, whereas substance XY dissolves as a molecular compound and has an *i* factor of 1. Therefore, substance XY has the lower ΔT_b and the lower boiling point.

b. According to Raoult's law, the vapor-pressure lowering is proportional to the mole fraction of the solute multiplied by the *i* factor. Since the *i* factor for substance AB is 2, and the *i* factor for substance XY is 1, you would not expect the vapor pressures of the two solutions to be the same. The vapor-pressure lowering is smaller for the substance with the smaller *i* factor. Therefore, the vapor pressure of a solution of XY will be higher than the vapor pressure of a solution of AB.

c. To make the two solutions have the same boiling point, you would have to make the concentration of particles in the two solutions the same. This can be accomplished by doubling the concentration of XY, thereby making the factor $i \times m$ equal for both solutions.

d. The boiling point of 250 mL of the AB(*aq*) solution will be the same as that of the original solution. The boiling point of a solution is independent of the volume of the sample and depends only on the concentration of solute particles.

e. Freezing-point depression depends on the concentration of the solute. As the solvent evaporates, the solute concentration increases, and the freezing-point depression gets larger, resulting in a lower melting point. Thus, after the water evaporates, the melting point of the resulting solution will be lower than for the original solution.

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12.26.

a. Even though the two solutions were prepared using equal moles, they can have different freezing points if the two substances dissolve into a different number of solute particles. Since sample A freezes at −0.50°C and sample B freezes at −1.00°C, sample B must dissolve into twice as many particles as sample A.

b. The sample with substance B still has the same freezing point as the original sample, so the difference is exactly the same.

c. Since equal numbers of moles of A and B were used, both solutions have the same molality. Using substance A, with $i = 1$, you get

$$m = \frac{\Delta T_f}{K_f} = \frac{0.50°\text{C}}{1.858°\text{C}/m} = 0.2\underline{6}9 = 0.27\ m$$

d. If another 1.0 kg of water were added to solution B, the molality would be reduced to one-half the original molality, and ΔT_f would also be reduced by one-half. The new solution would have a freezing point of −0.50°C.

e. To get a solution of A with a freezing point of −0.25°C, you would need the following molality:

$$m = \frac{\Delta T_f}{K_f} = \frac{0.25°\text{C}}{1.858°\text{C}/m} = 0.1\underline{3}4 = 0.13\ m$$

f. The boiling point of A will be lower than that of B, the vapor pressure of A will be higher than that of B, and the osmotic pressure of A will be lower than that of B.

■ ANSWERS TO CONCEPTUAL PROBLEMS

12.27. The amount of oxygen dissolved in water decreases as the temperature increases. Thus, at the lower temperatures, there is enough oxygen dissolved in the water to support both bass and trout. But as the temperature rises above 23°C, there is not enough dissolved oxygen in the warm water to support the trout, which need more O_2 than bass.

12.28. The salt that would best accomplish the task would be the salt that lowers the freezing point of water the most. This, in turn, will be the salt with the largest *i* factor. Ideally, if each salt dissolved completely, KCl, $MgSO_4$, and AgCl would have $i = 2$. Similarly, $CaCl_2$ and PbS_2 would have $i = 3$. Of the latter two salts, $CaCl_2$ is more soluble than PbS_2, so its *i* factor is closer to 3. Therefore, the salt with the largest *i* factor is $CaCl_2$, so it would lower the freezing point of water the most and would best accomplish the task.

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12.29. The two main factors to consider when trying to determine the solubility of an ionic compound in water are ionic size and lattice energy. Ionic size is inversely related to the energy of hydration; the smaller the ion, the greater the energy of hydration. Keep in mind that the greater the energy of hydration, the more likely it is for a compound to dissolve. The amount of lattice energy is directly related to the solubility of the compound; the lower the lattice energy, the more likely it is for the compound to dissolve.

Taking into account these factors, in order to increase the solubility of a compound you need to decrease the ionic size and decrease the lattice energy. Since the energy of hydration of the Y^+ ion is greater than that of the X^+ ion (making XZ less soluble), in order for XZ to be more soluble than YZ, the lattice energy must be less for the XZ compound.

12.30.

a. According to Raoult's law, the addition of a nonvolatile nonelectrolyte to a solvent will lower the vapor pressure of the solvent, so we would expect the vapor pressure of such a solution to be lower than that of the pure solvent (water in this case). When a volatile solute is added to a solvent, the vapor pressure of the solution is dependent on the mole fraction of the solute and solvent and on the vapor pressures of both the solute and the solvent. Since the solute is volatile (a high vapor pressure relative to water), the solution must have a higher vapor pressure than pure water.

b. Keeping in mind that a solution will boil when the vapor pressure equals the pressure pushing on the surface of the solution, the solution with the lower vapor pressure will boil at a higher temperature. Thus, the solution with the nonvolatile solute will boil at the higher temperature.

12.31. Smoke particles carry a small net charge that prevents them from forming larger particles that would settle to the bottom of the smokestack. The charged smoke particles are neutralized by the current, which then allows them to aggregate into large particles. These large particles are too big to be carried out of the stack.

12.32.

a. Since beaker B contains more solute particles, according to Raoult's law, it will boil at a higher temperature than beaker A.

b. More particles in solution lead to lower vapor pressure, which in turn lowers the freezing point of a solution. Since beaker B contains more solute particles, it will freeze at a lower temperature than beaker A.

c. When separated by a semipermeable membrane, the solvent from the less concentrated solution flows into the more concentrated solution. Because of this, the water will flow from beaker A to beaker B, causing an increase in the concentration of NaCl in beaker A.

12.33. Vinegar is a solution of acetic acid (solute) and water (solvent). Because the salt concentration is higher outside the lettuce leaf than inside, water will pass out of the lettuce leaf into the dressing via osmosis. The result is that the lettuce will wilt.

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12.34. As a solution freezes, pure solvent forms without any of the solute present. This means that as ocean water freezes to make icebergs, it freezes as pure water without the salt present.

12.35. To answer these questions, it is necessary to determine the relative concentrations of solute particles in each beaker. With equal moles and equal volumes, the solution concentration will be directly proportional to the van't Hoff factor, i, for that compound. Urea, a nonelectrolyte, has $i = 1$. NaCl, which is ionic, has $i = 2$, and $CaCl_2$, which is also ionic, has $i = 3$.

a. The highest boiling point will correspond to the largest boiling-point elevation, ΔT_b. Since $\Delta T_b = iK_b m$, the largest ΔT_b will correspond to the highest value of i. Thus, the solution with $CaCl_2$ ($i = 3$) will have the highest boiling point.

b. The highest freezing point will correspond to the smallest freezing-point depression, ΔT_f. Since $\Delta T_f = iK_f m$, the smallest ΔT_f will correspond to the smallest value of i. Thus, the solution with urea ($i = 1$) will have the highest freezing point.

12.36. To answer these questions, it is necessary to determine the relative concentrations of solute particles in each beaker. In order to compare volumes, use the lines on the sides of the beakers. Beaker A has a concentration of five atoms per two volume units, 5/2 or 2.5/1. Beaker B has a concentration of ten atoms per two volume units, 10/2 or 5/1. Beaker C has a concentration of five atoms per volume unit, 5/1. Comparing the concentrations,
beaker B = beaker C = 2 x beaker A.

a. Since $P_A = X_A P_A°$, the solution with the highest vapor pressure is the solution with the highest mole fraction of solvent, or, conversely, the lowest concentration of solute particles. Thus, the solution in beaker A will have the highest vapor pressure.

b. The lowest boiling point will correspond to the smallest boiling point increase, ΔT_b. Since $\Delta T_b = K_b m$, the smallest ΔT_b will correspond to the smallest concentration of solute particles (molality here). Thus, the solution in beaker A will have the lowest boiling point.

c. For each solution to have the same freezing point, they all need the same concentration of solute particles. This can be accomplished by doubling the volume in beakers B and C.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off. Atomic masses are rounded to two decimal places, except for that of hydrogen.

12.37. An example of a liquid solution prepared by dissolving a gas in a liquid is household ammonia, which consists of ammonia (NH_3) gas dissolved in water.

12.38. An example of a solid solution prepared from two solids is almost any alloy, such as 18-kt gold, which consists of 25 percent silver dissolved in 75% gold.

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12.39. Boric acid would be more soluble in ethanol because this acid is polar and is more soluble in a more polar solvent. It can also hydrogen-bond to ethanol but not to benzene.

12.40. Naphthalene is more soluble in benzene because nonpolar naphthalene must break the strong hydrogen bonds between ethanol molecules and replace them with weaker London forces.

12.41. The order of increasing solubility is $H_2O < CH_2OHCH_2OH < C_{10}H_{22}$. The solubility in nonpolar hexane increases with the decreasing polarity of the solute.

12.42. Acetic acid is more soluble because it is polar like ethanol and can form hydrogen bonds to it. Stearic acid also has a polar, H-bonding end, but it also has a long hydrocarbon part which is nonpolar and unlike ethanol.

12.43. The Al^{3+} ion has both a greater charge and a smaller ionic radius than Mg^{2+}, so Al^{3+} should have a greater energy of hydration.

12.44. The F^- ion has a smaller radius than the Cl^- ion, so F^- should have a greater hydration energy.

12.45. The order is $Ba(IO_3)_2 < Sr(IO_3)_2 < Ca(IO_3)_2 < Mg(IO_3)_2$. The iodate ion is fairly large, so the lattice energy for all these iodates should change to a smaller degree than the hydration energy of the cations. Therefore, solubility should increase with decreasing cation radius.

12.46. Fluorides (smaller anion): As the cation radius increases, the lattice energy of the fluoride salts decreases to a greater degree than the cation hydration energy decreases. Permanganates (larger anion): As the cation radius increases, the lattice energy of the permanganate salts decreases to a smaller degree than the cation hydration energy decreases. Therefore, the solubility of the fluorides increases with increasing cation radius, whereas the solubility of the permanganates decreases with increasing cation radius.

12.47. Using Henry's law, let S_1 = the solubility at 1.00 atm (P_1), and S_2 = the solubility at 5.50 atm (P_2).

$$S_2 = \frac{P_2 S_1}{P_1} = \frac{(5.50 \text{ atm})(0.161 \text{ g /100 mL})}{1.00 \text{ atm}} = 0.88\underline{5}5 = 0.886 \text{ g/100 mL}$$

12.48. The partial pressure of N_2 in air at 4.79 atm is

$$4.79 \text{ atm} \times 0.781 = 3.7\underline{4}099 \text{ atm}$$

Substituting this for P_2 in $S_2 = S_1 \times P_2/P_1$ (Henry's law), you obtain

$$S_2 = (0.00175 \text{ g/100 mL}) \times \frac{3.74099 \text{ atm}}{1.00 \text{ atm}} = 0.006\underline{5}46 = 0.00655 \text{ g/100 mL}$$

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12.49. First, calculate the mass of KI in the solution; then calculate the mass of water needed.

$$\text{Mass KI} = 72.5 \text{ g} \times \frac{5.00 \text{ g KI}}{100 \text{ g solution}} = 3.6\underline{2}50 = 3.63 \text{ g KI}$$

$$\text{Mass } H_2O = 72.5 \text{ g soln} - 3.6250 \text{ g KI} = 68.\underline{8}75 = 68.9 \text{ g } H_2O$$

Dissolve 3.63 g KI in 68.9 g of water.

12.50. First, calculate the mass of Na_2SO_4 in the solution; then calculate the mass of water needed.

$$\text{Mass of } Na_2SO_4 = 455 \text{ g solution} \times \frac{6.50 \text{ g } Na_2SO_4}{100 \text{ g solution}} = 29.\underline{5}7 \text{ g } Na_2SO_4$$

$$\text{Mass of water} = 455 \text{ g soln} - 29.57 \text{ g } Na_2SO_4 = 42\underline{5}.43 \text{ g water}$$

Dissolve 29.$\underline{5}$7 g Na_2SO_4 in 42$\underline{5}$.43 g of water.

12.51. Multiply the mass of KI by 100 g of solution per 5.00 g KI (reciprocal of percentage).

$$0.258 \text{ g KI} \times \frac{100 \text{ g solution}}{5.00 \text{ g KI}} = 5.1\underline{6}0 = 5.16 \text{ g solution}$$

12.52. Multiply the mass of sodium sulfate by 100 g of solution per 6.50 g Na_2SO_4 (reciprocal of percentage).

$$1.50 \text{ g } Na_2SO_4 \times \frac{100 \text{ g solution}}{6.50 \text{ g } Na_2SO_4} = 23.\underline{0}7 = 23.1 \text{ g solution}$$

12.53. Convert mass of vanillin ($C_8H_8O_3$, molar mass 152.14 g/mol) to moles, convert mg of ether to kg, and divide for molality.

$$0.0391 \text{ g vanillin} \times \frac{1 \text{ mol vanillin}}{152.14 \text{ g vanillin}} = 2.5\underline{7}0 \times 10^{-4} \text{ mol vanillin}$$

$$168.5 \text{ mg ether} \times 1 \text{ kg}/10^6 \text{ mg} = 168.5 \times 10^{-6} \text{ kg ether}$$

$$\text{Molality} = \frac{2.570 \times 10^{-4} \text{ mol vanillin}}{168.5 \times 10^{-6} \text{ kg ether}} = 1.5\underline{2}52 = 1.53 \textit{ m} \text{ vanillin}$$

12.54. Convert mass of lauryl alcohol (LA, $C_{12}H_{25}OH$, molar mass 186.33 g/mol) to moles, convert g of ethanol to kg, and divide.

$$17.1 \text{ g LA} \times \frac{1 \text{ mol LA}}{186.3 \text{ g LA}} = 9.1\underline{7}7 \times 10^{-2} \text{ mol LA}$$

$$165 \text{ g ethanol} \times 1 \text{ kg}/10^3 \text{ g} = 165 \times 10^{-3} \text{ kg ethanol}$$

$$\text{Molality} = \frac{9.1\underline{7}7 \times 10^{-2} \text{ mol LA}}{165 \times 10^{-3} \text{ kg ethanol}} = 0.55\underline{6}1 = 0.556 \textit{ m} \text{ LA}$$

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12.55. Convert mass of fructose ($C_6H_{12}O_6$, molar mass 180.16 g/mol) to moles, and then multiply by one kg H_2O per 0.125 mol fructose (the reciprocal of molality).

$$1.75 \text{ g fructose} \times \frac{1 \text{ mol fructose}}{180.16 \text{ g fructose}} \times \frac{1 \text{ kg } H_2O}{0.125 \text{ mol fructose}} = 0.07770 \text{ kg} \quad (77.7 \text{ g } H_2O)$$

12.56. Multiply the kg of $CHCl_3$ by the molality to get moles of caffeine; then convert moles to mass.

$$0.0450 \text{ kg } CHCl_3 \times \frac{0.0946 \text{ mol caffeine}}{1 \text{ kg } CHCl_3} \times \frac{194.2 \text{ g caffeine}}{1 \text{ mol caffeine}}$$

$$= 0.8267 = 0.827 \text{ g caffeine}$$

12.57. Convert masses to moles, and then calculate the mole fractions.

$$65.0 \text{ g alc.} \times \frac{1 \text{ mol alc.}}{60.09 \text{ g alc.}} = 1.0817 \text{ mol alc.}$$

$$35.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 1.9422 = 1.94 \text{ mol } H_2O$$

$$\text{Mole fraction alc.} = \frac{\text{mol alc.}}{\text{total mol}} = \frac{1.0817 \text{ mol}}{3.0239 \text{ mol}} = 0.3577 = 0.358$$

$$\text{Mole fraction } H_2O = \frac{\text{mol } H_2O}{\text{total mol}} = \frac{1.9422 \text{ mol}}{3.0239 \text{ mol}} = 0.6422 = 0.642$$

12.58. Convert masses to moles, and then calculate the mole fractions.

$$2.50 \times 10^3 \text{ g glycol} \times \frac{1 \text{ mol glycol}}{62.07 \text{ g glycol}} = 40.277 \text{ mol glycol}$$

$$2.00 \times 10^3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 110.98 \text{ mol } H_2O$$

$$\text{Total moles} = 40.277 + 110.98 = 151.26 \text{ mol}$$

$$\text{Mole fraction } H_2O = \frac{\text{mol } H_2O}{\text{total mol}} = \frac{110.98 \text{ mol}}{151.26 \text{ mol}} = 0.7336 = 0.734$$

$$\text{Mole fraction glycerol} = \frac{\text{mol glycerol}}{\text{total mol}} = \frac{40.277 \text{ mol}}{151.26 \text{ mol}} = 0.2662 = 0.266$$

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12.59. In the solution, for every 0.650 mol of NaClO there is 1.00 kg, or 1.00 x 10^3 g, of H_2O, so

$$1.00 \times 10^3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 55.\underline{4}9 \text{ mol } H_2O$$

$$\text{Total mol} = 55.\underline{4}9 \text{ mol } H_2O + 0.650 \text{ mol NaClO} = 56.\underline{1}4 \text{ mol}$$

$$\text{Mole fraction NaClO} = \frac{\text{mol NaClO}}{\text{total mol}} = \frac{0.650 \text{ mol}}{56.\underline{1}4 \text{ mol}} = 0.011\underline{5}7 = 0.0116$$

12.60. In the solution, for every 0.600 mol of H_2O_2, there is 1.00 kg, or 1.00 x 10^3 g, of H_2O, so

$$1.00 \times 10^3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 55.\underline{4}9 \text{ mol } H_2O$$

$$\text{Total mol} = 55.49 \text{ mol } H_2O + 0.600 \text{ mol } H_2O_2 = 56.\underline{0}93 \text{ mol}$$

$$\text{Mole fraction } H_2O_2 = \frac{\text{mol } H_2O_2}{\text{mol solution}} = \frac{0.600 \text{ mol}}{56.093 \text{ mol}} = 0.010\underline{6}9 = 0.0107$$

12.61. The total moles of solution = 3.31 mol H_2O + 1.00 mol HCl = 4.31 mol

$$\text{Mole fraction HCl} = \frac{1 \text{ mol HCl}}{4.31 \text{ mol}} = 0.232\underline{0}1 = 0.232$$

$$3.31 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} \times \frac{1 \text{ kg } H_2O}{10^3 \text{ g } H_2O} = 5.9\underline{6}5 \times 10^{-2} \text{ kg } H_2O$$

$$\text{Molality} = \frac{1.00 \text{ mol HCl}}{5.965 \times 10^{-2} \text{ kg } H_2O} = 16.\underline{7}6 = 16.8 \textit{ m}$$

12.62. The total moles of solution = 1.00 mol NH_3 + 2.44 mol H_2O = 3.44 mol

$$\text{Mole fraction } NH_3 = \frac{1 \text{ mol } NH_3}{3.44 \text{ mol}} = 0.29\underline{0}6 = 0.291$$

$$2.44 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} \times \frac{1 \text{ kg } H_2O}{10^3 \text{ g } H_2O} = 4.3\underline{9}7 \times 10^{-2} \text{ kg } H_2O$$

$$\text{Molality} = \frac{1.00 \text{ mol } NH_3}{4.397 \times 10^{-2} \text{ kg } H_2O} = 22.\underline{7}4 = 22.7 \textit{ m}$$

12.63. The mass of 1.000 L of solution is 1.022 kg. In the solution, there is 0.580 mol $H_2C_2O_4$ (OA) for every 1.0000 kg of water. Convert this number of moles to mass.

$$0.580 \text{ mol OA} \times \frac{90.04 \text{ g OA}}{1 \text{ mol OA}} \times \frac{1 \text{ kg OA}}{10^3 \text{ g OA}} = 0.052\underline{2}2 \text{ kg OA}$$

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The total mass of the solution containing 1.000 kg H_2O and 0.580 mol OA is calculated as follows:

$$\text{Mass} = 1.0000 \text{ kg } H_2O + 0.05222 \text{ kg OA} = 1.052\underline{2}2 \text{ kg}$$

Use this to relate the mass of 1.000 L (1.022 kg) of solution to the amount of solute:

$$1.022 \text{ kg solution} \times \frac{0.580 \text{ mol OA}}{1.05222 \text{ kg solution}} = 0.56\underline{3}3 \text{ mol OA}$$

$$\text{Molarity} = \frac{0.5633 \text{ mol OA}}{1.00 \text{ L solution}} = 0.56\underline{3}3 = 0.563\ M$$

12.64. In the solution, there is 0.688 mol of citric acid (CA) for every 1.000 kg of water. Convert this number of moles to mass.

$$0.688 \text{ mol CA} \times \frac{192.1 \text{ g CA}}{1 \text{ mol CA}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.13\underline{2}1 \text{ kg CA}$$

The total mass of solution containing 1.000 kg H_2O and 0.688 mol CA is

$$\text{Mass} = 1.0000 \text{ kg } H_2O + 0.13\underline{2}1 \text{ kg CA} = 1.13\underline{2}1 \text{ kg} = 113\underline{2}.1 \text{ g}$$

Now, use the density of the solution (1.049 g/mL) to convert this mass to liters of solution.

$$\text{Volume} = 113\underline{2}.1 \text{ g} \times \frac{1 \text{ mL}}{1.049 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.07\underline{9}2 \text{ L}$$

Since there is 0.688 mol CA in this volume, you can now calculate the molarity of the solution.

$$\text{Molarity} = \frac{\text{mol CA}}{\text{Volume}} = \frac{0.688 \text{ mol}}{1.07\underline{9}2 \text{ L}} = 0.63\underline{7}46 = 0.637\ M$$

12.65. In 1.000 L of vinegar, there is 0.763 mol of acetic acid. The total mass of the 1.000-L solution is 1.004 kg. Start by calculating the mass of acetic acid (AA) in the solution.

$$0.763 \text{ mol AA} \times \frac{60.05 \text{ g AA}}{1 \text{ mol AA}} = 45.\underline{8}2 \text{ g AA} \quad (0.045\underline{8}2 \text{ kg AA})$$

The mass of water may be found by difference:

$$\text{Mass } H_2O = 1.004 \text{ kg soln} - 0.04582 \text{ kg AA} = 0.95\underline{8}2 \text{ kg } H_2O$$

$$\text{Molality} = \frac{0.763 \text{ mol AA}}{0.9582 \text{ kg } H_2O} = 0.79\underline{6}2 = 0.796\ m$$

12.66. In 1.000 L of beverage, there is 0.265 mol of tartaric acid. The total mass of the 1.000-L beverage is 1.016 kg. Start by calculating the mass of tartaric acid (TA) in the beverage.

$$0.265 \text{ mol TA} \times \frac{150.1 \text{ g TA}}{1 \text{ mol TA}} = 39.\underline{7}7 \text{ g TA} \quad (0.039\underline{7}7 \text{ kg TA})$$

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The mass of water may be found by difference:

$$\text{Mass } H_2O = 1.016 \text{ kg soln} - 0.03977 \text{ kg TA} = 0.9762 \text{ kg } H_2O$$

$$\text{Molality} = \frac{0.265 \text{ mol TA}}{0.9762 \text{ kg } H_2O} = 0.2714 = 0.271\ m$$

12.67. To find the mole fraction of sucrose, first find the amounts of both sucrose (suc.) and water:

$$20.2 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.30 \text{ g sucrose}} = 0.05901 \text{ mol sucrose}$$

$$70.1 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 3.890 \text{ mol } H_2O$$

$$X_{\text{sucrose}} = \frac{0.05901 \text{ mol sucrose}}{(3.890 + 0.05901) \text{ mol}} = 0.01494$$

From Raoult's law, the vapor pressure (P) and lowering (ΔP) are

$$P = P^\circ_{H_2O} X_{H_2O} = P^\circ_{H_2O} (1 - X_{\text{suc.}}) = (42.2 \text{ mmHg})(1 - 0.01494)$$

$$= 41.569 = 41.6 \text{ mmHg}$$

$$\Delta P = P^\circ_{H_2O} X_{\text{suc.}} = (42.2 \text{ mmHg})(0.01494) = 0.6306 = 0.631 \text{ mmHg}$$

12.68. To find the mole fraction of benzene, first find the amounts of both benzene (ben.) and naphthalene (nap.):

$$1.20 \text{ g nap.} \times \frac{1 \text{ mol nap.}}{128.2 \text{ g nap.}} = 0.0093603 \text{ mol nap.}$$

$$25.6 \text{ g ben.} \times \frac{1 \text{ mol ben.}}{78.11 \text{ g ben.}} = 0.3277 \text{ mol ben.}$$

$$X_{\text{nap.}} = \frac{0.0093603 \text{ mol nap.}}{(0.3277 + 0.0093603) \text{ mol}} = 0.02777$$

From Raoult's law, the vapor pressure (P) and lowering (ΔP) are

$$P = P^\circ_{\text{ben.}} (1 - X_{\text{nap.}}) = (86.0 \text{ mmHg})(1 - 0.02777) = 83.61 = 83.6 \text{ mmHg}$$

$$\Delta P = P^\circ_{\text{ben.}} X_{\text{nap.}} = (86.0 \text{ mmHg})(0.02777) = 2.388 = 2.39 \text{ mmHg}$$

12.69. Find the molality of glycerol (gly.) in the solution first:

$$0.150 \text{ g gly.} \times \frac{1 \text{ mol gly.}}{92.095 \text{ g gly.}} = 0.001628 \text{ mol gly.}$$

$$\text{Molality} = \frac{0.001628 \text{ mol gly.}}{0.0200 \text{ kg solvent}} = 0.081437\ m$$

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Substitute $K_b = 0.512°C/m$ and $K_f = 1.858\ °C/m$ (Table 12.3) into equations for ΔT_b and ΔT_f:

$$\Delta T_b = K_b m = 0.512°C/m \text{ x } 0.081\underline{4}37\ m = 0.041\underline{6}9°C$$

$$T_b = 100.000 + 0.04169 = 100.04\underline{1}69 = 100.042°C$$

$$\Delta T_f = K_f m = 1.858°C/m \text{ x } 0.081\underline{4}37\ m = 0.15\underline{1}31°C$$

$$T_f = 0.000 - 0.15\underline{1}31 = -0.15\underline{1}31 = -0.151°C$$

12.70. Find the molality of the solution first:

$$0.834 \text{ g } S_8 \text{ x } \frac{1 \text{ mol } S_8}{256.52 \text{ g } S_8} = 0.003\underline{2}51 \text{ mol } S_8$$

$$\text{Molality} = \frac{0.003251 \text{ mol } S_8}{0.1000 \text{ kg solvent}} = 0.03\underline{2}51\ m$$

Substitute $K_b = 3.08°C/m$ and $K_f = 3.59°C/m$ (Table 12.3) into equations for ΔT_b and ΔT_f:

$$\Delta T_b = K_b m = \frac{3.08°C}{m\ S_8} \text{ x } 0.03251\ m\ S_8 = 0.10\underline{0}1°C$$

$$T_b = 118.5°C + 0.1001°C = 118.\underline{6}00 = 118.6°C$$

$$\Delta T_f = K_f m = \frac{3.59°C}{m\ S_8} \text{ x` } 0.03251\ m\ S_8 = 0.11\underline{6}7°C$$

$$T_f = 16.60°C - 0.1167°C = 16.4\underline{8}3 = 16.48°C$$

12.71. Calculate ΔT_f, the freezing-point depression, and, using $K_f = 1.858°C/m$ (Table 12.3), the molality, c_m.

$$\Delta T_f = 0.000°C - (-0.086°C) = 0.086°C$$

$$c_m = \frac{\Delta T_f}{K_f} = \frac{0.086°C}{1.858°C/m} = 4.\underline{6}28 \text{ x } 10^{-2} = 4.6 \text{ x } 10^{-2}\ m$$

12.72. Calculate ΔT_f, the freezing-point depression, and, using $K_f = 1.858°C/m$ (Table 12.3), the molality, c_m.

$$\Delta T_f = 0.000°C - (-0.085°C) = 0.085°C$$

$$c_m = \frac{\Delta T_f}{K_f} = \frac{0.085°C}{1.858°C/m} = 0.04\underline{5}7\ m$$

Now, find the amount of urea in the solution from the definition of molality:

$$\text{Mol}_{\text{urea}} = c_m \text{ x } (\text{kg } H_2O) = \frac{0.0457 \text{ mol urea}}{1 \text{ kg } H_2O} \text{ x } 0.1000 \text{ kg } H_2O = 0.004\underline{5}7 \text{ mol}$$

$$0.00457 \text{ mol urea } \text{x } \frac{60.06 \text{ g urea}}{1 \text{ mol urea}} = 0.2\underline{7}4 = 0.27 \text{ g urea}$$

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12.73. Find the moles of unknown solute from the definition of molality:

$$\text{Mol}_{\text{solute}} = m \text{ x kg solvent} = \frac{0.0698 \text{ mol}}{1 \text{ kg solvent}} \text{ x } 0.002135 \text{ kg solvent} = 1.490 \text{ x } 10^{-4} \text{ mol}$$

$$\text{Molar mass} = \frac{0.0182 \text{ g}}{1.490 \text{ x } 10^{-4} \text{ mol}} = 122.1 = 122 \text{ g/mol}$$

The molecular mass is 122 amu.

12.74. Find the moles of the solute from the definition of molality:

$$\text{Mol}_{\text{solute}} = m \text{ x kg solvent} = \frac{0.0368 \text{ mol}}{1 \text{ kg solvent}} \text{ x } 0.00831 \text{ kg solvent} = 3.058 \text{ x } 10^{-4} \text{ mol}$$

$$\text{Molar mass} = \frac{0.0653 \text{ g}}{3.058 \text{ x } 10^{-4} \text{ mol}} = 213.5 = 214 \text{ g/mol}$$

The molecular mass is 214 amu.

12.75. Calculate ΔT_f, the freezing-point depression, and, using $K_f = 1.858°\text{C}/m$ (Table 12.3), the molality, c_m.

$$\Delta T_f = 26.84°\text{C} - 25.70°\text{C} = 1.14°\text{C}$$

$$c_m = \frac{\Delta T_f}{K_f} = \frac{1.14°\text{C}}{8.00°\text{C}/m} = 0.1425 \, m$$

Find the moles of solute by rearranging the definition of molality:

$$\text{Mol} = m \text{ x kg solvent} = \frac{0.1425 \text{ mol}}{1 \text{ kg solvent}} \text{ x } 103 \text{ x } 10^{-6} \text{ kg solvent} = 1.467 \text{ x } 10^{-5} \text{ mol}$$

$$\text{Molar mass} = \frac{2.39 \text{ x } 10^{-3} \text{ g}}{1.467 \text{ x } 10^{-5} \text{ mol}} = 162.9 = 163 \text{ g/mol}$$

The molecular mass is 163 amu.

12.76. Calculate ΔT_f, the freezing-point depression, and, using $K_f = 5.065°\text{C}/m$ (Table 12.3), the molality, c_m.

$$\Delta T_f = 5.455°\text{C} - 4.880°\text{C} = 0.575°\text{C}$$

$$c_m = \frac{\Delta T_f}{K_f} = \frac{0.575°\text{C}}{5.065°\text{C}/m} = 0.1135 \, m$$

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Find the moles of solute by rearranging the definition of molality:

$$\text{Mol} = m \text{ x kg solvent} = \frac{0.1135 \text{ mol}}{1 \text{ kg solvent}} \text{ x } 0.1000 \text{ kg solvent} = 0.011\underline{3}5 \text{ mol}$$

$$\text{Molar mass} = \frac{2.500 \text{ g}}{0.01135 \text{ mol}} = 22\underline{0}.2 = 2.20 \text{ x } 10^2 \text{ g/mol}$$

The molecular mass is 2.20×10^2 amu.

12.77. Use the equation for osmotic pressure (π) to solve for the molarity of the solution.

$$M = \frac{\pi}{RT} = \frac{1.47 \text{ mmHg x } \left(\frac{1 \text{ atm}}{760 \text{ mmHg}}\right)}{(0.0821 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(21 + 273)\text{K}} = 8.0\underline{1}3 \times 10^{-5} \text{ mol/L}$$

Now, find the number of moles in 106 mL (0.106 L) using the molarity.

$$0.106 \text{ L x } \frac{8.013 \times 10^{-5} \text{ mol}}{1 \text{ L}} = 8.4\underline{9}4 \times 10^{-6} \text{ mol}$$

$$\text{Molar mass} = \frac{0.582 \text{ g}}{8.494 \times 10^{-6} \text{ mol}} = 6.8\underline{5}1 \times 10^4 = 6.85 \times 10^4 \text{ g/mol}$$

The molecular mass is 6.85×10^4 amu.

12.78. Use the equation for osmotic pressure (π) to solve for the molarity of the solution.

$$M = \frac{\pi}{RT} = \frac{3.70 \text{ mmHg x } \left(\frac{1 \text{ atm}}{760 \text{ mmHg}}\right)}{(0.0821 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(25 + 273)\text{K}} = 1.9\underline{8}9 \times 10^{-4} \text{ mol/L}$$

Now, find the number of moles in 100.0 mL (0.1000 L) using the molarity.

$$0.100 \text{ L x } \frac{1.989 \times 10^{-4} \text{ mol}}{1 \text{ L}} = 1.9\underline{8}9 \times 10^{-5} \text{ mol}$$

$$\text{Molar mass} = \frac{0.0216 \text{ g}}{1.989 \times 10^{-5} \text{ mol}} = 1.0\underline{8}59 \times 10^3 = 1.09 \times 10^3 \text{ g/mol}$$

The molecular mass is 1.09×10^3 amu.

12.79. Begin by noting that $i = 3$. Then calculate ΔT_f from the product of $iK_f c_m$:

$$3 \text{ x } \frac{1.858^\circ\text{C}}{m} \text{ x } 0.0075 \, m = 0.041\underline{8}^\circ\text{C}$$

The freezing point = 0.000°C − 0.0418°C = −0.041$\underline{8}$ = −0.042°C.

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12.80. Start by noting that $i = 4$. Then calculate ΔT_f from the product of $iK_f c_m$:

$$4 \text{ x } \frac{1.858°C}{m} \text{ x } 0.0091\ m = 0.06\underline{7}6\ °C$$

The freezing point = 0.000°C − 0.06$\underline{7}$6°C = −0.06$\underline{7}$6 = −0.068°C.

12.81. Begin by calculating the molarity of $Cr(NH_3)_5Cl_3$.

$$1.40 \text{ x } 10^{-2} \text{ g } Cr(NH_3)_5Cl_3 \text{ x } \frac{1 \text{ mol } Cr(NH_3)_5Cl_3}{243.5 \text{ g } Cr(NH_3)_5Cl_3} = 5.7\underline{4}9 \text{ x } 10^{-5} \text{ mol } Cr(NH_3)_5Cl_3$$

$$\text{Molarity} = \frac{5.749 \text{ x } 10^{-5} \text{ mol } Cr(NH_3)_5Cl_3}{0.0250 \text{ L}} = 0.002\underline{2}99\ M$$

Now find the hypothetical osmotic pressure, assuming $Cr(NH_3)_5Cl_3$ does not ionize:

$$\pi = MRT = (2.30 \text{ x } 10^{-3}\ M) \text{ x } \frac{0.0821 \text{ L} \bullet \text{atm}}{\text{K} \bullet \text{mol}} \text{ x } 298 \text{ K} \text{ x } \frac{760 \text{ mmHg}}{1 \text{ atm}} = 42.\underline{7}7 \text{ mmHg}$$

The measured osmotic pressure is greater than the hypothetical osmotic pressure. The number of ions formed per formula unit equals the ratio of the measured pressure to the hypothetical pressure:

$$i = \frac{119 \text{ mmHg}}{42.77 \text{ mmHg}} = 2.7\underline{8}2 \cong 3 \text{ ions/formula unit}$$

12.82. Begin by calculating the molality of the solution after rearranging $\Delta T_b = K_b c_m$:

$$c_m = \frac{\Delta T_b}{K_b} = \frac{5°C}{0.512°C/m} = \underline{9}.76\ m$$

The 9.76 *m* is the molality of the ions, not of the NaCl. The molality of the NaCl will be 9.76 *m* ÷ 2 = 4.88 *m* because $i = 2$. Thus, 4.88 mol of NaCl must be dissolved in the 1 kg of water. This is converted to mass using the molar mass of NaCl:

$$\underline{4}.88 \text{ mol NaCl} \text{ x } \frac{58.5 \text{ g NaCl}}{1 \text{ mol NaCl}} = \underline{2}85 = 3 \text{ x } 10^2 \text{ g NaCl}$$

12.83.

a. Aerosol (liquid water in air)

b. Sol [solid $Mg(OH)_2$ in liquid water]

c. Foam (air in liquid soap solution)

d. Sol (solid silt in liquid water)

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12.84.

a. Aerosol (liquid water in air)

b. Foam (air in liquid egg white)

c. Aerosol (solid dust particles in air)

d. Emulsion (liquid oil in liquid vinegar)

12.85. Because the As_2S_3 particles are negatively charged, the effective coagulation requires a highly charged cation, so $Al_2(SO_4)_3$ is the best choice.

12.86. The K_3PO_4 contains highly charged PO_4^{3-} ions that will be strongly attracted to the positively charged solution and will cause it to coagulate.

SOLUTIONS TO GENERAL PROBLEMS

12.87. Using Henry's law [$S_2 = S_1 \times (P_2/P_1)$, where $P_1 = 1.00$ atm], find the solubility of each gas at P_2, its partial pressure. For N_2, $P_2 = 0.800 \times 1.00$ atm $= 0.800$ atm; for O_2, $P_2 = 0.200$ atm.

$$N_2: S_1 \times \frac{P_2}{P_1} = (0.0175 \text{ g/L } H_2O) \times \frac{0.800 \text{ atm}}{1.00 \text{ atm}} = 0.014\underline{0}0 \text{ g/L } H_2O$$

$$O_2: S_2 \times \frac{P_2}{P_1} = (0.0393 \text{ g/L } H_2O) \times \frac{0.200 \text{ atm}}{1.00 \text{ atm}} = 0.007\underline{8}60 \text{ g/L } H_2O$$

In 1.00 L of the water, there are 0.0140 g of N_2 and 0.00786 g of O_2. If the water is heated to drive off both dissolved gases, the gas mixture that is expelled will contain 0.0140 g of N_2 and 0.00786 g of O_2.

Convert both masses to moles using the molar masses:

$$0.0140 \text{ g } N_2 \times \frac{1 \text{ mol } N_2}{28.01 \text{ g } N_2} = 4.9\underline{9}8 \times 10^{-4} \text{ mol}$$

$$0.00786 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 2.4\underline{5}6 \times 10^{-4} \text{ mol}$$

Now calculate the mole fraction of each gas:

$$X_{N_2} = \frac{\text{mol } N_2}{\text{total mol}} = \frac{4.998 \times 10^{-4} \text{ mol}}{(4.998 + 2.456) \times 10^{-4} \text{ mol}} = 0.67\underline{0}51 = 0.671$$

$$X_{O_2} = 1 - X_{N_2} = 1 - 0.67\underline{0}51 = 0.32\underline{9}49 = 0.329$$

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12.88. Using Henry's law [$S_2 = S_1$ x (P_2/P_1), where P_1 = 1.00 atm], find the solubility of each gas at P_2, its partial pressure. For CH_4, P_2 = 0.900 x 1.00 atm = 0.900 atm; for C_2H_6, P_2 = 0.100 x 1.00 atm = 0.100 atm.

$$CH_4: S_1 \text{ x } \frac{P_2}{P_1} = (0.023 \text{ g/L } H_2O) \text{ x } \frac{0.900 \text{ atm}}{1.00 \text{ atm}} = 0.02\underline{0}7 \text{ g/L } H_2O$$

$$C_2H_6: S_1 \text{ x } \frac{P_2}{P_1} = 0.059 \text{ g/L } H_2O \text{ x } \frac{0.100 \text{ atm}}{1.00 \text{ atm}} = 0.005\underline{9}0 \text{ g/L } H_2O$$

When 1.00 L of the water saturated with the gas mixture is heated, 0.0207 g of CH_4 and 0.0059 g of C_2H_6 will be expelled.

Convert these to moles using molar masses:

$$0.0207 \text{ g } CH_4 \text{ x } \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} = 1.2\underline{9}1 \text{ x } 10^{-3} \text{ mol}$$

$$0.0059 \text{ g } C_2H_6 \text{ x } \frac{1 \text{ mol } C_2H_6}{30.07 \text{ g } C_2H_6} = 1.\underline{9}62 \text{ x } 10^{-4} \text{ mol}$$

Now, find the mole fraction of each gas:

$$X_{CH_4} = \frac{\text{mol } CH_4}{\text{total mol}} = \frac{1.\underline{2}91 \text{ x } 10^{-3} \text{ mol}}{(1.291 + 0.196) \text{ x } 10^{-3} \text{ mol}} = 0.8\underline{6}819 = 0.87$$

$$X_{C_2H_6} = 1 - X_{CH_4} = 1 - 0.086819 = 0.1\underline{3}181 = 0.13$$

12.89. Assume a volume of 1.000 L whose mass is then 1.024 kg. Use the percent composition given to find the mass of each of the components of the solution.

$$1.024 \text{ kg soln x } \frac{8.50 \text{ kg } NH_4Cl}{100.00 \text{ kg soln}} = 0.087\underline{0}4 \text{ kg } NH_4Cl$$

$$\text{Mass of } H_2O = 1.024 \text{ kg soln} - 0.08704 \text{ kg } NH_4Cl = 0.9370 \text{ kg } H_2O$$

Convert mass of NH_4Cl and water to moles:

$$87.04 \text{ g } NH_4Cl \text{ x } \frac{1 \text{ mol } NH_4Cl}{53.49 \text{ g } NH_4Cl} = 1.6\underline{2}7 \text{ mol } NH_4Cl$$

$$937.0 \text{ g } H_2O \text{ x } \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} = 52.\underline{0}1 \text{ mol } H_2O$$

$$\text{Molarity} = \frac{\text{mol } NH_4Cl}{\text{L solution}} = \frac{1.627 \text{ mol}}{1.00 \text{ L}} = 1.6\underline{2}7 = 1.63 \, M$$

$$\text{Molality} = \frac{\text{mol } NH_4Cl}{\text{kg } H_2O} = \frac{1.627 \text{ mol}}{0.9370 \text{ kg } H_2O} = 1.7\underline{3}6 = 1.74 \, m$$

$$X_{NH_4Cl} = \frac{\text{mol } NH_4Cl}{\text{total moles}} = \frac{1.627 \text{ mol}}{(52.01 + 1.627) \text{ mol}} = 0.030\underline{3}3 = 0.0303$$

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12.90. Assume a volume of 1.000 L whose mass is then 1.127 kg. Use the percent composition given to find the mass of each of the components of the solution.

$$1.127 \text{ kg soln} \times \frac{27.0 \text{ kg LiCl}}{100.00 \text{ kg soln}} = 0.3042 \text{ kg} = 304.2 \text{ g LiCl}$$

$$\text{Mass of } H_2O = 1.127 \text{ kg soln} - 0.3042 \text{ kg LiCl} = 0.8227 \text{ kg} = 822.7 \text{ g } H_2O$$

Convert mass of LiCl and water to moles:

$$304.2 \text{ g LiCl} \times \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}} = 7.178 \text{ mol LiCl}$$

$$822.7 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g } H_2O} = 45.66 \text{ mol } H_2O$$

$$\text{Total moles} = 7.178 + 45.66 = 52.838 \text{ mol}$$

The various quantities can now be calculated.

$$\text{Molarity} = \frac{\text{mol LiCl}}{\text{L soln}} = \frac{7.178 \text{ mol LiCl}}{1.000 \text{ L soln}} = 7.178 = 7.18\ M$$

$$\text{Molality} = \frac{\text{mol LiCl}}{\text{kg } H_2O} = \frac{7.178 \text{ mol LiCl}}{0.8227 \text{ kg } H_2O} = 8.7249 = 8.72\ m$$

$$X_{\text{LiCl}} = \frac{\text{mol LiCl}}{\text{total moles}} = \frac{7.178 \text{ mol LiCl}}{52.838 \text{ mol}} = 0.1358 = 0.136$$

12.91. In 1.00 mol of gas mixture, there are 0.51 mol of propane (pro.) and 0.49 mol of butane (but.). First, calculate the masses of these components.

$$0.51 \text{ mol pro.} \times \frac{44.10 \text{ g pro.}}{1 \text{ mol pro.}} = 22.491 \text{ g pro.}$$

$$0.49 \text{ mol but.} \times \frac{58.12 \text{ g but.}}{1 \text{ mol but.}} = 28.478 \text{ g but.}$$

The mass of 1.00 mol of gas mixture is the sum of the masses of the two components:

$$22.491 \text{ g pro.} + 28.478 \text{ g but.} = 50.969 \text{ g mixture}$$

Therefore, in 50.969 g of the mixture, there are 22.491 g of propane and 28.478 g of butane.

For a sample with a mass of 55 g,

$$55 \text{ g mixture} \times \frac{22.491 \text{ g pro.}}{50.969 \text{ g mixture}} = 24.26 = 24 \text{ g pro.}$$

$$55 \text{ g mixture} \times \frac{28.478 \text{ g but.}}{50.969 \text{ g mixture}} = 30.73 = 31 \text{ g but.}$$

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12.92. In 1.000 mol of gas mixture, there are 0.036 mol O_2, 0.056 mol N_2, and 0.908 mol He. Calculate the masses of these components first.

$$0.036 \text{ mol } O_2 \text{ x } \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 1.\underline{1}5 \text{ g } O_2$$

$$0.056 \text{ mol } N_2 \text{ x } \frac{28.01 \text{ g } N_2}{1 \text{ mol } N_2} \quad 1.\underline{5}7 \text{ g } N_2$$

$$0.908 \text{ mol He x } \frac{4.0026 \text{ g He}}{1 \text{ mol He}} = 3.6\underline{3}4 \text{ g He}$$

The mass of 1.000 mol of the gas mixture is the sum of the masses of the components:

$$1.15 \text{ g } O_2 + 1.57 \text{ g } N_2 + 3.634 \text{ g He} = 6.35 \text{ g mixture}$$

For a sample with a mass of 8.32 g,

$$8.32 \text{ g mixture x } \frac{1.15 \text{ g } O_2}{6.35 \text{ g mixture}} = 1.\underline{5}0 = 1.5 \text{ g } O_2$$

$$8.32 \text{ g mixture x } \frac{1.57 \text{ g } N_2}{6.35 \text{ g mixture}} = 2.\underline{0}5 = 2.1 \text{ g } N_2$$

$$8.32 \text{ g mixture x } \frac{3.634 \text{ g He}}{6.35 \text{ g mixture}} = 4.\underline{7}6 = 4.8 \text{ g He}$$

12.93. $P_{ED} = P°_{ED}(X_{ED}) = 173 \text{ mmHg } (0.25) = 4\underline{3}.25 \text{ mmHg}$

$P_{PD} = P°_{PD}(X_{PD}) = 127 \text{ mmHg } (0.75) = 9\underline{5}.25 \text{ mmHg}$

$P = P_{ED} + P_{PD} = 4\underline{3}.25 + 9\underline{5}.25 = 13\underline{8}.50 = 139 \text{ mmHg}$

12.94. $P_B = P°_B(X_B) = 75 \text{ mmHg } (0.30) = 2\underline{2}.5 \text{ mmHg}$

$P_T = P°_T(X_T) = 22 \text{ mmHg } (0.70) = 1\underline{5}.4 \text{ mmHg}$

$P = P_B + P_T = 22.5 + 15.4 = 3\underline{7}.9 = 38 \text{ mmHg}$

12.95. Calculate the moles of $KAl(SO_4)_2 \cdot 12H_2O$ using its molar mass of 474.4 g/mol, and use this to calculate the three concentrations.

a. The moles of $KAl(SO_4)_2 \cdot 12H_2O$ are calculated below, using the abbreviation "Hyd" for the formula of $KAl(SO_4)_2 \cdot 12H_2O$.

$$\text{moles Hyd} = 0.1186 \text{ g Hyd x } \frac{1 \text{ mol Hyd}}{474.4 \text{ g Hyd}} = 0.00025\underline{0}0 = 0.0002500 \text{ mol}$$

Note that 1 mol of $KAl(SO_4)_2 \cdot 12H_2O$ contains 1 mole of $KAl(SO_4)_2$, so the molarity of $KAl(SO_4)_2$ can be calculated using the moles of $KAl(SO_4)_2 \cdot 12H_2O$.

$$\frac{\text{mol}}{\text{L}} = \frac{0.0002500 \text{ mol Hyd}}{1.000 \text{ L soln}} \text{ x } \frac{1 \text{ mol } KAl(SO_4)_2}{1 \text{ mol Hyd}} = 0.0002500 \, M \, KAl(SO_4)_2$$

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b. The molarity of the SO_4^{2-} ion will be twice that of the $KAl(SO_4)_2$.

$$\frac{\text{mol } SO_4^{2-}}{\text{L}} = 0.0002500\ M\ KAl(SO_4)_2 \times \frac{2\text{ mol } SO_4^{2-}}{1\text{ mol } KAl(SO_4)_2} = 0.0005000\ M$$

c. Since the density of the solution is 1.00 g/mL, the mass of 1.000 L of solution is 1000 g, or 1.000 kg. Since molality is moles per 1.000 kg of solvent, the molality of $KAl(SO_4)_2$ equals 0.0002500 mol divided by 1.000 kg or 0.0002500 *m* (the same as the molarity).

12.96. Calculate the moles of $Al_2(SO_4)_3 \cdot 18H_2O$ using its molar mass of 666.46 g/mol, and use this to calculate the three concentrations.

a. The moles of $Al_2(SO_4)_3 \cdot 18H_2O$ are calculated below, using the abbreviation "Hyd" for the formula of $Al_2(SO_4)_3 \cdot 18H_2O$.

$$\text{moles of Hyd} = 0.1593\text{ g Hyd} \times \frac{1\text{ mol Hyd}}{666.46\text{ g Hyd}} = 2.39\underline{0}2 \times 10^{-4}\text{ mol}$$

Note that 1 mole of $Al_2(SO_4)_3 \cdot 18H_2O$ contains 1 mole of $Al_2(SO_4)_3$, so the molarity of $Al_2(SO_4)_3$ can be calculated using the moles of $Al_2(SO_4)_3 \cdot 18H_2O$.

$$\text{Molarity} = \frac{\text{mol Hyd}}{\text{L soln}} = \frac{2.3902 \times 10^{-4}\text{ mol}}{1.000\text{ L soln}} = 2.39\underline{0}2 \times 10^{-4} = 2.390 \times 10^{-4}\ M$$

b. The molarity of the SO_4^{2-} ion will be three times that of the $Al_2(SO_4)_3$:

$$2.3902 \times 10^{-4}\text{ mol } Al_2(SO_4)_3 \times \frac{3\text{ mol } SO_4^{2-}}{1\text{ mol } Al_2(SO_4)_3} = 7.17\underline{0}7 \times 10^{-4} = 7.171 \times 10^{-4}\ M$$

c. Since the density of the solution is 1.00 g/mL, the mass of 1.000 L of the solution is 10$\underline{0}$0. g. Of this, 0.1593 g is solute; however, since the compound is a hydrate, 0.07751 grams of this mass of solute is water. Therefore the mass of just the $Al_2(SO_4)_3$ is

$$1000. - (0.1593 - 0.07751) = 99\underline{9}.91\text{ g} = 0.99\underline{9}91\text{ kg } H_2O$$

The molality of $Al_2(SO_4)_3$ can now be calculated.

$$\text{Molality} = \frac{\text{mol } Al_2(SO_4)_3}{\text{kg } H_2O} = \frac{2.3902 \times 10^{-4}\text{ mol}}{0.99\underline{9}91\text{ kg}} = 2.3\underline{9}04 \times 10^{-4} = 2.39 \times 10^{-4}\ M$$

12.97. In 1.00 kg of a saturated solution of urea, there are 0.41 kg of urea (a molecular solute) and 0.59 kg of water. First, convert the mass of urea to moles.

$$0.41 \times 10^3\text{ g urea} \times \frac{1\text{ mol urea}}{60.06\text{ g urea}} = 6.\underline{8}26\text{ mol urea}$$

Then find the molality of the urea in the solution:

$$\text{Molality} = \frac{\text{mol urea}}{\text{kg } H_2O} \times \frac{6.826\text{ mol urea}}{0.59\text{ kg}} = 1\underline{1}.57\ m$$

$$\Delta T_f = K_f c_m = (1.858°\text{C}/m)(11.57\ m) = 2\underline{1}.4°\text{C}$$

$$T_f = 0.0°\text{C} - 21.4°\text{C} = -2\underline{1}.4 = -21°\text{C}$$

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12.98. In 1.00 kg of a saturated solution of $CaCl_2$, there are 0.32 kg of $CaCl_2$ (ionic) and 0.68 kg of water. First, convert the mass of $CaCl_2$ to moles.

$$0.32 \times 10^3 \text{ g } CaCl_2 \times \frac{1 \text{ mol } CaCl_2}{111.0 \text{ g } CaCl_2} = 2.\underline{8}8 \text{ mol } CaCl_2$$

Then find the molality of the $CaCl_2$ in the solution:

$$\text{Molality} = \frac{\text{mol } CaCl_2}{\text{kg } H_2O} \times \frac{2.88 \text{ mol } CaCl_2}{0.68 \text{ kg}} = 4.\underline{2}4 \ m$$

For ionic solutions,

$$\Delta T_f = iK_f c_m$$

Calcium chloride dissolves to give three ions; thus $i = 3$, and

$$\Delta T_f = (1.858°C/m)(3)(4.24 \ m) = 2\underline{3}.6°C$$

$$T_f = 0.0°C - 2\underline{3}.6°C = -24°C$$

12.99. $$M = \frac{\pi}{RT} = \frac{7.7 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(37 + 273)\text{K}} = 0.3\underline{0}2 = 0.30 \text{ mol/L}$$

12.100. $$M = \frac{\pi}{RT} = \frac{5.50 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(25 + 273)\text{K}} = 0.22\underline{4}8 = 0.225 \text{ mol/L}$$

12.101. Consider the equation $\Delta T_f = iK_f c_m$. For $CaCl_2$, $i = 3$; for glucose, $i = 1$. Because $c_m = 0.10$ for both solutions, the product of i and c_m will be larger for $CaCl_2$, as will ΔT_f. The solution of $CaCl_2$ will thus have the lower freezing point.

12.102. Consider the equation $\Delta T_b = iK_b c_m$. For $CaCl_2$, $i = 3$; for KCl it is 2. The product of i and c_m will be larger for $CaCl_2$, as will ΔT_b. The solution of KCl will thus have the lower boiling point.

12.103. Assume there is 1.000 L of the solution, which will contain 18 mol H_2SO_4, molar mass 98.09 g/mol. The mass of the solution is

$$\text{Mass solution} = \frac{18 \text{ mol} \times 98.09 \text{ g/mol}}{0.98} = 1\underline{8}02 \text{ g}$$

Thus, the density of the solution is

$$d = \frac{1802 \text{ g}}{1000 \text{ mL}} = 1.8\underline{0}2 = 1.8 \text{ g/mL}$$

The mass of water in the solution is

$$\text{Mass } H_2O = 1802 \text{ g} \times 0.02 = \underline{3}6.0 \text{ g} = 0.0\underline{3}60 \text{ kg}$$

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Thus, the molality of the solution is

$$m = \frac{18 \text{ mol } H_2SO_4}{0.0360 \text{ Kg}} = \underline{5}00 = 5 \times 10^2 \, m$$

12.104. Assume there is 1.000 L of the solution, which will contain 15 mol H_3PO_4, molar mass 97.99 g/mol. The mass of the solution is

$$\text{Mass solution} = \frac{15 \text{ mol} \times 97.99 \text{ g/mol}}{0.85} = 1\underline{7}29 \text{ g}$$

Thus, the density of the solution is

$$d = \frac{1729 \text{ g}}{1000 \text{ mL}} = 1.\underline{7}29 = 1.7 \text{ g/mL}$$

The mass of water in the solution is

$$\text{Mass } H_2O = 1729 \text{ g} \times 0.15 = 2\underline{5}9 \text{ g} = 0.2\underline{5}9 \text{ kg}$$

Thus, the molality of the solution is

$$m = \frac{15 \text{ mol } H_3PO_4}{0.0259 \text{ Kg}} = 5\underline{7}.9 = 58 \, m$$

12.105. Use the freezing-point-depression equation to find the molality of the solution. The freezing point of pure cyclohexane is 6.55°C, and $K_f = 20.0°C/m$. Thus

$$m = \frac{\Delta T_f}{K_f} = \frac{(6.55 - 5.28)°C}{20.0°C/m} = 0.063\underline{5}0 \, m$$

The moles of the compound are

$$\text{Moles of compound} = \frac{0.06350 \text{ mol}}{1 \text{ kg solvent}} \times 0.00538 \text{ kg} = 3.4\underline{1}6 \times 10^{-4} \text{ mol}$$

The molar mass of the compound is

$$\text{Molar mass} = \frac{0.125 \text{ g}}{3.416 \times 10^{-4} \text{ mol}} = 36\underline{5}.8 \text{ g/mol}$$

The moles of the elements in 100 g of the compound are

$$\text{Moles of Mn} = 28.17 \text{ g Mn} \times \frac{1 \text{ mol}}{54.94 \text{ g Mn}} = 0.5127\underline{4} \text{ mol}$$

$$\text{Moles of C} = 30.80 \text{ g C} \times \frac{1 \text{ mol}}{12.01 \text{ g C}} = 2.56\underline{4}5 \text{ mol}$$

$$\text{Moles of O} = 41.03 \text{ g O} \times \frac{1 \text{ mol}}{16.00 \text{ g O}} = 2.56\underline{4}4 \text{ mol}$$

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This gives mole ratios of 1 mol Mn to 5 mol C to 5 mol O. Therefore, the empirical formula of the compound is MnC_5O_5. The mass of this formula unit is approximately 195 amu. Since the molar mass of the compound is 366. g/mol, the value of *n* is

$$n = \frac{366\ \text{g/mol}}{195\ \text{g/unit}} = 1.88, \text{ or } 2$$

Therefore, the formula of the compound is $Mn_2C_{10}O_{10}$.

12.106. Use the freezing-point-depression equation to find the molality of the solution. The freezing point of pure cyclohexane is 6.55°C, and $K_f = 20.0°C/m$. Thus

$$m = \frac{\Delta T_f}{K_f} = \frac{(6.55 - 5.23)°C}{20.0°C/m} = 0.06600\ m$$

The moles of the compound are

$$\text{Moles of compound} = \frac{0.06600\ \text{mol}}{1\ \text{kg solvent}} \times 0.00672\ \text{kg} = 4.435 \times 10^{-4}\ \text{mol}$$

The molar mass of the compound is

$$\text{Molar mass} = \frac{0.147\ \text{g}}{4.435 \times 10^{-4}\ \text{mol}} = 331.4\ \text{g/mol}$$

The moles of the elements in 100 g of the compound are

$$\text{Moles of Co} = 34.47\ \text{g Co} \times \frac{1\ \text{mol}}{58.93\ \text{g Co}} = 0.58493\ \text{mol}$$

$$\text{Moles of C} = 28.10\ \text{g C} \times \frac{1\ \text{mol}}{12.01\ \text{g C}} = 2.3397\ \text{mol}$$

$$\text{Moles of O} = 37.43\ \text{g O} \times \frac{1\ \text{mol}}{16.00\ \text{g O}} = 2.3394\ \text{mol}$$

This gives mole ratios of 1 mol Co to 4 mol C to 4 mol O. Therefore, the empirical formula of the compound is CoC_4O_4. The mass of this formula unit is approximately 171 amu. Since the molar mass of the compound is 331. g/mol, the value of *n* is

$$n = \frac{331\ \text{g/mol}}{171\ \text{g/unit}} = 1.93, \text{ or } 2$$

Therefore, the formula of the compound is $Co_2C_8O_8$.

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12.107.

a. Use the freezing-point-depression equation to find the molality of the solution. The freezing point of pure water is 0°C and K_f = 1.858°C/*m*. Thus

$$m = \frac{\Delta T_f}{K_f} = \frac{[0 - (-2.2)]°C}{1.858°C/m} = 1.\underline{1}84\ m$$

The moles of the compound are

$$\text{Moles of compound} = \frac{1.184\ \text{mol}}{1\ \text{kg solvent}} \times 0.100\ \text{kg} = 0.1\underline{1}84\ \text{mol}$$

The molar mass of the compound is

$$\text{Molar mass} = \frac{18.0\ \text{g}}{0.1184\ \text{mol}} = 1\underline{5}2.0\ \text{g/mol}$$

The moles of the elements in 100 g of the compound are

$$\text{Moles of C} = 48.64\ \text{g C} \times \frac{1\ \text{mol}}{12.01\ \text{g C}} = 4.05\underline{0}0\ \text{mol}$$

$$\text{Moles of H} = 8.16\ \text{g H} \times \frac{1\ \text{mol}}{1.008\ \text{g H}} = 8.0\underline{9}5\ \text{mol}$$

$$\text{Moles of O} = 43.20\ \text{g O} \times \frac{1\ \text{mol}}{16.00\ \text{g O}} = 2.70\underline{0}0\ \text{mol}$$

This gives mole ratios of 1.5 mol C to 3 mol H to 1 mol O. Multiplying by 2 gives ratios of 3 mol C to 6 mol H to 2 mol O. Therefore, the empirical formula of the compound is $C_3H_6O_2$. The mass of this formula unit is approximately 74 amu. Since the molar mass of the compound is 152.0. g/mol, the value of *n* is

$$n = \frac{152.0\ \text{g/mol}}{74\ \text{g/unit}} = 2.05, \text{ or } 2$$

Therefore, the formula of the compound is $C_6H_{12}O_4$.

b. The molar mass of the compound is (to the nearest tenth of a gram)

$$6(12.01) + 12(1.008) + 4(16.00) = 148.\underline{1}56 = 148.2\ \text{g/mol}$$

12.108.

a. Use the freezing-point-depression equation to find the molality of the solution. The freezing point of naphthalene is 80.0 °C and K_f = 6.8°C/*m*. Thus

$$m = \frac{\Delta T_f}{K_f} = \frac{(80.0 - 78.0)°C}{6.8°C/m} = 0.2\underline{9}4\ m$$

The moles of the compound are

$$\text{Moles of compound} = \frac{0.294\ \text{mol}}{1\ \text{kg solvent}} \times 0.00750\ \text{kg} = 2.\underline{2}1 \times 10^{-3}\ \text{mol}$$

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The molar mass of the compound is

$$\text{Molar mass} = \frac{0.855\ \text{g}}{2.21 \times 10^{-3}\ \text{mol}} = 3\underline{8}7\ \text{g/mol}$$

The moles of the elements in 100 g of the compound are

$$\text{Moles of C} = 39.50\ \text{g C} \times \frac{1\ \text{mol}}{12.01\ \text{g C}} = 3.28\underline{8}9\ \text{mol}$$

$$\text{Moles of H} = 2.21\ \text{g H} \times \frac{1\ \text{mol}}{1.008\ \text{g H}} = 2.1\underline{9}2\ \text{mol}$$

$$\text{Moles of Cl} = 58.30\ \text{g Cl} \times \frac{1\ \text{mol}}{35.45\ \text{g Cl}} = 1.64\underline{4}6\ \text{mol}$$

This gives mole ratios of 2 mol C to 1.33 mol H to 1 mol Cl. Multiplying by 3 gives ratios of 6 mol C to 4 mol H to 3 mol Cl. Therefore, the empirical formula of the compound is $C_6H_4Cl_3$. The mass of this formula unit is approximately 182.5 amu. Since the molar mass of the compound is 387. g/mol, the value of n is

$$n = \frac{387\ \text{g/mol}}{182.5\ \text{g/unit}} = 2.12, \text{ or } 2$$

Therefore, the formula of the compound is $C_{12}H_8Cl_6$.

b. The molar mass of the compound is (to the nearest tenth of a gram)

$$12(12.01) + 8(1.008) + 6(35.45) = 364.\underline{8}84 = 364.9\ \text{g/mol}$$

12.109. Use the freezing-point-depression equation to find the molality of the solution. The freezing point of pure water is 0°C, and $K_f = 1.86°\text{C}/m$. Thus

$$m = \frac{\Delta T_f}{K_f} = \frac{[0 - (-2.3)]°\text{C}}{1.86°\text{C}/m} = 1.\underline{2}4\ m$$

Since this is a relatively dilute solution, we can assume the molarity and molality of the fish blood are approximately equal. The calculated molarity is for the total number of particles, assuming they behave ideally.

$$\pi = MRT = 1.\underline{2}4\ \text{mol/L} \times 0.08206\ \text{L•atm/K•mol} \times 298.2\ \text{K} = 3\underline{0}.3 = 30.\ \text{atm}$$

12.110. Use the osmotic-pressure equation to find the molarity of the solution.

$$M = \frac{\pi}{RT} = \frac{17\ \text{atm}}{0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol} \times 295.2\ \text{K}} = 0.7\underline{0}1\ M$$

Since this is a relatively dilute solution, we can assume the molality and molarity of the solution are approximately equal and that the electrolyte (salt) is behaving ideally. The calculated temperature change is

$$\Delta T = K_f m = 1.86°\text{C}/m \times 0.701\ m = 1.\underline{3}0°\text{C}$$

Therefore, the solution will freeze at −1.3°C.

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12.111. Hemoglobin is the substance in red blood cells that carries oxygen. Hemoglobin is normally present in solution within the red blood cells. But in people with sickle-cell anemia, the unoxygenated hemoglobin readily comes out of solution. It produces a fibrous precipitate that deforms the cell, giving it the characteristic sickle shape. Normal and sickle-cell hemoglobins are almost exactly alike, except that each β chain of the hemoglobin responsible for sickle-cell anemia differs from normal hemoglobin in one place. In this place, the normal hemoglobin has the group that helps confer water solubility on the molecule because of the polarity of the group and its ability to form hydrogen bonds.

12.112. In people with the disease, the red blood cells tend to become elongated (sickle-shaped) when the concentration of oxygen (O_2) is low, as it is in the venus blood supply. Once the red blood cells have sickled, they can no longer function in their normal capacity as oxygen carriers, and they often break apart. Moreover, the sickled cells clog capillaries, interfering with the blood supply to vital organs.

12.113. Like a soap ion, a phospholipid has a hydrophobic end (the two hydrocarbon groups) and a hydrophilic end (an ionic portion containing a phosphate group, $-PO_4^-$–). Like soap ions, phospholipid molecules in water tend to associate so that their hydrophilic (or ionic) heads dip into the water, with their hydrophobic (or hydrocarbon) tails pointing away. However, the hydrocarbon tails of a phospholipid molecule are too bulky to associate into micelles and instead form a bilayer, a layer two molecules thick.

12.114. Recently, chemists have prepared cell-like structures (lipid vesicles) from phospholipids and have used them to carry out chemical reactions by combining the contents of two lipid vesicles, with diameters from about 50 nanometers to several micrometers. These lipid vesicles are the world's smallest test tubes. In one experiment, two phospholipid vesicles, each about a micrometer in diameter and containing different reactant substances, were brought together under a special microscope. When the vesicles just touched, the researchers delivered an electrical pulse to them that opened a small pore in each vesicle. The two vesicles coalesced into one, and their contents reacted.

SOLUTIONS TO STRATEGY PROBLEMS

12.115. $$\text{Moles solute} = \frac{\Delta T_f}{K_f} \text{ x kg solvent} = \frac{1.34°\text{C}}{1.858°\text{C/m}} \text{ x } 0.878 \text{ kg} = 0.6332 \text{ mol}$$

$$\text{Molar mass} = \frac{\text{mass}}{\text{moles}} = \frac{79.3 \text{ g}}{0.6332 \text{ mol}} = 125.2 = 125 \text{ g/mol}$$

The molecular mass of the compound is 125 amu.

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12.116. First calculate the moles and molality of magnesium chloride. Use a molar mass of 95.21 g/mol.

$$\text{Moles} = \frac{6.69\text{ g}}{95.21\text{ g/mol}} = 0.070\underline{2}6\text{ mol}$$

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.07026\text{ mol}}{0.2433\text{ kg}} = 0.28\underline{8}8\ m$$

Next calculate the boiling-point elevation. For magnesium chloride, $MgCl_2$, $i = 3$.

$$\Delta T_b = iK_bm = (3)\text{ x }(0.512°\text{C}/m)\text{ x }(0.2888\ m) = 0.44\underline{3}6 = 0.444°\text{C}.$$

Finally, the boiling point of the solution is

$$T_b = T_b° + \Delta T_b = 100°\text{C} + 0.4436°\text{C} = 100.44\underline{3}6 = 100.444°\text{C}$$

12.117. $S_2 = S_1 \text{ x } \frac{P_2}{P_1} = 15.6\text{ g/L x } \frac{24.6\text{ atm}}{2.14\text{ atm}} = 17\underline{9}.3 = 179\text{ g/L}$

If the temperature of the liquid were increased, the solubility of the gas would decrease.

12.118. First calculate the mass of each component in a solution containing 1 mol. The molar mass of methanol (CH_3OH) is 32.042 g/mol, and the molar mass of water is 18.015 g/mol.

$$\text{Mass } CH_3OH = 0.520\text{ mol x } \frac{32.042\text{ g}}{1\text{ mol}} = 16.\underline{6}61\text{ g}$$

$$\text{Mass } H_2O = 0.480\text{ mol x } \frac{18.015\text{ g}}{1\text{ mol}} = 8.6\underline{4}7\text{ g}$$

The mass percentage water can now be calculated.

$$\text{Mass \% } H_2O = \frac{\text{mass water}}{\text{mass solution}} = \frac{8.647\text{ g}}{8.647\text{ g} + 16.661\text{ g}} = \frac{8.647\text{ g}}{25.309\text{ g}} = 0.34\underline{1}6 = 0.342$$

12.119. The molar mass of potassium chloride (KCl) is 74.55 g/mol. The mass required is

$$(0.110\ m)\text{ x }(0.372\text{ kg})\text{ x }(74.55\text{ g/mol}) = 3.0\underline{5}0 = 3.05\text{ g}$$

12.120. The molar mass of barium chloride ($BaCl_2$) is 208.23 g/mol.

$$427\text{ g x }0.0317\text{ x }\frac{1\text{ mol}}{208.23\text{ g}} = 0.065\underline{0}0 = 0.0650\text{ mol}$$

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12.121. First calculate the moles of each substance. The molar mass of ethanol (C_2H_5OH) is 46.068 g/mol, and the molar mass of water is 18.015 g/mol.

$$\text{Moles of } C_2H_5OH = 4.76 \text{ g} \times \frac{1 \text{ mol}}{46.068 \text{ g}} = 0.10\underline{3}3 \text{ mol}$$

$$\text{Moles of } H_2O = 50.0 \text{ g} \times \frac{1 \text{ mol}}{18.015 \text{ g}} = 2.7\underline{7}54 \text{ mol}$$

The mole fraction of ethanol can now be calculated.

$$X_{C_2H_5OH} = \frac{\text{mol } C_2H_5OH}{\text{total mol}} = \frac{0.1033 \text{ mol}}{0.1033 \text{ mol} + 2.775 \text{ mol}} = 0.035\underline{8}9 = 0.0359$$

12.122. First, calculate the moles and molarity of the starch.

$$\text{Moles} = 0.759 \text{ g} \times \frac{1 \text{ mol}}{3.20 \times 10^4 \text{ g}} = 2.3\underline{7}1 \times 10^{-5} \text{ mol}$$

$$\text{Molarity} = \frac{2.371 \times 10^{-5} \text{ mol}}{0.112 \text{ L}} = 2.1\underline{1}7 \times 10^{-4} \, M$$

The osmotic pressure can now be calculated.

$$\pi = MRT = 2.117 \times 10^{-4} \text{ mol/L} \times 0.08206 \text{ L•atm/K•mol} \times 298.15 \text{ K} \times \frac{760 \text{ torr}}{1 \text{ atm}}$$

$$= 3.9\underline{3}7 = 3.94 \text{ torr}$$

12.123. Assume 1 L of solution. The molar mass of magnesium chloride ($MgCl_2$) is 95.21 g/mol. The mass of magnesium chloride, the mass of water, and the mass of the solution are

$$\text{Mass } MgCl_2 = 0.797 \text{ mol} \times \frac{95.21 \text{ g}}{1 \text{ mol}} = 75.\underline{8}82 \text{ g}$$

$$\text{Mass solution} = d \times V = 1.108 \text{ g/mL} \times 1000 \text{ mL} = 1108 \text{ g}$$

$$\text{Mass water} = 1108 \text{ g} - 75.882 \text{ g} = 1032.\underline{1}1 \text{ g} = 1032.1 \text{ g} = 1.0321 \text{ kg}$$

The molality can now be calculated.

$$\text{Molality} = \frac{0.797 \text{ mol}}{1.0321 \text{ kg}} = 0.77\underline{2}1 = 0.772 \, m$$

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12.124. First calculate the molarity of the solution. For $CaCl_2$ use $i = 3$.

$$\text{Molarity} = \frac{\pi}{iRT} = \frac{16 \text{ atm}}{3 \text{ x } 0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol x } 298.15 \text{ K}} = 0.2\underline{1}80 \ M$$

Next, determine the molality of the solution. Assume 1 L of solution. The molar mass of calcium chloride ($CaCl_2$) is 110.98 g/mol. The mass of calcium chloride, the mass of water, and the mass of the solution are

$$\text{Mass } CaCl_2 = 0.2180 \text{ mol x } \frac{110.98 \text{ g}}{1 \text{ mol}} = 2\underline{4}.19 \text{ g}$$

$$\text{Mass solution} = d \text{ x } V = 1.108 \text{ g/mL x } 100 \text{ mL} = 1108 \text{ g}$$

$$\text{Mass } H_2O = 1108 \text{ g} - 24.19 \text{ g} = 108\underline{3}.8 \text{ g} = 1.08\underline{3}8 \text{ kg}$$

The molality of the solution is

$$\text{Molality} = \frac{0.2180 \text{ mol}}{1.0838 \text{ kg}} = 0.2\underline{0}11 \ m$$

For $CaCl_2$, $i = 3$ The freezing-point depression is

$$\Delta T_f = iK_f m = (3) \text{ x } (1.858°\text{C}/m) \text{ x } (0.2011 \ m) = 1.\underline{1}21 = 1.1°\text{C}$$

The freezing point of the solution can now be calculated.

$$T_f = T_f° - \Delta T_f = 0°\text{C} - 1.121°\text{C} = -1.\underline{1}21 = -1.1°\text{C}$$

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

12.125. First, determine the initial moles of each ion present in the solution before any reaction has occurred. There are five ions present: Na^+, 2 x 0.375 = 0.750 mol; CO_3^{2-}, 0.375 mol; Ca^{2+}, 0.125 mol; Ag^+, 0.200 mol; and NO_3^-, 0.200 + 2 x 0.125 = 0.450 mol. Two precipitates form: $CaCO_3$ and Ag_2CO_3. The balanced net ionic equations for their formation are

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

$$2Ag^+(aq) + CO_3^{2-}(aq) \rightarrow Ag_2CO_3(s)$$

There is sufficient CO_3^{2-} to precipitate all of the Ca^{2+} and all of the Ag^+ ions. The moles of excess CO_3^{2-} are calculated as follows: 0.375 − 0.125 − 1/2 x 0.200 = 0.150 mol remaining. Since the volume is 2.000 L, the molarities of the various ions are

$$M \text{ of } CO_3^{2-} \text{ left} = 0.150 \text{ mol} \div 2.000 \text{ L} = 0.0750 \ M$$

$$M \text{ of } NO_3^- \text{ left} = 0.450 \text{ mol} \div 2.000 \text{ L} = 0.225 \ M$$

$$M \text{ of } Na^+ \text{ left} = 0.750 \text{ mol} \div 2.000 \text{ L} = 0.375 \ M$$

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12.126. First, determine the initial moles of each ion present in the solution before any reaction has occurred. There are five ions present: Na^+, 3 x 0.310 = 0.930 mol; PO_4^{3-}, 0.310 mol; Ca^{2+}, 0.100 mol; Ag^+, 0.150 mol; and NO_3^-, 0.150 + 2 x 0.100 = 0.350 mol. Two precipitates form: $Ca_3(PO_4)_2$ and Ag_3PO_4. The balanced net ionic equations for their formation are

$$3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$$

$$3\ Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$$

There is sufficient PO_4^{3-} to precipitate all of the Ca^{2+} and all of the Ag^+ ions. The moles of excess PO_4^{3-} is calculated as follows: 0.310 − 2/3 x 0.100 − 1/3 x 0.150 = 0.193̲3 mol remaining. Since the volume is 4.000 L, the molarities of the various ions are

$$M \text{ of } PO_4^{3-} \text{ left} = 0.193\underline{3} \text{ mol} \div 4.000 \text{ L} = 0.048\underline{3}3 = 0.0483\ M$$

$$M \text{ of } NO_3^- \text{ left} = 0.350 \text{ mol} \div 4.000 \text{ L} = 0.0875\ M$$

$$M \text{ of } Na^+ \text{ left} = 0.930 \text{ mol} \div 4.000 \text{ L} = 0.23\underline{2}5 = 0.233\ M$$

12.127.

$Na^+(g) + Cl^-(g)$	$\rightarrow$	$NaCl(s)$	$\Delta H = 787$ kJ/mol
$NaCl(s)$	$\rightarrow$	$Na^+(aq) + Cl^-(aq)$	$\Delta H = +4$ kJ/mol
$Na^+(g) + Cl^-(g)$	$\rightarrow$	$Na^+(aq) + Cl^-(aq)$	$\Delta H = 783$ kJ/mol

The heat of hydration of Na^+ is

$Na^+(g) + Cl^-(g)$	$\rightarrow$	$Na^+(aq) + Cl^-(aq)$	$\Delta H = 783$ kJ/mol
$Cl^-(aq)$	$\rightarrow$	$Cl^-(g)$	$\Delta H = +338$ kJ/mol
$Na^+(g)$	$\rightarrow$	$Na^+(aq)$	$\Delta H = 445$ kJ/mol

12.128.

$K^+(g) + Cl^-(g)$	$\rightarrow$	$KCl(s)$	$\Delta H = 717$ kJ/mol
$KCl(s)$	$\rightarrow$	$K^+(aq) + Cl^-aq)$	$\Delta H = +18$ kJ/mol
$K^+(g) + Cl^-(g)$	$\rightarrow$	$K^+(aq) + Cl^-aq)$	$\Delta H = 699$ kJ/mol

The heat of hydration of K^+ is

$K^+(g) + Cl^-(g)$	$\rightarrow$	$K^+(aq) + Cl^-aq)$	$\Delta H = 699$ kJ/mol
$Cl^-(aq)$	$\rightarrow$	$Cl^-g)$	$\Delta H = +338$ kJ/mol
$K^+(g)$	$\rightarrow$	$K^+(aq)$	$\Delta H = 361$ kJ/mol

Less heat is evolved in the hydration of $K^+(g)$ than in that of $Na^+(g)$ because smaller ions have larger hydration energies.

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12.129. $15.0 \text{ g } MgSO_4 \cdot 7H_2O \times \frac{1 \text{ mol}}{246.5 \text{ g}} = 0.060\underline{8}54 \text{ mol } MgSO_4 \cdot 7H_2O$

$$0.060854 \text{ mol } MgSO_4 \cdot 7H_2O \times \frac{7 \text{ mol } H_2O}{1 \text{ mol hydrate}} \times \frac{18.0 \text{ g } H_2O}{1 \text{ mol } H_2O} = 7.6\underline{6}7 \text{ g } H_2O$$

$$\text{kg } H_2O = (100.0 \text{ g } H_2O + 7.667 \text{ g } H_2O) \times \frac{1 \text{ kg } H_2O}{1000 \text{ g } H_2O} = 0.107\underline{6}6 \text{ kg } H_2O$$

$$m = \frac{0.060854 \text{ mol } MgSO_4}{0.10766 \text{ kg } H_2O} = 0.56\underline{5}2 \text{ mol/kg} = 0.565 \, m$$

12.130. $15.0 \text{ g } Na_2CO_3 \cdot 10H_2O \times \frac{1 \text{ mol}}{286.2 \text{ g}} = 0.052\underline{4}1 \text{ mol } Na_2CO_3 \cdot 10H_2O$, or Na_2CO_3

$$0.05241 \text{ mol } Na_2CO_3 \cdot 10H_2O \times \frac{10 \text{ mol } H_2O}{1 \text{ mol hydrate}} \times \frac{18.0 \text{ g } H_2O}{1 \text{ mol } H_2O} = 9.4\underline{3}4 \text{ g } H_2O$$

$$\text{kg } H_2O = (100 \text{ g } H_2O + 9.434 \text{ g } H_2O) \times \frac{1 \text{ kg } H_2O}{1000 \text{ g } H_2O} = 0.109\underline{4}3 \text{ kg } H_2O$$

$$m = \frac{0.05241 \text{ mol } Na_2CO_3}{0.10943 \text{ kg } H_2O} = 0.47\underline{8}9 \text{ mol/kg} = 0.479 \, m$$

12.131. $15.0 \text{ g } CuSO_4 \cdot 5H_2O \times \frac{1 \text{ mol}}{249.7 \text{ g}} = 0.060\underline{0}7 \text{ mol } CuSO_4 \cdot 5H_2O$, or $CuSO_4$

$$100 \text{ g soln} \times \frac{1 \text{ mL soln}}{1.167 \text{ g soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.085\underline{6}89 \text{ L}$$

$$M = \frac{0.06007 \text{ mol } CuSO_4}{0.085689 \text{ L}} = 0.70\underline{1}02 = 0.701 \text{ mol/L}$$

12.132. $20.0 \text{ g } Na_2S_2O_3 \cdot 5H_2O \times \frac{1 \text{ mol}}{248.2 \text{ g}} = 0.080\underline{5}8 \text{ mol } Na_2S_2O_3 \cdot 5H_2O$, or $Na_2S_2O_3$

$$100 \text{ g soln} \times \frac{1 \text{ mL soln}}{1.174 \text{ g soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.085\underline{1}7 \text{ L}$$

$$M = \frac{0.08058 \text{ mol } Na_2S_2O_3}{0.08517 \text{ L}} = = 0.946\underline{1} = 0.946 \text{ mol/L}$$

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12.133. $0.159°C \times \frac{m}{1.858°C} = 0.08557\ m = \frac{0.08557 \text{ mol AA} + H^+}{1000 \text{ g (or 1000 mL) } H_2O}$

Note that 0.0830 mol AA + mol H^+ = 0.08557 mol/L (AA + H^+).

Moles of H^+ = 0.08557 − 0.0830 = 0.00257 mol

Percent dissoc. = $\frac{\text{mol } H^+}{\text{mol AA}} \times 100\% = \frac{0.00257 \text{ mol}}{0.0830 \text{ mol}} \times 100\% = 3.09 = 3.1\%$

12.134. $0.210°C \times \frac{m}{1.858°C} = 0.1130\ m = \frac{0.1130 \text{ mol FA} + H^+}{1000 \text{ g (or 1000 mL) } H_2O}$

Note that 0.109 mol FA + mol H^+ = 0.113 mol/L (FA + H^+).

Moles of H^+ = 0.113 − 0.109 = 0.0040 mol

Percent dissoc. = $\frac{\text{mol } H^+}{\text{mol FA}} \times 100\% = \frac{0.0040 \text{ mol}}{0.109 \text{ mol}} \times 100\% = 3.69 = 4$ percent

12.135. Calculate the empirical formula first, using the masses of C, O, and H in 1.000 g:

$1.434 \text{ g } CO_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g } CO_2} = 0.39132 \text{ g C}$

$0.783 \text{ g } H_2O \times \frac{2.016 \text{ g H}}{18.016 \text{ g } H_2O} = 0.08761 \text{ g H}$

g O = 1.000 g − 0.39132 g − 0.08761 g = 0.5211 g O

Mol C = 0.39132 g C x 1 mol/12.01 g = 0.03258 mol C (lowest integer = 1)

Mol H = 0.08761 g H x 1 mol/1.008 g = 0.08691 mol H (lowest integer = 8/3)

Mol O = 0.5211 g O x 1 mol/16.00 g = 0.03257 mol O (lowest integer = 1)

Therefore, the empirical formula is $C_3H_8O_3$. The formula mass from the freezing point is calculated by first finding the molality:

$0.0894°C \times (m/1.858°C) = 0.04811 = (0.04811 \text{ mol}/1000 \text{ g } H_2O)$

$(0.04811 \text{ mol}/1000 \text{ g } H_2O) \times 25.0 \text{ g } H_2O = 0.001203 \text{ mol (in 25.0 g } H_2O)$

Molar mass = M_m = 0.1107 g/0.001203 mol = 92.02 g/mol

Because this is also the formula mass, the molecular formula is also $C_3H_8O_3$.

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12.136. Calculate the empirical formula first, using the masses of C, O, and H in 1.000 g:

$$1.418 \text{ g } CO_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g } CO_2} = 0.3870 \text{ g C}$$

$$0.871 \text{ g } H_2O \times \frac{2.016 \text{ g H}}{18.016 \text{ g } H_2O} = 0.09746 \text{ g H}$$

$$\text{g O} = 1.000 \text{ g} - 0.3870 \text{ g} - 0.09746 \text{ g} = 0.5155 \text{ g O}$$

$$\text{Mol C} = 0.3870 \text{ g C} \times 1 \text{ mol}/12.01 \text{ g} = 0.0322 \text{ mol C (lowest integer = 1)}$$

$$\text{Mol H} = 0.09746 \text{ g H} \times 1 \text{ mol}/1.008 \text{ g} = 0.09668 \text{ mol H (lowest integer = 3)}$$

$$\text{Mol O} = 0.5155 \text{ g O} \times 1 \text{ mol}/16.00 \text{ g} = 0.03222 \text{ mol O (lowest integer = 1)}$$

The empirical formula is CH_3O. For the freezing-point calculation, the molality is calculated as follows:

$$0.0734°\text{C} \times (m/1.858°\text{C}) = 0.039505 = (0.39505 \text{ mol}/1000 \text{ g } H_2O)$$

$$(0.39504 \text{ mol}/1000 \text{ g } H_2O) \times 45.0 \text{ g } H_2O = 0.001778 \text{ mol}$$

$$\text{Molar mass} = M_m = 0.1103 \text{ g}/0.0017778 \text{ mol} = 62.04 \text{ g/mol}$$

Because the formula mass of CH_3O is 31.02, the molecular formula is $C_2H_6O_2$.

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CHAPTER 13

Rates of Reaction

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

13.1. Rate of formation of $NO_2F = \Delta[NO_2F]/\Delta t$. Rate of reaction of $NO_2 = -\Delta[NO_2]/\Delta t$. Divide each rate by the coefficient of the corresponding substance in the equation:

$$1/2\,\frac{\Delta[NO_2F]}{\Delta t} = -1/2\,\frac{\Delta[NO_2]}{\Delta t};\ \text{or}\ \frac{\Delta[NO_2F]}{\Delta t} = -\frac{\Delta[NO_2]}{\Delta t}$$

13.2. $$\text{Rate} = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[0.00101\ \text{M} - 0.00169\ \text{M}]}{8.00\ \text{s} - 2.00\ \text{s}} = 1.\underline{1}3 \times 10^{-4} = 1.1 \times 10^{-4}\ M/\text{s}$$

13.3. The order with respect to CO is zero and with respect to NO_2 is 2. The overall order is 2, the sum of the exponents in the rate law.

13.4. By comparing Experiments 1 and 2, you see the rate is quadrupled when the $[NO_2]$ is doubled. Thus, the reaction is second order in NO_2, and the rate law is

$$\text{Rate} = k[NO_2]^2$$

The rate constant may be found by substituting experimental values into the rate-law expression. Based on values from Experiment 1,

$$k = \frac{\text{rate}}{[NO_2]^2} = \frac{7.1 \times 10\ \text{mol/(L}\bullet\text{s)}}{(0.010\ \text{mol/L})^2} = 0.7\underline{1}0 = 0.71\ \text{L/(mol}\bullet\text{s)}$$

13.5.

a. For $[N_2O_5]$ after 6.00×10^2 s, use the first-order rate law, and solve for the concentration at time *t*:

$$\ln\frac{[N_2O_5]_t}{[1.65 \times 10^{-2}\ \text{M}]} = -(4.80 \times 10^{-4}\ \text{/s})(6.00 \times 10^2\ \text{s}) = -0.28\underline{8}0$$

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Take the antilog of both sides to get

$$\frac{[N_2O_5]_t}{[1.65 \times 10^{-2}\ M]} = e^{-0.2880} = 0.74\underline{9}76$$

Hence,

$$[N_2O_5]_t = 1.65 \times 10^{-2}\ M \times 0.74976 = 0.012\underline{3}7 = 0.0124\ \text{mol/L}$$

b. Substitute the values into the rate equation to get

$$\ln\frac{10.0\%}{100.0\%} = -(4.80 \times 10^{-4}/\text{s}) \times t$$

Taking the log on the left side gives ln(0.100) = −2.30258. Hence,

$$-2.30\underline{2}58 = -(4.80 \times 10^{-4}\ /\text{s}) \times t$$

Or,

$$t = \frac{2.30258}{4.80 \times 10^{-4}/\text{s}} = 47\underline{9}7 = 4.80 \times 10^{3}\ \text{s (80.0 min)}$$

13.6. Substitute $k = 9.2/\text{s}$ into the equation relating k and $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{9.2/\text{s}} = 0.07\underline{5}3 = 0.075\ \text{s}$$

By definition, the half-life is the amount of time it takes to decrease the amount of substance present by one-half. Thus, it takes 0.07$\underline{5}$3 s for concentration to decrease by 50% and another 0.07$\underline{5}$3 s for the concentration to decrease by 50% of the remaining 50% (to 25% left), for a total of 0.15$\underline{0}$6, or 0.151 s.

13.7. Solve for E_a by substituting the given values into the two-temperature Arrhenius equation:

$$\ln\frac{2.14 \times 10^{-2}}{1.05 \times 10^{-3}} = \frac{E_a}{8.31\ \text{J/(mol}\bullet\text{K)}}\left(\frac{1}{759\ \text{K}} - \frac{1}{836\ \text{K}}\right)$$

$$3.01\underline{4}6 = \frac{E_a}{8.31\ \text{J/(mol}\bullet\text{K)}}\ (1.2\underline{1}35 \times 10^{-4}\ /\text{K})$$

$$E_a = \frac{3.0146 \times 8.31\ \text{J/mol}}{1.2135 \times 10^{-4}} = 2.0\underline{6}4 \times 10^{5} = 2.06 \times 10^{5}\ \text{J/mol}$$

Solve for the rate constant, k_2, at 865 K by using the same equation and using $E_a = 2.064 \times 10^5$ J/mol:

$$\ln\frac{k_2}{2.14 \times 10^{-2}/(\text{M}^{1/2}\bullet\text{s})} = \frac{2.064 \times 10^{5}\ \text{J/mol}}{8.31\ \text{J/(mol}\bullet\text{K)}}\left(\frac{1}{836\ \text{K}} - \frac{1}{865\ \text{K}}\right) = 0.99\underline{6}23$$

Taking antilogarithms,

$$\frac{k_2}{2.14 \times 10^{-2}/(\text{M}^{1/2}\bullet\text{s})} = \text{e}^{0.99623} = 2.7\underline{0}80$$

$$k_2 = 2.7080 \times (2.14 \times 10^{-2})/(M^{1/2}\bullet\text{s}) = 5.7\underline{9}52 \times 10^{-2} = 5.80 \times 10^{-2}\ (M^{1/2}\bullet\text{s})$$

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13.8. The net chemical equation is the overall sum of the two elementary reactions:

$$H_2O_2 + I^- \rightarrow H_2O + IO^-$$
$$\underline{H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-}$$
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The IO^- is an intermediate; I^- is a catalyst. Neither appears in the net equation.

13.9. The reaction is bimolecular because it is an elementary reaction that involves two molecules.

13.10. For $NO_2 + NO_2 \rightarrow N_2O_4$, the rate law is

$$\text{Rate} = k[NO_2]^2$$

(The rate must be proportional to the concentration of both reactant molecules.)

13.11. The first step is the slow, rate-determining step. Therefore, the rate law predicted by the mechanism given is

$$\text{Rate} = k_1 [H_2O_2][I^-]$$

13.12. According to the rate-determining (slow) step, the rate law is

$$\text{Rate} = k_2[NO_3][NO]$$

Eliminate NO_3 from the rate law by looking at the first step, which is fast and reaches equilibrium. At equilibrium, the forward rate and the reverse rate are equal.

$$k_1[NO][O_2] = k_{-1}[NO_3]$$

Therefore, $[NO_3] = (k_1/k_{-1})[NO][O_2]$, so

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [NO]^2[O_2] = k[NO]^2[O_2]$$

where $k_2(k_1/k_{-1})$ has been replaced by k, which represents the experimentally observed rate constant.

■ ANSWERS TO CONCEPT CHECKS

13.1.

a. Since the slope is steeper at point A, point A must be a faster instantaneous rate.

b. Since the curve is not a flat line, the rate of reaction must be constantly changing over time. Therefore, the rate for the reaction cannot be constant at all points in time.

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13.2.

a. Keeping in mind that all reactant species must be present in some concentration for a reaction to occur, the reaction with [Q] = 0 is the slowest because no reaction occurs. The other two reactions are equal in rate because the reaction is zero order with respect to [Q]; as long as there is some amount of Q present, the reaction rate depends on the [R], which is constant in this case.

b. Since $[Q]^0 = 1$, you can rewrite the rate law as follows: Rate = $k[R]^2$.

13.3.

a. A possible rate law is Rate of aging = $(\text{diet})^w(\text{exercise})^x(\text{sex})^y(\text{occupation})^z$. Your rate law probably will be different; however, the general form should be the same.

b. You will need a sample of people who have all the factors the same except one. For example, using the equation given in part a, you could determine the effect of diet if you had a sample of people who were the same sex, exercised the same amount, and had the same occupation. You would need to isolate each factor in this fashion to determine the exponent on each factor.

c. The exponent on the smoking factor would be 2 since you see a fourfold rate increase: $[2]^2 = 4$.

13.4. The half-life of a first-order reaction is constant over the course of the reaction. The half-life of a second-order reaction depends on the initial concentration and becomes longer as time elapses. Thus, the reaction must be second order because the half-life increases from 20 s to 40 s after time has elapsed.

13.5.

a. Since the "hump" is larger, the A + B reaction has a higher activation energy.

b. Since the activation energy is lower, the E + F reaction would have the larger rate constant. Keep in mind the inverse relationship between the activation energy, E_a, and the rate constant, k.

c. Since, in both cases, energy per mole of the reactants is greater than that of the products, both reactions are exothermic.

13.6.

a. Her finding should increase the rate since the activation energy, E_a, is inversely related to the rate constant, k; a decrease in E_a results in an increase in the value of k.

b. This is possible because the rate law does not have to reflect the overall stoichiometry of the reaction.

c. No. Since the rate law is based on the slow step of the mechanism, it should be Rate = $k[Y]^2$.

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ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

13.1. The four variables that can affect rate are (1) the concentrations of the reactants, although in some cases a particular reactant's concentration does not affect the rate; (2) the presence and concentration of a catalyst; (3) the temperature of the reaction; and (4) the surface area of any solid reactant or solid catalyst.

13.2. The rate of reaction of HBr can be defined as the decrease in HBr concentration (or the increase in Br_2 product formed) over the time interval, Δt:

$$\text{Rate} = -1/4\,\frac{\Delta[\text{HBr}]}{\Delta t} = 1/2\,\frac{\Delta[\text{Br}_2]}{\Delta t} \quad \text{or} \quad -\frac{\Delta[\text{HBr}]}{\Delta t} = 2\,\frac{\Delta[\text{Br}_2]}{\Delta t}$$

13.3. Two physical properties used to determine the rate are color, or absorption of electromagnetic radiation, and pressure. If a reactant or product is colored, or absorbs a different type of electromagnetic radiation than the other species, then measurement of the change in color (change in absorption of electromagnetic radiation) may be used to determine the rate. If a gas reaction involves a change in the number of gaseous molecules, measurement of the pressure change may be used to determine the rate.

13.4. Use the general example of a rate law in Section 13.3, where A and B react to give D and E with C as a catalyst:

$\text{Rate} = k\,[\text{A}]^m\,[\text{B}]^n\,[\text{C}]^p$

Note that the exponents *m*, *n*, and *p* are the orders of the individual reactants and catalyst. Assuming that *m* and *n* are positive numbers, the rate law predicts that increasing the concentrations of A and/or B will increase the rate. In addition, the rate will be increased by increasing the surface of the solid catalyst (making it as finely divided as possible, etc.). Finally, increasing the temperature will increase the rate constant, *k*, and increase the rate.

13.5. An example that illustrates that exponents have no relationship to coefficients is the reaction of nitrogen monoxide and hydrogen from Example 13.12 in the text.

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$.

The experimental rate law given there is

$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$

Thus, the exponent for hydrogen is 1, not 2 like the coefficient, and the overall order is 3, not 4 like the sum of the coefficients.

13.6. The rate law for this reaction of iodide ion, arsenic acid, and hydrogen ion is

$\text{Rate} = k[\text{I}^-][\text{H}_3\text{AsO}_4]\,[\text{H}^+]$

The overall order is 1 + 1 + 1 = 3 (third order).

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13.7. Use *m* to symbolize the reaction order as is done in the text. Then, from the table for *m* and the change in rate in the text, *m* is 2 when the rate is quadrupled (increased fourfold). Using the equation in the text gives the same result:

2^m = new rate/old rate = 4/1; thus, $m = 2$

13.8. Use *m* to symbolize the reaction order as is done in the text. The table for *m* and the change in rate in the text cannot be used in this case. When $m = 0.5$, the new rate should be found using the equation in the text:

$2^{0.50} = \sqrt{2} = 1.41$ = new rate/old rate

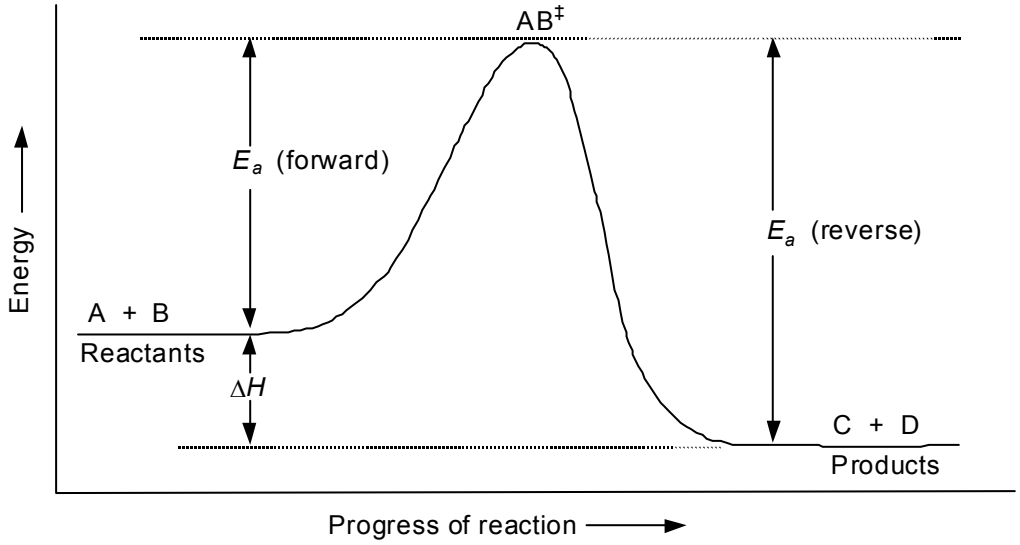
Thus, the new rate is 1.41 times the old rate.

13.9. Use the half-life concept to answer the question without an equation. If the half-life for the reaction of A(*g*) is 25 s, then the time for A(*g*) to decrease to 1/4 the initial value is two half-lives, or 2 x 25 = 50 s. The time for A(*g*) to decrease to 1/8 the initial value is three half-lives, or 3 x 25 = 75 s.

13.10. The half-life equation for a first-order reaction is $t_{1/2} = 0.693/k$. The half-life for the reaction is constant, independent of the reactant concentration. For a second-order reaction, the half-life equation is $t_{1/2} = 1/(k[A]_o)$, and it depends on the initial reactant concentration.

13.11. According to transition-state theory, the two factors that determine whether a collision results in reaction or not are (1) the molecules must collide with the proper orientation to form the activated complex, and (2) the activated complex formed must have a kinetic energy greater than the activation energy.

13.12. The potential-energy diagram for the exothermic reaction of A and B to give activated complex $AB^{\ddagger}$ and products C and D is given below.



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13.13. The activated complex for the reaction of NO_2 with NO_3 to give NO, NO_2, and O_2 has the structure below (dashed lines represent bonds about to form or break):

O–N–O–O–N(–O)$_2$

13.14. The Arrhenius equation expressed with the base *e* is

$$k = A\, e^{-E_a/RT}$$

The *A* term is the frequency factor and is equal to the product of *p* and *Z* from collision theory. The term *p* is the fraction of collisions with properly oriented reactant molecules, and *Z* is the frequency of collisions. Thus, *A* is the number of collisions with the molecules properly oriented. The E_a term is the activation energy, the minimum energy of collision required for two molecules to react. The *R* term is the gas constant, and *T* is the absolute temperature.

13.15. In the reaction of $NO_2(g)$ with $CO(g)$, an example of an intermediate is the temporary formation of NO_3 from the reaction of two NO_2 molecules in the first step:

$$NO_2 + NO_2 \rightarrow NO_3 + NO$$

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

13.16. It is generally impossible to predict the rate law from the equation alone, because most reactions consist of several elementary steps whose combined result is summarized in the rate law. If these elementary steps are unknown, the rate law cannot be predicted.

13.17. The mechanism cannot be $2NO_2Cl \rightarrow 2NO_2 + Cl_2$ because the reaction is first order in NO_2Cl. The order in NO_2Cl would have to reflect the total number of molecules (two) for the proposed mechanism, but it does not.

13.18. The characteristic of the rate-determining step in a mechanism is that it is, relatively speaking, the slowest step of all the elementary steps (even though it may occur in seconds). Thus, the rate of disappearance of reactant(s) is limited by the rate of this step.

13.19. For the rate of decomposition of N_2O_4,

$$\text{Rate} = k_1[N_2O_4]$$

For the rate of formation of N_2O_4,

$$\text{Rate} = k_{-1}[NO_2]^2$$

At equilibrium the rates are equal, so

$$k_1[N_2O_4] = k_{-1}[NO_2]^2$$

$$[N_2O_4] = (k_{-1}/k_1)\,[NO_2]^2$$

13.20. A catalyst operates by providing a pathway (mechanism) that occurs faster than the uncatalyzed pathway (mechanism) of the reaction. The catalyst is not consumed because after reacting in an early step, it is regenerated in a later step.

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13.21. In physical adsorption, molecules adhere to a surface through *weak* intermediate forces, whereas in chemisorption, the molecules adhere to the surface by *stronger* chemical bonding.

13.22. In the first step of catalytic hydrogenation of ethylene, the ethylene and hydrogen molecules diffuse to the catalyst surface and undergo chemisorption. Then the *pi* electrons of ethylene form temporary bonds to the metal catalyst, and the hydrogen molecule breaks into two hydrogen atoms. The hydrogen atoms next migrate to an ethylene held in position on the metal catalyst surface, forming ethane. Finally, because it cannot bond to the catalyst, the ethane diffuses away from the surface.

13.23. The answer is c, [A] = 0.0250 *M*, [B] = 0.0400 *M*.

13.24. The answer is e, I and III only.

13.25. The answer is e; if the rate law for the reaction is Rate = $k[E]^2[F]$, then doubling the concentration of E will cause the rate to increase by a factor of 4 (4 times faster).

13.26. The answer is c, doubling the $[C]_o$ while keeping the $[A]_o$ and $[B]_o$ constant.

■ ANSWERS TO CONCEPT EXPLORATIONS

13.27.

a. Rate = $k[A]^2[B]$

b. The greatest reaction rate will be for the container with the largest value of $[A]^2[B]$. For container W, this product is $(2)^2(3) = 12$, for container X it is $(2)^2(4) = 16$, for container Y it is $(3)^2(2) = 18$, and for container Z it is $(5)^2(0) = 0$. Therefore, container Y will have the greatest reaction rate.

c. The slowest reaction rate will be for container Z because the concentration of one of the reactants (B) is zero.

d. When the volume of the container is doubled from 1.0 L to 2.0 L, the concentrations of A and B are reduced by a factor of 2. This corresponds to a reduction in rate of $(1/2)^2(1/2) = 1/8$. Thus, the reaction rate in the larger container is 1/8 the rate in the smaller container.

e. Usually, reaction rates increase with an increase in temperature. At a higher temperature, molecules have a greater kinetic energy and collide with other molecules at a higher rate. Thus, the fraction of collisions with energy in excess of E_a is greater, and the reaction rate increases.

f. To double the reaction rate, the product $[A]^2[B]$ must also double. This can be accomplished by doubling [B] while leaving [A] unchanged. Another possibility is to double [A] and reduce [B] by one-half.

g. The slowest rate of formation of C is for container Z, where the reaction rate is zero.

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h. Since the reaction is second order in A and only first order in B, changes in the concentration of A will have the greater impact on the rate of reaction, so removing a unit of A will have the greater impact on the rate of reaction in container W.

i. The reaction rates are

$$-\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t}$$

Thus, the rate of consumption of A is one-half the rate of consumption of B.

j. Since [C] does not appear in the rate law, removing C from the container should have no effect on the reaction rate.

13.28.

a. Since the graph is not linear, there is no way to determine the reaction order by inspection. A second-order reaction should exhibit linear behavior if a plot is made of 1/[A] vs time.

b. The data seem to better support a first-order reaction. As the time changes by 2 seconds, the concentration of A decreases by 10^2. This is the behavior expected for an exponential rate law like a first-order reaction rate law, $[A] = [A]_0 e^{-kt}$.

c. The rate constant is

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{0.35\text{ s}} = 1.98\underline{0} = 1.98\text{ /s}$$

d. A possible mechanism with intermediates X and Y is

$A \rightarrow X + Y$ (slow step)

$X + Y \rightarrow B + C$ (fast step)

e. The behavior of the rate constant *k* as a function of temperature is described by the Arrhenius equation.

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

As the temperature increases the rate constant also increases. More molecules collide with sufficient energy to overcome the potential energy barrier so the rate of reaction increases.

■ ANSWERS TO CONCEPTUAL PROBLEMS

13.29.

a. You can write the rate expression in terms of the depletion of A:

$$\text{Rate of depletion of A} = -\frac{\Delta[A]}{\Delta t}$$

or you can write the rate expression in terms of the formation of B:

$$\text{Rate of formation of B} = +\frac{\Delta[B]}{\Delta t}$$

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b. No. Consider the stoichiometry of the reaction, which indicates that the rate of depletion of A would be faster than the rate of formation of B; for every 3 moles of A that are consumed, 2 moles of B would be formed.

c. Taking into account the stoichiometry of the reaction, the two rate expressions that would give an equal rate when calculated over the same time interval are

$$\text{Rate} = -\frac{\Delta[\text{A}]}{3\Delta t} = \frac{\Delta[\text{B}]}{2\Delta t}$$

13.30. You cannot write the rate law for this reaction from the information given. The rate law can be determined only by experiment, not by the stoichiometry of the reaction.

13.31.

a. The rate law for a second-order reaction is Rate = $k[\text{A}]^2$.

b. The faster reaction rate will correspond to the container with the higher concentration of A. Both containers contain the same number of A particles, but the volume of the container on the right is only one-half the volume of the other. Therefore, the initial concentration of A in the container on the right is double the initial concentration of A in the left container. Thus, the reaction will be faster in the smaller container on the right.

c. For a second-order reaction, the relationship among the half-life, rate constant, and initial concentration of A is

$$t_{1/2} = \frac{1}{k[\text{A}]_\text{o}}$$

Since the half-life is inversely proportional to the initial concentration, the shorter half-life will correspond to the higher initial concentration of A, which is in the right container.

d. The relative rates of the reactions can be determined as follows. Since the initial concentration of A in the container on the right is double the initial concentration of A in the left container, the ratio of the rate in the right container to that on the left is

$$\frac{\text{Rate}_\text{R}}{\text{Rate}_\text{L}} = \frac{k[\text{A}]_{\text{o,R}}^2}{k[\text{A}]_{\text{o,L}}^2} = \left(\frac{[\text{A}]_{\text{o,R}}}{[\text{A}]_{\text{o,L}}}\right)^2 = \left(\frac{2[\text{A}]_{\text{o,L}}}{[\text{A}]_{\text{o,L}}}\right)^2 = 2^2 = 4$$

Thus, the reaction rate in the right container is four times the reaction rate of the container on the left.

e. Since both containers start with the same number of A particles, and the reaction rate is faster in the right container, more A particles will have reacted in this container, so it will contain fewer atoms.

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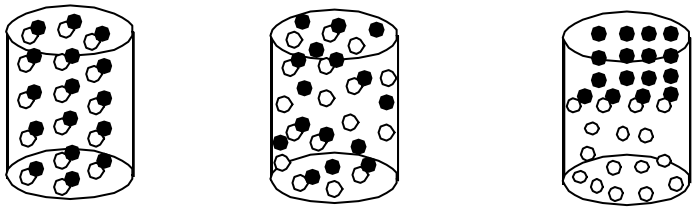
13.32.

a. The reaction is first order with a half-life of 10 seconds. Starting with 16 AB particles in the container, after 10 seconds (one half-life), 8 of the particles will have reacted and 8 will remain unreacted. After 20 seconds (two half-lives), 12 of the particles will have reacted and 4 will remain unreacted. The pictures are



$t = 0$ s $t = 10$ s $t = 20$ s

b. If the half-life is the same for the second-order reaction, the container $t = 20$ s will have more AB and fewer A and B particles than from part a.

c. After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the first-order case, the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[\text{A}]_{\text{o},0}}{k[\text{A}]_{\text{o},10}} = \frac{[\text{A}]_{\text{o},0}}{[\text{A}]_{\text{o},10}} = \frac{[\text{A}]_\text{o}}{1/2[\text{A}]_\text{o}} = 2$$

Thus, for the first-order case, after 10 seconds the rate is one-half the initial rate.

d. After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the second-order case, the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[\text{A}]^2_{\text{o},0}}{k[\text{A}]^2_{\text{o},10}} = \left(\frac{[\text{A}]_{\text{o},0}}{[\text{A}]_{\text{o},10}}\right)^2 = \left(\frac{[\text{A}]_\text{o}}{1/2[\text{A}]_\text{o}}\right)^2 = 2^2 = 4$$

Thus, for the second-order case, after 10 seconds, the rate is one-fourth the initial rate.

13.33.

a. If the concentration is tripled but there is no effect on the rate, the order of the reaction must be zero. Thus, $x = 0$.

b. If the concentration is doubled and the rate doubles, it is a first-order reaction. Thus, $x = 1$.

c. If the concentration is tripled and the rate goes up by a factor of 27, it is a third-order reaction. Thus, $x = 3$.

13.34.

a. E must be a product since its concentration increases with time. If E were a reactant, you would expect the concentration to decrease over time.

b. The average rate is faster between points A and B because the slope of the curve is steeper in this region. Remember, the steeper the curve, the greater the rate of change.

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13.35.

a. The rate has a constant value in region C because the slope of the curve is constant (flat) in this region.

b. The rate is the fastest in region A because the slope of the curve is steepest in this region.

13.36. Since NO_2 is a product in the reaction, its concentration must increase with time. The only graph that has $[NO_2]$ increasing with time is curve C.

13.37. A number of answers will work as long as you match one of the existing concentration of A. For example: [A] = 2.0 *M* with [B] = 2.0 *M*, or [A] = 1.0 *M* with [B] = 2.0 *M*.

13.38. The Arrhenius equation is

$$k = Ae^{-E_a/RT}$$

a. When the temperature is decreased, the rate constant, *k*, will also decrease. When *k* decreases, the rate also decreases.

b. When the activation energy is increased, the rate constant, *k*, also decreases. When *k* decreases, the rate also decreases.

c. Since the activation energy is in the numerator and the temperature is in the denominator, you cannot predict the effect without knowing the magnitude of the changes.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

13.39. For the reaction $2NO_2 \rightarrow 2NO + O_2$, the rate of decomposition of NO_2 and the rate of formation of O_2 are, respectively,

$$\text{Rate} = -\Delta[NO_2]/\Delta t$$

$$\text{Rate} = \Delta[O_2]/\Delta t$$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$-1/2\,\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

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13.40. For the reaction $H_2 + I_2 \rightarrow 2HI$, the rate of formation of HI and the rate of decomposition of H_2 are, respectively,

Rate = $\Delta[HI]/\Delta t$

Rate = $-\Delta[H_2]/\Delta t$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$-\frac{\Delta[H_2]}{\Delta t} = 1/2\,\frac{\Delta[HI]}{\Delta t}$$

13.41. For the reaction $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$, the rate of decomposition of Br^- and the rate of decomposition of BrO_3^- are, respectively,

Rate = $-\Delta[Br^-]/\Delta t$

Rate = $-\Delta[BrO_3^-]/\Delta t$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$1/5\,\frac{\Delta[Br^-]}{\Delta t} = \frac{\Delta[BrO_3^-]}{\Delta t}$$

13.42. For the reaction $3I^- + H_3AsO_4 + 2H^+ \rightarrow I_3^- + H_3AsO_3 + H_2O$, the rate of decomposition of I^- and the rate of formation of I_3^- are, respectively,

Rate = $-\Delta[I^-]/\Delta t$

Rate = $\Delta[I_3^-]/\Delta t$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$-1/3\,\frac{\Delta[I^-]}{\Delta t} = \frac{\Delta[I_3^-]}{\Delta t}$$

13.43. $$\text{Rate} = -\frac{\Delta[NH_4NO_2]}{\Delta t} = -\frac{[0.0432\,M \;-\; 0.500\,M]}{[3.00\text{ hr} \;-\; 0.00\text{ hr}]} = 2.\underline{2}7 \times 10^{-2} = 2.3 \times 10^{-2}\,M/\text{hr}$$

13.44. $$\text{Rate} = -\frac{\Delta[FeCl_3]}{\Delta t} = -\frac{[0.02638\,M \;-\; 0.3586\,M]}{[4.00\text{ min} \;-\; 0.00\text{ min}]} = 0.002\underline{37}0 = 0.00237\,M/\text{min}$$

13.45. $$\text{Rate} = -\frac{\Delta[\text{Azo.}]}{\Delta t} = -\frac{[0.0101\,M \;-\; 0.0150\,M]}{7.00\text{ min} \;-\; 0.00\text{ min}} \times \frac{1\text{ min}}{60\text{ sec}} = 1.\underline{16} \times 10^{-5} = 1.2 \times 10^{-5}\,M/\text{s}$$

13.46. $$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{[0.1076\,M \;-\; 0.1103\,M]}{60.0\text{ s} \;-\; 0.0\text{ s}} = 4.\underline{5}0 \times 10^{-5} = 4.5 \times 10^{-5}\,M/\text{s}$$

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13.47. If the rate law is Rate = $k[H_2S][Cl_2]$, the order with respect to H_2S is 1 (first order), and the order with respect to Cl_2 is also 1 (first-order). The overall order is 1 + 1 = 2, second-order.

13.48. If the rate law is Rate = $k[NO]^2[Cl_2]$, the order with respect to NO is 2 (second order), and the order with respect to Cl_2 is 1 (first-order). The overall order is 2 + 1 = 3, third-order.

13.49. If the rate law is Rate = $k[MnO_4^-][H_2C_2O_4]$, the order with respect to MnO_4^- is 1 (first order), the order with respect to $H_2C_2O_4$ is 1 (first order), and the order with respect to H^+ is zero. The overall order is 2, second order.

13.50. If the rate law is rate = $k[H_2O_2][Fe^{2+}]$, the order with respect to H_2O_2 is 1 (first order), the order with respect to Fe^{2+} is 1 (first order), and the order with respect to H^+ is zero. The overall order is 2, second order.

13.51. The reaction rate doubles when the concentration of CH_3NNCH_3 is doubled, so the reaction is first order in azomethane. The rate equation should have the form

$$\text{Rate} = k[CH_3NNCH_3]$$

Substituting values for the rate and concentration yields a value for k:

$$k = \frac{\text{rate}}{[\text{Azo.}]} = \frac{2.8 \times 10^{-6}\ M/\text{s}}{1.13 \times 10^{-2}\ M} = 2.\underline{4}7 \times 10^{-4} = 2.5 \times 10^{-4}/\text{s}$$

13.52. The reaction rate doubles when the concentration of ethylene oxide is doubled, so the reaction is first order in ethylene oxide. The rate equation should have the form

$$\text{Rate} = k[C_2H_4O]$$

Substituting values for the rate and concentration yields a value for k:

$$k = \frac{\text{rate}}{[\text{Et. Ox.}]} = \frac{5.57 \times 10^{-7}\ M/\text{s}}{2.72 \times 10^{-3}\ M} = 2.0\underline{4}7 \times 10^{-4} = 2.05 \times 10^{-4}/\text{s}$$

13.53. Doubling [NO] quadruples the rate, so the reaction is second order in NO. Doubling $[H_2]$ doubles the rate, so the reaction is first order in H_2. The rate law should have the form

$$\text{Rate} = k[NO]^2[H_2]$$

Substituting values for the rate and concentrations yields a value for k:

$$k = \frac{\text{rate}}{[NO]^2[H_2]} = \frac{2.6 \times 10^{-5}\ M/\text{s}}{[6.4 \times 10^{-3}\ M]^2[2.2 \times 10^{-3}\ M]} = 2.\underline{8}8 \times 10^2 = 2.9 \times 10^2/M^2\text{s}$$

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13.54. Doubling [NO] quadruples the rate, so the reaction is second order in NO. Doubling $[O_2]$ doubles the rate, so the reaction is first order in O_2. The rate law should have the form

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

Substituting values for the rate and concentrations yields a value for k:

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{0.0281\ M/\text{s}}{[0.0125\ M]^2[0.0253\ M]} = 7.1\underline{0}8 \times 10^3 = 7.11 \times 10^3/M^2\text{s}$$

13.55. By comparing Experiments 1 and 2, you see that tripling $[ClO_2]$ increases the rate ninefold; that is, $3^m = 9$, so $m = 2$ (and the reaction is second order in ClO_2). From Experiments 2 and 3, you see that tripling $[OH^-]$ triples the rate, so the reaction is first order in OH^-. The rate law is

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

Substituting values for the rate and concentrations yields a value for k:

$$k = \frac{\text{rate}}{[\text{ClO}_2]^2[\text{OH}^-]} = \frac{0.0248\ M/\text{s}}{[0.060\ M]^2[0.030\ M]} = 2.\underline{2}9 \times 10^2 = 2.3 \times 10^2/M^2\text{s}$$

13.56. By comparing Experiments 2 and 3, you see that doubling $[I^-]$ doubles the rate, so the reaction is first order in I^-. From Experiments 1 and 3, you see that doubling $[ClO^-]$ also doubles the rate, so the reaction is first order in ClO^-. From Experiments 3 and 4, you see that doubling $[OH^-]$ halves the rate; that is, $2^m = 1/2$. Hence $m = -1$, and the rate is inversely proportional to the first power of OH^-. The rate law is

$$\text{Rate} = k[\text{I}^-][\text{ClO}^-]/[\text{OH}^-]$$

Substituting values for the rate and concentrations yields a value for k:

$$k = \frac{\text{rate}\ [\text{OH}^-]}{[\text{ClO}^-][\text{I}^-]} = \frac{6.1 \times 10^{-2}\ M/\text{s}\ [0.010\ M]}{[0.010\ M]\ [0.010\ M]} = 6.\underline{1}0 = 6.1\ /\text{s}$$

13.57. Let $[SO_2Cl_2]_o = 0.0248\ M$ and $[SO_2Cl_2]_t$ = the concentration after 2.0 hr. Substituting these and $k = 2.2 \times 10^{-5}$/s into the first-order rate equation gives

$$\ln \frac{[\text{SO}_2\text{Cl}_2]_t}{[0.0248\ M]} = -(2.2 \times 10^{-5}/\text{s})\left(2.0\ \text{hr} \times \frac{3600\ \text{s}}{1\ \text{hr}}\right) = -0.1\underline{5}84$$

Taking the antilog of both sides gives

$$\frac{[\text{SO}_2\text{Cl}_2]_t}{[0.0248\ M]} = e^{-0.1584} = 0.8\underline{5}35$$

Solving for $[SO_2Cl_2]_t$ gives

$$[\text{SO}_2\text{Cl}_2]_t = 0.8\underline{5}25 \times [0.0248\ M] = 0.02\underline{1}16 = 0.021 = 2.1 \times 10^{-2}\ M$$

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13.58. Let $[C_3H_6]_o = 0.0226\ M$ and $[C_3H_6]_t$ = the concentration after 899 s. Substituting these concentrations and $k = 6.0 \times 10^{-4}$/s into the first-order rate equation gives

$$\ln \frac{[C_3H_6]_t}{[0.0226\ M]} = -(6.0 \times 10^{-4}/\text{s})(899\ \text{s}) = -0.5\underline{3}94$$

Taking the antilog of both sides gives

$$\frac{[C_3H_6]_t}{[0.0226\ M]} = e^{-0.5394} = 0.5\underline{8}30$$

Solving for $[C_3H_6]_t$ gives

$$[C_3H_6]_t = 0.5\underline{8}30 \times [0.0226\ M] = 0.01\underline{3}1 = 0.013\ M$$

13.59. The second-order integrated rate law is

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

Using a rate constant value of 0.225 L/(mol•s) and an initial concentration of 0.293 mol/L, after 35.4 s the concentration of A is

$$\frac{1}{[A]_t} = 0.225\ \text{L/(mol•s)} \times 35.4\ \text{s} + \frac{1}{0.293\ \text{mol/L}}$$

$$\frac{1}{[A]_t} = 7.9\underline{6}5\ \text{L/mol} + 3.4\underline{1}2\ \text{L/mol} = 11.3\underline{7}7\ \text{L/mol}$$

$$[A]_t = \frac{1}{11.377\ \text{L/mol}} = 0.087\underline{8}89 = 0.08789\ M$$

13.60. The second-order integrated rate law is

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

Using a rate constant value of 0.169 L/(mol•s) and an initial concentration of 0.159 mol/L, the time it would take for [A] to decrease to 6.07×10^{-3} mol/L is

$$\frac{1}{6.07 \times 10^{-3}\ \text{mol/L}} = 0.169\ \text{L/(mol•s)} \times t + \frac{1}{0.159\ \text{mol/L}}$$

$$0.169\ \text{L/(mol•s)} \times t = \frac{1}{6.07 \times 10^{-3}\ \text{mol/L}} - \frac{1}{0.159\ \text{mol/L}} = 15\underline{8}.45\ \text{L/mol}$$

$$t = \frac{158.45\ \text{L/mol}}{0.169\ \text{L/(mol•s)}} = 93\underline{7}.6 = 938\ \text{s}$$

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13.61. First, find the rate constant, k, by substituting experimental values into the first-order rate equation. Let $[\text{Et. Cl.}]_o = 0.00100\ M$, $[\text{Et. Cl.}]_t = 0.00067\ M$, and $t = 155$ s. Solving for k yields

$$k = -\frac{\ln \dfrac{[0.00067\ \text{M}]_t}{[0.00100\ \text{M}]_o}}{155\ \text{s}} = 2.\underline{5}83 \times 10^{-3}/\text{s}$$

Now let $[\text{Et. Cl.}]_t$ = the concentration after 256 s, $[\text{Et. Cl.}]_o$ again = 0.00100 M, and use the value of k of $1.5\underline{6}4 \times 10^{-3}$/s to calculate $[\text{Et. Cl.}]_t$.

$$\ln \frac{[\text{Et. Cl.}]_t}{[0.00100\ \text{M}]} = -(2.584 \times 10^{-3}/\text{s})(256\ \text{s}) = -0.6\underline{6}14$$

Converting both sides to antilogs gives

$$\frac{[\text{Et. Cl.}]_t}{[0.00100\ \text{M}]} = 0.5\underline{1}61$$

$$[\text{Et. Cl.}]_t = 0.5161 \times [0.00100\ M] = 5.\underline{1}6 \times 10^{-4} = 5.2 \times 10^{-4}\ M$$

13.62. First, find the rate constant, k, by substituting experimental values into the first-order rate equation. Let $[\text{Cyb.}]_o = 0.00150\ M$, $[\text{Cyb.}]_t = 0.00119\ M$, and $t = 455$ s.

$$-k(455\ \text{s}) = \ln \frac{[0.00119\ \text{M}]}{[0.00150\ \text{M}]} = -0.23\underline{1}51$$

Solving gives $k = 5.0\underline{8}8 \times 10^{-4}$/s. Now let $[\text{Cyb.}]_t$ = the concentration after 750 s and $[\text{Cyb.}]_o = 0.00150\ M$, and calculate $[\text{Cyb.}]_t$.

$$\ln \frac{[\text{Cyb.}]_t}{[0.00150\ \text{M}]} = -(5.088 \times 10^{-4}\ /\text{s})(750\ \text{s}) = -0.38\underline{1}6$$

Taking the antilog of both sides yields

$$\frac{[\text{Cyb.}]_t}{[0.00150\ \text{M}]} = 0.68\underline{2}75$$

Solving for $[\text{Cyb.}]_t$ gives

$$[\text{Cyb.}]_t = 0.68275 \times [0.00150\ M] = 1.0\underline{2}4 \times 10^{-3} = 1.02 \times 10^{-3}\ M$$

13.63. For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$$t_{1/2} = 0.693/(6.3 \times 10^{-4}/\text{s}) = 1.\underline{1}0 \times 10^3 = 1.1 \times 10^3\ \text{s}\ (1\underline{8}.3\ \text{min})$$

Now, use the half-life to determine the concentrations. When the concentration decreases to 50.0% of its initial value, this is equal to the half-life.

$$t_{50.0\%\ \text{left}} = t_{1/2} = 1.10 \times 10^3\ \text{s}$$

When the concentration decreases to 25.0% of its initial value, this is equal to two half-lives.

$$t_{25.0\%\ \text{left}} = t_{1/4\ \text{left}} = 2 \times t_{1/2} = 2 \times (1.10 \times 10^3\ \text{s}) = 2.\underline{2}0 \times 10^3\ \text{s}\ (37\ \text{min})$$

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13.64. For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$t_{1/2} = 0.693/(6.2 \times 10^{-4}/\text{min}) = 1.\underline{1}17 \times 10^3 = 1.1 \times 10^3$ min (1$\underline{8}$.6 hr)

$t_{25.0\%\text{ left}} = t_{1/4\text{ left}} = 2 \times t_{1/2} = 2 \times (1.117 \times 10^3\text{ min}) = 2.\underline{2}35 \times 10^3 = 2.2 \times 10^3$ min

$t_{12.5\%\text{ left}} = t_{1/8\text{ left}} = 3 \times t_{1/2} = 3 \times (1.117 \times 10^3\text{ min}) = 3.\underline{3}53 \times 10^3 = 3.4 \times 10^3$ min

13.65. For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$t_{1/2} = 0.693/(2.0 \times 10^{-6}/\text{s}) = 3.\underline{4}65 \times 10^5$ s (9$\underline{6}$.25 or 96 hr)

$t_{25\%\text{ left}} = t_{1/4\text{ left}} = 2 \times t_{1/2} = 2 \times 96.25\text{ hr} = 1\underline{9}2.5 = 1.9 \times 10^2$ hr

$t_{12.5\%\text{ left}} = t_{1/8\text{ left}} = 3 \times t_{1/2} = 3 \times 96.25\text{ hr} = 2\underline{8}8.75 = 2.9 \times 10^2$ hr

$t_{6.25\%\text{ left}} = t_{1/16\text{ left}} = 4 \times t_{1/2} = 4 \times 96.25\text{ hr} = 3\underline{8}5.0 = 3.9 \times 10^2$ hr

$t_{3.125\%\text{ left}} = t_{1/32\text{ left}} = 5 \times t_{1/2} = 5 \times 96.25\text{ hr} = 4\underline{8}1.25 = 4.8 \times 10^2$ hr

13.66. For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$t_{1/2} = 0.693/(1.27/\text{s}) = 0.54\underline{5}6$ s

$t_{25\%\text{ left}} = t_{1/4\text{ left}} = 2 \times t_{1/2} = 2 \times 0.5456\text{ s} = 1.0\underline{9}1 = 1.09$ s

$t_{12.5\%\text{ left}} = t_{1/8\text{ left}} = 3 \times t_{1/2} = 3 \times 0.5456\text{ s} = 1.6\underline{3}6 = 1.64$ s

$t_{6.25\%\text{ left}} = t_{1/16\text{ left}} = 4 \times t_{1/2} = 4 \times 0.5456\text{ s} = 2.1\underline{8}2 = 2.18$ s

$t_{3.125\%\text{ left}} = t_{1/32\text{ left}} = 5 \times t_{1/2} = 5 \times 0.5456\text{ s} = 2.7\underline{2}8 = 2.73$ s

13.67. The half-life for a second-order reaction is

$$t_{1/2} = \frac{1}{k[\text{A}]_o}$$

Using a rate constant of 0.413 L/(mol•s) and an initial A concentration of 5.25×10^{-3} mol/L, the half-life is

$$t_{1/2} = \frac{1}{(0.413\text{ L/(mol}\bullet\text{s)})(5.25 \times 10^{-3}\text{ mol/L})} = 46\underline{1}.2 = 461\text{ s}$$

13.68. The rate constant for a second-order reaction is related to the half-life by

$$k = \frac{1}{t_{1/2}[\text{A}]_o}$$

Using a half-life of 425 s and an initial A concentration of 5.99×10^{-3} mol/L, the rate constant is

$$k = \frac{1}{(425\text{ s})(5.99 \times 10^{-3}\text{ mol/L})} = 0.39\underline{2}8 = 0.393\text{ L/(mol}\bullet\text{s)}$$

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13.69. Use the first-order rate equation, and solve for time, t. Let $[Cr^{3+}]_o = 100.0\%$; then the concentration at time t, $[Cr^{3+}]_t$, = (100.0% − 85.0%, or 15.0%). Use $k = 2.0 \times 10^{-6}$/s.

$$\ln \frac{[15.0]}{[100.0]} = -(2.0 \times 10^{-6}/\text{s})\, t$$

$$t = -\frac{\ln(0.150)}{2.0 \times 10^{-6}/\text{s}} = 9.\underline{4}8 \times 10^{5} \text{ s, or } 2.6 \times 10^{2} \text{ hr}$$

13.70. Use the first-order rate equation, and solve for time, t. Let $[Fe^{3+}]_o = 100.0\%$; then the concentration at time t, $[Fe^{3+}]_t$, = (100.0% − 90.0%, or 10.0%). Use $k = 1.27$/s.

$$\ln \frac{[\ 10.0\%]}{[\ 100.0\%]} = -(1.27/\text{s})\, t$$

$$t = -\frac{\ln(0.100)}{1.27/\text{s}}\ 1.8\underline{1}3 = 1.81 \text{ s}$$

13.71. The rate law for a zero-order reaction is

$$[A] = -kt + [A]_o.$$

Using a rate constant of 8.1×10^{-2} mol/(L•s) and an initial concentration of 0.10 M, the time it would take for the concentration to change to 1.0×10^{-2} M is

$$1.0 \times 10^{-2}\ M = -8.1 \times 10^{-2} \text{ mol/(L•s)} \times t + 0.10\ M$$

$$t = \frac{0.10 \text{ M} - 1.0 \times 10^{-2} \text{ M}}{8.1 \times 10^{-2} \text{ M/s}} = 1.\underline{1}1 = 1.1 \text{ s}$$

13.72. The rate law for a zero-order reaction is

$$[A] = -kt + [A]_o.$$

Using a time of 4.3×10^{2} s to go from an initial concentration of 0.50 M to 0.25 M, the rate constant is

$$0.25\ M = -k \times 4.3 \times 10^{2} \text{ s} + 0.50\ M$$

$$k = \frac{0.50 \text{ M} - 0.25 \text{ M}}{4.3 \times 10^{2} \text{ s}} = 5.\underline{8}1 \times 10^{-4} = 5.8 \times 10^{-4}\ M/\text{s}$$

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13.73. For the first-order plot, follow Figure 13.9, and plot ln [ClO_2] versus the time in seconds. The data used for plotting are

***t*, sec**	**[ClO_2], *M***	**ln [ClO_2]**
0.00	4.77×10^{-4}	−7.647
1.00	4.31×10^{-4}	−7.749
2.00	3.91×10^{-4}	−7.846
3.00	3.53×10^{-4}	−7.949
5.00	2.89×10^{-4}	−8.149
10.00	1.76×10^{-4}	−8.645
30.00	2.4×10^{-5}	−10.63
50.00	3.2×10^{-5}	−12.65

The plot yields an approximate straight line, demonstrating the reaction is first order in [ClO_2]. The slope of the line may be calculated from the difference between the last point and the first point:

$$\text{Slope} = \frac{[(-12.65) - (-7.647)]}{[50.00 - 0.00]\text{s}} = -0.10\underline{0}1/\text{s}$$

Just as the slope, *m*, was obtained for the plot in Figure 13.9, you can also equate *m* to −*k*, and calculate *k* as follows:

$k = -\text{slope} = 0.10\underline{0}1 = 0.100/\text{s}$

13.74. For the first-order plot, follow Figure 13.9, and plot ln [MA], the methyl acetate concentration, versus time in minutes. This plot does not yield a straight line, so the reaction is not first order. For the second-order plot, follow Figure 13.10, and plot 1/[MA] versus time in minutes. The data used for plotting are

***t*, min**	**[MA], *M***	**1/[MA]**
0.00	0.01000	100.0
3.00	0.00740	135.1
4.00	0.00683	146.4
5.00	0.00634	157.7
10.00	0.00463	215.9
20.00	0.00304	328.9
30.00	0.00224	446.4

The plot requires a graph with too many lines to be reproduced here, but it yields a straight line, demonstrating that the reaction is second order in [MA]. The slope of the line may be calculated from the difference between the last point and the first point:

$$\text{Slope} = \frac{[446.4 - 100.0]/M}{[30.00 - 0.00]\text{min}} = \frac{11.54}{M \bullet \text{min}} = \frac{0.192}{M \bullet \text{s}}$$

In this case, the slope equals the rate constant, so $k = 11.5/(M\bullet\text{m})$, or $0.192/(M\bullet\text{s})$.

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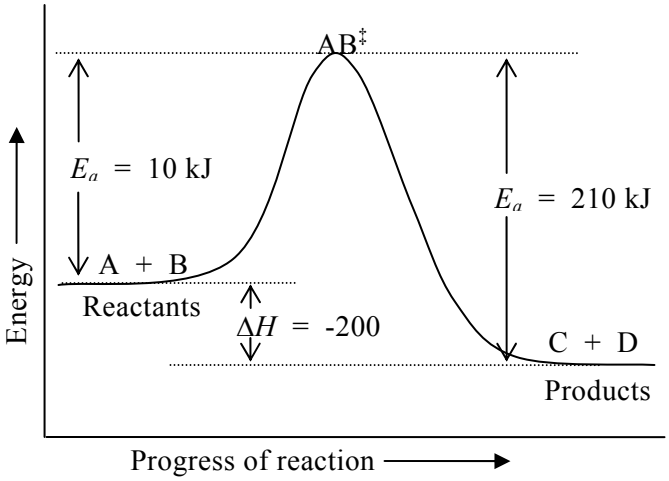
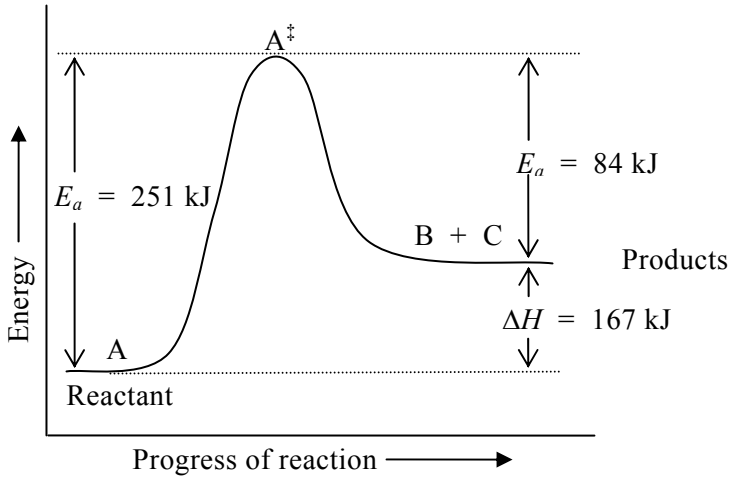
13.75. The potential-energy diagram, not drawn to scale, is below. Because the activation energy for the forward reaction is +10 kJ, and $\Delta H° = -200$ kJ, the activation energy for the reverse reaction is +210 kJ.



13.76. The potential-energy diagram, not drawn to scale, is below. Because the activation energy for the forward reaction is +251 kJ, and $\Delta H°$ is +167 kJ, the activation energy for the reverse reaction is +84 kJ.



13.77. Solve the two-temperature Arrhenius equation for E_a by substituting $T_1 = 308$ K (from 35°C), $k_1 = 1.4 \times 10^{-4}$/s, $T_2 = 318$ K (from 45°C), and $k_2 = 5.0 \times 10^{-4}$/s:

$$\ln \frac{5.0 \times 10^{-4}}{1.4 \times 10^{-4}} = \frac{E_a}{8.31 \text{ J/(mol} \bullet \text{K)}} \left(\frac{1}{308 \text{ K}} - \frac{1}{318 \text{ K}} \right)$$

Rearranging E_a to the left side and calculating [1/308 − 1/318] give

$$E_a = \frac{8.31 \text{ J/K} \times \ln(3.5714)}{1.0209 \times 10^{-4}/\text{K}} = 1.037 \times 10^5 = 1.0 \times 10^5 \text{ J/mol}$$

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To find the rate at 55°C (328 K), use the first equation. Let k_2 in the numerator be the unknown and solve:

$$\ln \frac{k_2}{1.4 \times 10^{-4}} = \frac{1.037 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \bullet \text{K)}} \left(\frac{1}{308 \text{ K}} - \frac{1}{328 \text{ K}} \right) = 2.\underline{4}68$$

$$\frac{k_2}{1.4 \times 10^{-4}} = 1\underline{1}.80$$

$$k_2 = 11.80 \times (1.4 \times 10^{-4}/\text{s}) = 1.\underline{6}52 \times 10^{-3} = 1.7 \times 10^{-3}/\text{s}$$

13.78. Solve the two-temperature Arrhenius equation for E_a by making these substitutions: $T_1 = 350$ K, $k_1 = 9.3 \times 10^{-6}$/s, $T_2 = 400$ K, and $k_2 = 6.9 \times 10^{-4}$/s.

$$\ln \frac{6.9 \times 10^{-4}/\text{s}}{9.3 \times 10^{-6}/\text{s}} = \frac{E_a}{8.31 \text{ J/(mol} \bullet \text{K)}} \left(\frac{1}{350 \text{ K}} - \frac{1}{400 \text{ K}} \right)$$

Rearranging and solving for E_a give

$$E_a = \frac{8.31 \text{ J/(mol} \bullet \text{K)} \times \ln \left(\frac{6.9 \times 10^{-4}}{9.3 \times 10^{-6}} \right)}{\left(\frac{1}{350 \text{ K}} - \frac{1}{400 \text{ K}} \right)} = 1.00\underline{2} \times 10^5 = 1.00 \times 10^5 \text{ J/mol (100. kJ/mol)}$$

To find the rate constant at 435 K, use the first equation with k_2 as the symbol for the rate constant at 475 K and $E_a = 1.00\underline{2} \times 10^5$ J/mol:

$$\ln \frac{k_2}{9.3 \times 10^{-6}/\text{s}} = \frac{1.002 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \bullet \text{K)}} \left(\frac{1}{350 \text{ K}} - \frac{1}{435 \text{ K}} \right) = 6.7\underline{3}2$$

Taking the antilog of both sides gives

$$\frac{k_2}{9.3 \times 10^{-6}/\text{s}} = e^{6.732} = 8\underline{3}9.05$$

Solving for k_2 gives

$$k_2 = 839.05 \times (9.3 \times 10^{-6}/\text{s}) = 0.007\underline{8}0 = 0.0078 \text{ /s}$$

13.79. Because the rate constant is proportional to the rate of a reaction, tripling the rate at 25°C means that the rate constant at 25°C is also tripled. Thus, $k_{35} = 3k_{25}$, and the latter can be substituted for k_{25} in the Arrhenius equation:

$$\ln \frac{3\,k_{25}}{k_{25}} = \frac{E_a}{8.31 \text{ J/(mol} \bullet \text{K)}} \left(\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right)$$

$$1.0986 = (1.3\underline{1}1 \times 10^{-5} \text{ mol/J})\, E_a$$

$$E_a = \frac{1.0986}{1.311 \times 10^{-5} \text{ mol/J}} = 8.3\underline{7}9 \times 10^4 \text{ J/mol} = 83.8 \text{ kJ/mol}$$

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13.80. Because the rate constant is proportional to the rate of a reaction, quadrupling the rate at 25°C means that the rate constant at 25°C is also quadrupled. Thus, $k_{35} = 4k_{25}$, and the latter can be substituted for k_{35} in the Arrhenius equation:

$$\ln \frac{4\,k_{25}}{k_{25}} = \frac{E_a}{8.31\ \text{J/(mol}\bullet\text{K)}} \left(\frac{1}{298\ \text{K}} - \frac{1}{308\ \text{K}} \right)$$

$$1.3862 = (1.311 \times 10^{-5}\ \text{mol/J})\ E_a$$

$$E_a = \frac{1.3862}{1.311 \times 10^{-5}\ \text{mol/J}} = 1.0572 \times 10^5\ \text{J/mol} = 106\ \text{kJ/mol}$$

13.81. For plotting ln k versus $1/T$, the data below are used:

k	**ln *k***	***1/T* (1/K)**
0.527	−0.64055	1.686×10^{-3}
0.776	−0.25360	1.658×10^{-3}
1.121	0.11422	1.631×10^{-3}
1.607	0.47436	1.605×10^{-3}

The plot yields an approximately straight line. The slope of the line is calculated from the difference between the last and the first points:

$$\text{Slope} = \frac{(0.47436) - (-0.64055)}{[1.605 \times 10^{-3} - 1.686 \times 10^{-3}]/\text{K}} = -13764\ \text{K}$$

Because the slope = $-E_a/R$, you can solve for E_a using $R = 8.31$ J/K:

$$\frac{-E_a}{8.31\ \text{J/ (K}\bullet\text{mol)}} = -13764\ \text{K}$$

$E_a = 13764\ \text{K} \times 8.31\ \text{J/K} = 1.143 \times 10^5\ \text{J/mol}$, or 1.1×10^2 kJ/mol

13.82. For plotting ln k versus $1/T$, the data below are used:

k	ln k	1/T (K)
2.69×10^{-3}	−5.918	1.402×10^{-3}
6.21×10^{-3}	−5.081	1.364×10^{-3}
1.40×10^{-2}	−4.268	1.328×10^{-3}
3.93×10^{-2}	−3.236	1.294×10^{-3}

The plot yields an approximately straight line. The slope of the line may be calculated from the difference between the last point and the first point:

$$\text{Slope} = \frac{(-3.236) - (-5.918)}{[1.294 \times 10^{-3} - 1.402 \times 10^{-3}]/\text{K}} = -2.483 \times 10^4\ \text{K}$$

Because the slope = $-E_a/R$, you can solve for E_a using $R = 8.31$ J/K•mol:

$$\frac{-E_a}{8.31\ \text{J/ (K}\bullet\text{mol)}} = 2.483 \times 10^4\ \text{K}$$

$E_a = 2.483 \times 10^4\ \text{K} \times 8.31\ \text{J/K} \bullet \text{mol} = 2.063 \times 10^5\ \text{J/mol}$ (2.1×10^2 kJ/mol)

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13.83. The $NOCl_2$ is a reaction intermediate that is produced in the first reaction and consumed in the second. The overall reaction is the sum of the two elementary reactions:

$$NO + Cl_2 \rightarrow NOCl_2$$
$$\underline{NOCl_2 + NO \rightarrow 2NOCl}$$
$$2NO + Cl_2 \rightarrow 2NOCl$$

13.84. The O atom is a reaction intermediate that is produced in the first reaction and consumed in the second. The overall reaction is the sum of the two elementary reactions:

$$O_3 \rightarrow O_2 + O$$
$$\underline{O_3 + O \rightarrow 2O_2}$$
$$2O_3 \rightarrow 3O_2$$

13.85.

a. Bimolecular
b. Bimolecular
c. Unimolecular
d. Termolecular

13.86.

a. Termolecular
b. Bimolecular
c. Bimolecular
d. Unimolecular

13.87.

a. Only O_3 occurs on the left side of the equation, so the rate law is
   Rate = $k[O_3]$
b. Both $NOCl_2$ and NO occur on the left side of the equation, so the rate law is
   Rate = $k[NOCl_2][NO]$

13.88.

a. Only CS_2 occurs on the left side of the equation, so the rate law is
   Rate = $k[CS_2]$

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b. Both CH_3Br and OH^- occur on the left side of the equation, so the rate law is

Rate = $k[CH_3Br][OH^-]$

13.89. Step 1 of the isomerization of cyclopropane, C_3H_6, is slow, so the rate law for the overall reaction will be the rate law for this step, with $k_1 = k$, the overall rate constant:

Rate = $k[C_3H_6]^2$

13.90. Step 1 of the decomposition of NO_2Cl is slow, so the rate law for the overall reaction will be the rate law for this step, with $k_1 = k$, the overall rate constant:

Rate = $k[NO_2Cl]$

13.91. Step 2 of this reaction is slow, so the rate law for the overall reaction would appear to be the rate law for this step:

Rate = $k_2[I]^2[H_2]$

However, the rate law includes an intermediate, the I atom, and cannot be used unless the intermediate is eliminated. This can be done only using an equation for Step 1. At equilibrium, you can write the following equality for Step 1:

$k_1[I_2] = k_{-1}[I]^2$

Rearranging and then substituting for the $[I]^2$ term yield

$$[I]^2 = [I_2]\frac{k_1}{k_{-1}}$$

Rate = $k_2(k_1/k_{-1})[I_2][H_2] = k[I_2][H_2]$ (k = the overall rate constant)

13.92. Step 2 of this reaction is slow, so the rate law for the overall reaction would appear to be the rate law for this step:

Rate = $k_2[O_3][O]$

However, the rate law includes an intermediate, the O atom, and cannot be used unless the intermediate is eliminated. This can be done only using an equation for Step 1. At equilibrium, you can write the following equality for Step 1:

$k_1[O_3] = k_{-1}[O_2][O]$

Rearranging and then substituting for the [O] term yield

$$[O] = \left[\frac{k_1}{k_{-1}}\right]\frac{[O_3]}{[O_2]}$$

$$\text{Rate} = k_2[O_3]\left[\frac{k_1}{k_{-1}}\right]\frac{[O_3]}{[O_2]}$$

$$\text{Rate} = k_2\left[\frac{k_1}{k_{-1}}\right]\frac{[O_3]^2}{[O_2]} = k\frac{[O_3]^2}{[O_2]}$$ (k = overall rate constant)

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13.93. The Br^- ion is the catalyst. It is consumed in the first step and regenerated in the second step. It speeds up the reaction by providing a pathway with a lower activation energy than that of a reaction pathway involving no Br^-. The overall reaction is obtained by adding the two steps together:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Bromide ion is added to the mixture to give the catalytic activity, and BrO^- is an intermediate.

13.94. The OH^- ion is the catalyst. It is consumed in the first step and regenerated in the second step. It speeds up the reaction by providing a pathway with a lower activation energy than that of a reaction pathway involving no OH^- ion. The overall reaction is obtained by adding the two steps together:

$$NH_2NO_2 \rightarrow N_2O + H_2O$$

You could add NaOH to give the catalytic activity.

■ SOLUTIONS TO GENERAL PROBLEMS

13.95. All rates of reaction are calculated by dividing the decrease in concentration by the difference in times; hence, only the setup for the first rate (after 10 minutes) is given below. This setup is

$$\text{Rate (10 min)} = -\frac{(1.29 - 1.50) \times 10^{-2}\ \text{M}}{(10 - 0)\ \text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 3.5 \times 10^{-6}\ M/\text{s}$$

A summary of the times and rates is given in the table.

Time, min	Rate
10	$3.\underline{5}0 \times 10^{-6} = 3.5 \times 10^{-6}\ M/\text{s}$
20	$3.\underline{1}7 \times 10^{-6} = 3.2 \times 10^{-6}\ M/\text{s}$
30	$2.\underline{5}0 \times 10^{-6} = 2.5 \times 10^{-6}\ M/\text{s}$

13.96. All rates of reaction are calculated by dividing the decrease in concentration by the difference in times; only the setup for the first rate after 1.0 min is given below:

$$\text{Rate (1.0 min)} = -\frac{(0.1076 - 0.1103)\ \text{M}}{(1.0 - 0)\ \text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 4.\underline{5}0 \times 10^{-5} = 4.5 \times 10^{-5}\ M/\text{s}$$

A summary of the times and rates is given in the table.

Time, min	Rate
1.0	$4.\underline{5}0 \times 10^{-5} = 4.5 \times 10^{-5}\ M/\text{s}$
2.0	$4.\underline{3}3 \times 10^{-5} = 4.3 \times 10^{-5}\ M/\text{s}$
3.0	$4.\underline{0}0 \times 10^{-5} = 4.0 \times 10^{-5}\ M/\text{s}$

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13.97. The calculation of the average concentration and the division of the rate by the average concentration are the same for all three time intervals. Thus, only the setup for the first interval is given:

$$k_{10\ \text{min}} = \frac{\text{rate}}{\text{avg. conc.}} = \frac{3.50 \times 10^{-6}\ M/\text{s}}{\left[\frac{(1.50 + 1.29) \times 10^{-2}\ M}{2}\right]} = 2.508 \times 10^{-4}/\text{s}$$

A summary of the times, rate constants, and average rate constant is given in the table.

Time	Rate	*k*
10 min	3.50×10^{-6} *M*/s	2.508×10^{-4}/s
20 min	3.17×10^{-6} *M*/s	2.652×10^{-4}/s
30 min	2.50×10^{-6} *M*/s	2.439×10^{-4}/s
-----	---- average *k*	$2.533 \times 10^{-4} = 2.5 \times 10^{-4}$/s

13.98. The calculation of the average concentration and the division of the rate by the average concentration are the same for all three time intervals. Thus, only the setup for the first interval is given:

$$k_{1.0\ \text{min}} = \frac{\text{rate}}{\text{avg. conc.}} = \frac{4.50 \times 10^{-5}\ M/\text{s}}{\left(\frac{0.1103\ M\ +\ 0.1076\ M}{2}\right)^2} = 3.79 \times 10^{-3}/(M\bullet\text{s})$$

A summary of the times, rate constants, and average rate constant is given in the table.

Time	Rate	*k*
1.0 min	4.50×10^{-5} *M*/s	$3.79 \times 10^{-3}/(M\bullet\text{s})$
2.0 min	4.33×10^{-5} *M*/s	$3.83 \times 10^{-3}/(M\bullet\text{s})$
3.0 min	4.00×10^{-5} *M*/s	$3.71 \times 10^{-3}/(M\bullet\text{s})$
-----	---- average *k* =	$3.78 \times 10^{-3} = 3.8 \times 10^{-3}/(M\bullet\text{s})$

13.99. Use the first-order rate equation $k = 1.26 \times 10^{-4}$/s, the initial methyl acetate $[\text{MA}]_o = 100\%$, and $[\text{MA}]_t = (100\% - 65\%, \text{ or } 35\%)$.

$$t = -\frac{\ln \frac{35\%}{100\%}}{1.26 \times 10^{-4}/\text{s}} = 8.3319 \times 10^3 = 8.33 \times 10^3\ \text{s}$$

13.100. Use the first-order rate equation; substitute $k = 4.3 \times 10^{-5}$/s, the initial benzene diazonium chloride $[\text{BC}]_o = 100\%$, and $[\text{BC}]_t = (100\% - 75\%, \text{ or } 25\%)$.

$$t = -\frac{\ln \frac{25\%}{100\%}}{4.3 \times 10^{-5}/\text{s}} = 3.223 \times 10^4 = 3.2 \times 10^4\ \text{s}$$

13.101. Use $k = 1.26 \times 10^{-4}$/s, and substitute into the $t_{1/2}$ equation:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.26 \times 10^{-4}/\text{s}} = 5.500 \times 10^3 = 5.50 \times 10^3\ \text{s (1.53 hr)}$$

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13.102. Use $k = 4.3 \times 20^{-5}$/s, and substitute into the $t_{1/2}$ equation:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.3 \times 10^{-5}/\text{s}} = 1.\underline{6}1 \times 10^4 = 1.6 \times 10^4 \text{ s (4.5 hr)}$$

13.103. First, find the rate constant from the first-order rate equation, substituting the initial concentration of $[\text{comp.}]_o = 0.0350\ M$, and the $[\text{comp.}]_t = 0.0250\ M$.

$$\ln \frac{0.0250\ M}{0.0350\ M} = -k\ (65 \text{ s})$$

Rearranging and solving for k give

$$k = \frac{\left(\ln \frac{0.0250\ M}{0.0350\ M}\right)}{65 \text{ s}} = 5.\underline{1}7 \times 10^{-3}/\text{s}$$

Now, arrange the first-order rate equation to solve for $[\text{comp.}]_t$; substitute the above value of k, again using $[\text{comp.}]_o = 0.0350\ M$.

$$\ln \frac{[\text{comp.}]_t}{0.0350\ M} = -(5.18 \times 10^{-3}/\text{s})(88 \text{ s}) = -0.4\underline{5}58$$

Taking the antilog of both sides gives

$$\frac{[\text{comp.}]_t}{0.0350\ M} = e^{-0.4558} = 0.6\underline{3}39$$

$$[\text{comp}]_t = 0.6\underline{3}39 \times [0.0350\ M]_o = 0.02\underline{2}1 = 0.022\ M$$

13.104. First, find the rate constant from the rearranged first-order rate equation, substituting the initial concentration of $[\text{comp.}]_o = 0.1180\ M$ and the $[\text{comp.}]_t = 0.0950\ M$. Use k to find the fraction.

$$k = \frac{\left(\ln \frac{0.0950\ M}{0.1180\ M}\right)}{5.2 \text{ min}} = 4.\underline{1}69 \times 10^{-2}/\text{min}$$

$$\ln \frac{[\text{comp.}]_t}{0.1180\ M} = -(4.169 \times 10^{-3}/\text{s})(7.1 \text{ min}) = -0.2\underline{9}60$$

Taking the antilogarithm of both sides yields

$$\frac{[\text{comp.}]_t}{0.1180\ M} = 0.7\underline{4}37 = 0.74 \text{ (fraction remaining)}$$

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13.105.

a. The rate constant for a second-order reaction is related to the half-life by

$$k = \frac{1}{t_{1/2}[\mathrm{A}]_o}$$

Using a half-life of 5.92 x 10^{-2} s and an initial A concentration of 0.50 mol/L, the rate constant is

$$k = \frac{1}{(5.92 \times 10^{-2}\ \mathrm{s})(0.50\ \mathrm{mol/L})} = 33.78 = 34\ \mathrm{L/(mol \cdot s)}$$

b. The second-order integrated rate law is

$$\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_o}$$

Using an initial concentration of C_4H_8 (A) of 0.010 *M*, after 3.6 x 10^2 s, the concentration will be

$$\frac{1}{[\mathrm{A}]_t} = 33.78\ \mathrm{L/(mol \cdot s)}(3.6 \times 10^2\ \mathrm{s}) + \frac{1}{0.010\ \mathrm{mol/L}}$$

$$\frac{1}{[\mathrm{A}]_t} = 12{,}162\ \mathrm{L/mol} + 100.0\ \mathrm{L/mol} = 12{,}262\ \mathrm{L/mol}$$

$$[\mathrm{A}]_t = \frac{1}{12{,}262\ \mathrm{L/mol}} = 8.155 \times 10^{-5} = 8.2 \times 10^{-5}\ M$$

13.106.

a. A plot of 1/[A] versus time is a straight line for a second-order reaction.

b. The second-order integrated rate law is

$$\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_o}$$

After 57 s, the concentration of A dropped 40% of its initial value, so $[\mathrm{A}]_t = 0.60[\mathrm{A}]_o$, or (0.60)(0.50 *M*) = 0.30 *M*. Using these values gives

$$\frac{1}{0.30\ \mathrm{mol/L}} = k \times (57\ \mathrm{s}) + \frac{1}{0.50\ \mathrm{mol/L}}$$

$$k \times (57\ \mathrm{s}) = \frac{1}{0.30\ \mathrm{mol/L}} - \frac{1}{0.50\ \mathrm{mol/L}} = 1.333\ \mathrm{L/mol}$$

$$k = \frac{1.333\ \mathrm{L/mol}}{57\ \mathrm{s}} = 0.0233 = 0.023\ \mathrm{L/(mol \cdot s)}$$

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13.107. The second-order integrated rate law is

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

The starting concentration of NO_2 (A) is 0.050 *M*. Using a rate constant of 0.775 L/(mol•s), after 2.5 x 10^2 s the concentration of NO_2 will be

$$\frac{1}{[A]_t} = 0.775 \text{ L/(mol•s)}(2.5 \times 10^2 \text{ s}) + \frac{1}{0.050 \text{ mol/L}}$$

$$\frac{1}{[A]_t} = 193 \text{ L/mol} + 20.0 \text{ L/mol} = 213. \text{ L/mol}$$

$$[A]_t = \frac{1}{213 \text{ L/mol}} = 4.67 \times 10^{-3} = 4.7 \times 10^{-3} \, M$$

The half-life is

$$t_{1/2} = \frac{1}{k[A]_o}$$

Using a rate constant of 0.775 L/(mol•s) and an initial A concentration of 0.10 mol/L, the half-life is

$$t_{1/2} = \frac{1}{(0.775 \text{ L/(mol} \bullet \text{s)}(0.050 \text{ mol/L})} = 25.80 = 26 \text{ s}$$

13.108. The second-order integrated rate law is

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

The starting concentration is 0.10 *M*. Using a rate constant of 3.1 x 10^{-2} L/(mol•s), after 1.0 x 10^2 s the concentration will be

$$\frac{1}{[A]_t} = 3.1 \times 10^{-2} \text{ L/(mol•s)}(1.0 \times 10^2 \text{ s}) + \frac{1}{0.10 \text{ mol/L}}$$

$$\frac{1}{[A]_t} = 3.1 \text{ L/mol} + 10.0 \text{ L/mol} = 13.1. \text{ L/mol}$$

$$[A]_t = \frac{1}{13.1 \text{ L/mol}} = 0.0763 = 0.076 \, M$$

The half-life is

$$t_{1/2} = \frac{1}{k[A]_o}$$

Using a rate constant of 3.1 x 10^{-2} L/(mol•s) and an initial concentration of 0.10 mol/L, the half-life is

$$t_{1/2} = \frac{1}{(3.1 \times 10^{-2} \text{ L/(mol} \bullet \text{s)}(0.10 \text{ mol/L})} = 322.5 = 3.2 \times 10^2 \text{ s}$$

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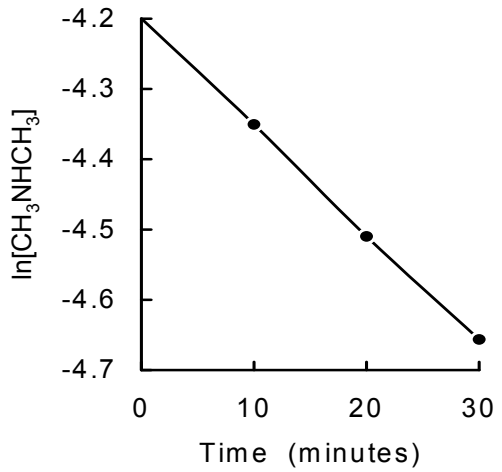
13.109. The ln[CH_3NNCH_3] and time data for the plot are tabulated below.

***t* min**	**ln[CH_3NNCH_3]**
0	−4.1997
10	−4.3505
20	−4.5098
30	−4.6564



The slope, *m*, is calculated from the graph:

$$m = \frac{(-4.6564) - (-4.1997)}{(30 - 0)\ \text{min}}$$

$$= -0.01522\ /\text{min}$$

Because the slope also = −*k*, this gives

$$k = -(-0.01522/\text{min})(1\ \text{min}/60\ \text{s}) = 2.53 \times 10^{-4} = 2.5 \times 10^{-4}/\text{s}$$

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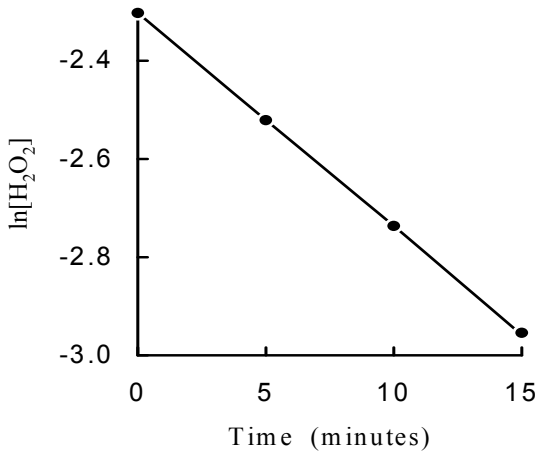
13.110. The ln $[H_2O_2]$ and time data for the plot are tabulated below.

t min	ln$[H_2O_2]$
0.0	−2.3025
5.0	−2.5207
10.0	−2.7364
15.0	−2.9584



The slope, *m*, is calculated from the graph:

$$m = \frac{(-2.9584) - (-2.3025)}{(15.0 - 0)\ \text{min}}$$

$$= -0.04372/\text{min}$$

Because the slope also = −*k*, this gives

$$k = -(-0.04372/\text{min})(1\ \text{min}/60\ \text{s}) = 7.287 \times 10^{-4} = 7.29 \times 10^{-4}/\text{s}$$

13.111. The rate law for a zero-order reaction is

$$[A] = -kt + [A]_o.$$

Using a rate constant of 3.7×10^{-6} mol/(L•s) and an initial concentration of 5.0×10^{-4} *M*, the time it would take for the concentration to drop to 5.0×10^{-5} *M* is

$$5.0 \times 10^{-5}\ M = -8.1 \times 10^{-2}\ \text{mol/(L•s)} \times t + 5.0 \times 10^{-4}\ \text{M}$$

$$t = \frac{(5.0 \times 10^{-4}\ \text{M}) - (5.0 \times 10^{-5}\ M)}{3.7 \times 10^{-6}\ M/\text{s}} = 121.6 = 1.2 \times 10^2\ \text{s}$$

The half-life for a zero-order reaction is

$$t_{1/2} = \frac{[A]_o}{2k} = \frac{5.0 \times 10^{-4}\ M}{2(3.7 \times 10^{-6}\ M/\text{s})} = 67.57 = 68\ \text{s}$$

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13.112. The rate law for a zero-order reaction is

$$[A] = -kt + [A]_o.$$

If it takes 3.3×10^2 s for the initial concentration of B to go from 0.50 *M* to 0.20 *M*, the rate constant is

$$0.20\ M = -k \times 3.3 \times 10^2\ \text{s} + 0.50\ M$$

$$k = \frac{(0.50\ M) - (0.20\ M)}{3.3 \times 10^2\ \text{s}} = 9.\underline{0}9 \times 10^{-4} = 9.1 \times 10^{-4}\ \text{mol/(L•s)}$$

The half-life for a zero-order reaction is

$$t_{1/2} = \frac{[A]_o}{2k} = \frac{0.50\ M}{2(9.09 \times 10^{-4}\ M/\text{s})} = 2\underline{7}5 = 2.8 \times 10^2\ \text{s}$$

13.113. Rearrange the two-temperature Arrhenius equation to solve for E_a in joules, using $k_1 = 0.498\ M/\text{s}$ at $T_1 = 592$ K (319°C) and $k_2 = 1.81\ M/\text{s}$ at 627 K (354°C). Assume $(1/T_1 - 1/T_2)$ has three significant figures.

$$E_a = \frac{(8.31\ \text{J/mol•K}) \ln\left(\frac{1.81}{0.498}\right)}{\left(\frac{1}{592\ \text{K}} - \frac{1}{627\ \text{K}}\right)} = 1.1\underline{3}7 \times 10^5\ \text{J/mol} = 114\ \text{kJ/mol}$$

To obtain *A*, rearrange the ln form of the one-temperature Arrhenius equation; substitute the value of E_a obtained above, and use $k_1 = 0.498\ M/\text{s}$ at $T_1 = 592$ K.

$$\ln A = \ln 0.498 + \frac{1.137 \times 10^5\ \text{J/mol}}{8.31\ \text{J/(mol•K)} \times 592\ \text{K}} = 22.\underline{4}20$$

$$A = \underline{5}.46 \times 10^9 = 5 \times 10^9$$

To obtain *k* at 420°C (693 K), also use the ln form of the one-temperature Arrhenius equation:

$$\ln k = 22.420 - \frac{1.137 \times 10^5\ \text{J/ mol}}{8.31\ \text{J/(mol•K)} \times 693\ \text{K}} = 2.\underline{6}71$$

$$k = e^{2.671} = 1\underline{4}.45 = 14\ M/\text{s}$$

13.114. Rearrange the two-temperature Arrhenius equation; solve for E_a using $k_1 = 8.7 \times 10^{-4}/(M\text{•s})$ at $T_1 = 303$ K (30°C) and $k_2 = 1.8 \times 10^{-3}$ (*M*•s) at 313 K (40°C).

$$E_a = \frac{8.31\ \text{J/(mol•K)} \times \ln\left(\frac{1.8 \times 10^{-3}/(\text{M•s})}{8.7 \times 10^{-4}/(\text{M•s})}\right)}{\left(\frac{1}{303\ \text{K}} - \frac{1}{313\ \text{K}}\right)} = 5.\underline{7}29 \times 10^4\ (57\ \text{kJ/mol})$$

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To obtain A, rearrange the ln form of the one-temperature Arrhenius equation; substitute the value of E_a obtained above and use $k_1 = 8.7 \times 10^{-4}/(M \cdot s)$ at $T_1 = 303$ K.

$$\ln A = \ln[8.7 \times 10^{-4}] + \frac{5.729 \times 10^4 \text{ J/ mol}}{8.31 \text{ J/ (mol} \bullet \text{K)} \times 303 \text{ K}} = 15.70$$

$$A = e^{15.70} = 6.646 \times 10^6 /(M \cdot s)$$

To obtain k at 45°C (318 K), also use the ln form of the one-temperature Arrhenius equation:

$$\ln k = 15.70 - \frac{5.729 \times 10^4 \text{ J/ mol}}{8.31 \text{ J/ (mol} \bullet \text{K)} \times 318 \text{ K}} = -5.970$$

$$k = e^{-5.970} = 2.551 \times 10^{-3} = 3 \times 10^{-3}/(M \cdot s)$$

13.115. If the reaction occurs in one step, the coefficients of NO_2 and CO in this elementary reaction are each one, so the rate law should be

$$\text{Rate} = k[NO_2][CO]$$

13.116. If the reaction occurs in one step, the coefficients of CH_3Cl and OH^- in this elementary reaction are each 1, so the rate law should be

$$\text{Rate} = k[CH_3Cl][OH^-]$$

13.117. The slow step determines the observed rate, so the overall rate constant, k, should be equal to the rate constant for the first step, and the rate law should be

$$\text{Rate} = k[NO_2Br]$$

13.118. The slow step determines the observed rate, so the overall rate constant, k, should be equal to the rate constant for the first step, and the rate law should be

$$\text{Rate} = k[(CH_3)_3CCl]$$

13.119. The slow step determines the observed rate; assuming k_2 is the rate constant for the second step, the rate law would appear to be

$$\text{Rate} = k_2[NH_3][HOCN]$$

However, this rate law includes two intermediate substances that are neither reactants nor products. The rate law cannot be used unless both are eliminated. This can be done only using an equation from Step 1. At equilibrium in Step 1, you can write the following equality, assuming k_1 and k_{-1} are the rate constants for the forward and back reactions, respectively:

$$k_1[NH_4^+][OCN^-] = k_{-1}[NH_3][HOCN]$$

Rearranging and then substituting for the $[NH_3][HOCN]$ product give

$$[NH_3][HOCN] = (k_1/k_{-1})[NH_4^+][OCN^-]$$

$$\text{Rate} = k_2(k_1/k_{-1})[NH_4^+][OCN^-] = k[NH_4^+][OCN^-]$$ (k = overall rate constant)

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13.120. The slow step determines the observed rate; assuming k_2 is the rate constant for the second step and using $[HA^+]$ for $[CH_3C(OH^+)CH_3]$, the rate law would appear to be

$$\text{Rate} = k_2[HA^+][H_2O]$$

However, this rate law includes the intermediates HA^+ and H_2O that are neither reactants nor products. The rate law cannot be used unless both are eliminated. This can be done only using an equation from Step 1. At equilibrium in Step 1, you can write the following equality, assuming k_1 and k_{-1} are the rate constants for the forward and back reactions, respectively:

$$k_1[A][H_3O^+] = k_{-1}[HA^+][H_2O]$$

Rearranging and then substituting for the $[HA^+][H_2O]$ product give

$$\text{Rate} = k_2(k_1/k_{-1})[A][H_3O^+] = k[A][H_3O^+] \ (k = \text{overall rate constant})$$

13.121.

a. The reaction is first order in O_2 because the rate doubled with a doubling of the oxygen concentration. The reaction is second order in NO because the rate increased by a factor of 8 when both the NO and O_2 concentrations were doubled.

$$\text{Rate} = k[NO]^2[O_2]$$

b. The initial rate of the reaction for Experiment 4 can be determined by first calculating the value of the rate constant using Experiment 1 for the data.

$$0.80 \times 10^{-2}\ M/\text{s} = k[4.5 \times 10^{-2}\ M]^2[2.2 \times 10^{-2}\ M]$$

Solving for the rate constant gives

$$k = 1.\underline{7}96 \times 10^2\ M^{-2}\text{s}^{-1}$$

Now, use the data in Experiment 4 and the rate constant to determine the initial rate of the reaction.

$$\text{Rate} = 1.796 \times 10^2\ M^{-2}\text{s}^{-1}\ [3.8 \times 10^{-1}\ M]^2[4.6 \times 10^{-3}\ M]$$

$$\text{Rate} = 0.1\underline{1}9 = 0.12\ \text{mol/L}\bullet\text{s}$$

13.122.

a. From the information given, the rate law is

$$\text{Rate} = k[CH_3Cl][H_2O]^2$$

Using just the units for each term in the rate law will give the units for the rate constant.

$$M/\text{s} = k(M)(M)^2$$

Thus, the units for k must be

$$k = M^{-2}\text{s}^{-1}$$

b. Plugging into the rate equation gives

$$1.50\ M/\text{s} = k[0.40\ M][0.40\ M]^2$$

$$k = 2\underline{3}.43 = 23\ M^{-2}\text{s}^{-1}$$

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13.123.

a.

i) Rate will decrease because OH^- will react with H_3O^+ and lower its concentration.

ii) Rate will decrease because the dilution with water will decrease both the H_3O^+ and the CH_3CSNH_2 concentration.

b.

i) The catalyst will provide another pathway, and *k* will increase because E_a will be smaller.

ii) The rate constant changes with temperature, and it will decrease with a decrease in temperature, because fewer molecules will have enough energy to react.

13.124.

a.

i) The $[H_3O^+]$ is increased, so the rate will increase.

ii) The $[H_3O^+]$ and $[CH_3COOCH_3]$ concentrations will be decreased, so the rate of reaction will decrease.

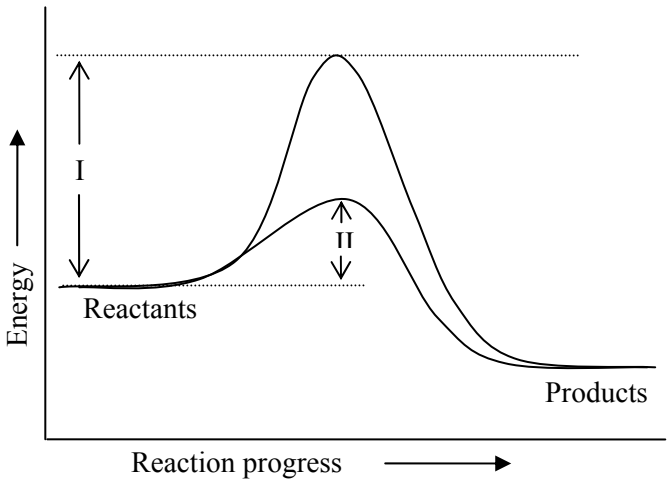
b.

i) The rate of reaction will increase, but the rate constant will remain the same.

ii) The rate constant will increase as more molecules have enough energy to react.

13.125.

a. The diagram:



b. In the diagram, I represents the activation energy for the uncatalyzed reaction, and II represents the activation energy for the catalyzed reaction. A catalyst provides another pathway for a chemical reaction, and with a lower activation energy, more molecules have enough energy to react, so the reaction will be faster.

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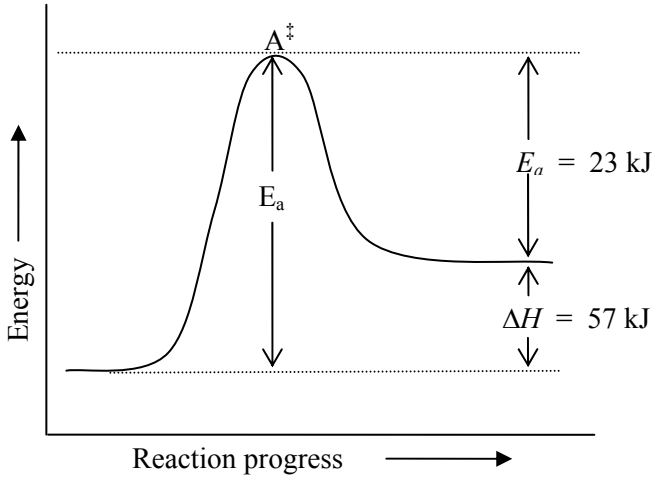
13.126.

a. The diagram:



b. $E_a = E_{ar} + \Delta H$

$E_a = 23 + 57 = 80$ kJ

c. The forward reaction will be more sensitive to a temperature change because it has the larger activation energy. When E_a is large, the ratio of the number of molecules that have enough energy to react is larger than when E_a is smaller.

13.127.

a. The rate of a chemical reaction is the change in the concentration of a reactant or product with time. For a reactant,

$-\Delta c/\Delta t$ or $-d[c]/dt$

b. The rate changes because the concentration of the reactant has changed.

Rate = $k[A]^m$

c. Rate = $k[A]^m[B]^n$

The rate will equal k when the reactants all have 1.00 M concentrations, or if the reaction is zeroth order.

13.128. .Factors that affect the rates of reactions:

i) Concentrations of the reactants

ii) Temperature

iii) Catalysts

At higher concentrations, more molecules can undergo effective collisions and give more product per unit of time. The temperature affects the number of molecules that have enough energy to react. The higher the temperature, the larger the fraction of molecules that have enough energy to react.

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Catalysts provide another pathway for reaction that has a lower activation energy, so more molecules have the minimum energy to react. The value of the rate constant for a particular reaction depends on the temperature and the activation energy. The concentration of catalyst and of the solvent, if the reaction occurs in solution, can affect E_a.

13.129. The experiment involves using a laser, first to send a pump pulse to excite a reactant molecule to a higher energy state. Then, a weaker laser pulse or probe pulse of properly chosen wavelength is used to detect the molecule as it transforms to products. By varying the time between the pump pulse and the probe pulse, the experimenter can follow a molecule throughout the course of its reaction. The change of wavelength of the probe pulse tells the experimenter something about the change in character of the molecules as it reacts.

13.130. The diagram shows the cyclobutane molecule going first to an intermediate molecule (between the two peaks). In this intermediate molecule, one carbon-carbon bond is broken. When the intermediate molecule goes over to products, another bond breaks, giving two ethylene molecules.

■ SOLUTIONS TO STRATEGY PROBLEMS

13.131. Use the Arrhenius equation.

$$\ln\frac{k_2}{1.4 \text{ x } 10^{-5} \text{ /M} \bullet \text{min}} = \frac{2.11 \text{ x } 10^3 \text{ J/mol}}{8.314 \text{ J/K} \bullet \text{mol}}\left(\frac{1}{483 \text{ K}} - \frac{1}{611 \text{ K}}\right) = 0.11\underline{0}08$$

$$k_2 = (1.4 \text{ x } 10^{-5} \text{ /}M\bullet\text{min})e^{0.11008} = 1.5\underline{6}2 \text{ x } 10^{-5} = 1.56 \text{ x } 10^{-5} \text{ /}M\bullet\text{min}$$

13.132.

a. $k = \dfrac{\ln 2}{t_{1/2}} = \dfrac{0.693}{17.0 \text{ min}} = 0.040\underline{7}6 = 0.0408 \text{ /min}$

b. When 86.0% of the H_2O_2 is decomposed, the concentration remaining is $0.140[H_2O_2]_o$. Now use the first-order rate law, rearranged to solve for t.

$$t = -\frac{1}{k}\ln\frac{[A]_t}{[A]_o} = -\frac{1}{0.04076 \text{ /min}}\ln\frac{0.14[A]_o}{[A]_o} = 48.\underline{2}3 = 48.2 \text{ min}$$

c. $[A] = [A]_o e^{-kt} = (0.100\ M)e^{-(0.04076 \text{ /min})(15.0 \text{ min})} = 0.054\underline{2}5 = 0.0543\ M$

13.133. $k = \dfrac{1}{t_{1/2}[A]_o} = \dfrac{1}{(307 \text{ s})(1.87 \text{ x } 10^{-2} \text{ M})} = 0.17\underline{4}1 = 0.174 \text{ /}M\bullet\text{s}$

13.134. Rate = $k[I]^2[H_2]$

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13.135. First write the rate law in terms of the slow step.

$$\text{Rate} = k_2[NOCl_2][NO]$$

Next, set the forward rate equal to the reverse rate for the fast equilibrium.

$$\text{Rate}_f = k_f[NO][Cl_2] = \text{Rate}_r = k_r[NOCl_2]$$

Rearrange this equation and solve for $[NOCl_2]$.

$$[NOCl_2] = \frac{k_f}{k_r}[NO][Cl_2]$$

Finally, substitute into the rate law above to eliminate $[NOCl_2]$. This gives the following rate equation.

$$\text{Rate} = k_2\left\{\frac{k_f}{k_r}[NO][Cl_2]\right\}[NO] = k[NO]^2[Cl_2]$$

13.136. The rate law for this elementary is

$$\text{Rate} = k[A]^2[B]$$

Rearrange this equation and solve for the rate constant k.

$$k = \frac{\text{Rate}}{[A]^2[B]} = \frac{16\ M/\text{s}}{(2.0\ M)^2(1.0\ M)} = 4.\underline{0}0 = 4.0\ /M^2\bullet\text{s}$$

13.137. You can set up an expression for the ratio of the two rates as follows. Use $[B]_2 = 2[B]_1$.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^{\,2}[B]_2^{\,3}}{k[A]_1^{\,2}[B]_1^{\,3}} = \left[\frac{[B]_2}{[B]_1}\right]^3 = \left[\frac{2[B]_1}{[B]_1}\right]^3 = 2^3 = 8$$

Therefore, the rate of the second run is eight times the rate of the first run.

13.138.

a. Since ΔH is positive, the reaction is endothermic.

b. The activation energy for the reverse reaction is

$$E_{a,r} = E_{a,f} - \Delta H = 100\text{ kJ} - 38\text{ kJ} = 62\text{ kJ}$$

c. If a catalyst were added to the reaction, the activation energy would be lowered.

13.139.

a. The overall reaction is

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

b. The catalyst is I^-, and the intermediate is IO^-.

c. No, the rate law can not be specified until the rate-determining step is established.

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13.140.

a. The rate law for this reaction is Rate = $k[A]^x[B]^y$. To determine the value of x, find the ratio of the rates for Experiments 1 and 2. In these experiments, [B] is constant. This gives

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^x[B]_2^y}{k[A]_1^x[B]_1^y} = \left[\frac{[A]_2}{[A]_1}\right]^x$$

$$\frac{3.0 \times 10^{-3}\ M/\text{s}}{1.0 \times 10^{-3}\ M/\text{s}} = \left(\frac{0.0300\ M}{0.0100\ M}\right)^x$$

This reduces to $3 = 3^x$, or $x = 1$. To determine the value of y, find the ratio of the rates for Experiments 2 and 3. In these experiments, [A] is constant. This gives

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{k[A]_3^x[B]_3^y}{k[A]_2^x[B]_2^y} = \left[\frac{[B]_3}{[B]_2}\right]^y$$

$$\frac{2.7 \times 10^{-2}\ M/\text{s}}{3.0 \times 10^{-3}\ M/\text{s}} = \left(\frac{0.0300\ M}{0.0100\ M}\right)^x$$

This reduces to $9 = 3^y$, or $y = 2$. The rate law is therefore

$$\text{Rate} = k[A]^x[B]^y = k[A][B]^2$$

b. The rate constant can be calculated using the date from Experiment 1.

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{1.0 \times 10^{-3}\ M/\text{s}}{(0.0100\ M)(0.100\ M)^2} = 1\underline{0}.0 = 10.\ /M^2 \bullet \text{s}$$

c. Rate = $k[A][B]^2$ = $(10.\ /M^2 \bullet \text{s})(0.200\ M)(0.200\ M)^2$ = $0.08\underline{0}0$ = $0.080\ M/\text{s}$

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

13.141. The balanced equation is

$$2N_2O_5 \rightarrow 4NO_2 + O_2.$$

Note that the number of moles of O_2 formed will be one-half the number of moles of N_2O_5 decomposed. Now use the integrated form of the first-order rate law to calculate the fraction of the 1.00 mol N_2O_5 decomposing in 20.0 hr, or 1200 min.

$$\ln\frac{[N_2O_5]_t}{[N_2O_5]_o} = -kt = -(6.2 \times 10^{-4}/\text{min})(1200\ \text{min}) = -0.7\underline{4}4$$

$$\frac{[N_2O_5]_t}{[N_2O_5]_o} = e^{-0.744} = 0.4\underline{7}52$$

Fraction of N_2O_5 decomposed = $1.000 - 0.4\underline{7}52 = 0.5\underline{2}48$

Since there is 1.00 mol of N_2O_5 present at the start, the moles of N_2O_5 decomposed is $0.5\underline{2}48$ mol. Thus,

Moles of O_2 formed = $(1\ O_2/2\ N_2O_5)$ x 0.5248 mol N_2O_5 = $0.2\underline{6}237$ mol O_2

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Now, use the ideal gas law to calculate the volume of this number of moles of O_2 gas at 45°C and 780 mmHg.

$$V = \frac{nRT}{P} = \frac{(0.26237 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/ (K} \bullet \text{mol))(318 K)}}{(770/760) \text{ atm}} = 6.\underline{7}58 = 6.8 \text{ L}$$

13.142. The balanced equation is

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Note that the moles of O_2 formed will be equal to one-half that of the moles of H_2O_2 decomposed. Now, use the integrated form of the first-order rate law to calculate the fraction of the 1.00 mol H_2O_2 decomposing in 20.0 min, or 1200 s.

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_o} = -kt = -(7.40 \text{ x } 10^{-4}/\text{s})(1200 \text{ s}) = -0.88\underline{8}0$$

$$\frac{[H_2O_2]_t}{[H_2O_2]_o} = e^{-0.8880} = 0.41\underline{1}47$$

Fraction of H_2O_2 decomposed = 1.00 − 0.41147 = 0.5$\underline{8}$852

Since there is 1.00 mol of H_2O_2 present at the start, the moles of H_2O_2 decomposed are 0.5$\underline{8}$852 mol. Thus,

Moles of O_2 formed = (1 O_2/2 H_2O_2) x 0.5$\underline{8}$852 mol H_2O_2 = 0.2$\underline{9}$426 mol O_2

Now, use the ideal gas law to calculate the volume of this number of moles of O_2 gas at 25°C and 740 mmHg.

$$V = \frac{nRT}{P} = \frac{(0.29426 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/(K} \bullet \text{mol))(298 K)}}{(740/760) \text{ atm}} = 7.\underline{3}9 = 7.4 \text{ L}$$

13.143. Using the first-order rate law, the initial rate of decomposition is given by

Rate = $k[H_2O_2]$ = (7.40 x 10^{-4}/s) x (1.50 M H_2O_2) = 1.110 x 10^{-3} M H_2O_2/s

The heat liberated per second per mol H_2O_2 can be found by first calculating the standard enthalpy of the decomposition of 1 mol H_2O_2:

	$H_2O_2(aq)$	$\rightarrow$	$H_2O(l)$ +	$1/2\ O_2(g)$
$\Delta H_f°$ =	-191.2 kJ/mol		-285.8 kJ/mol	0 kJ/mol

For the reaction, the standard enthalpy change is

$\Delta H°$ = −285.8 kJ/mol − (−191.2 kJ/mol) = −94.$\underline{6}$0 kJ/mol H_2O_2

The heat liberated per second is

$$\frac{94.60 \text{ kJ}}{\text{mol } H_2O_2} \text{ x } \frac{1.110 \text{ x } 10^{-3} \text{ mol } H_2O_2}{\text{L} \bullet \text{s}} \text{ x } 2.00 \text{ L} = 0.21\underline{0}01 = 0.210 \text{ kJ/s}$$

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13.144. Using the second-order rate law, the initial rate of reaction of NO_2 is

$$\text{Rate} = k[NO_2]^2 = 0.515 \text{ L/(mol•s)} \times [0.0250\ M\ NO_2]^2 = 3.2\underline{1}8 \times 10^{-4}\ M\ NO_2/\text{s}$$

The heat liberated per second per mol of NO_2 can be found by first calculating the standard enthalpy for the reaction of 1 mol NO_2:

	$NO_2(g)$	+	$CO(g)$	$\rightarrow$	$NO(g)$	+	$CO_2(g)$
$\Delta H_f°$ =	33.10 kJ/mol		-110.5 kJ/mol		90.29 kJ/mol		-393.5 kJ/mol

For the reaction, the change in standard enthalpy is

$$\Delta H° = 90.29 - 393.5 - (33.10) - (-110.5) = -225.\underline{8}1 \text{ kJ/mol } NO_2$$

The heat liberated per second is

$$\frac{225.81 \text{ kJ}}{\text{mol } NO_2} \times \frac{3.218 \times 10^{-4} \text{ mol } NO_2}{\text{L} \bullet \text{s}} \times 3.50 \text{ L} = 0.25\underline{4}3 = 0.254 \text{ kJ/s}$$

13.145. Use the ideal gas law ($P/RT = n/V$) to calculate the mol/L of each gas:

$$[O_2] = \frac{(345/760) \text{ atm}}{0.082057 \text{ L} \bullet \text{atm/(K} \bullet \text{mol)} \times 612 \text{ K}} = 0.00903\underline{9} \text{ mol } O_2/\text{L}$$

$$[NO] = \frac{(155/760) \text{ atm}}{0.082057 \text{ L} \bullet \text{atm/(K} \bullet \text{mol)} \times 612 \text{ K}} = 0.00406\underline{1} \text{ mol NO/L}$$

The rate of decrease of NO is

$$\frac{1.16 \times 10^{-5} \text{ L}^2}{\text{mol}^2 \bullet \text{s}} \times \left(\frac{4.061 \times 10^{-3} \text{ mol}}{1 \text{ L}}\right)^2 \times \frac{9.039 \times 10^{-3} \text{ mol}}{1 \text{ L}} = 1.7\underline{2}9 \times 10^{-12} \text{ mol/(L•s)}$$

The rate of decrease in atm/s is found by multiplying by RT:

$$\frac{1.729 \times 10^{-12} \text{ mol}}{\text{L} \bullet \text{s}} \times \frac{0.082057 \text{ L} \bullet \text{atm}}{\text{K} \bullet \text{mol}} \times 612 \text{ K} = 8.6\underline{8}2 \times 10^{-11} \text{ atm/s}$$

The rate of decrease in mmHg/s is

$$8.682 \times 10^{-11} \text{ atm/s} \times (760 \text{ mmHg/atm}) = 6.598 \times 10^{-8} = 6.60 \times 10^{-8} \text{ mmHg/s}$$

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13.146. Use the ideal gas law ($P/RT = n/V$) to calculate the mol/L of each gas:

$$[H_2] = \frac{(324/760)\text{ atm}}{0.082057\text{ L}\bullet\text{atm/(K}\bullet\text{mol)} \times 1099\text{ K}} = 0.004727\text{ mol } H_2/\text{L}$$

$$[NO] = \frac{(144/760)\text{ atm}}{0.082057\text{ L}\bullet\text{atm/(K}\bullet\text{mol)} \times 1099\text{ K}} = 0.002101\text{ mol NO/L}$$

The rate of NO decrease is twice the rate of H_2 decrease, so

$$2 \times \frac{1.10 \times 10^{-7}\text{ L}^2}{\text{mol}^2\bullet\text{s}} \times \left(\frac{2.101 \times 10^{-3}\text{ mol}}{1\text{ L}}\right)^2 \times \frac{4.727 \times 10^{-3}\text{ mol}}{1\text{ L}} = 4.5905 \times 10^{-15}\text{ mol/(L}\bullet\text{s)}$$

The rate of decrease in atm/s is found by multiplying by RT:

$$\frac{4.5905 \times 10^{-15}\text{ mol}}{\text{L}\bullet\text{s}} \times \frac{0.082057\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times 1099\text{ K} = 4.139 \times 10^{-13}\text{ atm/s}$$

The rate of decrease in mmHg/s is

$$4.139 \times 10^{-13}\text{ atm/s} \times (760\text{ mmHg/atm}) = 3.146 \times 10^{-10} = 3.15 \times 10^{-10}\text{ mmHg/s}$$

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CHAPTER 14

Chemical Equilibrium

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

14.1. Use the table approach, and give the starting numbers, the change, and the equilibrium number of moles of each.

Amt. (mol)	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
Starting	1.00	1.00	0	0
Change	$-x$	$-x$	$+x$	$+x$
Equilibrium	$(1.00 - x)$	$(1.00 - x)$	x	$x = 0.43$

Because we are given that $x = 0.43$ in the statement of the problem, we can use that to calculate the equilibrium amounts of the reactants and products:

Equilibrium amount CO $= 1.00 - 0.43 = 0.57$ mol

Equilibrium amount $H_2O = 1.00 - 0.43 = 0.57$ mol

Equilibrium amount $CO_2 = x = 0.43$ mol

Equilibrium amount $H_2 = x = 0.43$ mol

14.2. For the equation $2NO_2 + 7H_2 \rightarrow 2NH_3 + 4H_2O$, the expression for the equilibrium constant, K_c, is

$$K_c = \frac{[NH_3]^2[H_2O]^4}{[NO_2]^2[H_2]^7}$$

Notice that each concentration term is raised to a power equal to its coefficient in the chemical equation.

For the equation $NO_2 + 7/2H_2 \rightarrow NH_3 + 2H_2O$, the expression for the equilibrium constant, K_c, is

$$K_c = \frac{[NH_3][H_2O]^2}{[NO_2][H_2]^{7/2}}$$

Note the correspondence between the power and coefficient for each molecule.

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14.3. The chemical equation for the reaction is

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

The expression for the equilibrium constant for this reaction is

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

We obtain the concentration of each substance by dividing the moles of substance by its volume. The equilibrium concentrations are as follows: [CO] = 0.057 *M*, [H_2O] = 0.057 *M*, [CO_2] = 0.043 *M*, and [H_2] = 0.043 *M*. Substituting these values into the equation for the equilibrium constant gives

$$K_c = \frac{(0.043)(0.043)}{(0.057)(0.057)} = 0.5\underline{6}9 = 0.57$$

14.4. Use the table approach, and give the starting concentrations, the change, and the equilibrium concentration of each by dividing moles by volume in liters.

Conc. (*M*)	$2H_2S(g)$ $\rightleftharpoons$	$2H_2(g)$ +	$S_2(g)$
Starting	0.0100	0	0
Change	$-2x$	$+2x$ (= 0.00285)	$+x$
Equilibrium	$0.0100 - 2x$	$2x$	x

Because the problem states that 0.00285 *M* H_2 was formed, we can use the 0.00285 *M* to calculate the other concentrations. The S_2 molarity should be one-half that, or 0.0014$\underline{2}$5 *M*, and the H_2S molarity should be 0.0100 − 0.00285, or 0.007$\underline{1}$5 *M*. Substituting into the equilibrium expression gives

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{(0.00285)^2(0.001425)}{(0.00715)^2} = 2.\underline{2}6 \times 10^{-4} = 2.3 \times 10^{-4}$$

14.5. Use the expression that relates K_c to K_p:

$$K_p = K_c(RT)^{\Delta n}$$

The Δn term is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants. In this case, $\Delta n = (2 - 1) = 1$, and K_p is

$$K_p = (3.26 \times 10^{-2})(0.0821 \times 464)^1 = 1.2\underline{4}1 = 1.24$$

14.6. For a heterogeneous equilibrium, the concentration terms for liquids and solids are omitted because such concentrations are constant at a given temperature and are incorporated into the measured value of K_c. For this case, K_c is defined as

$$K_c = \frac{[Ni(CO)_4]}{[CO]^4}$$

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14.7. Because the equilibrium constant is very large ($> 10^4$), the equilibrium mixture will contain mostly products. Rearrange the K_c expression to solve for $[NO_2]$.

$$[NO_2] = \sqrt{K_c[O_2][NO]^2} = \sqrt{(4.0 \times 10^{13})(2.0 \times 10^{-6})(2.0 \times 10^{-6})^2} = 1.\underline{7}8 \times 10^{-2}$$

$$= 1.8 \times 10^{-2} = 0.018\ M$$

14.8. First, divide moles by volume in liters to convert to molar concentrations, giving 0.00015 *M* CO_2 and 0.010 *M* CO. Substitute these values into the reaction quotient and calculate *Q*.

$$Q = \frac{[CO]^2}{[CO_2]} = \frac{(0.010)^2}{(0.00015)} = 0.6\underline{6}6 = 0.67$$

Because $Q = 0.67$ and is less than K_c, the reaction will go to the right, forming more CO.

14.9. Rearrange the K_c expression, and substitute for K_c (= 0.0415) and the given moles per 1.00 L to solve for moles per 1.00 L of PCl_5.

$$[PCl_5] = \frac{[PCl_3][Cl_2]}{K_c} = \frac{(0.020)(0.020)}{0.0415} = 9.\underline{6}3 \times 10^{-3} = 9.6 \times 10^{-3}\ M$$

Because the volume is 1.00 L, the moles of $PCl_5 = 0.0096$ mol.

14.10. Use the table approach, and give the starting number, the change, and the equilibrium number of moles of each.

Amt. (mol)	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Starting	0.500		0.500		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.500 - x$		$0.500 - x$		$2x$

Substitute the equilibrium concentrations into the expression for K_c (= 49.7).

$$K_c = \frac{[HI]^2}{[H_2][I_2]};\ 49.7 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)} = \frac{(2x)^2}{(0.500 - x)^2}$$

Taking the square root of both sides of the right-hand equation and solving for *x* gives

$$\pm 7.05 = \frac{2x}{(0.500 - x)},\ \text{or}\ \pm 7.05(0.500 - x) = 2x$$

Using the positive root, $x = 0.3\underline{9}0$.

Using the negative root, $x = 0.6\underline{9}8$ (this must be rejected because 0.698 is greater than the 0.500 starting number of moles).

Substituting $x = 0.3\underline{9}0$ mol into the last line of the table to solve for equilibrium concentrations gives these amounts: 0.11 mol H_2, 0.11 mol I_2, and 0.78 mol HI.

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14.11. Use the table approach for starting, change, and equilibrium concentrations of each species.

Conc. *(M)*	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Starting	1.00		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$1.00 - x$		x		x

Substitute the equilibrium-concentration expressions from the table into the equilibrium equation, and solve for x using the quadratic formula.

$$[PCl_3][Cl_2] = K_c \times [PCl_5] = 0.0211(1.00 - x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(-0.0211)}}{2} = \frac{-0.0211 \pm 0.2913}{2}$$

$x = -0.1562$ (impossible; reject), or $x = 0.13\underline{5}09 = 0.135\ M$ (logical)

Solve for the equilibrium concentrations using $x = 0.135\ M$: $[PCl_5] = 0.86\ M$, $[Cl_2] = 0.135\ M$, and $[PCl_3] = 0.135\ M$.

14.12.

a. Increasing the pressure will cause a net reaction to occur from right to left, and more $CaCO_3$ will form.

b. Increasing the concentration of hydrogen will cause a net reaction to occur from right to left, forming more Fe and H_2O.

14.13.

a. Because there are equal numbers of moles of gas on both sides of the equation, increasing the pressure will not increase the amount of product.

b. Because the reaction increases the number of moles of gas, increasing the pressure will decrease the amount of product.

c. Because the reaction decreases the number of moles of gas, increasing the pressure will increase the amount of product.

14.14. Because this is an endothermic reaction and absorbs heat, high temperatures will be more favorable to the production of carbon monoxide.

14.15. Because this is an endothermic reaction and absorbs heat, high temperatures will give the best yield of carbon monoxide. Because the reaction increases the number of moles of gas, decreasing the pressure will also increase the yield.

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■ ANSWERS TO CONCEPT CHECKS

14.1. The statement that when reactant A decreases by an amount x, product C increases by amount x implies that A and C have the same coefficients. The statement that when reactant B decreases by an amount x, product C increases by amount $2x$ implies that the coefficient of C is twice that of B. Therefore, the coefficient of A is twice that of B. The simplest equation satisfying these conditions is $2A + B \rightarrow 2C$.

14.2. To answer this question, find the relationship between the two species present, using the equilibrium-constant expression and its value. For the first reaction, $A(g) \rightleftharpoons B(g)$, with $K = 2$, this becomes

$$K = 2 = \frac{[B]}{[A]}$$

This reduces to $[B] = 2[A]$. This corresponds to the container that has twice as many balls of one color than of the other color, namely container IV. Here, the blue molecules are B (eight of them), and the red molecules are A (four of them).

For the second reaction, $X(g) \rightleftharpoons 2Y(g)$, with $K = 6$, this becomes

$$K = 6 = \frac{[Y]^2}{[X]}$$

This reduces to $[Y]^2 = 6[X]$. This corresponds to container I, where there are six of each color molecule. Since there are the same numbers of each molecule, you cannot determine which color corresponds to which molecule.

For the third reaction, $2C(g) \rightleftharpoons D(g)$, with $K = 1$, this becomes

$$K = 1 = \frac{[D]}{[C]^2}$$

which reduces to $[C]^2 = [D]$. This corresponds to container II. The red balls (nine of them) correspond to molecule D, and the blue balls (three of them) correspond to molecule C.

14.3. The concentration of each substance initially doubles. This means that each concentration factor in the reaction quotient expression is double that in the initial equilibrium mixture. Because this expression contains $[CO][H_2]^2$ in the denominator, the denominator increases by a factor of 2^3. However, the numerator contains only $[CH_3OH]$, which merely doubles. Thus, the reaction quotient equals two divided by two cubed, or one-quarter, times the equilibrium constant. To approach the equilibrium constant, the numerator of the reaction quotient must increase, and the denominator must decrease. This means that more CH_3OH must be produced. The reaction goes from left to right.

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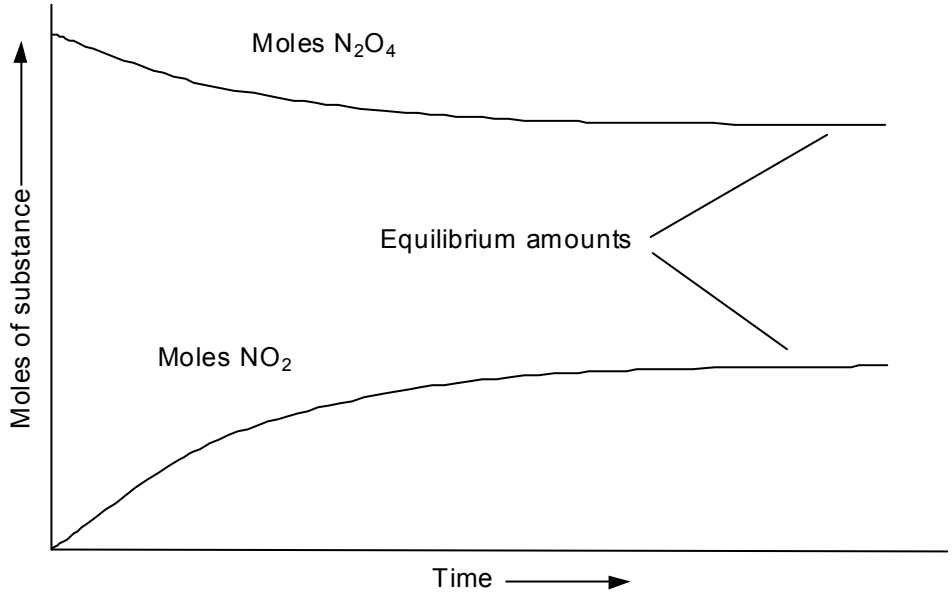
14.4. The equilibrium-constant expression is [C]/([A][B]). A new equilibrium is attained in which the equilibrium-constant expression is [C]′/([A]′[B]′) = [C]′/(2[A]2[B]), where primes indicate new equilibrium concentrations. The value of the equilibrium-constant expression, though, must remain fixed in value, so [C]′/(2[A]2[B]) equals [C]/([A][B]).This means that the new concentration of C, or [C]′, must be four times larger than the original equilibrium value. Thus, the concentration of C is quadrupled.

14.5. For an exothermic reaction, as the temperature is increased, the reaction shifts toward the reactant side to absorb the heat and counteract the temperature increase. This corresponds to the case where there are mostly reactant molecules and very few product molecules, namely container I. At lower temperatures, the reaction shifts toward the product side to release heat. This corresponds to the case where there is a larger ratio of product molecules to reactant molecules, namely container II.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

14.1. A reasonable graph showing the decrease in concentration of $N_2O_4(g)$ and the increase in concentration of $NO_2(g)$ is shown below.



At first, the concentration of N_2O_4 is large, and the rate of the forward reaction is large, but then as the concentration of N_2O_4 decreases, the rate of the forward reaction decreases. In contrast, the concentration of NO_2 builds up from zero to a low concentration. Thus, the initial rate of the reverse reaction is zero, but it steadily increases as the concentration of NO_2 increases. Eventually, the two rates become equal when the reaction reaches equilibrium. This is a dynamic equilibrium because both the forward and reverse reactions are occurring at all times, even though there is no net change in concentration at equilibrium.

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14.2. The 1.0 mol of $H_2(g)$ and 1.0 mol of $I_2(g)$ in the first mixture reach equilibrium when the amounts of reactants decrease to 0.50 mol each and when the amount of product increases to 1.0 mol. The total number of moles of the reactants at the start is 2.0 mol, which is the same number of moles as in the second mixture, the 2.0 mol of HI that is to be allowed to come to equilibrium. The second mixture should produce the same number of moles of H_2, I_2, and HI at equilibrium, because if the total number of moles is constant, it should not matter from which direction an equilibrium is approached.

14.3. The equilibrium constant for a gaseous reaction can be written using partial pressures instead of concentrations because all the reactants and products are in the same vessel. Therefore, at constant temperature, the pressure, P, is proportional to the concentration, n/V. (The ideal gas law says that $P = [n/V]RT$.)

14.4. The addition of reactions 1 and 2 yields reaction 3:

(Reaction 1)	HCN	+	OH^-	$\rightleftharpoons$	CN^-	+	H_2O
(Reaction 2)			H_2O	$\rightleftharpoons$	H^+	+	OH^-
(Reaction 3)			HCN	$\rightleftharpoons$	H^+	+	CN^-

The rule states that if a given equation can be obtained from the sum of other equations, the equilibrium constant for the given equation equals the product of the other equilibrium constants. Thus, K for reaction 3 is

$$K = K_1 \times K_2 = (4.9 \times 10^4) \times (1.0 \times 10^{-14}) = 4.9 \times 10^{-10}$$

14.5.

a. Homogeneous equilibrium. All substances are gases and thus exist in one phase, a mixture of gases.

b. Heterogeneous equilibrium. The two copper compounds are solids, but the other substances are gases. This fulfills the definition of a heterogeneous equilibrium.

c. Homogeneous equilibrium. All substances are gases and thus exist in one phase, a mixture of gases.

d. Heterogeneous equilibrium. The two copper-containing substances are solids, but the other substances are gases. This fulfills the definition of a heterogeneous equilibrium.

14.6. Pure liquids and solids can be ignored in an equilibrium-constant expression because their concentrations do not change. (If a solid is present, it has not dissolved in any gas or solution present.) In effect, concentrations of liquids and solids are incorporated into the value of K_c, as discussed in the chapter.

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14.7. A qualitative interpretation of the equilibrium constant involves using the magnitude of the equilibrium constant to predict the relative amounts of reactants and products at equilibrium. If K_c is around 1, the equilibrium mixture contains appreciable amounts (same order of magnitude) of reactants and products. If K_c is large, the equilibrium mixture is mostly products. If K_c is small, the equilibrium mixture is mostly reactants. The type of reaction governs what "large" and "small" values are; but for some types of reactions, "large" might be no less than 10^2 to 10^4, whereas "small" might be no more than 10^{-4} to 10^{-2}.

14.8. The reaction quotient, Q_c, is an expression that has the same form as the equilibrium-constant expression but whose concentrations are not necessarily equilibrium concentrations. It is useful in determining whether a reaction mixture is at equilibrium or, if not, what direction the reaction will go as it approaches equilibrium.

14.9. The ways in which the equilibrium composition of a mixture can be altered are (1) changing concentrations by removing some of the products and/or some of the reactants, (2) changing the partial pressure of a gaseous reactant and/or a gaseous product, and (3) changing the temperature of the reaction mixture. (Adding a catalyst cannot alter the equilibrium concentration; it can affect only the rate of reaction.)

14.10. The role of the platinum is that of a catalyst; it provides conditions (a surface) suitable for speeding up the attainment of equilibrium. The platinum has no effect on the equilibrium composition of the mixture even though it greatly increases the rate of reaction.

14.11. In some cases, a catalyst can affect the product in a reaction because it affects only the rate of one reaction out of several reactions that are possible. If two reactions are possible, and the uncatalyzed rate of one is much slower but that is the only reaction that is catalyzed, then the products with and without a catalyst will be different. The Ostwald process is a good example. In the absence of a catalyst, NH_3 burns in O_2 to form only N_2 and H_2O, even though it is possible for NH_3 to react to form NO and H_2O. Ostwald found that adding a platinum catalyst favors the formation of the NO and H_2O almost to the exclusion of the N_2 and H_2O.

14.12. Four ways in which the yield of ammonia can be improved are (1) removing the gaseous NH_3 from the equilibrium by liquefying it, (2) increasing the nitrogen or hydrogen concentration, (3) increasing the total pressure on the mixture (the moles of gas decrease), and (4) lowering the temperature ($\Delta H°$ is negative, so heat is evolved). Each causes a shift to the right in accordance with Le Châtelier's principle.

14.13. The answer is d, 2.10 moles.

14.14. The answer is a, 1.24.

14.15. The answer is c, 0.157.

14.16. The answer is b, $Q_c = 6.33 \times 10^{-4}$; the concentration of NOBr increases.

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■ ANSWERS TO CONCEPT EXPLORATIONS

14.17. **Part I**

a. $K_c = \dfrac{[E]^2}{[C][D]}$

b. A possible set of concentrations that you may observe in an equilibrium mixture is [C] = 2.0 *M*, [D] = 1.0 *M*, and [E] = 2.0 *M*. Another possible set of concentrations is [C] = 0.50 *M*, [D] = 0.25 *M*, and [E] = 0.50 *M*.

c. There are an infinite number of concentrations for C, D, and E possible at equilibrium. No matter what set of initial concentrations there are for C and D, the system will eventually reach equilibrium. There are no restrictions on the amounts of reactants required, as long as some of each of C and D are present.

d. The concentration of C cannot decrease to zero. When equilibrium is reached, each compound in the chemical equation must be present. No compound can disappear completely. The concentration of C can be determined as follows.

$$K_c = 2.0 = \frac{[E]^2}{[C][D]} = \frac{(2x)^2}{(1.0 - x)(1.0 - x)}$$

After taking the square root of each side, this reduces to

$$\sqrt{2.0} = \frac{2x}{(1.0 - x)}$$

Solving this equation for x gives

$$x = \frac{\sqrt{2.0}}{2.0 + \sqrt{2.0}} = \frac{1.414}{3.414} = 0.414 = 0.41\ M$$

Part II

a. When A and B are mixed together, a reaction occurs and proceeds from left to right. The concentrations of A and B will decrease, and the concentrations of F and G will increase.

b. When F and G are mixed together, a reaction occurs and proceeds from right to left. The concentrations of A and B will increase, and the concentrations of F and G will decrease.

c. When A and F are mixed together, no reaction occurs.

d. When B and G are mixed together, no reaction occurs.

e. When just B is placed in a container, no reaction occurs.

f. When just G is placed in a container, no reaction occurs.

In parts a and b, where a reaction occurs, the equilibrium composition is mostly A and B. The magnitude of the equilibrium constant (1.0×10^{-5}) suggests the equilibrium lies far to the left.

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14.18.

a. To study the equilibrium, create a saturated solution. Dissolve enough $Mg(OH)_2$ so that after mixing well, there is still excess solid that settles to the bottom of the container. As long as there is solid present in the flask, equilibrium is established. This solution could then be filtered and titrated with standardized HCl solution to determine $[OH^-]$.

b. $K_{sp} = [Mg^{2+}][OH^-]^2$

c. If more solid $Mg(OH)_2$ is added to a saturated solution, it will settle to the bottom of the container and not dissolve. It will have no effect on the concentrations of Mg^{2+} and OH^- ions.

d. Yes, If a solution is prepared from solid $Mg(OH)_2$, then $[Mg^{2+}] = 1/2[OH^-]$.

e. If OH^- is added to the equilibrium mixture, the reaction will shift to the left, causing more solid $Mg(OH)_2$ to form and reducing the Mg^{2+} ion concentration.

f. If some, but not all, of the solid $Mg(OH)_2$ is removed from the equilibrium mixture, it will have no effect on the concentrations of Mg^{2+} and OH^- ions.

g. If there is no solid $Mg(OH)_2$ on the bottom of the container, it is not likely to be at equilibrium. You could add more solid $Mg(OH)_2$ and stir until some excess solid settled to the bottom of the container. Alternatively, you could heat the solution to reduce the volume of water until a precipitate began to form. Once a solid is present, equilibrium has been reached.

h. The system is at dynamic equilibrium. This means that individual ions can find themselves at one time part of the solution and at another time part of the undissolved solid. The system is constantly changing on a microscopic level.

■ ANSWERS TO CONCEPTUAL PROBLEMS

14.19. For each three moles of H_2 that react, two moles of ammonia form. The mole ratio is

$$\frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2}$$

If x mol H_2 react, then the amount of ammonia that forms is

$$x \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} = \frac{2x}{3} \text{ mol } NH_3$$

14.20. The addition of a pure liquid does not affect an equilibrium. (The pure liquid does not appear in the equilibrium constant; in effect, the concentration of the liquid does not change.) Thus, the amount of water vapor does not change appreciably. (More precisely, the amount of vapor decreases slightly because the liquid takes up more room in the container.) If, instead, you add water vapor to the container, vapor condenses until the original vapor pressure is restored. Thus, the amount of liquid water in the container increases.

14.21. Hydrogen, H_2, is the limiting reactant, so the maximum amount of CH_3OH that could form is 1 mol. However, because the reaction comes to equilibrium before it can go to completion, less than 1 mol of CH_3OH forms. The answer is a.

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14.22. The system must exist as an equilibrium mixture of all four substances. The reaction can be represented as

$$Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)$$

If you pass $H_2(g)$ over iron oxide, the reaction shifts to the right, and metallic iron and water vapor form. If, instead, you pass water vapor over metallic iron, the reaction shifts to the left, and iron oxide and H_2 form. An excess of one reactant pushes the reaction in the opposite direction.

14.23.

a. The equilibrium-constant expression for this reaction is

$$K = \frac{[H_2][I_2]}{[HI]^2} = 2.0$$

The equilibrium case is where the reaction quotient, Q, is equal to the equilibrium constant, K. This occurs in picture III, where

$$Q = \frac{(2)(4)}{(2)^2} = 2.0 = K$$

b. For picture I, the reaction quotient is

$$Q = \frac{(2)(2)}{(4)^2} = 0.25 < K$$

Since $Q < K$, the reaction shifts toward the product ($H_2 + I_2$) side.

For picture II, the reaction quotient is

$$Q = \frac{(4)(4)}{(4)^2} = 1.0 < K$$

Since $Q < K$, the reaction shifts toward the product ($H_2 + I_2$) side.

14.24. Equilibrium has been reached when the concentration of reactants and products is constant. The equilibrium region on the graph is where the lines flatten out, indicating that the concentrations of reactants and products are not changing. At equilibrium, the concentration of A is approaching 2.0 *M*, and the concentration of B is approaching 1.0 *M*. Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[B]}{[A]^2} = \frac{1.0}{(2.0)^2} = 0.25$$

14.25.

a. When the volume is doubled, the pressure is reduced by one-half. A decrease in pressure results in the equilibrium shifting to the side of the reaction with the greater number of moles of gas. Note that in this reaction, there are 2 mol of gas reactants versus 1 mol of gas products. Since the pressure has been reduced, the reaction will shift to the left, toward the side of the reaction with the greater number of moles of gas.

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b. Since the reaction has been shifted to the left, the concentrations of A and B will increase, while the concentration of C will decrease.

14.26. For an endothermic reaction, as the temperature lowers, the reaction shifts toward the reactant side, producing heat and counteracting the lowering of the temperature. This corresponds to container I, where there is a smaller ratio of product molecules to reactant molecules. In terms of the reaction quotient, Q, the lower temperature corresponds to the container with the smaller value of Q (container I).

14.27. The formation of SO_3 can be represented by the following reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The first condition mentioned is the oxygen-enriched air. The higher concentration of O_2 drives the reaction to the right, increasing the yield of SO_3. Next, the reaction temperature is 420°C. Since the reaction is exothermic, the elevated temperature drives the reaction to the left, decreasing the yield of SO_3. The vanadium(V) oxide catalyst affects the rate of the reaction, but not the amount of SO_3 that forms at equilibrium. Finally, the SO_3 that forms in the reaction is absorbed by concentrated sulfuric acid and removed from the system. This causes the reaction to shift to the right, forming more SO_3.

Another condition that can be explored is a change in pressure. Since there are more moles of gas on the left side, an increase in pressure (or decrease in volume) should cause more SO_3 to form.

14.28. If you start with 1.00 mol CH_3OH, there will be 0.100 mol CH_3OH present at equilibrium. Assume the reaction could go to completion. Starting with 1.00 mol CO and 2.00 mol H_2, stoichiometry shows you would obtain 1.00 mol CH_3OH. Therefore, 1.00 mol CH_3OH is chemically equivalent to 1.00 mol CO and 2.00 mol H_2. At equilibrium, both starting with 1.00 mol CO and 2.00 mol H_2 and starting with 1.00 mol CH_3OH give the same equilibrium mixture, one containing 0.100 mol CH_3OH.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

14.29. Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Starting	2.500		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$2.500 - x$		$x = 0.338$		x

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Since the equilibrium amount of PCl_3 is given in the problem, this tells you $x = 0.338$. The equilibrium amounts for the other substances can now be determined.

Equilibrium amount $Cl_2 = x = 0.338$ mol

Equilibrium amount $PCl_5 = 2.500 - x = 2.500 - 0.338 = 2.162$ mol

Therefore, the amounts of the substances in the equilibrium mixture are 2.162 mol PCl_5, 0.338 mol PCl_3, and 0.338 mol Cl_2.

14.30. Because the amount of NO_2 at the start is zero, the 0.90 mol of NO_2 at equilibrium must also equal the change, x, in the moles of N_2O_3. Use the table approach, and insert the starting, change, and equilibrium number of moles.

Amt. (mol)	$N_2O_3(g)$ ⇌	$NO_2(g)$ +	$NO(g)$
Starting	3.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$3.00 - x$	$X = 0.90$	x

Since the equilibrium amount of NO_2 is given in the problem, this tells you $x = 0.90$. The equilibrium amounts for the other substances can now be determined.

Equilibrium amount $NO = x = 0.90$ mol

Equilibrium amount $N_2O_3 = 3.00 - x = 3.00 - 0.90 = 2.10$ mol

Therefore, the amounts of the substances in the equilibrium mixture are 2.10 mol N_2O_3, 0.90 mol NO_2, and 0.90 mol NO.

14.31. Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$N_2(g)$ +	$3H_2(g)$ ⇌	$2NH_3(g)$
Starting	0.600	1.800	0
Change	$-x$	$-3x$	$+2x$
Equilibrium	$0.600 - x$	$1.800 - 3x$	$2x = 0.048$

Since the equilibrium amount of NH_3 is given in the problem, this tells you $x = 0.024$. The equilibrium amounts for the other substances can now be determined.

Equilibrium amount $N_2 = 0.600 - 0.024 = 0.576$ mol

Equilibrium amount $H_2 = 1.800 - 3 \times (0.024) = 1.728$ mol

Therefore, the amounts of the substances in the equilibrium mixture are 0.576 mol N_2, 1.728 mol H_2, and 0.048 mol NH_3.

14.32. Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$2NO(g)$ +	$Br_2(g)$ ⇌	$2NOBr(g)$
Starting	0.0524	0.0262	0
Change	$-2x$	$-x$	$+2x$
Equilibrium	$0.0524 - 2x$	$0.0262 - x$	$2x = 0.0311$

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Since the equilibrium amount of NOBr is given in the problem, this tells you $x = 0.01555$. The equilibrium amounts for the other substances can now be determined.

Equilibrium amount NO = $0.0524 - 2 \times (0.01555) = 0.02130 = 0.0213$ mol

Equilibrium amount $Br_2 = 0.0262 - 0.01555 = 0.01065 = 0.0107$ mol

Therefore, the amounts of the substances in the equilibrium mixture are 0.0213 mol NO, 0.0107 mol Br_2, and 0.0311 mol NOBr.

14.33. Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Starting	0.0400		0.0200		0
Change	$-2x$		$-x$		$+2x$
Equilibrium	$0.0400 - 2x$		$0.0200 - x$		$2x$ (= 0.0296)

Therefore, $x = 0.0148$, and the amounts of substances at equilibrium are 0.0104 mol SO_2, 0.0052 mol O_2, and 0.0296 mol SO_3.

14.34. Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$CO(g)$	+	$2H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$
Starting	0.1500		0.3000		0
Change	$-x$		$-2x$		$+x$
Equilibrium	$0.1500 - x$ (= 0.1187)		$0.3000 - 2x$		x

Because $0.1500 - x = 0.1187$, $x = 0.0313$. Therefore, the amounts of substances at equilibrium are 0.1187 mol CO, 0.2374 mol H_2, and 0.0313 mol CH_3OH.

14.35.

a. $K_c = \dfrac{[NO_2]\,[NO]}{[N_2O_3]}$

b. $K_c = \dfrac{[H_2]^2\,[S_2]}{[H_2S]^2}$

c. $K_c = \dfrac{[NO_2]^2}{[NO]^2\,[O_2]}$

d. $K_c = \dfrac{[P(NH_2)_3]\,[HCl]^3}{[PCl_3]\,[NH_3]^3}$

14.36.

a. $K_c = \dfrac{[N_2H_4]}{[N_2]\,[H_2]^2}$

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b. $K_c = \dfrac{[NO]^2\,[Cl_2]}{[NOCl]^2}$

c. $K_c = \dfrac{[N_2]\,[H_2O]^2}{[NO]^2\,[H_2]^2}$

d. $K_c = \dfrac{[Cl_2]\,[H_2O]}{[HCl]^2\,[O_2]^{1/2}}$

14.37. The reaction is $2H_2S(g) + 3O_2(g) \rightleftharpoons 2H_2O(g) + 2SO_2(g)$.

14.38. The reaction is $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$.

14.39. When the reaction is halved, the equilibrium-constant expression is

$$K_c = \frac{[NO_2]^2\,[O_2]^{1/2}}{[N_2O_5]}$$

When the reaction is then reversed, the equilibrium-constant expression becomes

$$K_c = \frac{[N_2O_5]}{[NO_2]^2\,[O_2]^{1/2}}$$

14.40. When the reaction is halved, the equilibrium-constant expression is

$$K_c = \frac{[NH_3]^2\,[O_2]^{5/2}}{[NO]^2\,[H_2O]^3}$$

When the reaction is then reversed, the equilibrium-constant expression becomes

$$K_c = \frac{[NO]^2\,[H_2O]^3}{[NH_3]^2\,[O_2]^{5/2}}$$

14.41. Because $K_c = 1.84$ for $2HI \rightleftharpoons H_2 + I_2$, the value of K_c for $H_2 + I_2 \rightleftharpoons 2HI$ must be the reciprocal of K_c for the first reaction. Mathematically, this can be shown as follows:

Forward: $K_c = \dfrac{[H_2][I_2]}{[HI]^2} = 1.84$

Reverse: $K_c = \dfrac{[HI]^2}{[H_2][I_2]} = \dfrac{1}{\dfrac{[H_2][I_2]}{[HI]^2}} = \dfrac{1}{K_c(f)}$

Thus, for the reverse reaction, K_c is calculated as follows:

$K_c = 1 \div 1.84 = 5.434 \times 10^{-1} = 0.543$

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14.42. Because $K_c = 27.8$ for $CS_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2S$, the value of K_c for $1/2CH_4 + H_2S \rightleftharpoons 1/2CS_2 + 2H_2$, the second (2) reaction, must be the reciprocal of the square root of K_c for the first (1) reaction. Mathematically, this can be shown as follows:

$$K_c(1) = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$$

$$K_c(2) = \frac{[CS_2]^{1/2}[H_2]^2}{[CH_4]^{1/2}[H_2S]} = \left[\frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}\right]^{-1/2} = [K_c(1)]^{-1/2}$$

Thus, for the second (2) reaction, K_c is calculated as follows:

$$K_c = \frac{1}{\sqrt{27.8}} = 0.18\underline{9}6 = 0.190$$

14.43. First, calculate the molar concentration of each of the compounds in the equations:

$$[H_2] = 0.488 \text{ mol } H_2 \div 6.00 \text{ L} = 0.081\underline{3}3 \ M$$

$$[I_2] = 0.206 \text{ mol } I_2 \div 6.00 \text{ L} = 0.034\underline{3}3 \ M$$

$$[HI] = 2.250 \text{ mol HI} \div 6.00 \text{ L} = 0.37\underline{5}0 \ M$$

Now, substitute these into the K_c expression:

$$K_c = \frac{(0.3750)^2}{(0.08133)(0.03433)} = 50.\underline{3}6 = 50.4$$

14.44. First, calculate the molar concentration of each of the compounds in the equilibrium:

$$[PCl_5] = 0.0126 \text{ mol } PCl_5 \div 4.00 \text{ L} = 0.003\underline{1}50 \ M$$

$$[PCl_3] = 0.0148 \text{ mol } PCl_3 \div 4.00 \text{ L} = 0.003\underline{7}00 \ M$$

$$[Cl_2] = 0.0870 \text{ mol } Cl_2 \div 4.00 \text{ L} = 0.021\underline{7}5 \ M$$

Now, substitute these into the expression for K_c:

$$K_c = \frac{0.003150}{(0.003700)(0.02175)} = 39.\underline{1}4 = 39.1$$

14.45. Substitute the following concentrations into the K_c expression:

$$[SO_3] = 0.0296 \text{ mol} \div 2.000 \text{ L} = 0.014\underline{8}0 \ M$$

$$[SO_2] = 0.0104 \text{ mol} \div 2.000 \text{ L} = 0.005\underline{2}00 \ M$$

$$[O_2] = 0.0052 \text{ mol} \div 2.000 \text{ L} = 0.002\underline{6}0 \ M$$

$$K_c = \frac{(0.01480)^2}{(0.005200)^2(0.00260)} = 3.\underline{1}1 \times 10^3 = 3.1 \times 10^3$$

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14.46. Substitute the following concentrations into the K_c expression:

$[CH_3OH] = 0.0313 \text{ mol} \div 1.50 \text{ L} = 0.02086\ M$

$[CO] = 0.1187 \text{ mol} \div 1.50 \text{ L} = 0.07913\ M$

$[H_2] = 0.2374 \text{ mol} \div 1.50 \text{ L} = 0.1582\ M$

$$K_c = \frac{(0.02086)}{(0.07913)(0.1582)^2} = 10.53 = 10.5$$

14.47. For each mole of NOBr that reacts, (1.000 − 0.094 = 0.906) mol remains. Starting with 2.00 mol NOBr, this means that 2 x 0.906 mol NOBr, or 1.812 mol NOBr, remains. Because the volume is 1.00 L, the concentration of NOBr at equilibrium is 1.812 *M*. Assemble a table of starting, change, and equilibrium concentrations:

Conc. (*M*)	$2NOBr(g)$ ⇌	$2NO(g)$ +	$Br_2(g)$
Starting	2.00	0	0
Change	$-2x$	$+2x$	$+x$
Equilibrium	$2.00 - 2x$ (= 1.812)	$2x$	x

Because $2.00 - 2x = 1.812$, $x = 0.094\ M$. Therefore, the equilibrium concentrations are $[NOBr] = 1.812\ M$, $[NO] = 0.188\ M$, and $[Br_2] = 0.094\ M$.

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{(0.188)^2(0.094)}{(1.812)^2} = 1.01 \times 10^{-3} = 1.0 \times 10^{-3}$$

14.48. A decomposition of 6.0% of NO_2 means that 0.060 x 2.00 mol = 0.12 mol was decomposed, leaving 1.88 mol at equilibrium. Because the concentration at the start was 2.00 mol/80.0 L, or 0.0250 *M*, the concentration at equilibrium is 1.88 mol/80.0 L, or 0.0235 *M*. Assemble a table of starting, change, and equilibrium concentrations:

Conc. (*M*)	$2NO_2(g)$ ⇌		$2NO(g)$ +	$O_2(g)$
Starting	0.0250		0	0
Change	$-2x$		$+2x$	$+x$
Equilibrium	$0.0250 - 2x$	$2x$	$+2x$ (= 0.0235)	X

Because $0.0250 - 2x = 0.0235\ M$, $x = 0.00075\ M$; thus, $[NO_2] = 0.0235\ M$, $[NO] = 0.0015\ M$, and $[O_2] = 0.00075\ M$. The value of K_c is

$$K_c = \frac{(0.0015)^2(0.00075)}{(0.0235)^2} = 3.055 \times 10^{-6} = 3.1 \times 10^{-6}$$

14.49.

a. $$K_p = \frac{P_{HBr}^{\ 2}}{P_{H_2}\, P_{Br_2}}$$

b. $$K_p = \frac{P_{CH_4}\, P_{H_2S}^{\ 2}}{P_{CS_2}\, P_{H_2}^{\ 4}}$$

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c. $K_p = \dfrac{P_{H_2O}{}^2 \, P_{Cl_2}{}^2}{P_{HCl}{}^4 \, P_{O_2}}$

d. $K_p = \dfrac{P_{CH_3OH}}{P_{CO} \, P_{H_2}{}^2}$

14.50.

a. $K_p = \dfrac{P_{NO_2}{}^2}{P_{N_2O_4}}$

b. $K_p = \dfrac{P_{NOBr}{}^2}{P_{NO}{}^2 \, P_{Br_2}}$

c. $K_p = \dfrac{P_{SO_3}{}^2}{P_{SO_2}{}^2 \, P_{O_2}}$

d. $K_p = \dfrac{P_{NO}{}^4 \, P_{H_2O}{}^6}{P_{NH_3}{}^4 \, P_{O_2}{}^5}$

14.51. There are 3 mol of gaseous product for every 8 mol of gaseous reactant, so $\Delta n = 3 - 5 = -2$. Using this, calculate K_p from K_c:

$$K_p = K_c(RT)^{\Delta n} = 0.28\ (0.0821 \text{ x } 1173)^{-2} = 3.\underline{0}19 \text{ x } 10^{-5} = 3.0 \text{ x } 10^{-5}$$

14.52. There is 1 mol of gaseous product for every 3 mol of gaseous reactant, so $\Delta n = 3 - 1 = 2$. Using this, calculate K_p from K_c:

$$K_p = K_c(RT)^{\Delta n} = (0.0952)(0.0821 \text{ x } 500)^2 = 16\underline{0}.4 = 160.$$

14.53. For each 1 mol of gaseous product, there are 1.5 mol of gaseous reactants; thus, $\Delta n = 1 - 1.5 = -0.5$. Using this, calculate K_c from K_p:

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{6.55}{(0.0821 \text{ x } 900)^{-0.5}} = 6.55 \text{ x } (0.0821 \text{ x } 900)^{0.5} = 56.\underline{3}03 = 56.3$$

14.54. For each 1 mol of gaseous product, there is 0.5 mol of gaseous reactant; thus, $\Delta n = 1 - 0.5 = 0.5$. Using this, calculate K_c from K_p:

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{7.55 \text{ x } 10^{-2}}{(0.0821 \text{ x } 1115)^{0.5}} = 7.8\underline{9}1 \text{ x } 10^{-3} = 7.89 \text{ x } 10^{-3}$$

14.55.

a. $K_c = \dfrac{[CO]^2}{[CO_2]}$

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b. $K_c = \dfrac{[CO_2]}{[CO]}$

c. $K_c = \dfrac{[CO_2]}{[SO_2]\,[O_2]^{1/2}}$

d. $K_c = [Pb^{2+}]\,[I^-]^2$

14.56.

a. $K_c = [NH_3]\,[HCl]$

b. $K_c = \dfrac{[N_2O]^2}{[CO_2]\,[N_2]^2}$

c. $K_c = [H_2O]\,[CO_2]$

d. $K_c = \dfrac{1}{[Fe^{3+}]\,[OH^-]^3}$

14.57.

a. Not complete; K_c is very small (10^{-31}), indicating very little reaction.

b. Nearly complete; K_c is very large (10^{21}), indicating nearly complete reaction.

14.58.

a. Nearly complete; K_c is very large (10^{113}), indicating nearly complete reaction.

b. Not complete; K_c is very small (10^{-17}), indicating very little reaction.

14.59. K_c is extremely small, indicating very little reaction at room temperature. Because the decomposition of HF yields equal amounts of H_2 and F_2, at equilibrium $[H_2] = [F_2]$. So, for the decomposition of HF,

$$K_c = \frac{[H_2]\,[F_2]}{[HF]^2} = \frac{[H_2]^2}{[HF]^2}$$

$$[H_2] = K_c^{1/2}\,[HF] = (1.0 \times 10^{-95})^{1/2}\,(1.0\ M) = 3.16 \times 10^{-48} = 3.2 \times 10^{-48}\ \text{mol/L}$$

This result does agree with what is expected from the very small magnitude of K_c.

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14.60. K_c is extremely large, indicating nearly complete reaction at room temperature. The problem states that at equilibrium, $[SO_2] = [O_2]$. So, for the reaction of SO_2,

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{[SO_3]^2}{[SO_2]^3}$$

Solving for $[SO_2]$ yields

$$[SO_2] = \left[\frac{[SO_3]^2}{K_c}\right]^{1/3} = \left[\frac{(1.0)^2}{8.0 \times 10^{35}}\right]^{1/3} = 1.\underline{0}7 \times 10^{-12} = 1.1 \times 10^{-12}\ M$$

This agrees with what we expect from the magnitude of K_c.

14.61. Calculate Q, the reaction quotient, and compare it to the equilibrium constant ($K_c = 3.07 \times 10^{-4}$). If Q is larger, the reaction will go to the left; if Q is smaller, the reaction will go to the right; if they are equal, the reaction is at equilibrium. In all cases, Q is found by combining these terms:

$$Q = \frac{[NO]^2\,[Br_2]}{[NOBr]^2}$$

a. $$Q = \frac{(0.0162)^2(0.0123)}{(0.0720)^2} = 6.2\underline{2}6 \times 10^{-4} = 6.23 \times 10^{-4}$$

$Q > K_c$. The reaction should go to the left.

b. $$Q = \frac{(0.0159)^2(0.0139)}{(0.121)^2} = 2.4\underline{0}0 \times 10^{-4} = 2.40 \times 10^{-4}$$

$Q < K_c$. The reaction should go to the right.

c. $$Q = \frac{(0.0134)^2(0.0181)}{(0.103)^2} = 3.0\underline{6}3 \times 10^{-4} = 3.06 \times 10^{-4}$$

$Q = K_c$. The reaction should be at equilibrium.

d. $$Q = \frac{(0.0121)^2(0.0105)}{(0.0472)^2} = 6.9\underline{0}0 \times 10^{-4} = 6.90 \times 10^{-4}$$

$Q > K_c$. The reaction should go to the left.

14.62. Calculate Q, the reaction quotient, and compare it to the equilibrium constant ($K_c = 3.59$). If Q is larger, the reaction will go to the left; if Q is smaller, the reaction will go to the right; if they are equal, the reaction is at equilibrium. In all cases, Q is found by combining these terms:

$$Q = \frac{[CS_2]\,[H_2]^4}{[CH_4]\,[H_2S]^2}$$

a. $$Q = \frac{(1.43)(1.12)^4}{(1.26)(1.32)^2} = 1.0\underline{2}49 = 1.02$$

$Q < K_c$. The reaction should go to the right.

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b. $Q = \dfrac{(1.15)(1.73)^4}{(1.25)(1.52)^2} = 3.5\underline{6}6 = 3.57$

$Q = K_c$. The reaction should be at equilibrium.

c. $Q = \dfrac{(1.10)(1.20)^4}{(1.30)(1.41)^2} = 0.88\underline{2}5 = 0.883$

$Q < K_c$. The reaction should go to the right.

d. $Q = \dfrac{(1.23)(1.91)^4}{(1.56)(1.43)^2} = 5.1\underline{3}14 = 5.13$

$Q > K_c$. The reaction should go to the left.

14.63. Calculate Q, the reaction quotient, and compare it to the equilibrium constant. If Q is larger, the reaction will go to the left, and vice versa. Q is found by combining these terms:

$$Q = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(0.020)}{(0.010)(0.010)^2} = 2\underline{0}.0 \ (>10.5)$$

The reaction goes to the left.

14.64. Calculate Q, the reaction quotient, and compare it to the equilibrium constant. If Q is larger, the reaction will go to the left, and vice versa. Q is found by combining these terms:

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.40)^2}{(0.20)^2(0.10)} = 4\underline{0}.0 \ (>0.0417)$$

The reaction goes to the left.

14.65. Substitute into the expression for K_c and solve for $[COCl_2]$:

$$K_c = 1.23 \times 10^3 = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{[COCl_2]}{(0.012)(0.025)}$$

$$[COCl_2] = (1.23 \times 10^3)(0.012)(0.025) = 0.3\underline{6}9 = 0.37\ M$$

14.66. Substitute into the expression for K_c and solve for [NO]:

$$K_c = 0.0025 = \frac{[NO]^2}{[N_2][O_2]} = \frac{[NO]^2}{(0.031)(0.023)}$$

$$[NO] = [(0.0025)(0.031)(0.023)]^{1/2} = 1.\underline{3}3 \times 10^{-3} = 1.3 \times 10^{-3}\ M$$

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14.67. Divide moles of substance by the volume 5.0 L to obtain concentration. The starting concentrations are 3.0×10^{-4} *M* for both $[I_2]$ and $[Br_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$I_2(g)$	+	$Br_2(g)$	⇌	2 IBr(*g*)
Starting	3.0×10^{-4}		3.0×10^{-4}		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$(3.0 \times 10^{-4}) - x$		$(3.0 \times 10^{-4}) - x$		$2x$

Substituting into the equilibrium-constant expression gives

$$K_c = 1.2 \times 10^2 = \frac{[IBr]^2}{[I_2][Br_2]} = \frac{(2x)^2}{(3.0 \times 10^{-4} - x)(3.0 \times 10^{-4} - x)}$$

Taking the square root of both sides yields

$$10.95 = \frac{(2x)}{(3.0 \times 10^{-4} - x)}$$

Rearranging and simplifying the right side give

$$(3.0 \times 10^{-4} - x) = \frac{(2x)}{10.95} = (0.182\,x)$$

$$x = 2.53 \times 10^{-4}\ M$$

Thus, $[I_2] = [Br_2] = 4.70 \times 10^{-5} = 4.7 \times 10^{-5}$ *M*, and $[IBr] = 5.06 \times 10^{-4} = 5.1 \times 10^{-4}$ *M*.

14.68. Divide moles of substance by the volume 8.00 L to obtain concentration. The starting concentrations are 0.09937 *M* for both $[N_2]$ and $[O_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$N_2(g)$	+	$O_2(g)$	⇌	2NO(*g*)
Starting	0.09937		0.09937		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.09937 - x$		$0.09937 - x$		$2x$

$$K_c = 0.0123 = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(0.09937 - x)(0.09937 - x)}$$

Taking the square root of both sides gives

$$0.1109 = \frac{(2x)}{(0.09937 - x)}$$

Rearranging and simplifying the right side yield

$$(0.09937 - x) = \frac{(2x)}{0.1109} = (18.03\,x)$$

$$x = 5.222 \times 10^{-3}\ M$$

Thus $[N_2] = [O_2] = 0.09414 = 0.0941$ *M*, and $[NO] = 1.044 \times 10^{-2} = 1.04 \times 10^{-2}$ *M*.

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14.69. Divide moles of substance by the volume 1.25 L to obtain concentration. The starting concentration is 1.00 *M* for [CO_2], but the concentration of carbon, a solid, is omitted. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$CO_2(g)$	+	$C(s)$	$\rightleftharpoons$	$2CO(g)$
Starting	1.00				0
Change	$-x$				$+2x$
Equilibrium	$1.00 - x$				$2x$

Substituting into the equilibrium expression for K_c gives

$$K_c = 14.0 = \frac{[CO]^2}{[CO_2]} = \frac{(2x)^2}{(1.00 - x)}$$

Rearranging and solving for x yield

$$14.0 - 14.0x = 4x^2$$

$$4x^2 + 14.0x - 14.0 = 0 \text{ (quadratic equation)}$$

Using the solution to the quadratic equation gives

$$x = \frac{-14.0 \pm \sqrt{(14.0)^2 - 4(4)(-14.0)}}{2(4)}$$

$x = -4.31$ (impossible; reject), or $x = 0.81\underline{1}7 = 0.812$ *M* (logical)

Thus, $[CO_2] = 0.19$ *M*, and $[CO] = 1.62$ *M*.

14.70. Divide moles of substance by the volume 4.0 L to obtain concentration. The starting concentrations are 0.10 *M* for both [PCl_3] and [Cl_2]. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
Starting	0.10		0.10		0
Change	$-x$		$-x$		$+x$
Equilibrium	$0.10 - x$		$0.10 - x$		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 49 = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{x}{(0.10 - x)(0.10 - x)}$$

Rearranging and solving for x yield

$$49(0.10 - x)^2 = 49(x^2 - 0.20x + 0.010) = x$$

$$49x^2 - 10.8x + 0.49 = 0 \text{ (quadratic equation)}$$

Using the solution to the quadratic equation gives

$$x = \frac{10.8 \pm \sqrt{(10.8)^2 - 4(49)(0.49)}}{2(49)}$$

$x = 0.157$ (impossible; reject), or $x = 0.06\underline{3}89 = 0.064$ *M* (logical)

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Thus, $[PCl_3] = [Cl_2] = 0.036\ M$, and $[PCl_5] = 0.064\ M$; the vessel contains 0.14 mol PCl_3, 0.14 mol Cl_2, and 0.26 mol PCl_5.

14.71. Divide moles of substance by the volume 10.00 L to obtain concentration. The starting concentrations are 0.1000 *M* for [CO] and 0.3000 *M* for $[H_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$CO(g)$	+	$3H_2(g)$	⇌	$CH_4(g)$	+	$H_2O(g)$
Starting	0.1000		0.3000		0		0
Change	$-x$		$-3x$		$+x$		$+x$
Equilibrium	$0.1000 - x$		$0.3000 - 3x$		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 3.92 = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{x^2}{(0.1000 - x)[3(0.1000 - x)]^3} = \frac{x^2}{27(0.1000 - x)^4}$$

Multiplying both sides by 27 and taking the square root of both sides give

$$10.29 = \frac{x}{(0.1000 - x)^2}$$

Or,

$$10.29x^2 - 3.058x + 0.1029 = 0$$

Using the solution to the quadratic equation yields

$$x = \frac{3.058 \pm \sqrt{(-3.058)^2 - 4(10.29)(0.1029)}}{2(10.29)}$$

$x = 0.2585$ (can't be > 0.1000, so reject), or $x = 0.03868 = 0.0387\ M$ (use)

Thus, $[CO] = 0.0613\ M$, $[H_2] = 0.1839\ M$, $[CH_4] = 0.0387\ M$, and $[H_2O] = 0.0387\ M$.

14.72. Divide moles of substance by the volume 5.00 L to obtain concentration. The starting concentrations are 0.200 *M* for $[N_2]$ and 0.600 *M* for $[H_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$N_2(g)$	+	$3H_2(g)$	⇌	$2NH_3(g)$
Starting	0.200		0.600		0
Change	$-x$		$-3x$		$+2x$
Equilibrium	$0.200 - x$		$0.600 - 3x$		$2x$

Substituting into the equilibrium expression for K_c gives

$$K_c = 0.159 = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(0.200 - x)(0.600 - 3x)^3} = \frac{(2x)^2}{(0.200 - x)\,3^3\,(0.200 - x)^3}$$

Combining the value of K_c and 3^3 from the right-hand term gives

$$(3^3)(0.159) = \frac{(2x)^2}{(0.200 - x)^4}$$

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Taking the square root of both sides gives

$$2.0\underline{7}2 = \frac{2x}{(0.200 - x)^2}$$

$$0.08288 - 0.8288x + 2.072x^2 = 2x$$

$$2.072x^2 - 2.8288x + 0.08288 = 0 \quad \text{(quadratic equation)}$$

Using the solution to the quadratic equation yields

$$x = \frac{2.8288 \pm \sqrt{(-2.8288)^2 - 4(2.072)(0.08288)}}{2(2.072)}$$

$x = 1.335$ (larger than 0.200, so reject), or $x = 0.029\underline{9}5$ *M* (logical; use)

Thus, $[N_2] = 0.029\underline{9}5 = 0.0300$ *M*, $[H_2] = 0.089\underline{8}6 = 0.0899$ *M*, and $[NH_3] = 0.059\underline{9}1 = 0.0599$ *M*.

14.73. Forward direction

14.74.

a. Reverse direction

b. Forward direction

14.75.

a. A pressure increase has no effect because the number of moles of reactants equals that of products.

b. A pressure increase has no effect because the number of moles of reactants equals that of products.

c. A pressure increase causes the reaction to go to the left because the number of moles of reactants is less than that of products.

14.76.

a. Pressure increase

b. Pressure increase

c. Pressure decrease

14.77. The fraction would not increase because an increase in temperature decreases the amounts of products of an exothermic reaction.

14.78. The decomposition would be favorable at high temperatures because an increase in temperature increases the amounts of products of an endothermic reaction.

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14.79. The value of $\Delta H°$ is calculated from the $\Delta H_f°$ values below each substance in the reaction:

$$\underset{2(33.10)}{2NO_2(g)} + \underset{7(0)}{7H_2(g)} \rightleftharpoons \underset{2(-45.9)}{2NH_3(g)} + \underset{4(-241.8)}{4H_2O(g)}$$

$$\Delta H° = -967.2 + (-91.8) - 66.20 = -1125.2 \text{ kJ/2 mol } NO_2$$

The equilibrium constant will decrease with temperature because raising the temperature of an exothermic reaction causes the reaction to go farther to the left.

14.80. The value of $\Delta H°$ is calculated from the $\Delta H_f°$ values below each substance in the reaction:

$$\underset{-74.9}{CH_4(g)} + \underset{2(-20)}{2H_2S(g)} \rightleftharpoons \underset{117}{CS_2(g)} + \underset{4(0)}{4H_2(g)}$$

$$\Delta H° = 117 - (-40) - (-74.9) = 231.9 = 232 \text{ kJ/mol } CH_4$$

The equilibrium constant will increase with temperature because raising the temperature of an endothermic reaction causes the reaction to go farther to the right.

14.81. Because the reaction is exothermic, the formation of products will be favored by low temperatures. Because there are more molecules of gaseous products than of gaseous reactants, the formation of products will be favored by low pressures.

14.82. Because the reaction is exothermic, the formation of products will be favored by low temperatures. Because there are more molecules of gaseous reactants than of gaseous products, the formation of products will be favored by high pressures.

SOLUTIONS TO GENERAL PROBLEMS

14.83. Substitute the concentrations into the equilibrium expression to calculate K_c.

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(0.015)}{(0.096)(0.191)^2} = 4.28 = 4.3$$

14.84. Substitute the concentrations into the equilibrium expression to calculate K_c.

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = \frac{(0.0160)}{(0.0056)(0.0021)^{1/2}} = 62.3 = 62$$

14.85. Assume 100.00 g of gas: 90.55 g CO, and 9.45 g CO_2. The moles of each are

$$90.55 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} = 3.2328 \text{ mol COI}$$

$$9.45 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} = 0.2147 \text{ mol } CO_2$$

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Total moles of gas = (3.2328 + 0.2147) mol = 3.44$\underline{7}$5 mol. Use the ideal gas law to convert to the volume of gaseous solution:

$$V = \frac{nRT}{P} = \frac{(3.4475 \text{ mol})(0.082057 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(850 + 273)\text{K}}{1.000 \text{ atm}} = 317.\underline{6}9 \text{ L}$$

The concentrations are

$$[\text{CO}] = \frac{3.2328 \text{ mol CO}}{317.69 \text{ L}} = 0.010\underline{1}76 \ M$$

$$[\text{CO}_2] = \frac{0.2147 \text{ mol CO}_2}{317.69 \text{ L}} = 6.7\underline{5}8 \text{ x } 10^{-4} \ M$$

Find K_c by substituting into the equilibrium expression:

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.010\underline{1}76)^2}{(6.758 \text{ x } 10^{-4})} = 0.15\underline{3}2 = 0.153$$

14.86. Assume 100.0 g of gas: 65.8 g NO_2, and 34.2 g N_2O_4. The moles of each are

$$65.8 \text{ g NO}_2 \text{ x } \frac{1 \text{ mol NO}_2}{46.01 \text{ g NO}_2} = 1.4\underline{3}0 \text{ mol}$$

$$34.2 \text{ g N}_2\text{O}_4 \text{ x } \frac{1 \text{ mol N}_2\text{O}_4}{92.01 \text{ g N}_2\text{O}_4} = 0.37\underline{1}7 \text{ mol}$$

Total moles of gas = (1.430 + 0.3717) mol = 1.80$\underline{2}$ mol. Use the ideal gas law to convert to the volume of gaseous solution:

$$V = \frac{nRT}{P} = \frac{(1.802 \text{ mol})(0.082057 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(25 + 273)\text{K}}{1.00 \text{ atm}} = 44.\underline{0}6 \text{ L}$$

The concentrations are

$$[\text{NO}_2] = \frac{1.430 \text{ mol NO}_2}{44.06 \text{ L}} = 0.032\underline{4}6 \ M$$

$$[\text{N}_2\text{O}_4] = \frac{0.3717 \text{ mol N}_2\text{O}_4}{44.06 \text{ L}} = 0.008\underline{4}36 \ M$$

Find K_c by substituting into the equilibrium expression:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.03246)^2}{(0.008436)} = 0.12\underline{4}8 = 0.125 \ M$$

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14.87. After calculating the concentrations after mixing, calculate Q, the reaction quotient, and compare it with K_c.

$[N_2] = [H_2] = 1.00 \text{ mol} \div 2.00 \text{ L} = 0.500\ M$

$[NH_3] = 2.00 \text{ mol} \div 2.00 \text{ L} = 1.00\ M$

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.00)^2}{(0.500)(0.500)^3} = 16.\underline{0}0 = 16.0$$

Because Q is greater than K_c, the reaction will go in the reverse direction (to the left) to reach equilibrium.

14.88. To calculate the concentrations after mixing, the volume can be assumed to be 1.00 L, symbolized as V. Because the volumes in the numerator and denominator cancel each other, they do not matter. Assume a 1.00-L volume and calculate Q, the reaction quotient, and compare it with K_c.

$[I_2] = [Br_2] = 0.0010 \text{ mol}/1.00 \text{ L}$

$[IBr] = 0.200 \text{ mol} \div 1.00 \text{ L} = 0.200 \text{ mol}/1.00 \text{ L}$

$$Q = \frac{[IBr]^2}{[I_2][Br_2]} = \frac{(0.200 \text{ mol}/1.00 \text{ L})^2}{(0.0010 \text{ mol}/1.00 \text{ L})(0.0010 \text{ mol}/1.00 \text{ L})} = 4.\underline{0}0 \times 10^4$$

Because Q is greater than K_c, the reaction will go in the reverse direction (to the left) to reach equilibrium.

14.89. To calculate the concentrations after mixing, assume the volume to be 1.00 L, symbolized as V. Because the volumes in the numerator and denominator cancel each other, they do not matter. Assume a 1.00-L volume and calculate Q, the reaction quotient, and compare it with K_c.

$[CO] = [H_2O] = [CO_2] = [H_2] = 1.00 \text{ mol}/1.00 \text{ L}$

$$Q = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(1.00 \text{ mol}/1.00 \text{ L})(1.00 \text{ mol}/1.00 \text{ L})}{(1.000 \text{ mol}/1.00 \text{ L})(1.00 \text{ mol}/1.00 \text{ L})} = 1.\underline{0}0$$

Because Q is greater than K_c, the reaction will go in the reverse direction (left) to reach equilibrium.

14.90. After calculating the concentrations after mixing, calculate Q, the reaction quotient, and compare it with K_c.

$[CO] = 0.10 \text{ mol} \div 2.0 \text{ L} = 0.050\ M$

$[H_2] = 0.20 \text{ mol} \div 2.0 \text{ L} = 0.10\ M$

$[CH_3OH] = 0.50 \text{ mol} \div 2.0 \text{ L} = 0.25\ M$

$$Q = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{(0.25)}{(0.050)(0.10)^2} = 5.\underline{0}0 \times 10^2 = 5.0 \times 10^2$$

Because Q is greater than K_c, the reaction will go in the reverse direction (left) to reach equilibrium.

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14.91. Assemble a table of starting, change, and equilibrium concentrations, letting $2x$ = the change in [HBr].

Conc. (M)	$2HBr(g)$	$\rightleftharpoons$	$H_2(g)$	+	$Br_2(g)$
Starting	0.010		0		0
Change	$-2x$		$+x$		$+x$
Equilibrium	$0.010 - 2x$		X		x

$$K_c = 0.016 = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{(x)(x)}{(0.010 - 2x)^2}$$

$$0.126 = \frac{(x)}{(0.010 - 2x)}$$

$$1.26 \times 10^{-3} - (2.52 \times 10^{-1})x = x$$

$$x = (1.26 \times 10^{-3}) \div 1.252 = 1.006 \times 10^{-3} = 1.0 \times 10^{-3}\ M$$

Therefore, [HBr] = 0.008 M, or 0.008 mol; $[H_2]$ = 0.0010 M, or 0.0010 mol; and $[Br_2]$ = 0.0010 M, or 0.0010 mol.

14.92. The starting concentration of [IBr] = 0.010 mol ÷ 1.0 L = 0.010 M. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$2IBr(g)$	$\rightleftharpoons$	$I_2(g)$	+	$Br_2(g)$
Starting	0.010		0		0
Change	$-2x$		$+x$		$+x$
Equilibrium	$0.010 - 2x$		x		x

$$K_c = 0.026 = \frac{[I_2][Br_2]}{[IBr]^2} = \frac{(x)(x)}{(0.010 - 2x)^2}$$

$$0.161 - \frac{(x)}{(0.010 - 2x)}$$

$$1.61 \times 10^{-3} - (3.22 \times 10^{-1})x = x$$

$$x = (1.61 \times 10^{-3}) \div 1.322 = 1.217 \times 10^{-3} = 1.2 \times 10^{-3}\ M$$

Therefore, [IBr] = 0.0076 M, or 0.008 mol; $[I_2]$ = 0.00121 M, or 0.0012 mol; and $[Br_2]$ = 0.00121 M, or 0.0012 mol.

14.93. The starting concentration of $COCl_2$ = 1.00 mol ÷ 25.00 L = 0.0400 M. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$COCl_2(g)$	$\rightleftharpoons$	$Cl_2(g)$	+	$CO(g)$
Starting	0.0400		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.0400 - x$		x		x

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Substituting into the equilibrium expression for K_c gives

$$K_c = 8.05 \times 10^{-4} = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{(x)(x)}{(0.0400 - x)}$$

Rearranging and solving for x yield

$$3.22 \times 10^{-5} - (8.05 \times 10^{-4})x - x^2 = 0$$

$$x^2 + (8.05 \times 10^{-4})x - 3.22 \times 10^{-5} = 0 \text{ (quadratic equation)}$$

Using the solution to the quadratic equation gives

$$x = \frac{-(8.05 \times 10^{-4}) \pm \sqrt{(8.05 \times 10^{-4})^2 - 4(1)(-3.22 \times 10^{-5})}}{2(1)}$$

$x = -6.09 \times 10^{-3}$ (impossible; reject), or $x = 5.2\underline{8}6 \times 10^{-3}$ (logical; use)

Percent dissoc. = (change ÷ starting) x 100% = (0.005286 ÷ 0.0400) x 100%

= 13.$\underline{2}$1 = 13.2%

14.94. The starting concentration of N_2O_4 = 0.0300 mol ÷ 1.00 L = 0.0300 *M*. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$N_2O_4(g)$ ⇌	$2NO_2(g)$
Starting	0.0300	0
Change	$-x$	$+2x$
Equilibrium	$0.0300 - x$	$2x$

Substituting into the equilibrium expression for K_c gives

$$K_c = 0.125 = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.0300 - x)}$$

Rearranging and solving for x yield

$$4x^2 + 0.125x - 3.75 \times 10^{-3} = 0 \text{ (quadratic equation)}$$

Using the solution to the quadratic equation gives

$$x = \frac{-(0.125) \pm \sqrt{(0.125)^2 - 4(4)(-3.75 \times 10^{-3})}}{2(4)}$$

$x = -5.00 \times 10^{-2}$ (impossible; reject), or $x = 1.8\underline{7}5 \times 10^{-2}$ *M* (logical)

Percent dissoc. = (change ÷ starting) x 100% = (0.01875 ÷ 0.0300) x 100%

= 62.$\underline{5}$0 = 62.5%

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14.95. Using 1.00 mol/10.00 L, or 0.100 *M*, and 4.00 mol/10.00 L, or 0.400 *M*, for the respective starting concentrations for CO and H_2, assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$CO(g)$ +	$3H_2(g)$ ⇌	$CH_2(g)$ +	$H_2O(g)$
Starting	0.100	0.400	0	0
Change	$-x$	$-3x$	$+x$	$+x$
Equilibrium	$0.100 - x$	$0.400 - 3x$	X	x

Substituting into the equilibrium expression for K_c gives

$$K_c = 3.92 = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{x^2}{(0.100 - x)(0.400 - 3x)^3}$$

$$f(x) = \frac{x^2}{(0.100 - x)(0.400 - 3x)^3}$$

Because K_c is > 1 (> 50% reaction), choose $x = 0.05$ (about half of CO reacting), and use that for the first entry in the table of x, $f(x)$, and interpretations.

x	$f(x)$	Interpretation
0.05	3.20	$x > 0.05$
0.06	8.45	$x < 0.06$
0.055	5.18	$x < 0.055$
0.0525	4.07	$x < 0.0525$ (but close)
0.052	3.87	$f(x)$ of $3.87 \cong 3.92$

At equilibrium, concentrations and moles are CO: 0.048 *M* and 0.48 mol; H_2: 0.244 *M* and 2.44 mol; CH_4: 0.052 *M* and 0.52 mol; and H_2O: 0.052 *M* and 0.52 mol.

14.96. Using 1.00 mol/10.00 L, or 0.100 *M*, and 4.00 mol/10.00 L, or 0.400 *M*, for the respective starting concentrations for N_2 and H_2, assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$N_2(g)$ +	$3H_2(g)$ ⇌	$2NH_3(g)$
Starting	0.100	0.400	0
Change	$-x$	$-3x$	$+2x$
Equilibrium	$0.100 - x$	$0.400 - 3x$	$2x$

Substituting into the equilibrium expression for K_c gives

$$K_c = 0.153 = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(0.100 - x)(0.400 - 3x)^3}$$

$$f(x) = \frac{4x^2}{(0.100 - x)(0.400 - 3x)^3}$$

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Because K_c is < 1 (< 50% reaction), choose $x = 0.010$ (about 10% of N_2 reacting), and use that for the first entry in the table of x, f(x), and interpretations.

x	f(x)	Interpretation
0.010	0.0877	x too small
0.020	0.5089	x too big
0.015	0.237	x still too big
0.012	0.136	$x < 0.153$ (but close)
0.013	0.1651	f(x) of .1651 $\cong$ 0.153
0.0125	0.150	best f(x)

At equilibrium, concentrations and moles are N_2: 0.087 M and 0.87 mol; H_2: 0.362 M and 3.62 mol; and NH_3: 0.025 M and 0.25 mol.

14.97. The dissociation is endothermic.

14.98. The value of K_c and the ratio of products to reactants decrease with temperature, so the reaction must be exothermic.

14.99. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_p is defined in terms of pressures as

$$K_p = \frac{P_{NH_3}^{\ 2}}{P_{N_2} P_{H_2}^{\ 3}}$$

But by the ideal gas law, where [i] = mol/L,

$P_i = (n_i RT)/V$, or $P_i = [\ i\ ]RT$

Substituting the right-hand equality into the K_p expression gives

$$K_p = \frac{[NH_3]^2 (RT)^2}{[N_2](RT)\ [H_2]^3 (RT)^3} = \frac{[NH_3]^2}{[N_2][H_2]^3} (RT)^{-2}$$

$$K_p = K_c(RT)^{-2}, \text{ or } K_c = K_p (RT)^2$$

14.100. For $COCl_2 \rightleftharpoons CO + Cl_2$, K_p is defined in terms of pressure as

$$K_p = \frac{P_{CO} P_{Cl_2}}{P_{COCl_2}}$$

Substituting [i]$RT = P$ for each term as in the above problem yields

$$K_p = \frac{[CO](RT)[Cl_2](RT)}{[COCl_2](RT)} = \frac{[CO][Cl_2]}{[COCl_2]}(RT)$$

$$K_p = K_c RT, \text{ or } K_c = K_p/(RT)$$

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14.101.

a. The change in the number of moles of gas for the reaction is $\Delta n = 2 - 1 = 1$. Using this, calculate K_p from K_c:

$$K_p = K_c(RT)^{\Delta n} = 0.153\ (0.08206 \times 1123)^1 = 14.\underline{0}99 = 14.1$$

b. Use the table approach, and give the starting, change, and equilibrium pressures in atm.

Press. (atm)	C(*s*) +	$CO_2(g)$ ⇌	$2CO(g)$
Starting		1.50	0
Change		$-x$	$+2x$
Equilibrium		$1.50 - x$	$2x$

Substituting into the equilibrium-constant expression gives

$$K_p = 14.10 = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(2x)^2}{(1.50 - x)}$$

Rearranging and solving for x give a quadratic equation.

$$4x^2 + 14.10x - 21.15 = 0$$

Using the quadratic formula gives

$$x = \frac{-14.10 \pm \sqrt{(14.10)^2 - (4)(4)(-21.15)}}{2(4)}$$

$$x = 1.1\underline{3}5 \text{ (positive root)}$$

Thus, at equilibrium, the pressures of CO and CO_2 are

$$P_{CO_2} = 1.50 - 1.1\underline{3}5 = 0.3\underline{6}5 = 0.37 \text{ atm}$$

$$P_{CO} = 2x = 2(1.1\underline{3}5) = 2.2\underline{7}0 = 2.27 \text{ atm}$$

c. Because the reaction is endothermic, the equilibrium will shift to the left, and the pressure of CO will decrease.

14.102.

a. The change in the number of moles of gas for the reaction is $\Delta n = 2 - 1 = 1$. Using this, calculate K_p from K_c:

$$K_p = K_c(RT)^{\Delta n} = 0.238\ (0.08206 \times 1173)^1 = 22.\underline{9}09 = 22.9$$

b. The total pressure of the system at equilibrium is 6.40 atm. This equals the sum of the pressures of CO and CO_2. Thus, the pressure of CO_2 can be expressed as

$$P_{CO_2} = 6.40 - P_{CO}$$

Substituting into the equilibrium-constant expression gives

$$K_p = 22.91 = \frac{P_{CO}^2}{P_{CO_2}} = \frac{P_{CO}^2}{6.40 - P_{CO}}$$

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Rearranging and solving for x (= P_{CO}) give a quadratic equation.

$$x^2 + 22.91x - 146.6 = 0$$

Using the quadratic formula gives

$$x = \frac{-22.91 \pm \sqrt{(22.91)^2 - (4)(1)(-146.6)}}{2(1)}$$

$$x = 5.2\underline{1}3 \text{ (positive root)}$$

Thus, at equilibrium, the pressures of CO and CO_2 are

$$P_{CO_2} = 640 - 5.2\underline{1}3 = 1.1\underline{8}7 = 1.19 \text{ atm}$$

$$P_{CO} = x = 5.2\underline{1}3 = 5.21 \text{ atm}$$

c. Carbon doesn't appear in the equilibrium expression, so it doesn't have any effect on the position of the equilibrium.

14.103.

a. The molar mass of PCl_5 is 208.22 g/mol. Thus, the initial concentration of PCl_5 is

$$\frac{35.8 \text{ g } PCl_5 \text{ x } \frac{1 \text{ mol } PCl_5}{208.22 \text{ g } PCl_5}}{5.0 \text{ L}} = 0.03\underline{4}4 \ M$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$PCl_3(g)$ +	$Cl_2(g)$ ⇌	$PCl_5(g)$
Starting	0	0	$0.03\underline{4}4$
Change	x	x	$-x$
Equilibrium	x	x	$0.03\underline{4}4 - x$

Substituting into the equilibrium-constant expression gives

$$K_c = 4.1 = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.0344 - x}{x^2}$$

Rearranging and solving for x gives a quadratic equation.

$$4.1x^2 + x - 0.0344 = 0$$

Using the quadratic formula gives

$$x = \frac{-1 \pm \sqrt{(1)^2 - (4)(4.1)(-0.0344)}}{2(4.1)}$$

$$x = 0.03\underline{0}6 \text{ (positive root)}$$

Thus, at equilibrium, $[PCl_3] = [Cl_2] = x = 0.031\ M$. The concentration of PCl_5 is

$$[PCl_5] = .03\underline{4}4 - x = 0.0344 - 0.0306 = 0.00\underline{3}8 = 0.004\ M.$$

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b. The fraction of PCl_5 decomposed is

$$\text{Fraction decomposed} = \frac{0.0306\ \text{M}}{0.0344\ \text{M}} = 0.889 = 0.89$$

c. There would be a greater pressure, so, in order to minimize the increase in pressure, less PCl_5 would decompose.

14.104.

a. The total pressure at equilibrium is

$$P_{NH_3} + P_{H_2S} = 0.660\ \text{atm}$$

Since the pressures of NH_3 and H_2S are equal, this gives

$$P_{NH_3} = P_{H_2S} = \frac{0.660\ \text{atm}}{2} = 0.330\ \text{atm}$$

The equilibrium-constant expression is

$$K_p = P_{NH_3} \times P_{H_2S} = (0.330)^2 = 0.1089 = 0.109$$

b. Since $P_{H_2S} = 3P_{NH_3}$, the equilibrium-constant expression becomes

$$K_p = P_{NH_3} \times P_{H_2S} = 3P_{NH_3}^2 = 0.1089$$

$$P_{NH_3} = \sqrt{\frac{0.1089}{3}} = 0.1905 = 0.191\ \text{atm}$$

The partial pressure of H_2S is

$$P_{H_2S} = 3(0.1905) = 0.5715 = 0.572\ \text{atm}$$

c. Use the table approach, and give the starting, change, and equilibrium pressures in atm.

Press. (atm)	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
Starting			0.750		0.500
Change			$-x$		$-x$
Equilibrium			$0.750 - x$		$0.500 - x$

Substituting into the equilibrium-constant expression gives

$$K_p = P_{NH_3} \times P_{H_2S} = (0.750 - x)(0.500 - x) = 0.1089$$

Rearranging and solving for x give a quadratic equation.

$$x^2 - 1.250x + 0.2661 = 0$$

Using the quadratic formula gives

$$x = \frac{-(-1.250) \pm \sqrt{(-1.250)^2 - (4)(1)(0.2661)}}{2(1)}$$

$$x = 0.2721 \text{ (negative root)}$$

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Thus, at equilibrium, the partial pressures of NH_3 and H_2S are

$$P_{NH_3} = 0.750 - 0.2721 = 0.4779 = 0.478 \text{ atm}$$

$$P_{H_2S} = 0.500 - 0.2721 = 0.2279 = 0.228 \text{ atm}$$

For NH_4HS, use the ideal gas equation to convert atm (= x) to moles.

$$n = \frac{PV}{RT} = \frac{(0.2721 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(298 \text{ K})} = 0.01113 = 0.0111 \text{ mol}$$

14.105. The initial moles of $SbCl_5$ (molar mass 299.01 g/mol) are

$$65.4 \text{ g } SbCl_5 \text{ x } \frac{1 \text{ mol } SbCl_5}{299.01 \text{ g } SbCl_5} = 0.2187 \text{ mol}$$

The initial pressure of $SbCl_5$ is

$$P = \frac{nRT}{V} = \frac{(0.2187 \text{ mol})(0.08206 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(468 \text{ K})}{5.00 \text{ L}} = 1.680 \text{ atm}$$

Use the table approach, and give the starting, change, and equilibrium pressures in atm.

Press. (atm)	$SbCl_5(g)$	$\rightleftharpoons$	$SbCl_3(g)$	+	$Cl_2(g)$
Starting	1.680		0		0
Change	$-x$		x		x
Equilibrium	(1.680)(0.642)		(1.680)(0.358)		(1.680)(0.358)

At equilibrium, 35.8% of the $SbCl_5$ is decomposed, so x = (1.680)(0.358) in this table. The equilibrium-constant expression is

$$K_p = \frac{P_{SbCl_3} \bullet P_{Cl_2}}{P_{SbCl_5}} = \frac{(1.680 \text{ x } 0.358)^2}{1.680 \text{ x } 0.642} = 0.3354 = 0.335$$

14.106. Use the table approach, and give the starting, change, and equilibrium concentrations. The volume of the system is 1.00 L.

Conc. (M)	$SO_2(g)$	+	$1/2O_2(g)$	$\rightleftharpoons$	$SO_3(g)$
Starting	0.0216		0.0148		0
Change	$-x$		$-1/2x$		$+x$ (= 0.0175)
Equilibrium	0.0216 − 0.0175 = 0.00410		0.0148 − 1/2(0.0175) = 0.00605		0.0175

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = \frac{0.0175}{(0.00410)(0.00605)^{1/2}} = 54.87 = 54.9$$

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14.107.

a. The initial concentration of SO_2Cl_2 (molar mass 134.97 g/mol) is

$$\frac{8.25\text{ g } SO_2Cl_2 \text{ x } \dfrac{1\text{ mol } SO_2Cl_2}{134.97\text{ g } SO_2Cl_2}}{1.00\text{ L}} = 0.06112\ M$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$SO_2Cl_2(g)$	$\rightleftharpoons$	$SO_2(g)$	+	$Cl_2(g)$
Starting	0.06112		0		0
Change	$-x$		x		x
Equilibrium	$0.06112 - x$		x		x

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{x^2}{(0.06112 - x)} = 0.045$$

Rearranging and solving for x give a quadratic equation.

$$x^2 + 0.045x - 0.0027506 = 0$$

Using the quadratic formula gives

$$x = \frac{-(0.045) \pm \sqrt{(0.045)^2 - (4)(1)(-0.0027506)}}{2(1)}$$

$x = 0.03456$ (positive root)

The concentrations at equilibrium are $[SO_2] = [Cl_2] = x = 0.034\ M$. For SO_2Cl_2,

$[SO_2Cl_2] = 0.06112 - x = 0.06112 - 0.03456 = 0.02655 = 0.027$ M.

b. The fraction of SO_2Cl_2 decomposed is

$$\text{Fraction decomposed} = \frac{0.03456\ M}{0.06112\ M} = 0.565 = 0.57$$

c. This would shift the equilibrium to the left and decrease the fraction of SO_2Cl_2 that has decomposed.

14.108.

a. The initial concentration of $COCl_2$ (molar mass 98.91 g/mol) is

$$\frac{6.55\text{ g } COCl_2 \text{ x } \dfrac{1\text{ mol } COCl_2}{98.91\text{ g } COCl_2}}{1.00\text{ L}} = 0.06622\ M$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
Starting	0.06622		0		0
Change	$-x$		x		x
Equilibrium	$0.06622 - x$		x		x

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Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{x^2}{(0.06622 - x)} = 0.0046$$

Rearranging and solving for x give a quadratic equation.

$$x^2 + 0.0046x - 3.046 \times 10^{-4} = 0$$

Using the quadratic formula gives

$$x = \frac{-(0.0046) \pm \sqrt{(0.0046)^2 - (4)(1)(-3.046 \times 10^{-4})}}{2(1)}$$

$x = 0.01\underline{5}3$ (positive root)

The concentrations at equilibrium are $[CO] = [Cl_2] = x = 0.015\ M$. For $COCl_2$,

$[COCl_2] = 0.06622 - x = 0.06622 - 0.01\underline{5}3 = 0.05\underline{0}9 = 0.051\ M$.

b. The fraction of $COCl_2$ decomposed is

$$\text{Fraction decomposed} = \frac{0.0153\ M}{0.06622\ M} = 0.2\underline{3}1 = 0.23$$

c. This would shift the equilibrium to the left and decrease the fraction of $COCl_2$ that has decomposed.

14.109.

a. First, determine the initial concentration of the dimer assuming complete reaction. The reaction can be described as $2A \rightarrow D$. Therefore, the initial concentration of dimer is one-half of the concentration of monomer, or $2.0 \times 10^{-4}\ M$. Next, allow the dimer to dissociate into the monomer in equilibrium. Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	D(g) ⇌	2A(g)
Starting	2.0×10^{-4}	0
Change	$-x$	$2x$
Equilibrium	$2.0 \times 10^{-4} - x$	$2x$

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[A]^2}{[D]} = \frac{(2x)^2}{(2.0 \times 10^{-4} - x)} = \frac{1}{3.2 \times 10^4} = 3.125 \times 10^{-5}$$

Rearranging and solving for x give a quadratic equation.

$$4x^2 + (3.125 \times 10^{-5})\,x - (6.250 \times 10^{-9}) = 0$$

Using the quadratic formula gives

$$x = \frac{-(3.125 \times 10^{-5}) \pm \sqrt{(3.125 \times 10^{-5})^2 - (4)(4)(-6.250 \times 10^{-9})}}{2(4)}$$

$x = 3.\underline{5}8 \times 10^{-5}$ (positive root)

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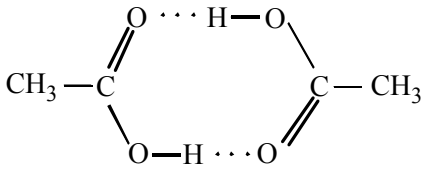
Thus, the concentrations at equilibrium are

$$[CH_3COOH] = 2x = 2\,(3.\underline{5}8 \times 10^{-5}) = 7.\underline{1}6 \times 10^{-5} = 7.2 \times 10^{-5}\ M$$

$$[\text{Dimer}] = 2.0 \times 10^{-4} - 3.\underline{5}8 \times 10^{-5} = 1.\underline{6}4 \times 10^{-4} = 1.6 \times 10^{-4}\ M$$

b. Some hydrogen bonding can occur that results in a more stable system. The proposed structure of the dimer is



c. An increase in the temperature would facilitate bond breaking and would decrease the amount of dimer. We could also use a Le Châtelier-type argument.

14.110.

a. First, determine the initial pressure of the dimer assuming complete reaction. The reaction can be described as $2A \rightarrow D$. Therefore, the initial pressure of the dimer is one-half of the pressure of monomer, or $3.\underline{7}5 \times 10^{-3}$ atm. Next, allow the dimer to dissociate into the monomer in equilibrium. Use the table approach, and give the starting, change, and equilibrium pressures.

Press. (atm)	D(*g*)	⇌	2A(*g*)
Starting	3.75×10^{-3}		0
Change	$-x$		$2x$
Equilibrium	$3.75 \times 10^{-3} - x$		$2x$

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{P_A^2}{P_D} = \frac{(2x)^2}{(3.75 \times 10^{-3} - x)} = \frac{1}{1.3 \times 10^{3}} = 7.692 \times 10^{-4}$$

Rearranging and solving for x give a quadratic equation.

$$4x^2 + (7.692 \times 10^{-4})\,x - (2.885 \times 10^{-6}) = 0$$

Using the quadratic formula gives

$$x = \frac{-(7.692 \times 10^{-4}) \pm \sqrt{(7.692 \times 10^{-4})^2 - (4)(4)(-2.885 \times 10^{-6})}}{2(4)}$$

$$x = 7.\underline{5}9 \times 10^{-4} \text{ (positive root)}$$

Thus, the concentrations at equilibrium are

$$[CH_3COOH] = 2x = 2\,(7.\underline{5}9 \times 10^{-4}) = 1.\underline{5}2 \times 10^{-3} = 1.5 \times 10^{-3}\ \text{atm}$$

$$[\text{Dimer}] = 3.75 \times 10^{-3} - 7.\underline{5}9 \times 10^{-4} = 2.\underline{9}9 \times 10^{-3} = 3.0 \times 10^{-3}\ \text{atm}$$

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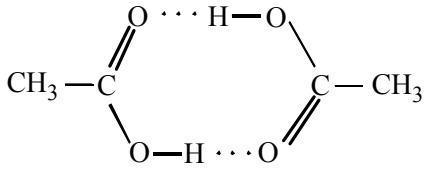
b. Some hydrogen bonding can occur that results in a more stable system. The proposed structure of the dimer is



c. A decrease in the temperature would decrease bond breaking in the dimer, so this would decrease the amount of dimer.

14.111. The molar mass of Br_2 is 159.82 g/mol. Thus, the initial concentration of Br_2 is

$$\frac{18.22\ \text{g Br}_2\ \text{x}\ \dfrac{1\ \text{mol Br}_2}{159.82\ \text{g Br}_2}}{1.00\ \text{L}} = 0.11\underline{4}0\ M$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	2NO(g)	+	Br_2(g)	⇌	2NOBr(g)
Starting	0.112		0.11$\underline{4}$0		0
Change	$-2x$		$-x$		$2x$
Equilibrium	$0.112 - 2x =$ 0.02$\underline{9}$60		$= 0.1140 - x$ 0.07$\underline{2}$80		$2x$ (= 0.0824 M) = 0.0824

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]} = \frac{(0.0824)^2}{(0.02960)^2(0.07280)} = 1\underline{0}6.4 = 1.1 \times 10^2$$

14.112. The molar mass of Br_2 is 159.82 g/mol. Thus, the initial moles of Br_2 are

$$1.52\ \text{g Br}_2\ \text{x}\ \frac{1\ \text{mol Br}_2}{159.82\ \text{g Br}_2} = 9.5\underline{1}1 \times 10^{-3}\ \text{mol}$$

The initial pressures of NO and Br_2 are

$$P_{NO} = \frac{nRT}{V} = \frac{(0.0322\ \text{mol})(0.08206\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K})}{1.00\ \text{L}} = 0.78\underline{7}4\ \text{atm}$$

$$P_{Br_2} = \frac{nRT}{V} = \frac{(9.511 \times 10^{-3}\ \text{mol})(0.08206\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K})}{1.00\ \text{L}} = 0.23\underline{2}6\ \text{atm}$$

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Use the table approach, and give the starting, change, and equilibrium pressures.

Press. (atm)	$2NO(g)$	+	$Br_2(g)$	⇌	$2NOBr(g)$
Starting	0.787<u>4</u>		0.232<u>6</u>		0
Change	$-2x$		$-x$		$2x$
Equilibrium	$0.787\underline{4} - 2x =$ $0.349\underline{4}$		$0.232\underline{6} - x =$ $0.013\underline{6}$		2x (= 0.438 atm) = 0.438

Substituting into the equilibrium-constant expression gives

$$K_p = \frac{P^2_{NOBr}}{P^2_{NO}\,P_{Br_2}} = \frac{(0.438)^2}{(0.3494)^2\,(0.0136)} = 11\underline{5}.5 = 1.2 \times 10^2$$

14.113. Chemists have shown that oscillation reactions occur by two different mechanisms, first by one, then by the other. These mechanisms are repeated in space or time, depending on the concentrations of intermediate substances. During the reaction, an indicator changes color depending on which mechanism is active. Although the complete set of elementary steps is complicated, the overall reaction occurs just as you would expect. The initial reactants continue to decrease over time, and the final products increase as the substances come to equilibrium.

14.114. An oscillating mechanism appears to be at work in the aggregation phase of cellular slime molds. During the initial stages of aggregation the amoebas form a distinctive pattern reminiscent of that seen by chemists in an oscillating reaction. One theory of the formation of fur patterns in animals, such as leopard's spots, assumes that an oscillating reaction occurs in the skin of the embryo, which eventually generates the fur pattern you see in the adult. A similar theory has been used to explain striped patterns on seashells.

■ SOLUTIONS TO STRATEGY PROBLEMS

14.115. First write out the equilibrium expression K_p. Then write each of the partial pressures in terms of its mole fraction, $P_i = X_i P_{tot}$.

$$K_p = \frac{P_{COF_2}{}^2}{P_{CO_2}\,P_{CF_4}} = \frac{(X_{COF_2}P_{tot})^2}{(X_{CO_2}P_{tot})\,(X_{CF_4}P_{tot})} = \frac{X_{COF_2}{}^2}{X_{CO_2}\,X_{CF_4}}$$

The mole fraction of CO_2 is $1 - 0.40 - 0.20 = 0.40$. Substitute the mole fractions and get

$$K_p = \frac{(0.20)^2}{(0.40)(0.40)} = 0.2\underline{5}0 = 0.25$$

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14.116. First write out the equilibrium expression K_p. Then write each of the partial pressures in terms of its moles, $P_i = (RT/V)n_i$.

$$K_p = \frac{P_{NO}^{\ 2}}{P_{N_2}\,P_{O_2}} = \frac{(n_{NO}RT/V)^2}{(n_{N_2}RT/V)(n_{O_2}RT/V)} = \frac{(n_{NO})^2}{(n_{N_2})(n_{O_2})}$$

Now calculate Q when equal moles of N_2, O_2, and NO are placed in the flask.

$$Q_p = \frac{(n)^2}{(n)(n)} = 1.0$$

Since $Q_p > K_p$, the reaction is not at equilibrium and will undergo reaction to the left.

14.117. Let n be the initial moles of each substance, and set up the usual table.

Amt. (mol)	$N_2(g)$ +	$O_2(g)$ ⇌	$2NO(g)$
Starting	n	n	n
Change	$+x$	$+x$	$-2x$
Equilibrium	$n + x$	$n + x$	$n - 2x$

Substituting into the equilibrium-constant expression gives

$$K_p = 0.0123 = \frac{(n - 2x)^2}{(n + x)(n + x)}$$

Take the square root of each side.

$$0.11\underline{0}9 = \frac{(n - 2x)}{(n + x)}$$

Rearrange and solve for x.

$$0.1109(n + x) = n - 2x$$

$$x = \frac{1 - 0.1109}{2 + 0.1109}n = \frac{0.8890}{2.1109}n = 0.42\underline{1}19n = 0.421n$$

The equilibrium-composition mixture is

Moles of $N_2 = n + 0.4211n = 1.42\underline{1}1n$

Moles of $O_2 = = n + 0.421n = 1.42\underline{1}1n$

Moles of NO $= n - 2(0.421n) = 0.15\underline{7}6n$

Total moles $= 1.421n + 1.421n + 0.1576n = 2.99\underline{9}8n$

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The equilibrium-composition mixture is best expressed in terms of the mole fractions of the substances, since the equilibrium mixture is independent of the initial moles, as long as it is the same for all three substances.

$$X_{N_2} = \frac{1.4211n}{2.9998n} = 0.47\underline{3}7 = 0.474$$

$$X_{O_2} = \frac{1.4211n}{2.9998n} = 0.47\underline{3}7 = 0.474$$

$$X_{NO} = \frac{0.1576n}{2.9998n} = 0.052\underline{5}3 = 0.0525$$

14.118. Reverse the first equation (at 425°C) so that it is the same as the second equation (at 458°C). The equilibrium constant for the reverse reaction is $K_1 = 1/1.84 = 0.54\underline{3}4$. The equilibrium constant at the higher temperature is $K_2 = 49.7$. Since the equilibrium constant increases with increasing temperature, the reaction shifts to the right and is endothermic. Thus, increasing temperature favors the formation of HI. Since the change in the number of moles of gaseous substances, Δn, is zero for this reaction, increasing the pressure has no effect on the equilibrium.

14.119. This reaction requires the breaking of bonds, which requires energy and is an endothermic process. As you raise the temperature, the reaction shifts toward the formation of more $NO_2(g)$, so you would expect the reaction mixture to become more red-brown.

14.120. The initial concentration of PCl_3 is 0.0800 *M* and of Cl_2 is 0.120 *M*. Set up the usual table.

Conc. (*M*)	$PCl_3(g)$	+	$Cl_2(g)$	⇌	$PCl_5(g)$
Starting	0.0800		0.120		0
Change	$-x$		$-x$		$+x$
Equilibrium	$0.0800 - x$		$0.120 - x$		x

Substituting into the equilibrium-constant expression gives

$$K_c = 25.6 = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{x}{(0.0800 - x)(0.120 - x)}$$

Rearrange this expression into a quadratic equation in standard form.

$$25.6x^2 - 6.12x + 0.2457 = 0$$

$$x = \frac{-(-6.12) \pm \sqrt{(-6.12)^2 - (4)(25.6)(0.2457)}}{2(25.6)} = \frac{6.12 \pm 3.505}{51.2}$$

The positive root is 0.18$\underline{7}$9, which is not valid, so use the negative root, 0.051$\underline{0}$7 *M*. The equilibrium composition of the mixture is

$[PCl_3] = 0.0800\ M - x = 0.0800 - 0.05107 = 0.028\underline{9}3 = 0.0289\ M$

$[Cl_2] = 0.120 - x = 0.120 - 0.05107 = 0.06\underline{8}93 = 0.069\ M$

$[PCl_5] = x = 0.051\underline{0}7 = 0.0511\ M$

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14.121.

a. Removing some NH_3 from the flask would cause the reaction to shift from left to right, increasing the amount of H_2S produced.

b. Adding some NH_3 to the flask would cause the reaction to shift from right to left, decreasing the amount of H_2S gas produced.

c. Since NH_4HS is a solid, removing some of it would have no effect on the equilibrium, nor would it have any effect on the amount of H_2S produced.

d. Increasing the pressure in the flask by adding helium gas would have no effect on the equilibrium, nor would it have any effect on the amount of H_2S produced. Adding helium has no effect on the partial pressures of the gasses in the flask.

14.122. First calculate the initial concentrations of CO and Cl_2 in the flask.

$$[Cl_2] = 8.00 \text{ g } Cl_2 \times \frac{1 \text{ mol}}{70.90 \text{ g}} \times \frac{1}{10.00 \text{ L}} = 0.011\underline{2}8 \; M$$

$$[CO] = 1/2[Cl_2] = 0.005\underline{6}41 \; M$$

Now set up the table.

Conc. (M)	$CO(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$
Starting	0.005641		0.01128		0
Change	$-x$		$-x$		$+x$
Equilibrium	$0.005641 - x$		$0.01128 - x$		x

Substituting into the equilibrium-constant expression gives

$$K_c = 1.23 \times 10^3 = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{x}{(0.005641 - x)(0.01128 - x)}$$

Rearrange this expression into a quadratic equation in standard form.

$$x^2 - 0.01773x + 6.363 \times 10^{-5} = 0$$

$$x = \frac{-(-0.01773) \pm \sqrt{(-0.01773)^2 - (4)(1)(6.363 \times 10^{-5})}}{2(1)} = \frac{0.01773 \pm 0.007735}{2}$$

The positive root is 0.012$\underline{7}$3, which is not valid, so use the negative root, 0.004$\underline{9}$97 M. The partial pressure of phosgene ($COCl_2$) is calculated as follows. The temperature is 395°C, which is 668 K.

$$P = (n/V)RT = (0.004997 \; M)(0.08206 \text{ L•atm/K•mol})(668 \text{ K}) = 0.27\underline{3}9 = 0.274 \text{ atm}$$

14.123. The reaction involves breaking of bonds, which requires energy and is endothermic. This means that the equilibrium constant should be larger at higher temperatures. This allows you to assign $K_p = 0.001745$ at 700°C and $K_p = 0.01106$ at 800°C.

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14.124.

a. The moles are equal to the mass, m, divided by the molar mass, M_m. This gives

$$PV = nRT = (m/M_m)RT$$

Rearrange this expression and solve for the mass of the gas.

$$m = \frac{PVM_m}{RT}$$

b. The mass of gas A and the mass of gas B are

$$m_A = \frac{P_A V M_{mA}}{RT} \quad m_B = \frac{P_B V M_{mB}}{RT}$$

The total mass of the gas is

$$m = m_A + m_B = \frac{P_A V M_{mA}}{RT} + \frac{P_B V M_{mB}}{RT} = \frac{V(P_A M_{mA} + P_B M_{mB})}{RT}$$

The density of the gas is

$$d = \frac{m}{V} = \frac{(P_A M_{mA} + P_B M_{mB})}{RT}$$

c. If A is NO_2 and B is N_2O_4, then $M_{mB} = 2M_{mA}$. Also, $P_B = P - P_A$. Plug these relations into the result above to obtain

$$dRT = P_A M_{mA} + (P - P_A)(2M_{mA}) = 2PM_{mA} - P_A M_{mA}$$

This equation can be solved for P_A.

$$P_A = 2P - \frac{dRT}{M_{mA}}$$

d. The partial pressures of NO_2 and N_2O_4 are

$$P_{NO_2} = 2(1.00 \text{ atm}) - \frac{(2.86 \text{ g/L})(0.082058 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(308.15 \text{ K})}{46.01 \text{ g/mol}}$$

$$= 0.4282 = 0.428 \text{ atm}$$

$$P_{N_2O_4} = P - P_{NO_2} = 1.00 \text{ atm} - 0.4282 \text{ atm} = 0.5718 = 0.572 \text{ atm}$$

The equilibrium constant is

$$K_p = \frac{P_{N_2O_4}}{P_{NO_2}^2} = \frac{0.5718}{(0.4282)^2} = 3.118 = 3.12$$

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■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

14.125. For $Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$ [$+3Pb^{2+} \rightarrow 3PbS(s) + 6H^+$]:

Starting M of $H_2(g)$ = 0.0100 mol ÷ 2.50 L = 0.00400 M H_2

1.029 g PbS ÷ 239.26 g PbS/mol H_2S = 4.30$\underline{0}$7 x 10^{-3} mol H_2S

4.3007 x 10^{-3} mol H_2S ÷ 2.50 L = [1.7203 x 10^{-3}] = M of H_2S

Conc. (M)	$3H_2(g)$	+	$Sb_2S_3(s)$	$\rightleftharpoons$	$3H_2S(g)$	+	$2Sb(s)$
Starting	0.00400				0		
Change	−0.0017203				+0.0017203		
Equilibrium	0.0022797				0.0017203		

Substituting into the equilibrium expression for K_c gives

$$K_c = \frac{[H_2S]^3}{[H_2]^3} = \frac{(0.0017203)^3}{(0.0022797)^3} = 0.42\underline{9}7 = 0.430$$

14.126. For $LaCl_3 + H_2O \rightleftharpoons LaOCl(s) + 2HCl(g)$ [$+2Ag^+ \rightarrow 2AgCl(s) + 2H^+$]:

Starting M of $H_2O(g)$ = 0.0250 mol ÷ 1.25 L = 0.0200 M H_2O

3.59 g AgCl ÷ 143.32 g AgCl/mol AgCl = 0.025$\underline{0}$48 mol AgCl

0.025048 mol AgCl ÷ 1.25 L = 0.020$\underline{0}$39 M

Conc. (M)	$H_2O(g)$	+	$LaCl_3(s)$	$\rightleftharpoons$	$2HCl(g)$	+	$LaOCl(s)$
Starting	0.0200				0		
Change	−0.0100195				+0.020039		
Equilibrium	0.009$\underline{9}$805				0.020$\underline{0}$39		

$$K_c = \frac{[HCl]^2}{[H_2O]} = \frac{(0.020039)^2}{(0.0099805)} = 4.\underline{0}23 \times 10^{-2} = 4.0 \times 10^{-2}$$

14.127. for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$:

Starting M of PCl_5 = 0.0100 mol ÷ 2.00 L = 0.00500 M

Conc. (M)	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Starting	0.00500		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	0.00500 − x		x		x

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Substituting into the equilibrium expression for K_c gives

$$K_c = 4.15 \times 10^{-2} = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)(x)}{(0.00500 - x)}$$

$$x^2 + (4.15 \times 10^{-2})x - 2.075 \times 10^{-4} = 0 \text{ (quadratic)}$$

Solving the quadratic equation gives $x = -4.60 \times 10^{-2}$ (impossible) and $x = 4.51 \times 10^{-3}$ *M* (use).

Total *M* of gas = 0.00451 + 0.00451 + 0.00049 = 0.009510 *M*

$P = (n/V)RT = (0.009510\ M)[0.082057\ \text{L•atm/(K•mol)}](523\ \text{K}) = 0.4081 = 0.408\ \text{atm}$

14.128. For $SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$:

Starting *M* of $SbCl_5$ = 0.0125 mol ÷ 3.50 L = 0.003571 *M*

Conc. (*M*)	$SbCl_5(g)$	$\rightleftharpoons$	$SbCl_3(g)$	+	$Cl_2(g)$
Starting	0.003571		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.003571 - x$		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 2.50 \times 10^{-2} = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{(x)(x)}{(0.003751 - x)}$$

$$x^2 + (2.50 \times 10^{-2})x - 8.927 \times 10^{-5} = 0 \text{ (quadratic)}$$

Solving the quadratic equation gives $x = -2.817 \times 10^{-2}$ (impossible) and $x = 3.17 \times 10^{-3}$ *M* (use).

Total *M* of gas = 0.00317 + 0.00317 + 0.00040 = 0.006740 *M*

$P = (n/V)RT = (0.00674\ M)[0.082057\ \text{L•atm/(K•mol)}](521\ \text{K}) = 0.2881 = 0.288\ \text{atm}$

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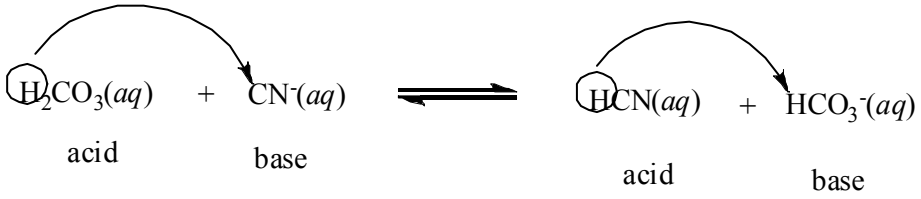
CHAPTER 15

Acids and Bases

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

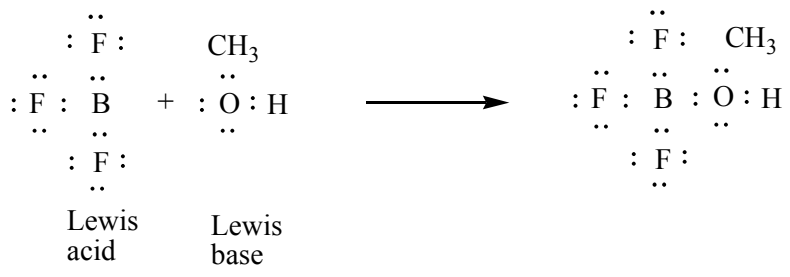
15.1. See labels below reaction:



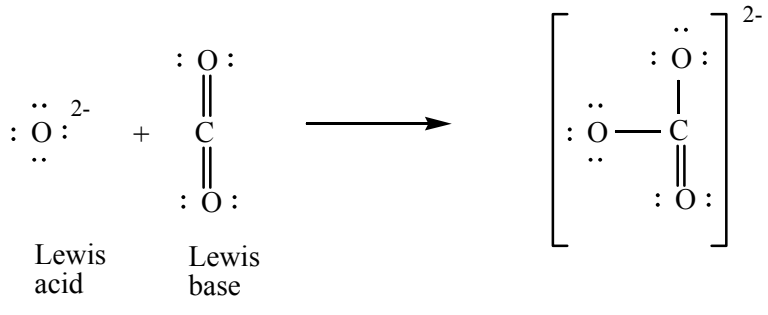
H_2CO_3 is the proton donor (Brønsted-Lowry acid) on the left, and HCN is the proton donor (Brønsted-Lowry acid) on the right. The CN^- and HCO_3^- ions are proton acceptors (Brønsted-Lowry bases). HCN is the conjugate acid of CN^-.

15.2. Part a involves molecules with all single bonds; part b does not, so bonds are drawn in.

a.



b.



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15.3. The $HC_2H_3O_2$ is a stronger acid than H_2S, and HS^- is a stronger base than the $C_2H_3O_2^-$ ion. The equilibrium favors the weaker acid and weaker base; therefore, the reactants are favored.

15.4.

a. PH_3

b. HI

c. H_2SO_3

d. $H_3AsO_4^-$

e. HSO_4^-

15.5. A 0.125 *M* solution of $Ba(OH)_2$, a strong base, ionizes completely to yield 0.125 *M* Ba^{2+} ion and 2 x 0.125 *M*, or 0.250 *M*, OH^- ion. Use the K_w equation to calculate the $[H_3O^+]$.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{(0.250)} = 4.\underline{0}0 \times 10^{-14} = 4.0 \times 10^{-14}\ M$$

15.6. Use the K_w equation to calculate the $[H_3O^+]$.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.\underline{0}0 \times 10^{-9} = 1.0 \times 10^{-9}\ M$$

Since the $[H_3O^+]$ concentration is less than 1.0×10^{-7}, the solution is basic.

15.7. Calculate the negative log of the $[H_3O^+]$:

$$pH = -\log [H_3O^+] = -\log (0.045) = 1.3\underline{4}6 = 1.35$$

15.8. Calculate the pOH of 0.025 *M* OH^-, and then subtract from 14.00 to find pH:

$$pOH = -\log [OH^-] = -\log (0.025) = 1.6\underline{0}2$$

$$pH = 14.00 - 1.602 = 12.3\underline{9}7 = 12.40$$

15.9. Because pH = 3.16, by definition $\log [H_3O^+] = -3.16$. Enter this on the calculator and convert to the antilog (number) of −3.16.

$$[H_3O^+] = \text{antilog}\ (-3.16) = 10^{-3.16} = 6.\underline{9}1 \times 10^{-4} = 6.9 \times 10^{-4}\ M$$

15.10. Find the pOH by subtracting the pOH from 14.00. Then enter −3.40 on the calculator to convert to the antilog (number) corresponding to −3.40.

$$pOH = 14.00 - 10.6 = 3.\underline{4}0$$

$$[H_3O^+] = \text{antilog}\ (-3.40) = 10^{-3.40} = \underline{3}.98 \times 10^{-4} = 4 \times 10^{-4}\ M$$

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ANSWERS TO CONCEPT CHECKS

15.1. In any aqueous solution, you should consider the autoionization of water. And because we have a solution of a weak acid in water, you should also consider the equilibrium between this acid and water. Here are the two equilibria:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$HCHO_2(aq) + H_2O(l) \rightleftharpoons CHO_2^-(aq) + H_3O^+(aq)$$

The species present in these equilibria are $H_2O(l)$, $H_3O^+(aq)$, $OH^-(aq)$, $HCHO_2(aq)$, and $CHO_2^-(aq)$.

15.2. The stronger acid gives up its proton more readily, and therefore, its conjugate base ion holds on to a proton less strongly. In other words, the stronger acid has the weaker conjugate base. Because formic acid is the stronger acid, the formate ion is the weaker base. Acetate ion is the stronger base.

15.3. Look at each solution, and determine whether it is acidic, basic, or neutral. In solution A, the numbers of H_3O^+ and OH^- ions are equal, so the solution is neutral. For solution B, the number of H_3O^+ ions is greater than the number of OH^- ions, so the solution is acidic. In solution C, the number of H_3O^+ ions is less than the number of OH^- ions, so the solution is basic. Therefore, the ranking from most acidic to least acidic (most basic) is B > A > C.

15.4. In order to answer this problem qualitatively, it is essential that all the solutions have the same solute concentrations. Bases produce solutions of pH greater than 7, whereas acids produce solutions of pH less than 7. NH_3 and NaOH are bases, and HCl and $HC_2H_3O_2$ are acids. NaOH is a stronger base than NH_3, so the NaOH solution would have the highest pH, followed by the NH_3 solution. $HC_2H_3O_2$ is a much weaker acid than HCl, so the $HC_2H_3O_2$ solution would have a higher pH than the HCl solution. Therefore, the ranking from highest to lowest pH for solutions with the same solute concentrations is NaOH > NH_3 > $HC_2H_3O_2$ > HCl.

ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

15.1. You can classify these acids using the information in Section 15.1. Also recall that all diatomic acids of Group VIIA halides are strong except for HF.

a. Weak

b. Weak

c. Strong

d. Strong

e. Weak

f. Weak

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15.2. In Section 15.1, we are told that all neutralizations involving strong acids and bases evolve 55.90 kJ of heat per mole of H_3O^+. Thus, the thermochemical evidence for the Arrhenius concept is based on the fact that when 1 mol of any strong acid (1 mol H_3O^+) is neutralized by 1 mole of any strong base (1 mol OH^-), the heat of neutralization is always the same ($\Delta H° = -55.90$ kJ/mol).

15.3. A Brønsted-Lowry acid is a molecule or ion that donates an H^+ ion (proton donor) to a base in a proton-transfer reaction. A Brønsted-Lowry base is a molecule or ion that accepts an H^+ ion (proton acceptor) from an acid in a proton-transfer reaction. An example of an acid-base equation:

$$\underset{\text{acid}}{HF(aq)} + \underset{\text{base}}{NH_3(aq)} \rightarrow \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{F^-(aq)}$$

15.4. The conjugate acid of a base is a species that differs from the base by only one H^+. Consider the base, HSO_3^-. Its conjugate acid would be H_2SO_3 but not H_2SO_4. H_2SO_4 differs from HSO_3^- by one H and one O.

15.5. You can write the equations by considering that $H_2PO_3^-$ is both a Brønsted-Lowry acid and a Brønsted-Lowry base. The $H_2PO_3^-$ acts as a Brønsted-Lowry acid when it reacts with a base such as OH^- :

$$H_2PO_3^-(aq) + OH^-(aq) \rightarrow HPO_3^{2-}(aq) + H_2O(l)$$

The $H_2PO_3^-$ acts as a Brønsted-Lowry base when it reacts with an acid such as HCl:

$$H_2PO_3^-(aq) + HCl(aq) \rightarrow H_3PO_3(aq) + Cl^-(aq)$$

15.6. The Brønsted-Lowry concept enlarges on the Arrhenius concept in the following ways: (1) It expands the concept of a base to include any species that accepts protons, not just the OH^- ion or compounds containing the OH^- ion. (2) It enlarges the concepts of acids and bases to include ions as well as molecules. (3) It enables us to write acid-base reactions in nonaqueous solutions as well as in aqueous solutions, whereas the Arrhenius concept applies only to aqueous solutions. (4) It allows some species to be considered as acids or bases, depending on the other reactant with which they are mixed.

15.7. According to the Lewis concept, an acid is an electron-pair acceptor and a base is an electron-pair donor. An example is

$$\underset{\text{acid}}{Ag^+(aq)} + \underset{\text{base}}{2(:NH_3)} \rightarrow Ag(NH_3)_2^+(aq)$$

15.8. Recall that the weaker the acid, the stronger it holds on to its proton(s). Thus, if a reaction mixture consists of a stronger acid and base and a weaker acid and base, the weaker-acid side will always be favored because the proton(s) will bond more strongly to the weaker acid.

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15.9. The two factors that determine the strength of an acid are (1) the polarity of the bond to which the H atom is attached, and (2) the strength of the bond, or how tightly the proton is held by the atom to which it is bonded. An increase in the polarity of the bond makes it easier to remove the proton, increasing the strength of the acid. An increase in the strength of the bond makes it more difficult to remove the proton, decreasing the strength of the acid. The strength of the bond depends in turn on the size of the atom, so larger atoms have weaker bonds, whereas smaller atoms have stronger bonds.

15.10. The self-ionization of water is the reaction of two water molecules in which a proton is transferred from one molecule to the other to form H_3O^+ and OH^- ions. At 25°C, the K_w expression is $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$.

15.11. The pH = −log $[H_3O^+]$ of an aqueous solution. Measure pH by using electrodes and a pH meter or by interpolating the pH from the color changes of a series of acid-base indicators.

15.12. A solution of pH 4 has a $[H_3O^+] = 1 \times 10^{-4}$ *M* and is more acidic than a solution of pH 5, which has a $[H_3O^+] = 1 \times 10^{-5}$ *M*.

15.13. For a neutral solution, $[H_3O^+] = [OH^-]$; thus, the $[H_3O^+]$ of a neutral solution at 37°C is the square root of K_w at 37°C:

$$[H_3O^+] = \sqrt{2.5 \times 10^{-14}} = 1.58 \times 10^{-7}\ M$$

$$\text{pH} = -\log (1.58 \times 10^{-7}) = 6.801 = 6.80$$

15.14. Because pH + pOH = pK_w at any temperature,

$$\text{pH} + \text{pOH} = -\log (2.5 \times 10^{-14}) = 13.60$$

15.15. The answer is a, F^-.

15.16. The answer is d, Fe^{3+}.

15.17. The answer is d, 3.8×10^{-13} *M*.

15.18. The answer is b, 3.5×10^{-5} *M*.

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■ ANSWERS TO CONCEPT EXPLORATIONS

15.19.

a. $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

b. The pH of the solution is around 3. Since the volume of the solution is 1.0 L, the molarity and the number of moles are numerically equal, 0.0010 *M*. The first nonzero digit is three places to the right of the decimal, and this is the approximate pH.

c. The H_3O^+ concentration and pH of the solution are

$$\frac{0.00100 \text{ mol HCl}}{1.0 \text{ L}} \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol HCl}} = 1.\underline{0}0 \times 10^{-3} \, M$$

$$\text{pH} = -\log(1.00 \times 10^{-3}) = 3.0\underline{0}0 = 3.00$$

d. Yes, there are OH^- ions present in every solution that uses water as a solvent. The concentration of OH^- can be determined using K_w. The OH^- comes from the autoionization of water.

e. If OH^- were added, the H_3O^+ ion concentration would decrease. Some of the added OH^- would react with the HCl present to form water, leaving less HCl remaining in the solution. Since the product $[H_3O^+][OH^-]$ is constant, as the OH^- ion concentration increases, the H_3O^+ ion concentration must decrease.

f. The pH of a sample removed from the original solution will have the same pH as the original solution. The pH does not depend on the volume of the solution being tested.

g. The two different volumes have the same concentration of HCl, and therefore the same pH. They contain different numbers of moles because they contain different volumes. Since moles = $M \times V$, different volumes of solution with the same concentration contain different moles of solute.

h. If 1.0 L of pure water were added to the solution, the volume would double, and the solution would decrease in molarity by a factor of one-half. Since the concentration of the solution is decreasing, the solution is less acidic and the pH is higher.

15.20.

a. The concentration of the two solutions is 0.10 *M*. The reactions are

$$HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$$

$$HB(aq) + H_2O(l) \rightarrow H_3O^+(aq) + B^-(aq)$$

b. You could measure the pH of each solution. The pH of the strong acid solution will be lower than the pH of the weak acid solution.

c. The strong acid will have a pH of 1.00. Since the HA solution has a pH of 3.7, it is the weaker of the two acids.

d. $[A^-] = [H_3O^+] = 10^{-\text{pH}} = 10^{-3.7} = 1.\underline{9}9 \times 10^{-4} = 2.0 \times 10^{-4} \, M$

e. If HB is a strong acid, then $[H_3O^+] = [B^-] = 0.10 \, M$.

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f. The greatest concentration should be for the H_3O^+. Since HB is an acid, $[H_3O^+] > [OH^-]$. Also, since HB is a strong acid, the concentration of HB should be zero. The H_3O^+ and B^- ions are formed from the acid in equal numbers, but since there is some H_3O^+ present in the water, it should have a slightly higher concentration than B^-.

g. Since HA is a weak acid, there should be more HA than either H_3O^+ or A^- ions. Also, since HA is an acid, $[H_3O^+] > [OH^-]$.

h. Adding 1.0 L of water to the HB solution would decrease the concentration of the acid by a factor of one-half, thereby raising the pH of the solution. As long as the concentration changes, the pH will also change. As the concentration of the acid goes down, the pH goes up.

i. A 200-mL sample of the solution will have the same pH as the original solution. The pH depends on the concentration, not on the volume of the sample tested.

■ ANSWERS TO CONCEPTUAL PROBLEMS

15.21. It is not necessary to have the species NH_4OH in order to have OH^- in the solution. When ammonia reacts with water, hydroxide ion forms in the reaction.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

15.22. A reaction where HPO_4^{2-} acts as an acid is

$$HPO_4^{2-}(aq) + OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + H_2O(l)$$

A reaction where HPO_4^{2-} acts as a base is

$$HPO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons H_2PO_4^-(aq) + H_2O(l)$$

15.23. The hydroxide ion acts as a base and donates a pair of electrons on the O atom, forming a bond with CO_2 to give HCO_3^-.

15.24. Nitrogen has a greater electronegativity than carbon. You would expect the H—O bond in the H—O—N group to be more polar (with the H atom having a positive partial charge) than the H—O bond in the H—O—C group. Thus, based on their structure, you would expect HNO_2 to be the stronger acid.

15.25. When you lower the temperature of pure water, the value of K_w decreases. In pure water, the hydronium-ion concentration equals the hydroxide-ion concentration, so $K_w = [H_3O^+]^2$. When K_w decreases, the hydronium-ion concentration decreases, and the corresponding pH increases.

15.26. Sodium hydroxide is a strong base, whereas ammonia is weak. As a strong base, NaOH exists in solution completely as ions, whereas NH_3 exists in solution as an equilibrium in which only part of the NH_3 has reacted to produce ions. Thus, a sodium hydroxide solution has a greater OH^- concentration than the same concentration solution of NH_3. At the same concentrations, the pH of the NaOH solution is greater (more basic) than that of the NH_3 solution.

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15.27. A strong monoprotic acid will dissolve completely in water to form hydronium ions (H_3O^+) and anions in equal number. None of the original monoprotic acid molecules will remain. This is represented by the picture in the middle. The picture on the left represents an undissociated acid. No ions are present in the solution. The picture on the right represents a weak acid where only some of the acid molecules have dissociated to form ions.

15.28. A weak acid will dissolve to form a solution that has some hydronium ions present, some anions present, and some undissociated acid molecules present. This is represented by beaker A. The solution in beaker B is a weak base, and the solution in beaker C is a strong acid.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

15.29. The reaction with labels of "acid" and "base" written below is as follows:

$$\underset{\text{base}}{OH^-(aq)} + \underset{\text{acid}}{HF(aq)} \rightleftharpoons \underset{\text{base}}{F^-(aq)} + \underset{\text{acid}}{H_2O(l)}$$

15.30. The reaction with labels of "acid" and "base" written below is as follows:

$$\underset{\text{acid}}{HOCl(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{OCl^-(aq)}$$

15.31.

a. PO_4^{3-}

b. HS^-

c. NO_2^-

d. $HAsO_4^{2-}$

15.32.

a. SeO_4^{2-}

b. PH_3

c. S^{2-}

d. OCl^-

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15.33.

a. $HClO$

b. AsH_4^+

c. H_3PO_4

d. $HTeO_3^-$

15.34.

a. H_2Se

b. NH_3

c. $HClO_2$

d. $N_2H_5^+$

15.35. Each equation is given below with the labels for acid and base:

a. $HSO_4^-(aq) + NH_3(aq) \rightleftharpoons SO_4^{2-}(aq) + NH_4^+(aq)$

acid base acid base

The conjugate acid-base pairs are HSO_4^-, SO_4^{2-}, and NH_4^+, NH_3.

b. $HPO_4^{2-}(aq) + NH_4^+(aq) \rightleftharpoons H_2PO_4^-(aq) + NH_3(aq)$

base acid base acid

The conjugate acid-base pairs are $H_2PO_4^-$, HPO_4^{2-}, and NH_4^+, NH_3.

c. $Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$

acid base acid base

The conjugate acid-base pairs are $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(OH)^{2+}$, and H_3O^+, H_2O.

d. $SO_3^{2-}(aq) + NH_4^+(aq) \rightleftharpoons HSO_3^-(aq) + NH_3(aq)$

base acid base acid

The conjugate acid-base pairs are HSO_3^-, SO_3^{2-}, and NH_4^+, NH_3.

15.36. Each equation is given below with the labels for acid and base:

a. $HPO_4^{2-}(aq) + HCO_3^-(aq) \rightleftharpoons PO_4^{3-}(aq) + H_2CO_3(aq)$

acid base base acid

The conjugate acid-base pairs are HPO_4^{2-}, PO_4^{3-}, and H_2CO_3, HCO_3^-.

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$$F^-(aq) + HSO_4^-(aq) \rightleftharpoons HF(aq) + SO_4^{2-}(aq)$$

b. base acid acid base

The conjugate acid-base pairs are HF, F^-, and HSO_4^-, SO_4^{2-}.

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

c. acid base base acid

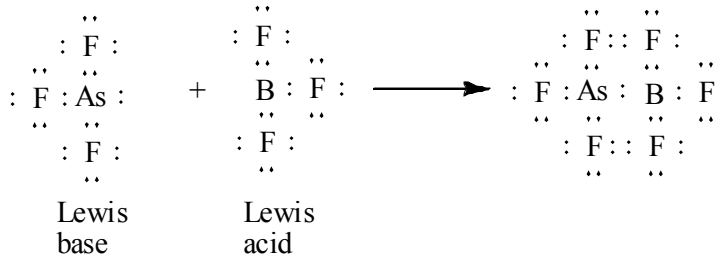
The conjugate acid-base pairs are HSO_4^-, SO_4^{2-}, and H_3O^+, H_2O.

$$HS^-(aq) + CN^-(aq) \rightleftharpoons S^{2-}(aq) + HCN(aq)$$

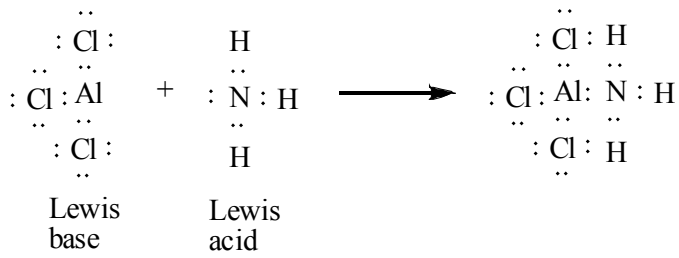
d. acid base base acid

The conjugate acid-base pairs are HS^-, S^{2-}, and HCN, CN^-.

15.37. The reaction is



15.38. The reaction is



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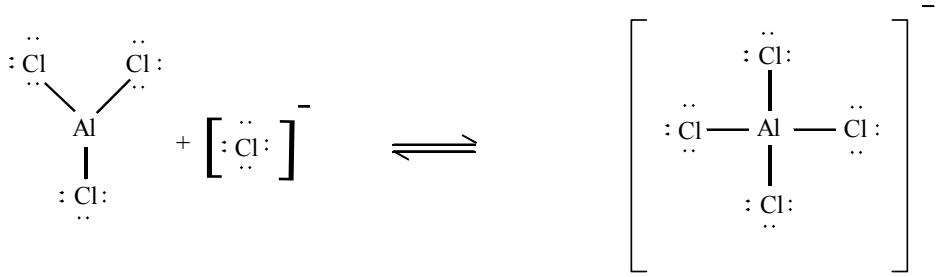
15.39.

a. The completed equation is

$$AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$$

The Lewis formula representation is

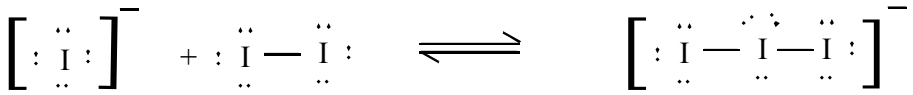


$AlCl_3$ is the electron-pair acceptor and is the acid. Cl^- is the electron-pair donor and is the base.

b. The completed equation is

$$I^- + I_2 \rightleftharpoons I_3^-$$

The Lewis formula representation is



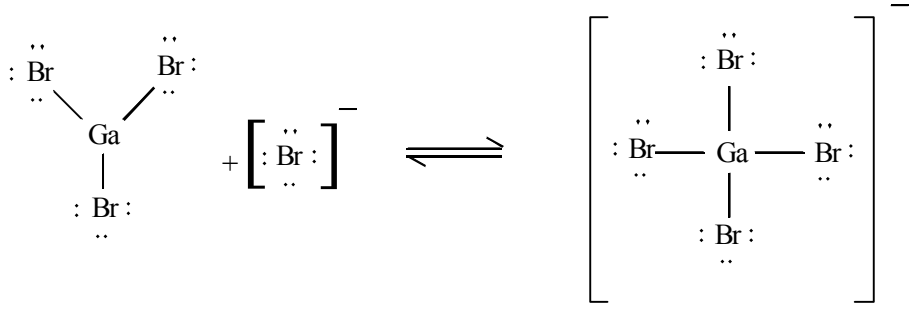
I_2 is the electron-pair acceptor and is the acid. The I^- ion is the electron-pair donor and is the base.

15.40.

a. The completed equation is

$$GaBr_3 + Br^- \rightleftharpoons GaBr_4^-$$

The Lewis formula representation is



$GaBr_3$ is the electron-pair acceptor and is the acid. The Br^- ion is the electron-pair donor and is the base.

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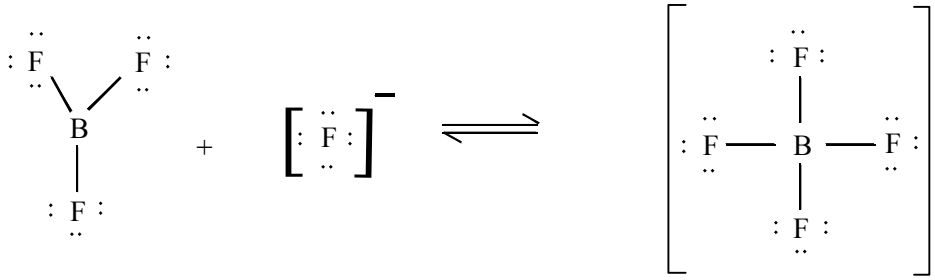
b. The completed equation is

$$BF_3 + F^- \rightleftharpoons BF_4^-$$

The Lewis formula representation is



BF_3 is the electron-pair acceptor and is the acid. The F^- ion is the electron-pair donor and is the base.

15.41.

a. Each water molecule donates a pair of electrons to copper(II), making the water molecule a Lewis base and the Cu^{2+} ion a Lewis acid.

b. The AsH_3 donates a pair of electrons to the boron atom in BBr_3, making AsH_3 a Lewis base and the BBr_3 molecule a Lewis acid.

15.42.

a. Each F^- ion donates a pair of electrons to Be in BeF_2, making F^- a Lewis base and BeF_2 a Lewis acid.

b. Each Cl^- ion donates a pair of electrons to $SnCl_4$, making Cl^- ion a Lewis base and $SnCl_4$ a Lewis acid.

15.43. The equation is $H_2S + HOCH_2CH_2NH_2 \rightarrow HOCH_2CH_2NH_3^+ + HS^-$. The H_2S is a Lewis acid, and $HOCH_2CH_2NH_2$ is a Lewis base. The hydrogen ion from H_2S accepts a pair of electrons from the N atom in $HOCH_2CH_2NH_2$.

15.44. The equation is $CaO + SO_2 \rightarrow CaSO_3$. The CaO is a Lewis base, and SO_2 is a Lewis acid. The oxide ion from CaO donates a pair of electrons to the sulfur of SO_2, forming the SO_3^{2-} ion in $CaSO_3$.

15.45. The reaction is $HSO_4^- + ClO^- \rightarrow HClO + SO_4^{2-}$. According to Table 15.2, HClO is a weaker acid than HSO_4^-. Because the equilibrium for this type of reaction favors formation of the weaker acid (or weaker base), the reaction occurs to a significant extent.

15.46. The reaction is $HCN + SO_4^{2-} \rightarrow CN^- + HSO_4^-$. According to Table 15.2, HCN is a weaker acid than HSO_4^-. Because the equilibrium for this type of reaction favors formation of the weaker acid (or weaker base), the reaction occurs in the opposite direction.

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15.47.

a. NH_4^+ is a weaker acid than H_3PO_4, so the left-hand species are favored at equilibrium.

b. HCN is a weaker acid than H_2S, so the left-hand species are favored at equilibrium.

c. H_2O is a weaker acid than HCO_3^-, so the right-hand species are favored at equilibrium.

d. H_2O is a weaker acid than $Al(H_2O)_6^{3+}$, so the right-hand species are favored at equilibrium.

15.48.

a. H_2CO_3 is a stronger acid than NH_4^+, so the left-hand species are favored at equilibrium.

b. H_2S is a weaker acid than H_2CO_3, so the left-hand species are favored at equilibrium.

c. H_2O is a weaker acid than HCN, so the left-hand species are favored at equilibrium.

d. HCN is a stronger acid than HCO_3^-, so the left-hand species are favored at equilibrium.

15.49. Trichloroacetic acid is the stronger acid because, in general, the equilibrium favors the formation of the weaker acid, which is formic acid in this case.

15.50. The BF_4^- ion is the weaker base because the equilibrium favors the formation of the weaker base.

15.51.

a. H_2S is stronger because acid strength decreases with increasing anion charge for polyprotic acid species.

b. H_2SO_3 is stronger because, for a series of oxoacids, acid strength increases with increasing electronegativity.

c. HBr is stronger because Br is more electronegative than Se. Within a period, acid strength increases as electronegativity increases.

d. HIO_4 is stronger because acid strength increases with the number of oxygen atoms bonded to the central atom.

e. H_2S is stronger because, within a group, acid strength increases with the increasing size of the central atom in binary acids.

15.52.

a. $HBrO_3 < HBrO_4$: Acid strength increases with the number of oxygen atoms bonded to the central atom.

b. $HCO_3^- < H_2CO_3$: Acid strength decreases with increasing anion charge for polyprotic acid species.

c. $H_2S < H_2Te$: Within a group, acid strength increases with increasing size of the central atom for binary acids.

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d. $H_2Se < HBr$: Within a period, acid strength increases with increasing electronegativity of the central atom for binary acids.

e. $H_3AsO_4 < H_3PO_4$: For a series of oxoacids, acid strength increases with increasing electronegativity.

15.53.

a. $[H_3O^+] = 1.2\ M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.2} = 8.\underline{3}3 \times 10^{-15} = 8.3 \times 10^{-15}\ M$$

b. $[OH^-] = 0.32\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.32} = 3.\underline{1}2 \times 10^{-14} = 3.1 \times 10^{-14}\ M$$

c. $[OH^-] = 2 \times (0.085\ M) = 0.170\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.170} = 5.\underline{8}8 \times 10^{-14} = 5.9 \times 10^{-14}\ M$$

d. $[H_3O^+] = 0.38\ M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.38} = 2.\underline{6}3 \times 10^{-14} = 2.6 \times 10^{-14}\ M$$

15.54.

a. $[OH^-] = 1.65\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{1.65} = 6.0\underline{6}0 \times 10^{-15} = 6.06 \times 10^{-15}\ M$$

b. $[OH^-] = 2 \times (0.35\ M) = 0.70\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.70} = 1.\underline{4}2 \times 10^{-14} = 1.4 \times 10^{-14}\ M$$

c. $[H_3O^+] = 0.045\ M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.045} = 2.\underline{2}2 \times 10^{-13} = 2.2 \times 10^{-13}\ M$$

d. $[H_3O^+] = 0.58\ M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{0.58} = 1.\underline{7}2 \times 10^{-14} = 1.7 \times 10^{-14}\ M$$

15.55. The $[H_3O^+] = 0.050\ M$ (HCl is a strong acid); using K_w, the $[OH^-] = 2.0 \times 10^{-13}\ M$.

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15.56. The $[H_3O^+]$ = 0.020 *M* (HNO_3 is a strong acid); using K_w, the $[OH^-]$ = 5.0×10^{-13} *M*.

15.57. Because the $Ba(OH)_2$ forms two OH^- per formula unit, the $[OH^-] = 2 \times 0.0085 = 0.017$ *M*.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.017} = 5.\underline{8}8 \times 10^{-13} = 5.9 \times 10^{-13}\ M$$

15.58. Because $Mg(OH)_2$ forms two OH^- per formula unit, the $[OH^-] = 2 \times 3.2 \times 10^{-4} = 6.4 \times 10^{-4}$ *M*.

$$[H_3O^+] = K_w \div [OH^-] = (1.0 \times 10^{-14}) \div (6.4 \times 10^{-4}) = 1.\underline{5}6 \times 10^{-11} = 1.6 \times 10^{-11}\ M$$

15.59

a. 5×10^{-6} *M* $H_3O^+ > 1.0 \times 10^{-7}$, so the solution is acidic.

b. Use K_w to determine $[H_3O^+]$.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{5 \times 10^{-9}} = \underline{2}.0 \times 10^{-6} = 2 \times 10^{-6}\ M$$

Since 2×10^{-6} *M* $> 1.0 \times 10^{-7}$, the solution is acidic.

c. When $[OH^-] = 1.0 \times 10^{-7}$ *M*, $[H_3O^+] = 1.0 \times 10^{-7}$ *M*, and the solution is neutral.

d. 2×10^{-9} *M* $H_3O^+ < 1.0 \times 10^{-7}$, so the solution is basic.

15.60.

a. Use K_w to determine $[H_3O^+]$.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{2 \times 10^{-11}} = \underline{5}.0 \times 10^{-4} = 5 \times 10^{-4}\ M$$

Since 5×10^{-4} *M* $> 1.0 \times 10^{-7}$, the solution is acidic.

b. 2×10^{-9} *M* $< 1.0 \times 10^{-7}$, so the solution is basic.

c. Use K_w to determine $[H_3O^+]$.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{6 \times 10^{-5}} = \underline{1}.6 \times 10^{-10} = 2 \times 10^{-10}\ M$$

Since 2×10^{-10} *M* $< 1.0 \times 10^{-7}$, the solution is basic.

d. 6×10^{-3} *M* $> 1.0 \times 10^{-7}$ *M*, so the solution is acidic.

15.61. The $[H_3O^+]$ calculated below is $> 1.0 \times 10^{-7}$ *M*, so the solution is acidic.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.\underline{6}6 \times 10^{-6} = 6.7 \times 10^{-6}\ M$$

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15.62. The $[H_3O^+]$ calculated below is $< 1.0 \times 10^{-7}$ *M*, so the solution is basic.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{8.4 \times 10^{-5}} = 1.\underline{1}9 \times 10^{-10} = 1.2 \times 10^{-10}\ M$$

15.63.

a. pH 4.6, acidic solution

b. pH 7.0, neutral solution

c. pH 1.6, acidic solution

d. pH 10.5, basic solution

15.64.

a. pH 5.6, acidic solution

b. pH 2.5, acidic solution

c. pH 13.2, basic solution

d. pH 8.3, basic solution

15.65.

a. Acidic (3.5 < 7.0)

b. Neutral (7.0 = 7.0)

c. Basic (9.0 > 7.0)

d. Acidic (5.5 < 7.0)

15.66.

a. Basic (12.0 > 7.0)

b. Neutral (7.0 = 7.0)

c. Acidic (4.0 < 7.0)

d. Acidic (5.7 < 7.0)

15.67. Record the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

a. $-\log (1.0 \times 10^{-8}) = 8.0\underline{0}0 = 8.00$

b. $-\log (5.0 \times 10^{-12}) = 11.3\underline{0}1 = 11.30$

c. $-\log (7.5 \times 10^{-3}) = 2.1\underline{2}4 = 2.12$

d. $-\log (6.35 \times 10^{-9}) = 8.19\underline{7}2 = 8.197$

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15.68. Record the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

a. $-\log (2.5 \times 10^{-4}) = 3.6\underline{0}2 = 3.60$

b. $-\log (5.7 \times 10^{-10}) = 9.2\underline{4}4 = 9.24$

c. $-\log (4.6 \times 10^{-5}) = 4.3\underline{3}7 = 4.34$

d. $-\log (2.91 \times 10^{-11}) = 10.53\underline{6}1 = 10.536$

15.69. Record the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

$-\log (7.5 \times 10^{-3}) = 2.1\underline{2}49 = 2.12$

15.70. Record the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

$-\log (5.0 \times 10^{-3}) = 2.3\underline{0}1 = 2.30$

15.71.

a. $pOH = -\log (5.25 \times 10^{-9}) = 8.27\underline{9}8$; $pH = 14.00 - 8.2798 = 5.7\underline{2}02 = 5.72$

b. $pOH = -\log (8.3 \times 10^{-3}) = 2.0\underline{8}09$; $pH = 14.00 - 2.0809 = 11.9\underline{1}908 = 11.92$

c. $pOH = -\log (3.6 \times 10^{-12}) = 11.44\underline{3}6$; $pH = 14.00 - 11.4436 = 2.5\underline{5}63 = 2.56$

d. $pOH = -\log (2.1 \times 10^{-8}) = 7.67\underline{7}7$; $pH = 14.00 - 7.6777 = 6.3\underline{2}2 = 6.32$

15.72.

a. $pOH = -\log (6.74 \times 10^{-11}) = 10.17\underline{1}3$; $pH = 14.00 - 10.1713 = 3.8\underline{2}8 = 3.83$

b. $pOH = -\log (5.8 \times 10^{-5}) = 4.2\underline{3}6$; $pH = 14.00 - 4.236 = 9.7\underline{6}3 = 9.76$

c. $pOH = -\log (3.4 \times 10^{-10}) = 9.4\underline{6}8$; $pH = 14.00 - 9.468 = 4.5\underline{3}1 = 4.53$

d. $pOH = -\log (7.1 \times 10^{-4}) = 3.1\underline{4}8$; $pH = 14.00 - 3.148 = 10.8\underline{5}1 = 10.85$

15.73. First, convert the $[OH^-]$ to $[H_3O^+]$ using the K_w equation. Then find the pH, recording the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

$[H_3O^+] = K_w \div [OH^-] = (1.0 \times 10^{-14}) \div (0.0040) = 2.\underline{5}0 \times 10^{-12}\ M$

$pH = -\log (2.50 \times 10^{-12}) = 11.6\underline{0}2 = 11.60$

15.74. First, convert the $[OH^-]$ to $[H_3O^+]$ using the K_w equation. Then find the pH, recording the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

$[H_3O^+] = K_w \div [OH^-] = (1.0 \times 10^{-14}) \div (0.050) = 2.\underline{0}0 \times 10^{-13}\ M$

$pH = -\log (2.00 \times 10^{-13}) = 12.6\underline{9}8 = 12.70$

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15.75. From the definition, pH = −log $[H_3O^+]$ and −pH = log $[H_3O^+]$, so enter the negative value of the pH on the calculator, and use the inverse and log keys (or 10^x) key to find the antilog of –pH.

$$\log [H_3O^+] = -pH = -5.12$$

$$[H_3O^+] = \text{antilog}(-5.12) = 10^{-5.12} = 7.\underline{5}8 \times 10^{-6} = 7.6 \times 10^{-6}\ M$$

15.76. From the definition, pH = −log $[H_3O^+]$ and −pH = log $[H_3O^+]$, so enter the negative value of the pH on the calculator, and use the inverse and log keys (or 10^x) key to find the antilog of –pH.

$$\log [H_3O^+] = -pH = -3.85$$

$$[H_3O^+] = \text{antilog}(-3.85) = 10^{-3.85} = 1.\underline{4}1 \times 10^{-4} = 1.4 \times 10^{-4}\ M$$

15.77. From the definition, pH = −log $[H_3O^+]$ and −pH = log $[H_3O^+]$, so enter the negative value of the pH on the calculator, and use the inverse and log keys (or 10^x) key to find the antilog of −pH. Then use the K_w equation to calculate $[OH^-]$ from $[H_3O^+]$.

$$\log [H_3O^+] = -pH = -11.63$$

$$[H_3O^+] = \text{antilog}(-11.63) = 10^{-11.63} = 2.\underline{3}4 \times 10^{-12}\ M$$

$$[OH^-] = K_w \div [H_3O^+] = (1.0 \times 10^{-14}) \div (2.34 \times 10^{-12}) = 4.\underline{2}7 \times 10^{-3} = 4.3 \times 10^{-3}\ M$$

15.78. From the definition, pH = −log $[H_3O^+]$ and −pH = log $[H_3O^+]$, so enter the negative value of the pH on the calculator, and use the inverse and log keys (or 10^x) key to find the antilog of −pH. Then use the K_w equation to calculate $[OH^-]$ from $[H_3O^+]$.

$$\log [H_3O^+] = -pH = -9.61$$

$$[H_3O^+] = \text{antilog}(-9.61) = 10^{-9.61} = 2.\underline{4}5 \times 10^{-10}\ M$$

$$[OH^-] = K_w \div [H_3O^+] = (1.0 \times 10^{-14}) \div (2.45 \times 10^{-10}) = 4.\underline{0}8 \times 10^{-5} = 4.1 \times 10^{-5}\ M$$

15.79. First, calculate the molarity of the OH^- ion from the mass of NaOH. Next, convert the $[OH^-]$ to $[H_3O^+]$ using the K_w equation. Then find the pH, recording the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

$$\frac{5.80\text{ g NaOH}}{1.00\text{ L}} \times \frac{1\text{ mol NaOH}}{40.01\text{ g NaOH}} = \frac{0.1450\text{ mol NaOH}}{1.00\text{ L}} = 0.14\underline{5}0\ M\ OH^-$$

$$[H_3O^+] = K_w \div [OH^-] = (1.0 \times 10^{-14}) \div (0.1450) = 6.\underline{8}96 \times 10^{-14}\ M$$

$$pH = -\log [H_3O^+] = -\log (6.896 \times 10^{-14}) = 13.1\underline{6}14 = 13.16$$

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15.80. First, calculate the molarity of the $Ba(OH)_2$ from the mass of $Ba(OH)_2$, and multiply the molarity of $Ba(OH)_2$ by 2 to obtain $[OH^-]$. Next, convert the $[OH^-]$ to $[H_3O^+]$ using the K_w equation. Then find the pH, recording the same number of places after the decimal point in the pH as the number of significant figures in the $[H_3O^+]$.

$$\frac{6.78 \text{ g } Ba(OH)_2}{1.00 \text{ L}} \times \frac{1 \text{ mol } Ba(OH)_2}{171.4 \text{ g } Ba(OH)_2} = \frac{0.039556 \text{ mol } Ba(OH)_2}{1.00 \text{ L}}$$

$[OH^-] = 2 \text{ mol } OH^-/1 \text{ mol } Ba(OH)_2 = 2 \times 0.039556 \, M \, Ba(OH)_2 = 0.07911 \, M$

$[H_3O^+] = K_w \div [OH^-] = (1.0 \times 10^{-14}) \div (0.07912) = 1.264 \times 10^{-13} \, M$

$pH = -\log [H_3O^+] = -\log (1.264 \times 10^{-13}) = 12.8982 = 12.90$

15.81. Figure 15.10 shows that the methyl-red indicator is yellow at pH values above about 5.5 (slightly past the midpoint of the range for methyl red). Bromthymol blue is yellow at pH values up to about 6.5 (slightly below the midpoint of the range for bromthymol blue). Therefore, the pH of the solution is between 5.5 and 6.5, and the solution is acidic.

15.82. Thymol blue is yellow at pH values above about 2.5. Bromphenol blue is yellow at pH values below about 3.5. Therefore, the pH of the aspirin solution must be in the range of 2.5 to 3.5. The solution is, of course, acidic.

■ SOLUTIONS TO GENERAL PROBLEMS

15.83.

a. BaO is a base; $BaO + H_2O \rightarrow Ba^{2+} + 2OH^-$

b. H_2S is an acid; $H_2S + H_2O \rightarrow H_3O^+ + HS^-$

c. CH_3NH_2 is a base; $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$

d. SO_2 is an acid; $SO_2 + 2H_2O \rightarrow H_3O^+ + HSO_3^-$

15.84.

a. P_4O_{10} is an acid; $P_4O_{10} + 10H_2O \rightarrow 4H_3O^+ + 4H_2PO_4^-$

b. K_2O is a base; $K_2O + H_2O \rightarrow 2K^+ + 2OH^-$

c. N_2H_4 is a base; $N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$

d. H_2Se is an acid; $H_2Se + H_2O \rightarrow H_3O^+ + HSe^-$

15.85.

a. $H_2O_2(aq) + S^{2-}(aq) \rightarrow HO_2^-(aq) + HS^-(aq)$

b. $HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$

c. $NH_4^+(aq) + CN^-(aq) \rightarrow NH_3(aq) + HCN(aq)$

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d. $H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$

15.86.

a. $H_2O(l) + HCl(aq) \rightarrow H_3O^+(aq) + Cl^-(aq)$

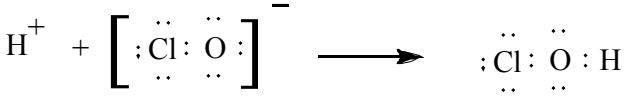
b. $HCO_3^-(aq) + HF(aq) \rightarrow H_2CO_3(aq) + F^-(aq)$

c. $NH_3(aq) + HBrO(aq) \rightarrow NH_4^+(aq) + BrO^-(aq)$

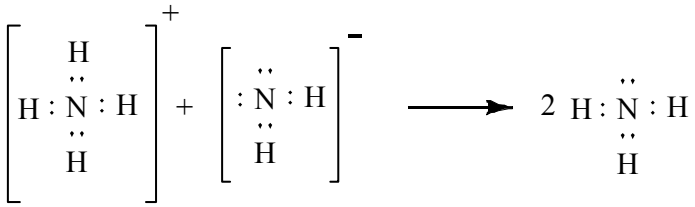
d. $H_2PO_4^-(aq) + H_2SO_3(aq) \rightarrow H_3PO_4(aq) + HSO_3^-(aq)$

15.87.

a. The ClO^- ion is a Brønsted base, and water is a Brønsted acid. The complete chemical equation is $ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$. The equilibrium does not favor the products because ClO^- is a weaker base than OH^-. In Lewis language, a proton from H_2O acts as a Lewis acid by accepting a pair of electrons on the oxygen of ClO^-.

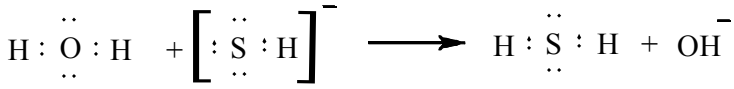


b. The NH_2^- ion is a Brønsted base, and NH_4^+ is a Brønsted acid. The complete chemical equation is $NH_4^+ + NH_2^- \rightleftharpoons 2NH_3$. The equilibrium favors the products because the reactants form the solvent, a weakly ionized molecule. In Lewis language, the proton from NH_4^+ acts as a Lewis acid by accepting a pair of electrons on the nitrogen of NH_2^-.

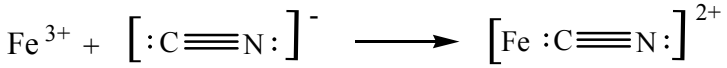


15.88.

a. The HS^- ion is a Brønsted base, and water is a Brønsted acid. The complete chemical equation is $HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$. The equilibrium does not favor the products because the HS^- ion is a weaker base than OH^-. In Lewis language, a proton from H_2O acts as a Lewis acid by accepting a pair of electrons on the sulfur of HS^-.



b. The complete chemical equation is $Fe^{3+}(aq) + CN^-(aq) \rightarrow Fe(CN)^{2+}$. The reaction cannot be described in Brønsted language because no proton transfer occurs. In Lewis language, Fe^{3+} acts as a Lewis acid by sharing a pair of electrons on the carbon of CN^-.



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15.89. Table 15.2 shows that HNO_2 is a stronger acid than HF. Because an acid-base reaction normally goes in the direction of the weaker acid, the reaction is more likely to go in the direction written

$$HNO_2 + F^- \rightleftharpoons HF + NO_2^-$$

15.90. The HS^- ion is acting as a base and will form its conjugate acid, H_2S. Table 15.2 shows that H_2S is a stronger acid than HCN. Because an acid-base reaction normally goes in the direction of the weaker acid, the reaction is more likely to go in the opposite direction:

$$HS^- + HCN \rightleftharpoons H_2S + CN^-$$

15.91. The order is $H_2S < H_2Se < HBr$. H_2Se is stronger than H_2S because, within a group, acid strength increases with increasing size of the central atom in binary acids. HBr is a strong acid, whereas the others are weak acids.

15.92. The order is $HBrO < HBrO_2 < HClO_2$. $HClO_2$ is stronger than $HBrO_2$ because, for oxoacids, acid strength increases with increasing electronegativity. $HBrO_2$ is stronger than HBrO because acid strength increases with increasing oxidation number of Br.

15.93. The KOH is a strong base and is fully ionized in solution, so you can use its formula and molar concentration to determine the $[OH^-]$ of the solution. Therefore, the 0.25 *M* KOH contains 0.25 *M* OH^-. The $[H_3O^+]$ is obtained from the K_w expression:

$$K_w = 1.0 \times 10^{-14} = [H_3O^+] \times 0.25\ M\ OH^-$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.25} = 4.\underline{0}0 \times 10^{-14} = 4.0 \times 10^{-14}\ M$$

15.94. The $Sr(OH)_2$ is a strong base and is fully ionized in solution, so you can use its formula and molar concentration to determine the $[OH^-]$ of the solution. Therefore, the 0.35 *M* $Sr(OH)_2$ contains $2 \times 0.35 = 0.70\ M\ OH^-$. The $[H_3O^+]$ is obtained from the K_w expression:

$$K_w = 1.0 \times 10^{-14} = [H_3O^+] \times 0.70\ M\ OH^-$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.70} = 1.42 \times 10^{-14} = 1.4 \times 10^{-14}\ M$$

15.95. Enter the H_3O^+ concentration of 1.5×10^{-3} into the calculator, press the log key, and press the sign key to change the negative log to a positive log. This follows the negative-log definition of pH. The number of decimal places of the pH should equal the significant figures in the H_3O^+.

$$pH = -\log [H_3O^+] = -\log (1.5 \times 10^{-3}) = 2.8\underline{2}3 = 2.82$$

15.96. Enter the H_3O^+ concentration of 2.5×10^{-2} into the calculator, press the log key, and press the sign key to change the negative log to a positive log. This follows the negative-log definition of pH. The number of decimal places of the pH should equal the significant figures in the H_3O^+.

$$pH = -\log [H_3O^+] = -\log (2.5 \times 10^{-2}) = 1.6\underline{0}2 = 1.60$$

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15.97. Find the pOH from the pH using pH + pOH = 14.00. Then calculate the $[OH^-]$ from the pOH by entering the pOH into the calculator, pressing the sign key to change the positive log to a negative log, and finding the antilog. On some calculators, the antilog is found by using the inverse of the log; on other calculators, the antilog is found using the 10^x key. The number of significant figures in the $[OH^-]$ should equal the number of decimal places in the pOH.

$$pOH = 14.00 - 3.15 = 10.85$$

$$[OH^-] = \text{antilog}(-10.85) = 10^{-10.85} = 1.\underline{4}12 \times 10^{-11} = 1.4 \times 10^{-11}\ M$$

15.98. Find the pOH from the pH using pH + pOH = 14.00. Then calculate the $[OH^-]$ from the pOH by entering the pOH into the calculator, pressing the sign key to change the positive log to a negative log, and finding the antilog. On some calculators, the antilog is found by using the inverse of the log; on other calculators, the antilog is found using the 10^x key. The number of significant figures in the $[OH^-]$ should equal the number of decimal places in the pOH.

$$pOH = 14.00 - 4.05 = 9.95$$

$$[OH^-] = \text{antilog}(-9.95) = 10^{-9.95} = 1.\underline{1}2 \times 10^{-10} = 1.1 \times 10^{-10}\ M$$

15.99.

a. $H_2SO_4(aq) + 2NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$ (molecular)

$H_3O^+(aq) + HCO_3^-(aq) \rightarrow CO_2(g) + 2H_2O(l)$ (net ionic)

b. The total moles of H_3O^+ from the H_2SO_4 is

$$\text{Moles of } H_3O^+ = \frac{0.437 \text{ mol } H_2SO_4}{1 \text{ L}} \times 0.02500 \text{ L} \times \frac{2 \text{ mol } H_3O^+}{1 \text{ mol } H_2SO_4}$$

$$= 0.021\underline{8}5 \text{ mol } H_3O^+$$

The moles of H_3O^+ that reacted with the NaOH is given by

$$\text{Moles of } H_3O^+ = \frac{0.108 \text{ mol NaOH}}{1 \text{ L}} \times 0.0354 \text{ L} = 0.003\underline{8}23 \text{ mol}$$

The moles of $NaHCO_3$ present in the original sample is equal to the moles of H_3O^+ that reacted with the HCO_3^-, which is given by

$$\text{Total moles } H_3O^+ - \text{moles } H_3O^+ \text{ reacted with the NaOH} = \text{moles } HCO_3^-$$

$$0.021\underline{8}5 \text{ mol} - 0.003823 \text{ mol} = 0.018\underline{0}3 = 0.0180 \text{ mol } NaHCO_3$$

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c. The mass of $NaHCO_3$ (molar mass 84.01 g/mol) present in the original sample is

$$0.01803 \text{ mol } NaHCO_3 \text{ x } \frac{84.01 \text{ g } NaHCO_3}{1 \text{ mol } NaHCO_3} = 1.5\underline{1}4 \text{ g}$$

Thus, the percent $NaHCO_3$ in the original sample is given by

$$\text{Percent } NaHCO_3 = \frac{1.514 \text{ g}}{2.500 \text{ g}} \text{ x } 100\% = 60.\underline{5}6 = 60.6\%$$

The percent KCl in the original sample is

$$\text{Percent KCl} = 100 - 60.56 = 39.\underline{4}4 = 39.4\%$$

15.100.

a. $CO_3^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 3\ H_2O\ (l) + CO_2(g)$

b. The total moles of H_3O^+ from the HCl is

$$\text{Moles of } H_3O^+ = \frac{0.798 \text{ mol HCl}}{1 \text{ L}} \text{ x } 0.02500 \text{ L} = 0.019\underline{9}5 \text{ mol}$$

The moles of H_3O^+ that reacted with the NaOH is given by

$$\text{Moles of } H_3O^+ = \frac{0.108 \text{ mol NaOH}}{1 \text{ L}} \text{ x } 0.0287 \text{ L} = 0.003\underline{1}00 \text{ mol}$$

The moles of Na_2CO_3 present in the original sample is equal to one-half that of the moles of H_3O^+ that reacted with the CO_3^{2-}, which is given by

$$\text{Moles } Na_2CO_3 = 1/2(\text{total moles } H_3O^+ - \text{moles } H_3O^+ \text{ reacted with the NaOH})$$
$$= 1/2(0.019\underline{9}5 \text{ mol} - 0.003100 \text{ mol}) = 0.008\underline{4}25 = 0.00843 \text{ mol}$$

c. The mass of Na_2CO_3 (molar mass 105.99 g/mol) present in the original sample is

$$0.008425 \text{ mol } Na_2CO_3 \text{ x } \frac{105.99 \text{ g } Na_2CO_3}{1 \text{ mol } Na_2CO_3} = 0.89\underline{2}9 \text{ g}$$

Thus, the percent Na_2CO_3 in the original sample is given by

$$\text{Percent } Na_2CO_3 = \frac{0.8929 \text{ g}}{2.500 \text{ g}} \text{ x } 100\% = 35.\underline{7}1 = 35.7\%$$

The percent NaCl in the original sample is

$$\text{Percent NaCl} = 100 - 35.71 = 64.\underline{2}8 = 64.3\%$$

15.101. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

$HCO_3^-(aq) + Na^+(aq) + OH^-(aq) \rightleftharpoons Na^+(aq) + CO_3^{2-}(aq) + H_2O(l)$

$HCO_3^-(aq) + H^+(aq) + Cl^-(aq) \rightleftharpoons H_2O(l) + CO_2(g) + Cl^-(aq)$

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15.102. $H_2PO_4^-$ is amphiprotic or amphoteric.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$$

$$H_2PO_4^-(aq) + K^+(aq) + OH^-(aq) \rightleftharpoons K^+(aq) + HPO_4^{2-}(aq) + H_2O(l)$$

$$H_2PO_4^-(aq) + H^+(aq) + NO_3^-(aq) \rightleftharpoons H_3PO_4(aq) + NO_3^-(aq)$$

15.103. $CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + 2H_2(g)$

The hydride ion is a stronger base because it took an H^+ from water, leaving the OH^- ion. Every time a strong base is added to water, it will react with the water, leaving the OH^- as the product, so a strong base cannot exist in water.

15.104. $Ca_3N_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s) + 2NH_3(g)$

$NaNH_2(s) + H_2O(l) \rightarrow NaOH(aq) + NH_3(g)$

N^{3-} is a stronger base than NH_2^- because it has more negative charge, so it will have a greater attraction for H^+. Also, we could consider that NH_2^- is a N^{3-} that has already reacted with two H^+'s. Stronger bases than OH^- will produce OH^- in aqueous solution.

15.105.

a. $2HF(l) \rightleftharpoons H_2F^+ + F^-$

b. NaF will be a base because F^- is a conjugate base of HF.

c. $HClO_4 + HF \rightarrow H_2F^+ + ClO_4^-$

The conjugate acid is H_2F^+.

15.106.

a. $2NH_3(l) \rightleftharpoons NH_4^+ + NH_2^-$

b. NH_2^- is the conjugate base of NH_3, so $NaNH_2$ will be a base.

c. $NaNH_2 + NH_4Cl \rightarrow 2NH_3 + NaCl$

15.107. The reaction of ammonia with water is given by

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The initial concentration of NH_3 (molar mass 17.03 g/mol) is

$$\text{Molarity} = \frac{4.25\ \text{g}\ NH_3\ \times\ \dfrac{1\ \text{mol}\ NH_3}{17.03\ \text{g}\ NH_3}}{0.2500\ \text{L}} = 0.9982\ M$$

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Since the NH_3 is 0.42% reacted, the concentration of OH^- is

$$[OH^-] = 0.9982\ M \times 0.0042 = 0.00419\ M$$

$$pOH = -\log [OH^-] = -\log (0.00419) = 2.378$$

$$pH = 14 - pOH = 14 - 2.378 = 11.622 = 11.62$$

15.108. The reaction of $C_2H_5NH_2$ with water is given by

$$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$$

The initial concentration of $C_2H_5NH_2$ (molar mass 45.09 g/mol) is given by

$$\text{Molarity} = \frac{0.675\ \text{g}\ C_2H_5NH_2 \times \dfrac{1\ \text{mol}\ C_2H_5NH_2}{45.09\ \text{g}\ C_2H_5NH_2}}{0.1000\ \text{L}} = 0.1497\ M$$

Since the $C_2H_5NH_2$ is 0.98 percent reacted, the concentration of OH^- is

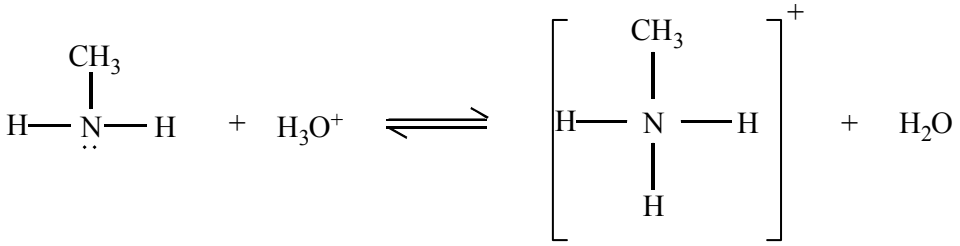
$$[OH^-] = 0.1497\ M \times 0.0098 = 0.00147\ M$$

$$pOH = -\log [OH^-] = -\log (0.00147) = 2.833$$

$$pH = 14 - pOH = 14 - 2.833 = 11.167 = 11.17$$

15.109. A bitter taste seems to be a common feature of a base. It is a fact that many medicinal substances are nitrogen bases, substances that organic chemists call amines, which are bases.

15.110. The nitrogen atom in an amine has a lone pair of electrons that can be donated to form a covalent bond, so an amine is a Lewis base. But like ammonia, an amine accepts a hydrogen ion from an acid to form an amine ion, so it is also a Brønsted-Lowry base.



15.111. Such solutions work by chemically reacting with fat and with hair, the usual ingredients of a stopped drain. When fat reacts with a strong base such as sodium hydroxide, it forms a salt of a fatty acid, a product otherwise known as soap. Hair is a protein material, and in the presence of a strong base, the protein breaks up into the salts of its constituent amino acid salts. That solution washes easily down the drain.

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15.112. Sodium hydroxide is produced commercially by sending a direct current through an aqueous solution of sodium chloride, a process referred to as electrolysis. Hydrogen gas is released at the negative pole, and chlorine gas is released at the positive pole. At the end of the electrolysis, the solution contains sodium hydroxide. The overall reaction is

$$2NaCl(aq) + 2H_2O(l) \xrightarrow{\text{electrolysis}} H_2(g) + Cl_2(g) + 2NaOH(aq)$$

■ SOLUTIONS TO STRATEGY PROBLEMS

15.113. Ethanol reacting as a Brønsted-Lowry acid with OH^- is

$$CH_3CH_2OH + OH^- \rightleftharpoons CH_3CH_2O^- + H_2O$$

Ethanol reacting as a Brønsted-Lowry base with H_3O^+ is

$$CH_3CH_2OH + H_3O^+ \rightleftharpoons CH_3CH_2OH_2^+ + H_2O$$

In both of these reactions, a proton is transferred from the acid to the base, which is in agreement with the Brønsted-Lowry definitions of an acid and a base. These reactions can also be considered Lewis acid-base reactions. In the first reaction, the oxygen atom of OH^- can act as an electron-pair donor, and the hydrogen of CH_3CH_2OH can act as an electron-pair acceptor. In the second reaction, the oxygen of CH_3CH_2OH acts as the electron-pair donor and the hydrogen of H_3O^+ as the electron-pair acceptor.

15.114. The self-ionization of ethanol is obtained by transferring a proton from one ethanol molecule to the other ethanol molecule.

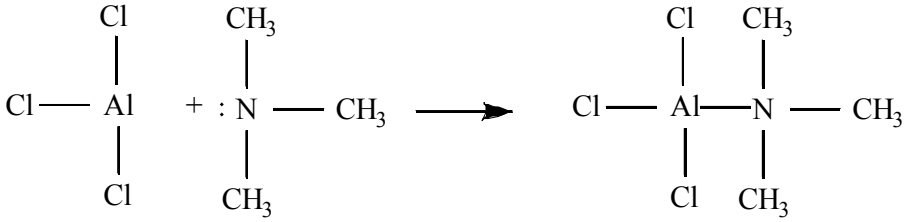
$$CH_3CH_2OH + CH_3CH_2OH \rightleftharpoons CH_3CH_2OH_2^+ + CH_3CH_2O^-$$

In pure ethanol, $[CH_3CH_2OH_2^+] = [CH_3CH_2O^-]$, so setting the concentration equal to x gives

$$K_{eth} = 1.0 \times 10^{-20} = [CH_3CH_2OH_2^+][CH_3CH_2O^-] = x^2$$

Solving for x gives 1.0×10^{-10} M for the concentration of each ion.

15.115. This is a Lewis acid-base reaction with $N(CH_3)_3$ the electron-pair donor (Lewis base) and $AlCl_3$ the electron-pair acceptor (Lewis acid). The product is $AlCl_3$–$N(CH_3)_3$.



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15.116.

a. Fe^{3+} is a stronger Lewis acid than Fe^{2+}. The higher the positive charge, the stronger the acid.

b. BF_3 is a stronger Lewis acid than BCl_3. Fluorine is more electronegative than chlorine. Thus, the bonds in BF_3 are more polar than the bonds in BCl_3. Acid strength increases with increasing bond polarity.

15.117.

a. $HBrO < HBrO_2 < HBrO_3$. For a series of oxoacids with the same central atom, acid strength increases with increasing number of oxygen atoms bonded to the central atom.

b. $H_2TeO_3 < H_2SeO_3 < H_2SO_3$. For a series of oxoacids having the same structure but different central atoms, acid strength increases with increasing electronegativity of the central atom. For elements in the same column on the periodic table, electronegativity decreases as you go down the column, so acid strength decreases as you go down the column.

c. $SbH_3 < H_2Te < HI$. For acids with the structure HX, acid strength increases with increasing electronegativity of atom X. Going across a row of elements on the periodic table, the electronegativity increases, the bond polarity increases, and the acid strength increases.

d. $H_2S < H_2Se < HBr$. For acids with the structure HX, acid strength increases with increasing electronegativity of atom X. In going down a column of the periodic table, the size of atom X increases, the bond strength decreases, and the acid strength increases. H_2S and H_2Se are in the same column, and Se has bigger atoms, so H_2Se is a stronger acid than H_2S. Also, going across a row of elements on the periodic table, the electronegativity increases, the bond polarity increases, and the acid strength increases. Se and Br are in the same row, and Br is more electronegative, so HBr is a stronger acid than H_2Se.

e. $HBrO_2 < HClO_2 < HClO_3$. For a series of oxoacids having the same structure but different central atoms, acid strength increases with increasing electronegativity of the central atom. For elements in the same column on the periodic table, electronegativity decreases as you go down the column, so acid strength decreases as you go down the column. Thus, $HClO_2$ is a stronger acid than $HBrO_2$. Also, for a series of oxoacids with the same central atom, acid strength increases with increasing number of oxygen atoms bonded to the central atom. Thus, $HClO_3$ is a stronger acid than $HClO_2$.

15.118. The acids in each column have the same central atom, so the strongest acid in each column is the one with the most oxygen atoms. The acids in each row have the same structure but different central atoms. Thus, the strongest acid is the one with the most electronegative central atom, which is Cl. Overall, the strongest acid is $HOClO_2$ ($HClO_3$) and the weakest acid is HOI.

15.119. First, determine the H_3O^+ concentration in the solution with pH 1.831.

$$[H_3O^+] = 10^{-pH} = 10^{-1.831} = 0.014\underline{7}57\ M$$

Now, use the dilution formula, $M_1V_1 = M_2V_2$, to solve for the final volume.

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(557\text{ mL})(0.0300\ M)}{(0.014757\ M)} = 11\underline{3}2.3\text{ mL} = 1.1\underline{3}2\text{ L} = 1.13\text{ L}$$

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15.120. Water dissociates into ions according to

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$$

$K_w = 1.00 \times 10^{-14}$, so the concentration of each ion is 1.00×10^{-7} *M*. The mass of water in dissociated form is

$$1.00 \text{ L} \times \frac{1.00 \times 10^{-7} \text{ mol}}{1 \text{ L}} \times \frac{18.01 \text{ g}}{1 \text{ mol } H_2O} = 1.801 \times 10^{-6} = 1.80 \times 10^{-6} \text{ g } H_2O$$

The number of H^+ ions in 1 L of pure water is

$$1.00 \text{ L} \times \frac{1.00 \times 10^{-7} \text{ mol}}{1 \text{ L}} \times \frac{6.02 \times 10^{23} \text{ } H^+ \text{ ions}}{1 \text{ mol}} = 6.02 \times 10^{16} \text{ } H^+ \text{ ions}$$

15.121. In a solution with pH 2.00, the H_3O^+ ion concentration is $1.00 \times 10^{-2} = 0.0100$ *M*. Since HCl is a strong acid, this would also be the concentration of HCl. The mass of HCl required is

$$3.00 \text{ L} \times \frac{0.0100 \text{ mol}}{1 \text{ L}} \times \frac{36.458 \text{ g}}{1 \text{ mol HCl}} = 1.0937 \text{ g HCl}$$

The solution is 37.2 mass percent HCl, so the mass of concentrated hydrochloric acid solution required is

$$\frac{1.097 \text{ g}}{0.372} = 2.940 = 2.94 \text{ g concentrated HCl}$$

15.122. In a solution of 1.00×10^{-7} *M* HCl, the amount of H^+ ions from HCl is comparable to the number obtained from water itself. This is like a common-ion problem, so set up a table and use K_w for the equilibrium.

Conc. (*M*)	$H_3O^+(aq)$	+	$OH^-(aq)$	$\rightleftharpoons$	$2H_2O(l)$
From HCl	1.00×10^{-7}		0		
From water	1.00×10^{-7}		1.00×10^{-7}		
Change	$-x$		$-x$		
Equilibrium	$2.00 \times 10^{-7} - x$		$1.00 \times 10^{-7} - x$		

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = (2.00 \times 10^{-7} - x)(1.00 \times 10^{-7} - x)$$

Rearrange this equation into standard quadratic form and use the quadratic equation to solve for *x*.

$$x^2 - 3.00 \times 10^{-7}x + 1.00 \times 10^{-14} = 0$$

$$x = \frac{-(-3.00 \times 10^{-7}) \pm \sqrt{(-3.00 \times 10^{-7})^2 - (4)(1)(1.00 \times 10^{-14})}}{2(1)}$$

$$= \frac{3.00 \times 10^{-7} \pm 2.236 \times 10^{-7}}{2}$$

The positive root is 2.618×10^{-7}, which is not allowed, so use the negative root, which is 0.382×10^{-7}. Therefore, the concentration of H_3O^+ and the pH are

$$[H_3O^+] = 2.00 \times 10^{-7} - 0.382 \times 10^{-7} = 1.618 \times 10^{-7} = 1.62 \times 10^{-7} \text{ } M$$

$$\text{pH} = -\log(1.618 \times 10^{-7}) = 6.791 = 6.79$$

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SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

15.123. For $(HO)_mYO_n$ acids, acid strength increases with n regardless of the number of OH's. The structure of H_3PO_4 is $(HO)_3PO$; because H_3PO_3 and H_3PO_4 have about the same acidity, H_3PO_3 must also have $n = 1$; thus, $m = 2$. This leaves one H, which must bond to phosphorus, giving a structure of $(HO)_2(O)PH$. Assuming that only two H's react with NaOH, the mass of NaOH that reacts with 1.00 g of H_3PO_3 (PA) is calculated as follows:

$$1.00 \text{ g PA} \times \frac{1 \text{ mol PA}}{81.994 \text{ g PA}} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol PA}} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}}$$

$$= 0.97\underline{5}6 = 0.976 \text{ g NaOH}$$

15.124. For $(HO)_mYO_n$ acids, acid strength increases with n regardless of the number of OH's. The structure of H_3PO_4 is $(HO)_3PO$; because H_3PO_2 and H_3PO_4 have the same acidity, H_3PO_2 must also have $n = 1$; thus, $m = 1$. This leaves two H's, which must bond to phosphorus, giving a structure of $(HO)(O)PH_2$. Assuming that only one H reacts with NaOH, the mass of NaOH that reacts with 1.00 g of H_3PO_2 (HA) is calculated as follows:

$$1.00 \text{ g HA} \times \frac{1 \text{ mol HA}}{65.994 \text{ g HA}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HA}} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}}$$

$$= 0.60\underline{6}1 = 0.606 \text{ g NaOH}$$

15.125. BF_3 acts as a Lewis acid, accepting an electron pair from NH_3:

$$BF_3 + :NH_3 \rightarrow F_3B{:}NH_3$$

The NH_3 acts as a Lewis base in donating an electron pair to BF_3. When 10.0 g of each are mixed, the BF_3 is the limiting reagent because it has the higher formula mass. The mass of $BF_3{:}NH_3$ formed is

$$10.0 \text{ g } BF_3 \times \frac{1 \text{ mol } BF_3}{67.81 \text{ g } BF_3} \times \frac{1 \text{ mol } BF_3{:}NH_3}{1 \text{ mol } BF_3} \times \frac{84.84 \text{ g } BF_3{:}NH_3}{1 \text{ mol } BF_3{:}NH_3}$$

$$= 12.\underline{5}1 = 12.5 \text{ g } BF_3{:}NH_3$$

15.126. BF_3 is the Lewis acid and accepts an electron pair from ether:

$$BF_3 + :OR_2 \rightarrow F_3B{:}OR_2$$

The ether ($:OR_2$) acts as a Lewis base in donating an electron pair to BF_3. When 10.0 g of BF_3 and 20.0 g of ether are mixed, the BF_3 is the limiting reagent because the formula masses are nearly equal. The mass of $BF_3{:}OR_2$ formed is

$$10.0 \text{ g } BF_3 \times \frac{1 \text{ mol } BF_3}{67.81 \text{ g } BF_3} \times \frac{1 \text{ mol } BF_3{:}OR_2}{1 \text{ mol } BF_3} \times \frac{141.93 \text{ g } BF_3{:}OR_2}{1 \text{ mol } BF_3{:}OR_2}$$

$$= 20.\underline{9}3 = 20.9 \text{ g } BF_3{:}OR_2$$

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CHAPTER 16

Acid-Base Equilibria

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

16.1. Abbreviate the formula of lactic acid as HL. To solve, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$HL + H_2O \rightleftharpoons$	$H_3O^+ +$	L^-
Starting	0.025	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.025 - x$	x	x

Substituting into the equilibrium-constant equation gives

$$K_a = \frac{[H_3O^+]\,[L^-]}{[HL]} = \frac{(x)^2}{(0.025 - x)}$$

The value of x equals the value of the molarity of the H_3O^+ ion, which can be obtained from the pH:

$$[H_3O^+] = \text{antilog}\,(-\text{pH}) = \text{antilog}\,(-2.75) = 0.00\underline{1}78\ M$$

Substitute this value for x into the equation to get

$$K_a = \frac{(x)^2}{(0.025 - x)} = \frac{(0.00178)^2}{(0.025 - 0.00178)} = 1.\underline{3}6 \times 10^{-4} = 1.4 \times 10^{-4}$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{0.00178}{0.025} = 0.071$$

16.2. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HAc as the symbol for acetic acid.

Conc. (M)	$HAc + H_2O \rightleftharpoons$	$H_3O^+ +$	Ac^-
Starting	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

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Now, substitute these concentrations and the value of K_a into the equilibrium-constant equation for acid ionization:

$$K_a = \frac{[H_3O^+]\,[Ac^-]}{[HAc]} = \frac{(x)^2}{(0.10 - x)} = 1.7 \times 10^{-5}$$

Solve the equation for x, assuming x is much smaller than 0.10, so $(0.10 - x) \cong 0.10$.

$$\frac{(x)^2}{(0.10)} \cong 1.7 \times 10^{-5}$$

$$x^2 = 1.7 \times 10^{-5} \times 0.10 = 1.7 \times 10^{-6}$$

$$x = 0.00130\ M$$

Check to make sure the assumption that $(0.10 - x) \cong 0.10$ is valid:

$0.10 - 0.00130 = 0.0987, = 0.10$ (to two significant figures)

The concentrations of hydronium ion and acetate ion are

$$[H_3O^+] = [Ac^-] = x = 0.0013 = 1.3 \times 10^{-3}\ M$$

The pH of the solution is

$$\text{pH} = -\log [H_3O^+] = -\log (0.00130) = 2.884 = 2.88$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{0.00130}{0.10} = 0.0130 = 0.013$$

16.3. Abbreviate the formula for pyruvic acid as HPy. To solve, assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	$HPy + H_2O$ ⇌	$H_3O^+ +$	Py^-
Starting	0.0030	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0030 - x$	x	x

Substitute the equilibrium concentrations and the value of K_a into the equilibrium-constant expression to get

$$K_a = \frac{[H_3O^+]\,[Py^-]}{[HPy]} = \frac{(x)^2}{(0.0030 - x)} = 1.4 \times 10^{-4}$$

Note that the concentration of acid divided by K_a is $0.0030/1.4 \times 10^{-4} = 21$, which is considerably smaller than 100. Thus, you can expect that x cannot be ignored compared with 0.0030. The quadratic formula must be used. Rearrange the preceding equation to put it into the form $ax^2 + bx + c = 0$.

$$x^2 + 1.4 \times 10^{-4}\,x - 4.20 \times 10^{-7} = 0$$

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Substitute into the quadratic formula to get

$$x = \frac{-1.4 \times 10^{-4} \pm \sqrt{(1.4 \times 10^{-4})^2 + 4(4.20 \times 10^{-7})}}{2} = \frac{-1.4 \times 10^{-4} \pm 1.303 \times 10^{-3}}{2}$$

Using the positive root, $x = [H_3O^+] = 5.81 \times 10^{-4}\ M$. Now you can calculate the pH.

$$pH = -\log [H_3O^+] = -\log (5.81 \times 10^{-4}) = 3.2350 = 3.24$$

16.4. To solve, note that $K_{a_1} = 1.3 \times 10^{-2} > K_{a_2} = 6.3 \times 10^{-8}$, and hence the second ionization and K_{a_2} can be ignored. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$H_2SO_3 + H_2O$ ⇌	$H_3O^+ +$	HSO_3^-
Starting	0.25	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.25 - x$	x	x

Substitute into the equilibrium-constant expression for the first ionization.

$$K_{a_1} = \frac{[H_3O^+]\,[HSO_3^-]}{[H_2SO_3]} = \frac{(x)^2}{(0.25 - x)} = 1.3 \times 10^{-2} = 0.013$$

This gives $x^2 + 0.013x - 0.00325 = 0$.

Note that the concentration of acid divided by K_a is 0.25/0.013 = 19, which is considerably smaller than 100. Thus, you can expect that x cannot be ignored compared with 0.25. Reorganize the above equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x = \frac{-0.013 \pm \sqrt{(0.013)^2 + 4(0.00325)}}{2} = \frac{-0.013 \pm 0.1147}{2}$$

Using the positive root, $x = [H_3O^+] = 0.05087\ M$.

$$pH = -\log (0.05087) = 1.293$$

To calculate $[SO_3^{2-}]$, which will be represented by y, use the second ionization. Assume the starting concentrations of H_3O^+ and HSO_3^- are those from the first equilibrium.

Conc. (*M*)	$HSO_3^- + H_2O$ ⇌	$H_3O^+ +$	SO_3^{2-}
Starting	0.0508	0.0508	0
Change	$-y$	$+y$	$+y$
Equilibrium	$0.0508 - y$	$0.0508 - y$	y

Now, substitute into the K_{a_2} expression for the second ionization.

$$K_{a_2} = \frac{[H_3O^+]\,[SO_3^{2-}]}{[HSO_3^-]} = \frac{(0.0508 + y)(y)}{(0.0508 - y)} = 6.3 \times 10^{-8}$$

Assuming y is much smaller than 0.0508, note that the $(0.0508 + y)$ cancels the $(0.0508 - y)$ term, leaving $y \cong K_{a_2}$, or

$$y = [SO_3^{2-}] \cong 6.3 \times 10^{-8}\ M$$

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16.5. Convert the pH first to pOH and then to $[OH^-]$:

$$pOH = 14.00 - pH = 14.00 - 9.84 = 4.16$$

$$[OH^-] = \text{antilog}(-4.16) = 6.\underline{9}2 \times 10^{-5}\ M$$

Using the symbol Qu for quinine, assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$Qu + H_2O$	$\rightleftharpoons$	HQu^+	+	OH^-
Starting	0.0015		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.0015 - x$		x		x

Note that $x = 6.\underline{9}2 \times 10^{-5}$. Substitute into the equilibrium-constant expression to get

$$K_b = \frac{[HQ^+]\,[OH^-]}{[Qu]} = \frac{(x)^2}{(0.0015 - x)} = \frac{(6.92 \times 10^{-5})^2}{(0.0015 - 6.92 \times 10^{-5})} = 3.\underline{3}46 \times 10^{-6}$$

$$= 3.3 \times 10^{-6}$$

16.6. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (*M*)	$NH_3 + H_2O$	$\rightleftharpoons$	NH_4^+	+	OH^-
Starting	0.20		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.20 - x$		x		x

Assume x is small enough to ignore compared with 0.20. Substitute into the equilibrium-constant expression to get

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = \frac{(x)^2}{(0.20 - x)} \cong \frac{(x)^2}{(0.20)} = 1.8 \times 10^{-5}$$

Solving for x gives

$$x^2 = (0.20) \times 1.8 \times 10^{-5} = 3.6 \times 10^{-6}$$

$$x = [OH^-] \cong 1.\underline{8}9 \times 10^{-3}\ M \text{ (Note that } x \text{ is negligible compared to 0.20.)}$$

Now calculate the hydronium-ion concentration.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.89 \times 10^{-3}} = 5.\underline{2}9 \times 10^{-12} = 5.3 \times 10^{-12}\ M$$

16.7.

a. Acidic. NH_4NO_3 is the salt of a weak base (NH_4OH) and a strong acid (HNO_3), so a solution of NH_4NO_3 is acidic because of the hydrolysis of NH_4^+.

b. Neutral. KNO_3 is the salt of a strong base (KOH) and a strong acid (HNO_3), so a solution of NH_4NO_3 is neutral because none of the ions hydrolyze.

c. Acidic. $Al(NO_3)_3$ is the salt of a weak base [$Al(OH)_3$] and a strong acid (HNO_3), so a solution of $Al(NO_3)_3$ is acidic because of the hydrolysis of Al^{3+}.

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16.8.

a. Calculate K_b of the F^- ion from the K_a of its conjugate acid, HF:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.\underline{4}7 \times 10^{-11} = 1.5 \times 10^{-11}$$

b. Calculate K_a of $C_6H_5NH_3^+$ from the K_b of its conjugate base, $C_6H_5NH_2$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.\underline{3}8 \times 10^{-5} = 2.4 \times 10^{-5}$$

16.9. Assemble the usual table, writing HBen for benzoic acid and Ben^- for the benzoate ion. Let $0.015 - x$ equal the equilibrium concentration of the benzoate anion.

Conc. (M)	$Ben^- + H_2O$ ⇌	HBen +	OH^-
Starting	0.015	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0015 - x$	x	x

Calculate K_b for the benzoate ion from K_a for HBen

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.\underline{5}8 \times 10^{-10}$$

Substitute into the equilibrium-constant expression. Assume x is much smaller than 0.015.

$$K_b = \frac{[HBen]\,[OH^-]}{[Ben^-]} = \frac{(x)^2}{(0.015 - x)} \cong \frac{(x)^2}{(0.015)} = 1.\underline{5}8 \times 10^{-10}$$

$x = [HBen] = [OH^-] \cong 1.\underline{5}39 \times 10^{-6}\ M$ (x is negligible compared to 0.015.)

Thus, the concentration of benzoic acid in the solution is $1.5 \times 10^{-6}\ M$. The pH is

$$pOH = -\log [OH^-] = -\log (1.539 \times 10^{-6}) = 5.8\underline{1}2$$

$$pH = 14.00 - 5.812 = 8.1\underline{8}8 = 8.19$$

16.10. Assemble the usual table, using starting $[H_3O^+] = 0.20\ M$ from $0.20\ M$ HCl and letting HFo symbolize $HCHO_2$.

Conc. (M)	$HFo + H_2O$ ⇌	H_3O^+ +	Fo^-
Starting	0.010	0.20	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	$0.20 + x$	x

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Assume x is negligible compared to 0.10 M and 0.20 M, and substitute into the equilibrium-constant expression to get

$$K_a = \frac{[H_3O^+][Fo^-]}{[HFo]} = \frac{(0.20 + x)(x)}{(0.10 - x)} \cong \frac{(0.20)(x)}{(0.10)} = 1.7 \times 10^{-4}$$

$$x = [Fo^-] = 8.\underline{5}0 \times 10^{-5} = 8.5 \times 10^{-5}\ M$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{8.50 \times 10^{-5}}{0.10} = 8.\underline{5}0 \times 10^{-4} = 8.5 \times 10^{-4}$$

16.11. Assemble the usual table, using a starting $[CHO_2^-]$ of 0.018 M from 0.018 M $NaCHO_2$ and symbolizing $HCHO_2$ as HFo and the CHO_2^- anion as Fo^-.

Conc. (M)	HFo + H_2O ⇌	H_3O^+ +	Fo^-
Starting	0.025	0	0.018
Change	$-x$	$+x$	$+x$
Equilibrium	$0.025 - x$	x	$0.018 + x$

Substitute into the equilibrium-constant expression. Assume x is negligible compared to 0.025 M and 0.018 M.

$$K_a = \frac{[H_3O^+][Fo^-]}{[HFo]} = \frac{(0.018 + x)(x)}{(0.025 - x)} \cong \frac{(0.018)(x)}{(0.025)} = 1.7 \times 10^{-4}$$

$$x = [H_3O^+] \cong 2.\underline{3}6 \times 10^{-4}\ M$$

The pH can now be calculated.

$$pH = -\log [H_3O^+] = -\log (2.36 \times 10^{-4}) = 3.6\underline{2}7 = 3.63$$

16.12. Let HOAc represent $HC_2H_3O_2$ and OAc^- represent $C_2H_3O_2^-$. The total volume of the buffer is

$$\text{Total volume} = 30.0\ mL + 70.0\ mL = 100.0\ mL = 0.1000\ L$$

The moles of HOAc and OAc^- in the buffer are

$$\text{mol HOAc} = 0.15\ M \times 0.0300\ L = 0.00450\ \text{mol}$$

$$\text{mol } OAc^- = 0.20\ M \times 0.0700\ L = 0.0140\ \text{mol}$$

The concentrations of HOAc and OAc^- in the buffer are

$$[HOAc] = \frac{0.00450\ \text{mol}}{0.1000\ L} = 0.04\underline{5}0\ M$$

$$[OAc^-] = \frac{0.0140\ \text{mol}}{0.1000\ L} = 0.1\underline{4}0\ M$$

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Now, assemble these starting concentrations into a table.

Conc. (M)	$HOAc + H_2O$	$\rightleftharpoons$	$H_3O^+ +$	OAc^-
Starting	0.0450		0	0.140
Change	−x		+x	+x
Equilibrium	0.0450 − x		x	0.140 + x

Substitute the equilibrium concentrations into the equilibrium-constant expression; then assume x is negligible compared to the starting concentrations of both HOAc and OAc^-.

$$K_a = \frac{[H_3O^+]\,[OAc^-]}{[HOAc]} = \frac{(0.140 + x)(x)}{(0.0450 - x)} \cong \frac{(0.140)(x)}{(0.0450)} = 1.7 \times 10^{-5}$$

$$x = [H_3O^+] \cong 5.\underline{4}6 \times 10^{-6}\ M$$

You can now calculate the pH.

$$pH = -\log [H_3O^+] = -\log (5.46 \times 10^{-6}) = 5.2\underline{6}2 = 5.26$$

16.13. First, do the stoichiometric calculation. From Exercise 16.11, [HFo] = 0.025 *M* and $[Fo^-]$ = 0.018 *M*. In 1 L of buffer, there are 0.025 mol HFo and 0.018 mol Fo^-. The moles of OH^- (equal to moles of NaOH) added are

$$(0.10\ M) \times 0.0500\ L = 0.00500\ \text{mol}\ OH^-$$

The total volume of solution is

$$\text{Total volume} = 1\ L + 0.0500\ L = 1.0500\ L$$

After reaction with the OH^-, the moles of HFo and Fo^- remaining in the solution are

$$\text{mol HFo} = (0.025 - 0.00500)\ \text{mol} = 0.0200\ \text{mol}$$

$$\text{mol}\ Fo^- = (0.018 + 0.00500)\ \text{mol} = 0.0230\ \text{mol}$$

The concentrations are

$$[HFo] = \frac{0.0200\ \text{mol}}{1.0500\ L} = 0.01\underline{9}0\ M$$

$$[Fo^-] = \frac{0.0230\ \text{mol}}{1.0500\ L} = 0.02\underline{1}9\ M$$

Now account for the ionization of HFo to Fo^- at equilibrium by assembling the usual table.

Conc. (M)	$HFo + H_2O$	$\rightleftharpoons$	$H_3O^+ +$	OAc^-
Starting	0.0190		0	0.0219
Change	$-x$		$+x$	$+x$
Equilibrium	$0.0190 - x$		x	$0.0219 + x$

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Assume x is negligible compared to 0.0190 M and 0.0219 M, and substitute into the equilibrium-constant expression to get

$$K_a = \frac{[H_3O^+]\,[Fo^-]}{[HFo]} = \frac{(0.0219 + x)(x)}{(0.0190 - x)} \cong \frac{(0.0219)(x)}{(0.0190)} = 1.7 \times 10^{-4}$$

$$x = [H_3O^+] = 1.\underline{4}7 \times 10^{-4}\ M$$

Now, calculate the pH.

$$pH = -\log [H_3O^+] = -\log (1.\underline{4}7 \times 10^{-4}) = 3.8\underline{3}1 = 3.83$$

16.14. All the OH^- reacts with the H_3O^+ from HCl. Calculate the stoichiometric amounts of OH^- and H_3O^+.

$$\text{mol } H_3O^+ = (0.10 \text{ mol/L}) \times 0.025 \text{ L} = 0.0025 \text{ mol}$$

$$\text{mol } OH^- = (0.10 \text{ mol NaOH/L}) \times 0.015 \text{ L} = 0.0015 \text{ mol}$$

The total volume of solution is

$$\text{Total volume} = 0.025 \text{ L} + 0.015 \text{ L} = 0.040 \text{ L}$$

Subtract the moles of OH^- from the moles of H_3O^+, and divide by the total volume to get the concentration of H_3O^+.

$$\text{mol } H_3O^+ \text{ left} = (0.0025 - 0.0015) \text{ mol} = 0.0010 \text{ mol}$$

$$[H_3O^+] = \frac{0.0010 \text{ mol}}{0.040 \text{ L}} = 0.02\underline{5}0\ M$$

Now calculate the pH.

$$pH = -\log [H_3O^+] = -\log (0.0250) = 1.6\underline{0}2 = 1.60$$

16.15. At the equivalence point, the solution will contain NaF. The molar amount of F^- is equal to the molar amount of HF and is calculated as follows:

$$(0.10 \text{ mol HF/L}) \times 0.025 \text{ L} = 0.0025 \text{ mol } F^-$$

The volume of 0.15 M NaOH added and the total volume of solution are calculated next.

$$\text{Volume NaOH} = \frac{M_{acid} V_{acid}}{M_{base}} = \frac{(0.10\ M)(25 \text{ mL})}{0.15\ M} = 1\underline{6}.6 \text{ mL}$$

$$\text{Total volume} = 25 \text{ mL} + 16.6 \text{ mL} = 4\underline{1}.6 \text{ mL} = 0.041\underline{6} \text{ L}$$

The concentration of F^- at the equivalence point can now be calculated.

$$[F^-] = \frac{0.0025 \text{ mol}}{0.0416 \text{ L}} = 0.06\underline{0}0\ M$$

Next, consider the hydrolysis of F^-. Start by calculating the hydrolysis constant of F^- from the K_a of its conjugate acid, HF.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.\underline{4}7 \times 10^{-11}$$

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Now, assemble the usual table of concentrations, assume x is negligible compared to 0.0600, and calculate $[OH^-]$.

Conc. (M)	$F + H_2O$	$\rightleftharpoons$	HF	+	OH^-
Starting	0.0600		0		0.0219
Change	$-x$		$+x$		$+x$
Equilibrium	$0.0600 - x$		x		x

Substitute into the equilibrium-constant expression to get

$$K_b = \frac{[HF]\,[OH^-]}{[F^-]} = \frac{(x)^2}{(0.0600 - x)} \cong \frac{(x)^2}{(0.0600)} = 1.\underline{4}7 \times 10^{-11}$$

$$x = [OH^-] = 9.\underline{3}9 \times 10^{-7}\ M$$

Finally, calculate the pOH and then the pH.

$$pOH = -\log [OH^-] = -\log (9.\underline{3}9 \times 10^{-7}) = 6.0\underline{2}6$$

$$pH = 14.00 - 6.0\underline{2}6 = 7.9\underline{7}4 = 7.97$$

16.16.

a. Assemble the usual table of concentrations.

Conc. (M)	$NH_3 + H_2O$	$\rightleftharpoons$	NH_4^+	+	OH^-
Starting	0.200		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.200 - x$		x		x

Now substitute into the equilibrium-constant expression, assume x is negligible compared to 0.200 M, and calculate $[OH^-]$.

$$K_b = \frac{(x)^2}{(0.200 - x)} = \frac{(x)^2}{(0.200)} = 1.8 \times 10^{-5}$$

$$x = [OH^-] = 1.8\underline{9}7 \times 10^{-3}\ M$$

Finally, calculate the pOH and then the pH.

$$pOH = -\log [OH^-] = -\log (1.8\underline{9}7 \times 10^{-3}) = 2.7\underline{2}1$$

$$pH = 14.00 - 2.721 = 11.2\underline{7}8 = 11.28$$

b. At the half-way point in the titration of a weak base with a strong acid, $pOH = pK_b$.

$$pOH = -\log (1.8 \times 10^{-5}) = 4.7\underline{4}4$$

$$pH = 14.00 - pOH = 14.00 - 4.744 = 9.2\underline{5}5 = 9.26$$

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c. At the equivalence point, the solution will contain NH_4Cl. The molar amount of NH_4^+ is equal to the molar amount of NH_3 and is calculated as follows:

$$(0.200\ M)\ \text{x}\ 0.0800\ \text{L} = 0.016\underline{0}0\ \text{mol}\ NH_4^+$$

The volume of 0.100 *M* HCl added and the total volume of solution are calculated next.

$$\text{Volume HCl} = \frac{M_{\text{base}}V_{\text{base}}}{M_{\text{acid}}} = \frac{(0.200\ M)(80.0\ \text{mL})}{0.100\ M} = 16\underline{0}.0\ \text{mL}$$

$$\text{Total volume} = 80.0\ \text{mL} + 160.0\ \text{mL} = 24\underline{0}.0\ \text{mL} = 0.24\underline{0}0\ \text{L}$$

The concentration of NH_4^+ at the equivalence point can now be calculated.

$$[NH_4^+] = \frac{0.01600\ \text{mol}}{0.2400\ \text{L}} = 0.0666\underline{6}\ M$$

Next, consider the hydrolysis of NH_4^+. Start by calculating the hydrolysis constant of NH_4^+ from the K_b of its conjugate base, NH_3.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}6 \times 10^{-10}$$

Now, assemble the usual table of concentrations, assume x is negligible compared to 0.06666, and calculate $[H_3O^+]$.

Conc. (M)	$NH_4^+ + H_2O$	$\rightleftharpoons$	$NH_3 + H_3O^+$
Starting	0.06666		0 + 0
Change	$-x$		$+x + x$
Equilibrium	$0.06666 - x$		$x + x$

Substitute into the equilibrium-constant expression to get

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = \frac{(x)^2}{(0.06666 - x)} \cong \frac{(x)^2}{(0.06666)} = 5.\underline{5}6 \times 10^{-10}$$

$$x = [H_3O^+] = 6.\underline{0}8 \times 10^{-6}\ M$$

Finally, calculate the pH.

$$\text{pH} = -\log [H_3O^+] = -\log (6.08 \times 10^{-6}) = 5.2\underline{1}5 = 5.22$$

d. Calculate the moles of acid added.

$$(0.100\ M)\ \text{x}\ 0.175\ \text{L} = 0.017\underline{5}0\ \text{mol}$$

The moles of base added are the same as for part c, 0.016$\underline{0}$0 mol. The excess moles of acid and the total volume are

$$\text{Moles of acid remaining} = 0.01750\ \text{mol} - 0.01600\ \text{mol} = 0.001\underline{5}0\ \text{mol}$$

$$V = 80.0\ \text{mL} + 175\ \text{mL} = 25\underline{5}.0\ \text{mL} = 0.25\underline{5}0\ \text{L}$$

The $[H_3O^+]$ concentration and the pH are

$$[H_3O^+] = \frac{0.00150\ \text{mol}}{0.2550\ \text{L}} = 5.\underline{8}82 \times 10^{-3}\ M$$

$$\text{pH} = -\log (5.882 \times 10^{-3}) = 2.2\underline{3}0 = 2.23$$

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■ ANSWERS TO CONCEPT CHECKS

16.1. You would probably guess that the pH's of the acid solutions depend on their respective K_a's; the larger the K_a, the greater the acidity, or the lower the pH. We can put this on a firm basis by looking at the acid-ionization equilibrium. An acid, HA, ionizes in water as follows:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The corresponding equilibrium constant, K_a, equals $[H_3O^+][A^-]/[HA]$. When you start with the same concentration of HA, the concentration of HA in solution is essentially the same for each acid. Also, $[H_3O^+] = [A^-]$. This means K_a is proportional to $[H_3O^+]^2$, or $pH = -\log [H_3O^+]$ is proportional to $-\log K_a$. Therefore, the larger the K_a, the lower the pH. As an example, compare two acids, one with K_a equal to 10^{-5} and the other with K_a equal to 10^{-4}. The corresponding $-\log K_a$ values are 5 and 4, respectively. The second acid (the one with the greater K_a) would have the lower pH. If you look at Table 16.1, the acid with the largest K_a of those listed in the problem statement is HF. So the ranking from highest to lowest pH is $HCN > HC_2H_3O_2 > HNO_2 > HF$.

16.2. By examining the contents of the beaker, you see there are three different species present: the ions BH^+ and OH^- and unreacted B molecules. This represents a weak base. The ionization reaction for this base is

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

16.3. Ammonia, NH_3, is a weak base; the other compounds are salts. You can decide the acidity or basicity of salt solutions by noting whether the corresponding acid and base are strong or weak. For example, NH_4Br is the salt of a weak base (NH_3) and a strong acid (HBr), so the salt is acidic. Similarly, NaF is basic (it is the salt of a strong base, NaOH, and a weak acid, HF). NaCl is neutral. This means two of the solutions are basic (NH_3 and NaF), one solution is neutral (NaCl), and the other is acidic (NH_4Br). Although a salt might be as basic as NH_3, this occurs only when the acid from which the salt formed is quite weak (for example, NaCN is quite basic). Thus, the solution with highest pH is 0.1 *M* NH_3 (a), and the solution of lowest pH is 0.1 *M* NH_4Br (b).

16.4. The amount of any substance in a solution is proportional to the volume times molarity. Let's look at each solution

a. The 1.5 mL of 1 *M* HCl just neutralizes 15 mL of 0.1 *M* NaOH, giving a solution of NaCl. Thus, the pH of the original solution changes from very basic to neutral (pH = 7) after the addition of HCl.

b. The solution of acetic acid changes from weakly acidic to strongly acidic with the addition of HCl.

c. Equal amounts of NaOH and $HC_2H_3O_2$ in the original solution exactly neutralize each other to produce the salt $NaC_2H_3O_2$, which is slightly basic. The addition of the strong acid HCl gives an acidic solution.

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d. The 30 mL of NaOH reacts with 30 mL of $HC_2H_3O_2$ to give the salt $NaC_2H_3O_2$, leaving an equal amount of the corresponding acid, $HC_2H_3O_2$. The result is a buffer solution. The addition of HCl to the buffer does not change the pH appreciably. (This is true as long as the amount of added acid does not overwhelm the capacity of the buffer. In this case, it does not. The amount of acid and base conjugates in the buffer is twice the amount of added acid.)

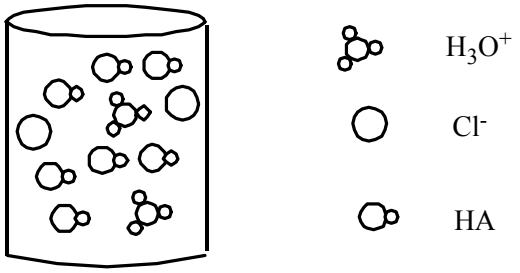
Only d does not change appreciably in pH.

16.5.

a. When two formula units of NaOH are added to the beaker on the left, a reaction occurs consuming two HA molecules and forming two A^- ions. This results in a solution with two HA molecules and five A^- ions, which is depicted in beaker Y.

b. Since the original buffer contains three A^- ions, three HCl molecules could be added before the buffer capacity would be exceeded.

c. The beaker would contain seven HA molecules. In addition, the extra HCl molecules would dissociate into H_3O^+ and Cl^- ions. This could be represented as follows:



■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

16.1. The equation is

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

The equilibrium-constant expression is

$$K_a = \frac{[H_3O^+]\,[CN^-]}{[HCN]}$$

16.2. HCN is the weakest acid. Its K_a of 4.9×10^{-10} is less than the K_a of 1.7×10^{-5} of $HC_2H_3O_2$; $HClO_4$ is a strong acid, of course.

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16.3. Both methods involve direct measurement of the concentrations of the hydronium ion and the anion of the weak acid and calculation of the concentration of the un-ionized acid. All concentrations are substituted into the K_a expression to obtain a value for K_a. In the first method, the electrical conductivity of a solution of the weak acid is measured. The conductivity is proportional to the concentration of the hydronium ion and anion. In the second method, the pH of a known starting concentration of weak acid is measured. The pH is converted to $[H_3O^+]$, which will be equal to [anion].

16.4. The degree of ionization of a weak acid decreases as the concentration of the acid added to the solution increases. Compared to low concentrations, at high concentrations, there is less water for each weak acid molecule to react with as the weak acid ionizes:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

16.5. You can neglect x if $C_a/K_a \geq 100$. In this case, $C_a/K_a = [(0.0010\ M \div 6.8 \times 10^{-4}) = 1.47]$, which is significantly less than 100, and x cannot be neglected in the $(0.0010 - x)$ term. This says the degree of ionization is significant.

16.6. The ionization of the first H_3O^+ is

$$H_2PHO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPHO_3^-(aq)$$

The equilibrium-constant expression is

$$K_{a_1} = \frac{[H_3O^+]\,[HPHO_3^-]}{[H_2PHO_3]}$$

The ionization of the second H_3O^+ is

$$HPHO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PHO_3^{2-}(aq)$$

The equilibrium-constant expression is

$$K_{a_2} = \frac{[H_3O^+]\,[PHO_3^{2-}]}{[HPHO_3^-]}$$

16.7. As shown in Example 16.4, the concentration of a −2 anion of a polyprotic acid in a solution of the diprotic acid alone is approximately equal to the value of K_{a_2}. For oxalic acid, begin by noting that $[H_3O^+] \cong [HC_2O_4^-]$. Then, substitute $[H_3O^+]$ for the $[HC_2O_4^-]$ term in the equilibrium-constant expression for K_{a_2}:

$$K_{a_2} = \frac{[H_3O^+]\,[C_2O_4^{2-}]}{[HC_2O_4^-]} \cong \frac{[H_3O^+]\,[C_2O_4^{2-}]}{[H_3O^+]} = [C_2O_4^{2-}]$$

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16.8. The balanced chemical equation for the ionization of aniline is

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

The equilibrium-constant equation, or expression for K_b, is defined without an $[H_2O]$ term; this term is included in the value for K_b, as discussed in Section 16.3. The expression is

$$K_b = \frac{[C_6H_5NH_3^+]\,[OH^-]}{[C_6H_5NH_2]}$$

16.9. First, decide whether any of the three is a strong base. Because all the molecules are among the nitrogen-containing weak bases listed in Table 16.2, none is a strong base. Next, recognize that the greater the $[OH^-]$, the stronger the weak base. Because $[OH^-]$ can be calculated from the square root of the product of K_b and concentration, the larger the K_b, the greater the $[OH^-]$ and the stronger the weak base. Thus, CH_3NH_2 is the strongest of these three weak bases because its K_b is the largest.

16.10. The solution of anilinium chloride is acidic. Anilinium chloride is a salt that contains the anilinium ion, $C_6H_5NH_3^+$, and the Cl^- ion. The chloride ion does not hydrolyze because it could form only HCl, a strong acid. The anilinium ion does hydrolyze as follows:

$$C_6H_5NH_3^+ + H_2O(l) \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

The equilibrium-constant expression for this reaction is

$$K_a = \frac{[C_6H_5NH_2]\,[H_3O^+]}{[C_6H_5NH_3^+]}$$

Obtain the value for K_a by calculating the value of K_w/K_b, where K_b is the ionization constant for aniline, $C_6H_5NH_2$.

16.11. The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that furnishes an ion that is common to, or takes part in, the equilibrium. If the equilibrium involves the ionization of a weak acid, then the common ion is usually the anion formed by the ionization of the weak acid. If the equilibrium involves the ionization of a weak base, then the common ion is usually the cation formed by the ionization of the weak base. An example is the addition of F^- ion (as NaF) to a solution of the weak acid HF, which ionizes as shown below:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

The effect of adding F^- to this equilibrium is that it causes a shift in the equilibrium composition to the left. The additional F^- reacts with H_3O^+, lowering its concentration and raising the concentration of HF.

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16.12. The addition of CH_3NH_3Cl to 0.10 *M* CH_3NH_2 exerts a common-ion effect that causes the equilibrium below to exhibit a shift in composition to the left:

$$CH_3NH_2\,(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

This shift lowers the equilibrium concentration of the OH^- ion, which increases the $[H_3O^+]$. An increase in $[H_3O^+]$ lowers the pH below 11.8. The shift in composition to the left occurs according to Le Châtelier's principle, which states that a system shifts to counteract any change in composition.

16.13. A buffer is most often a solution of a mixture of two substances that is able to resist pH changes when limited amounts of acid or base are added to it. A buffer must contain a weak acid and its conjugate (weak) base. Strong acids and/or bases cannot form effective buffers because a buffer acts by converting H_3O^+ (strong acid) to the un-ionized (weak) buffer acid and by converting OH^- (strong base) to the un-ionized (weak) buffer base. An example of a buffer pair is a mixture of H_2CO_3 and HCO_3^-, the principal buffer in the blood.

16.14. The capacity of a buffer is the amount of acid or base with which the buffer can react before exhibiting a significant pH change. (A significant change in blood pH might mean 0.01−0.02 pH unit; for other systems a significant change might mean 0.5 pH unit.) A high-capacity buffer might be of the type discussed for Figure 16.11: 1 mol of buffer acid and 1 mol of buffer base. A low-capacity buffer might involve quite a bit less than these amounts: 0.01−0.05 mol of buffer acid and buffer base.

16.15. The pH of a weak base before titration is relatively high, around pH 10 for a 0.1 *M* solution of a typical weak base. As a strong acid titrant is added, the $[OH^-]$ decreases, and the pH decreases. At 50% neutralization, a buffer of equal amounts of acid and base is formed. The $[OH^-]$ equals the K_b, or the pOH equals the pK_b. The equivalence point is the point in a titration when a stoichiometric amount of reactant has been added. At the equivalence point, the pH is governed by the hydrolysis of the salt of the weak base formed and is usually in the pH 4−6 region. After the equivalence point, the pH decreases to a level just greater than the pH of the strong acid titrant.

16.16. If the pH is 8.0, an indicator that changes color in the basic region would be needed. Of the indicators mentioned in the text, phenolphthalein (pH 8.2−10.0) and thymol blue would work. In actual practice, cresol red (pH 7.2−8.8) would be the best choice because the pH should be closer to the middle of the range than to one end.

16.17. The answer is a, NaF.

16.18. The answer is d, slightly acidic.

16.19. The answer is a, H_2S.

16.20. The answer is d, 5.05.

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■ ANSWERS TO CONCEPT EXPLORATIONS

16.21.

a. $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

$NaCN(s) \rightarrow Na^+(aq) + CN^-(aq)$

$KClO_2(s) \rightarrow K^+(aq) + ClO_2^-(aq)$

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

$KBr(s) \rightarrow K^+(aq) + Br^-(aq)$

$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$

b. The proton donors should be cations and should contain hydrogen. Thus, the only possible proton donor is NH_4^+. The proton acceptors are anions and are conjugate bases of weak acids. The possible proton acceptors are CN^-, ClO_2^-, and F^-.

c. $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

$ClO_2^-(aq) + H_2O(l) \rightleftharpoons HClO_2(aq) + OH^-(aq)$

$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$

d. You can get an idea of the extent of these reactions by looking at the K value for each reaction. All of the reactions above involve conjugate acids or bases. Recall that the smaller the K value for an acid or base, the larger the K value for its conjugate acid or base. The acid with the smallest K_a value will have a conjugate base that hydrolyzes to the greatest extent and have the greatest effect on the pH of the solution. For increasingly larger K_a values, the conjugate bases hydrolyze to a lesser degree, and have increasingly smaller effects on the pH of a solution.

e. For the solutions containing either NaCN, $KClO_2$, NH_4NO_3, or NaF, you would need the K_a or K_b value for the corresponding acid or base. For a solution of NaCl or KBr, no further information is needed. None of the ions hydrolyze, so the pH of the solution would be 7.00.

f. If 0.01 mol of NH_4CN were dissolved in enough water to make 1.0 L of solution, the concentration of the solution would be 0.010 M. Since NH_4CN is soluble, this would produce a solution that was 0.010 M in NH_4^+ and 0.010 M in CN^-. Both ions hydrolyze. The reactions are

$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

Since NH_4^+ would produce an acidic solution and CN^- would produce a basic solution, the ions have opposite effects on the pH of the solution. It will be necessary to compare the K value for the reactions. Whichever reaction has the larger K value will dominate the behavior. Both of these reactions involve a conjugate acid or base, so it will be necessary to compare the K values for the acid or base. The smaller the K value for an acid or base, the larger the K value for its conjugate. You will need the value of K_b for NH_3 and the value of K_a for HCN. If $K_a < K_b$, the solution will be basic, and if $K_b < K_a$, the solution will be acidic.

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16.22.

a. In the compound NaX, Na^+ is a neutral ion and X^- is a conjugate base of a weak acid. X^- hydrolyzes to give a basic solution in water with a pH of 9.12. In the compound ACl, Cl^- is a neutral ion and, since a solution of the salt is neutral, A^+ is also a neutral ion. Thus, a solution of AX will be basic, A^+ a neutral ion and X^- hydrolyzing to produce a solution with pH of 9.12, the same as for the solution of NaX.

b. Yes, OH^- is present in a solution of AX. Since the solution is basic, $[OH^-] > [H_3O^+]$.

c. Since there is 0.10 mol AX in 1.0 L, [AX] = 0.10 *M*. The hydrolysis of X^- is

$$\begin{array}{ccccc} X^-(aq) & + & H_2O(l) & \rightleftharpoons & HX(aq) & + & OH^-(aq) \\ 0.10 - x & & & & x & & x \end{array}$$

Use the pH to calculate $[OH^-]$, which is equal to *x*.

$$pOH = 14.00 - pH = 14.00 - 9.12 = 4.88$$

$$x = [OH^-] = 10^{-pOH} = 10^{-4.88} = 1.\underline{3}18 \times 10^{-5}$$

Now calculate K_b and K_a.

$$K_b = \frac{(x)^2}{0.10 - x} = \frac{(1.318 \times 10^{-5})^2}{0.10 - 1.318 \times 10^{-5}} = 1.\underline{7}3 \times 10^{-9} = 1.7 \times 10^{-9}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.73 \times 10^{-9}} = 5.\underline{7}5 \times 10^{-6} = 5.8 \times 10^{-6}$$

d. The added HCl will react with X^-, removing it from solution, replacing it with equal moles of HX. There is not enough added HCl to completely react with the X^- present, so the resulting solution will still be basic, but the pH will be lower. Since the solution of NaX and the solution of AX have the same conjugate base with the same concentration, the effect on both solutions is the same.

e. Here, equal moles of acid and conjugate base are present, so the solution is equivalent to a solution of HX and ACl with a concentration of 0.10 *M* for each. Since ACl does not affect the pH of the solution, the pH of the solution is due to the acid HX.

f. This is a solution of a strong base (NaOH) and a weak conjugate base (X^-). The strong base dominates the behavior. Since there is 0.10 mol NaOH in 1.0 L, [OH^- = 0.10 *M*]. This gives

$$pOH = -\log(0.10) = 1.0\underline{0}0 = 1.00$$

$$pH = 14.00 - pOH = 14.00 - 1.00 = 13.00$$

g. This is a solution of equal moles of a strong acid and a weak base. Students have the misconception that the strong acid dominates the behavior, but this is not the case. The acid and the base will react with each other and produce an equal number of moles of conjugate acid HX. Since the conjugate acid is a weak acid, you would not expect it to dissociate completely, so the pH would not be 1.00, which would be the case if it were a strong acid.

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■ ANSWERS TO CONCEPTUAL PROBLEMS

16.23. A solution of the weak acid, HA, will contain hydronium ions (H_3O^+) and anions (A^-) in equal amounts, as well as some undissociated acid (HA) molecules. This is represented by the solution in container A, which contains six HA molecules, two H_3O^+ ions, and two A^- ions. The solution in container B contains eight HA molecules and represents an undissociated acid. In container C, all of the HA molecules have dissociated, so this represents a strong acid.

16.24. For equal molar solutions,

a. The greater the pH of the solution, the less H_3O^+ present in solution. When comparing the three acid solutions of equal concentration were compared, HX produced the least amount of H_3O^+ in solution (highest pH), so it must be the least ionized.

b. When the three acids were compared, HZ was the most ionized in solution (lowest pH) producing the greatest concentration of H_3O^+. Therefore, HZ must be the strongest acid with the largest K_a.

16.25.

a. When HF is dissolved in water, the F^- hydrolyzes. The reaction is

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

b. When NaF is dissolved in water, F^- hydrolyzes. The reaction is

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

c. When $C_6H_5NH_2$ is dissolved in water, the following reaction occurs:

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

d. When $C_6H_5NH_3Cl$ is dissolved in water, $C_6H_5NH_3^+$ hydrolyzes. The reaction is

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$$

16.26. The KBr solution is made from a neutral salt. Thus, it should have a pH of 7.0. The HBr solution is a strong acid with pH < 7.0. The CH_3NH_2 solution is a weak base with pH > 7.0. The NH_4Cl solution is made from a salt with a weak acid cation, NH_4^+, with pH < 7.0. Therefore, the ranking from lowest to highest hydroxide concentrations is HBr < NH_4Cl < KBr < CH_3NH_2.

16.27. A solution of rantidine hydrochloride should be acidic. Let Ran represent rantidine. Then RanHCl is the chloride salt, rantidinium chloride. The cation rantidinium, $RanH^+$, should hydrolyze according to the equation

$$RanH^+(aq) + H_2O(l) \rightleftharpoons Ran(aq) + H_3O^+(aq)$$

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16.28. NH_3 is a weak base; therefore, the solution would have pH > 7. The NH_4Br solution is made from a salt with a weak acid cation, NH_4^+, with pH < 7.0. The NaF solution is made from a salt with a basic anion, F^-, with a pH > 7. The NaCl solution is made from a neutral salt; therefore, it should have a pH = 7. In order to rank the relative strengths of the F^- and NH_3, you should estimate K_b for each. Using data from Appendices E and F of your text, K_b is about 10^{-5} for NH_3 and about 10^{-10} for F^-, which indicates that NH_3 is a stronger base than F^-. Therefore, the ranking from highest to lowest pH is NH_3 > NaF > NaCl > NH_4Br.

16.29. To prepare a buffer solution that has a pH equal to the pK_a value of the acid, you need equal amounts of acid and conjugate base in the solution. The easiest way to make the buffer is to mix equal volumes of equal molar solutions of HA and NaA. Thus, mix 100 mL of 0.10 *M* NaA with the 100 mL of 0.10 *M* HA to prepare the buffer.

16.30. Of the three titrations, the weak base-strong acid titration is easiest to identify. The attributes to look for are a high pH at the start and a gradual decrease in pH as the titration proceeds. The other two titrations both start with low pH and increase in pH as the titration proceeds. Of the two, the strong acid-strong base titration should show a more rapid increase in pH before the endpoint is reached along with a well-defined, sharp equivalence point at pH 7. The weak acid-strong base titration will show a more gradual change in pH before the equivalence point, which should be less sharply defined and occur at a pH > 7.

16.31.

a. First, since the pH of the solution is less than 7 at the beginning of the titration, you can conclude that an acid is being titrated with a base.

b. The pH of the equivalence point is about 8.5. Therefore, the acid being titrated is a weak acid.

c. You need to pick an indicator that changes color in the pH range of about 7 to 10. Therefore, thymol blue or phenolphthalein would work fine for this titration.

16.32.

a. The balanced chemical equation for the titration of aqueous NaOH with HCl is

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

b. Beaker A contains four Cl^- ions and four water molecules. There are no OH^- ions present. This represents the equivalence point. Beaker B contains two OH^- and two Cl^- ions and two water molecules. Since some OH^- is still present, this represents the titration at a point before the equivalence point. Beaker C contains six Cl^- and two H_3O^+ ions and four water molecules. This represents the titration at a point after the equivalence point.

c. The solution in beaker A is at the equivalence point and is neutral. The solution in beaker B contains OH^- ions and is basic. The solution in beaker C contains H_3O^+ ions and is acidic.

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■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

16.33.

a. $HBrO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO^-(aq)$

b. $HClO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_2^-(aq)$

c. $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

d. $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

16.34.

a. $HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$

b. $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

c. $HN_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + N_3^-(aq)$

d. $HOCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OCN^-(aq)$

16.35. HAc will be used throughout as an abbreviation for acrylic acid and Ac^- for the acrylate ion. At the start, the H_3O^+ from the self-ionization of water is so small it is approximately zero. Once the acrylic acid solution is prepared, some of the 0.10 *M* HAc ionizes to H_3O^+ and Ac^-. Then, let x equal the mol/L of HAc that ionize, forming x mol/L of H_3O^+ and x mol/L of Ac^- and leaving $(0.10 - x)$ *M* HAc in solution. We can summarize the situation in tabular form:

Conc. (M)	$HAc + H_2O \rightleftharpoons$	H_3O^+ +	Ac^-
Starting	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

The equilibrium-constant expression is

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} = \frac{x^2}{(0.10 - x)}$$

The value of x can be obtained from the pH of the solution:

$$x = [H_3O^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-2.63) = 2.\underline{3}4 \times 10^{-3} = 0.00234\ M$$

Note that $(0.10 - x) = (0.10 - 0.00234) = 0.09766$, which is significantly different from 0.10, so x cannot be ignored in the calculation.

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Thus, we substitute for x in both the numerator and the denominator to obtain the value of K_a:

$$K_a = \frac{x^2}{(0.10 - x)} = \frac{(0.00234)^2}{(0.10 - 0.00234)} = 5.\underline{6}06 \times 10^{-5} = 5.6 \times 10^{-5}$$

16.36. HN_3 will be used throughout as an abbreviation for hydrazoic acid and N_3^- for the hydrazoate ion. At the start, the H_3O^+ from the self-ionization of water is so small it is approximately zero. Once the hydrazoic acid solution is prepared, some of the 0.20 M HN_3 ionizes to H_3O^+ and N_3^-. Then, let x equal the mol/L of HN_3 that ionizes, forming x mol/L of H_3O^+ and x mol/L of N_3^- and leaving (0.20 − x) M HN_3 in solution. We can summarize the situation in tabular form:

Conc. (M)	$HN_3 + H_2O$ ⇌	H_3O^+	+	N_3^-
Starting	0.20	0		0
Change	$-x$	$+x$		$+x$
Equilibrium	$0.20 - x$	x		x

The equilibrium-constant expression is

$$K_a = \frac{[H_3O^+][N_3^-]}{[HN_3]} = \frac{x^2}{(0.20 - x)}$$

The value of x can be obtained from the pH of the solution:

$$x = [H_3O^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-3.21) = 6.\underline{1}6 \times 10^{-4} = 0.000\underline{6}16\ M$$

Note that (0.20 − x) = (0.20 − 0.000616) = 0.1993, which is not significantly different from 0.20, so x can be ignored in the calculation. Thus, we substitute for x in only the numerator, not the denominator, to obtain the value of K_a:

$$K_a = \frac{x^2}{(0.20 - x)} \cong \frac{(0.000616)^2}{(0.20)} \cong 1.\underline{8}9 \times 10^{-6} = 1.9 \times 10^{-6}$$

16.37. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HBo as the symbol for boric acid and Bo^- as the symbol for $B(OH)_4^-$.

Conc. (M)	$HBo + H_2O$ ⇌	H_3O^+	+	Bo^-
Starting	0.021	0		0
Change	$-x$	$+x$		$+x$
Equilibrium	$0.021 - x$	x		x

The value of x equals the value of the molarity of the H_3O^+ ion, which can be obtained from the equilibrium-constant expression.

Substitute into the equilibrium-constant expression, and solve for x.

$$K_a = \frac{[H_3O^+][Bo^-]}{[HBo]} = \frac{(x)^2}{(0.021 - x)} = 5.9 \times 10^{-10}$$

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Solve the equation for x, assuming x is much smaller than 0.021.

$$\frac{(x)^2}{(0.021 - x)} \cong \frac{(x)^2}{(0.021)} = 5.9 \times 10^{-10}$$

$$x^2 = 5.9 \times 10^{-10} \times (0.021) = 1.\underline{2}39 \times 10^{-11}$$

$$x = [H_3O^+] = 3.\underline{5}19 \times 10^{-6}\ M$$

Check to make sure the assumption that $(0.021 - x) \cong 0.021$ is valid:

$$0.021 - (3.519 \times 10^{-6}) = 0.02099, \text{ or} \cong 0.021 \text{ to two sig. figs.}$$

$$\text{pH} = -\log [H_3O^+] = -\log (3.519 \times 10^{-6}) = 5.4\underline{5}3 = 5.45$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{3.519 \times 10^{-6}}{(0.021)} = 0.000167 = 0.00017 = 1.7 \times 10^{-4}$$

16.38. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HFo as the symbol for formic acid and Fo^- as the symbol for CHO_2^-.

Conc. (M)	$HFo + H_2O \rightleftharpoons$	$H_3O^+ +$	Fo^-
Starting	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

The value of x equals the value of the molarity of the H_3O^+ ion, which can be obtained from the equilibrium-constant expression. Substitute into the equilibrium-constant expression, and solve for x.

$$K_a = \frac{[H_3O^+]\,[Fo^-]}{[HFo]} = \frac{(x)^2}{(0.10 - x)} = 1.7 \times 10^{-4}$$

Solve the equation for x, assuming x is much smaller than 0.10.

$$\frac{(x)^2}{(0.10 - x)} = \frac{(x)^2}{(0.10)} = 1.7 \times 10^{-4}$$

$$x^2 = 1.7 \times 10^{-4} \times (0.10) = 1.7 \times 10^{-5}$$

$$x = [H_3O^+] = 4.\underline{1}23 \times 10^{-3} = 0.0041\ M$$

Check to make sure the assumption that $(0.10 - x) \cong 0.10$ is valid:

$$0.10 - (0.004123) = 0.0958, \text{ or} \cong 0.10 \text{ to two sig. figs}$$

$$\text{pH} = -\log [H_3O^+] = -\log (4.123 \times 10^{-3}) = 2.3\underline{8}4 = 2.38$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{0.0041}{(0.10)} = 0.04\underline{1}2 = 0.041$$

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16.39. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HPaba as a symbol for p-aminobenzoic acid (PABA), and use $Paba^-$ as the symbol for the −1 anion.

Conc. (*M*)	HPaba + H_2O	H_3O^+ +	Paba
Starting	0.055	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.055 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(0.055 - x)$:

$$K_a = \frac{[H_3O^+]\,[Paba^-]}{[HPaba]} = \frac{(x)^2}{(0.055 - x)} = 2.2 \times 10^{-5}$$

Solve the equation for x, assuming x is smaller than 0.055.

$x^2 = (2.2 \times 10^{-5}) \times 0.055 = 1.\underline{2}1 \times 10^{-6}$

$x = [H_3O^+] = [Paba^-] \cong 1.\underline{1}0 \times 10^{-3} = 0.0011 = 1.1 \times 10^{-3}\ M$

Check to make sure the assumption that $(0.055 - x) \cong 0.055$ is valid.

$0.055 - 0.00110 = 0.0539$, or 0.054

16.40. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HBar as a symbol for barbituric acid and Bar^- as the symbol for the −1 anion.

Conc. (*M*)	HBar + H_2O	H_3O^+ +	Bar^-
Starting	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(0.10 - x)$:

$$K_a = \frac{[H_3O^+]\,[Bar^-]}{[HBar]} = \frac{(x)^2}{(0.10 - x)} = 9.8 \times 10^{-5}$$

Solve the equation for x, assuming x is negligible compared to 0.15.

$x^2 \cong (9.8 \times 10^{-5}) \times 0.10 = 9.80 \times 10^{-6}$

$x = [H_3O^+] = [Bar^-] \cong 3.\underline{1}3 \times 10^{-3} = 0.0031\ M$

16.41. To solve, first convert the pH to $[H_3O^+]$, which also equals $[C_2H_3O_2^-]$, here symbolized as $[Ac^-]$. Then assemble the usual table, and substitute into the equilibrium-constant expression to solve for $[HC_2H_3O_2]$, here symbolized as [HAc].

$[H_3O^+] = \text{antilog}\,(-2.68) = 2.\underline{0}89 \times 10^{-3}\ M$

Conc. (*M*)	HAc + H^2O	H^3O^+ +	Ac^-
Starting	x	0	0
Change	-2.089×10^{-3}	$+2.089 \times 10^{-3}$	$+2.089 \times 10^{-3}$
Equilibrium	$x - (2.089 \times 10^{-3})$	2.089×10^{-3}	2.089×10^{-3}

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Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the $x - (2.089 \times 10^{-3})$ terms into the expression:

$$K_a = \frac{[H_3O^+]\,[Ac^-]}{[HAc]} = \frac{(2.089 \times 10^{-3})^2}{(x - 2.089 \times 10^{-3})} = 1.7 \times 10^{-5}$$

Solve the equation for x, assuming 0.002089 is much smaller than x.

$$x = [HAc] \cong \frac{(2.089 \times 10^{-3})^2}{(1.7 \times 10^{-5})} = 0.25\underline{6} = 0.26\ M$$

16.42. To solve, first convert the pH to $[H_3O^+]$, which also equals the $[C_3H_5O_3^-]$, here symbolized as $[Lac^-]$. Then assemble the usual table, and substitute into the equilibrium-constant expression to solve for $[HC_3H_5O_3]$, here symbolized as [HLac].

$[H_3O^+]$ = antilog (−2.51) = $3.09 \times 10^{-3}\ M$

Conc. (M)	HLac + H_2O ⇌	H_3O^+ +	Lac^-
Starting	x	0	0
Change	-3.09×10^{-3}	$+3.09 \times 10^{-3}$	$+3.09 \times 10^{-3}$
Equilibrium	$x - (3.09 \times 10^{-3})$	3.09×10^{-3}	3.09×10^{-3}

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the $x - (3.09 \times 10^{-3})$ terms into the expression:

$$K_a = \frac{[H_3O^+]\,[Lac^-]}{[HLac]} = \frac{(3.09 \times 10^{-3})^2}{(x - 3.09 \times 10^{-3})} = 1.4 \times 10^{-4}$$

Solve the equation for x. It appears that 3.09×10^{-3} is not much smaller than x, so do not ignore x in the denominator.

$$\frac{(3.09 \times 10^{-3})^2}{1.4 \times 10^{-4}} = 0.06\underline{8}2 = (x - 3.09 \times 10^{-3})$$

$$x = [HLac] = 0.0682 + 0.00309 = 0.07\underline{1}2 = 0.071\ M$$

16.43. To solve, assemble the usual table of starting, change, and equilibrium concentrations of HF and F^- ions.

Conc. (M)	HF + H_2O ⇌	H_3O^+ +	F^-
Starting	0.40	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.40 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(0.040 - x)$:

$$K_a = \frac{[H_3O^+]\,[F^-]}{[HF]} = \frac{(x)^2}{(0.040 - x)} = 6.8 \times 10^{-4}$$

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In this case, x cannot be ignored compared to 0.040 M. (If it is ignored, subtracting the calculated $[H_3O^+]$ from 0.040 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (6.8 \times 10^{-4})\,x - (2.72 \times 10^{-5}) = 0$$

$$x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 + 4(2.72 \times 10^{-5})}}{2}$$

$$x = \frac{-6.8 \times 10^{-4} \pm 0.01045}{2}$$

Use the positive root.

$$x = [H_3O^+] = 4.\underline{8}8 \times 10^{-3} = 0.0049 = 4.9 \times 10^{-3}\ M$$

$$\text{pH} = -\log(4.88 \times 10^{-3}) = 2.3\underline{1}1 = 2.31$$

16.44. To solve, assemble the usual table of starting, change, and equilibrium concentrations of $HC_2H_2ClO_2$, symbolized as HChl, and the $C_2H_2ClO_2^-$ ion, symbolized as Chl^-.

Conc. (M)	HChl + H_2O ⇌	H_3O^+ +	Chl^-
Starting	1.0020	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$1.0020 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(1.0020 - x)$:

$$K_a = \frac{[H_3O^+]\,[Chl^-]}{[HChl]} = \frac{(x)^2}{(1.0020 - x)} = 1.3 \times 10^{-3} = 0.0013$$

Assume x is negligible compared to 1.0020 and solve for x.

$$0.0013 = \frac{(x)^2}{(1.0020)}$$

$$x = 0.03\underline{6}09$$

$$\text{pH} = -\log(0.03609) = 1.4\underline{4}2 = 1.44$$

16.45. To solve, assemble the usual table of starting, change, and equilibrium concentrations of $(NO_2)_2C_6H_3CO_2H$, symbolized as HDin, and the $(NO_2)_2C_6H_3CO_2^-$ ion, symbolized as Din^-.

Conc. (M)	HDin + H_2O ⇌	H_3O^+ +	Din^-
Starting	2.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$2.00 - x$	x	x

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Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(2.00 - x)$:

$$K_a = \frac{[H_3O^+]\,[Din^-]}{[HDin]} = \frac{(x)^2}{(2.00 - x)} = 7.94 \times 10^{-2} = 0.0794$$

In this case, x cannot be ignored compared to 2.00 M. (If it is ignored, subtracting the calculated $[H_3O^+]$ from 2.00 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (0.0794)\,x - 0.1588 = 0$$

$$x = \frac{-0.0794 \pm \sqrt{(0.0794)^2 + 4(0.1588)}}{2}$$

$$x = \frac{-0.0794 \pm 0.8009}{2}$$

Use the positive root.

$$x = [H_3O^+] = 0.3607 = 0.361\ M$$

16.46. To solve, assemble the usual table of starting, change, and equilibrium concentrations of $BrC_6H_4CO_2H$, symbolized as HpBr, and the $BrC_6H_4CO_2^-$ ion, symbolized as pBr^-.

Conc. (M)	HpBr + H_2O	H_3O^+ +	pBr^-
Starting	2.00×10^{-4}	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(2.00 \times 10^{-4} - x)$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(2.00 \times 10^{-4} - x)$:

$$K_a = \frac{[H_3O^+]\,[pBr^-]}{[HpBr]} = \frac{(x)^2}{(2.00 \times 10^{-4} - x)} = 1.00 \times 10^{-4}$$

In this case, x cannot be ignored compared to 2.00×10^{-4} M. (If it is ignored, subtracting the calculated $[H_3O^+]$ from 2.00×10^{-4} yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (1.00 \times 10^{-4})\,x - 2.00 \times 10^{-8} = 0$$

Plugging into the quadratic formula gives

$$x = \frac{-1.00 \times 10^{-4} \pm \sqrt{(1.00 \times 10^{-4})^2 + 4(2.00 \times 10^{-8})}}{2}$$

$$x = \frac{-1.00 \times 10^{-4} \pm 3.00 \times 10^{-4}}{2}$$

Use the positive root.

$$x = [H_3O^+] = 1.000 \times 10^{-4} = 1.00 \times 10^{-4}\ M$$

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16.47.

a. To solve, note that $K_{a_1} = 1.2 \times 10^{-3} > K_{a_2} = 3.9 \times 10^{-6}$, and hence the second ionization and K_{a_2} can be neglected. Assemble a table of starting, change, and equilibrium concentrations. Let $H_2Ph = H_2C_8H_4O_4$ and $HPh^- = H\,C_8H_4O_4^-$.

Conc. (*M*)	$H_2Ph + H_2O$ ⇌	$H_3O^+ +$	HPh^-
Starting	0.015	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.015 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute x and $(0.015 - x)$:

$$K_{a_1} = \frac{[H_3O^+]\,[HPh^-]}{[H_2Ph]} = \frac{(x)^2}{(0.015 - x)} = 1.2 \times 10^{-3} = 0.0012$$

In this case, x cannot be ignored in the $(0.015\ M - x)$ term. (If it is ignored, the calculated $[H_3O^+]$ when subtracted from 0.0015 *M* yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (0.0012)\,x - 1.80 \times 10^{-5} = 0$$

$$x = \frac{-0.0012 \pm \sqrt{(0.0012)^2 - 4(-1.80 \times 10^{-5})}}{2}$$

$$x = \frac{-0.0012 \pm 0.008569}{2}$$

Use the positive root.

$$x = [H_3O^+] \cong 3.\underline{6}84 \times 10^{-3} = 0.0037 = 3.7 \times 10^{-3}\ M$$

b. Because $[HPh^-] \cong [H_3O^+]$, these terms cancel in the K_{a_2} expression. This reduces to

$$[Ph^{2-}] = K_{a_2} = 3.9 \times 10^{-6}\ M.$$

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16.48.

a. To solve, note that $K_{a_1} = 4.3 \times 10^{-7} > K_{a_2} = 4.8 \times 10^{-11}$, and hence the second ionization and K_{a_2} can be neglected. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$H_2CO_3 + H_2O$	$\rightleftharpoons$	$H_3O^+ +$	HCO_3^-
Starting	5.45×10^{-4}		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(5.45 \times 10^{-4} - x)$		x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute x and $(5.45 \times 10^{-4} - x)$:

$$K_{a_1} = \frac{[H_3O^+]\,[HCO_3^-]}{[H_2CO_3]} = \frac{(x)^2}{(5.45 \times 10^{-4} - x)} = 4.3 \times 10^{-7}$$

In this case, x cannot be ignored compared to 5.45×10^{-4} M. (If it is ignored, the calculated $[H_3O^+]$ when subtracted from 5.45×10^{-4} M yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (4.3 \times 10^{-7})\,x - 2.3435 \times 10^{-10} = 0$$

$$x = \frac{-4.3 \times 10^{-7} \pm \sqrt{(4.3 \times 10^{-7})^2 + 4(2.3435 \times 10^{-10})}}{2}$$

$$x = \frac{-4.3 \times 10^{-7} \pm 3.06 \times 10^{-5}}{2}$$

Use the positive root.

$$x = [H_3O^+] = 1.51 \times 10^{-5} = 1.5 \times 10^{-5}\ M$$

b. To calculate $[CO_3^{2-}] = y$, note from the equilibrium concentrations in the table above that $[HCO_3^-] \cong [H_3O^+]$. In exact terms, $[H_3O^+] = (1.5 \times 10^{-5} + y)$ from the ionization of HCO_3^-, and $[HCO_3^-] = (1.5 \times 10^{-5} - y)$ from ionization. Substituting into the K_{a_2} expression gives

$$K_{a_2} = \frac{[H_3O^+]\,[CO_3^{2-}]}{[HCO_3^-]} = \frac{(1.5 \times 10^{-5} + y)(y)}{(1.5 \times 10^{-5} - y)} = 4.8 \times 10^{-11}$$

Assuming y is much smaller than 1.5×10^{-5}, note that the $(1.5 \times 10^{-5}) + y$ term cancels the $(1.5 \times 10^{-5}) - y$ term, leaving

$$[CO_3^{2-}] \cong K_{a_2} = 4.8 \times 10^{-11}\ M$$

16.49. The equation is

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

The K_b expression is

$$K_b = \frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]}$$

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16.50. The equation is

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

The K_b expression is

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

16.51. To solve, convert the pH to $[OH^-]$:

$$pOH = 14.00 - pH = 14.00 - 11.34 = 2.66$$

$$[OH^-] = \text{antilog}(-2.66) = 2.\underline{1}88 \times 10^{-3}\ M$$

Using the symbol EtN for ethanolamine, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$EtN + H_2O$	$\rightleftharpoons$	$HEtN^+$	+	OH^-
Starting	0.15		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.15 - (2.188 \times 10^{-3})$		2.188×10^{-3}		2.188×10^{-3}

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms, and solve for K_b:

$$K_b = \frac{[HEtN^+][OH^-]}{[EtN]} = \frac{(2.188 \times 10^{-3})^2}{(0.15 - 2.188 \times 10^{-3})} = 3.\underline{2}3 \times 10^{-5} = 3.2 \times 10^{-5}$$

16.52. To solve, convert the pH to $[OH^-]$:

$$pOH = 14.00 - pH = 14.00 - 11.63 = 2.37$$

$$[OH^-] = \text{antilog}(-2.37) = 4.\underline{2}66 \times 10^{-3}\ M$$

Using the symbol TMeN for trimethylamine, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$TmeN + H_2O$	$\rightleftharpoons$	$HTMeN^+$	+	OH^-
Starting	0.25		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.25 - (4.266 \times 10^{-3})$		4.266×10^{-3}		4.266×10^{-3}

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms, and solve for K_b:

$$K_b = \frac{[HTMeN^+][OH^-]}{[TMeN]} = \frac{(4.266 \times 10^{-3})^2}{(0.25 - 4.266 \times 10^{-3})} = 7.\underline{4}0 \times 10^{-5} = 7.4 \times 10^{-5}$$

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16.53. To solve, assemble a table of starting, change, and equilibrium concentrations:

Conc. (*M*)	$CH_3NH_2 + H_2O$ ⇌	$CH_3NH_3^+ +$	OH^-
Starting	0.060	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.060 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and the value of K_b:

$$K_b = \frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]} = \frac{(x)^2}{(0.060 - x)} = 4.4 \times 10^{-4}$$

In this case, x cannot be ignored compared to 0.060 *M*. (If it is ignored, subtracting the calculated $[OH^-]$ from 0.060 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (4.4 \times 10^{-4})x - 2.64 \times 10^{-5} = 0$$

$$x = \frac{-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 + 4(2.64 \times 10^{-5})}}{2}$$

$$x = \frac{-4.4 \times 10^{-4} \pm 0.01028}{2}$$

Use the positive root.

$$x = [OH^-] = 4.\underline{9}2 \times 10^{-3} = 0.0049 = 4.9 \times 10^{-3}\ M$$

$$\text{pOH} = -\log (4.92 \times 10^{-3}) = 2.3\underline{0}7$$

$$\text{pH} = 14.00 - 2.307 = 11.6\underline{9}2 = 11.69$$

16.54. To solve, assemble a table of starting, change, and equilibrium concentrations:

Conc. (*M*)	$HONH_2 + H_2O$ ⇌	$HONH_3^+ +$	OH^-
Starting	0.18	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.18 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and the value of K_b:

$$K_b = \frac{[HONH_3^+]\,[OH^-]}{[HONH_2]} = \frac{(x)^2}{(0.18 - x)} = 1.1 \times 10^{-8}$$

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Solve the equation for x, assuming x can be ignored compared to 0.18 M.

$$\frac{(x)^2}{(0.18 - x)} \cong \frac{(x)^2}{(0.18)} = 1.1 \times 10^{-8}$$

$$x^2 = 1.1 \times 10^{-8} \times (0.18)$$

$$x = [OH^-] = 4.\underline{4}4 \times 10^{-5} = 4.4 \times 10^{-5}\ M$$

$$pOH = -\log (4.44 \times 10^{-5}) = 4.3\underline{5}1$$

$$pH = 14.00 - 4.351 = 9.6\underline{4}8 = 9.65$$

16.55.

a. No hydrolysis occurs because the nitrate ion (NO_3^-) is the anion of a strong acid.

b. Hydrolysis occurs. Equation:

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

Equilibrium-constant expression:

$$K_b = \frac{K_w}{K_a} = \frac{[HOCl]\,[OH^-]}{[OCl^-]}$$

c. Hydrolysis occurs. Equation:

$$NH_2NH_3^+ + H_2O \rightleftharpoons H_3O^+ + NH_2NH_2$$

Equilibrium-constant expression:

$$K_a = \frac{K_w}{K_b} = \frac{[H_3O^+]\,[NH_2NH_2]}{[NH_2NH_3^+]}$$

d. No hydrolysis occurs because the bromide ion (Br^-) is the anion of a strong acid.

16.56.

a. Hydrolysis occurs. Equation:

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

Equilibrium-constant expression:

$$K_a = \frac{K_w}{K_b} = \frac{[H_3O^+]\,[CH_3NH_2]}{[CH_3NH_3^+]}$$

b. No hydrolysis occurs because the iodide ion (I^-) is the anion of a strong acid.

c. Hydrolysis occurs. Equation:

$$ClO_2^- + H_2O \rightleftharpoons HClO_2 + OH^-$$

Equilibrium-constant expression:

$$K_b = \frac{K_w}{K_a} = \frac{[HClO_2]\,[OH^-]}{[ClO_2^-]}$$

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d. Hydrolysis occurs. Equation:

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$

Equilibrium-constant expression:

$$K_b = \frac{K_w}{K_{a_3}} = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]}$$

16.57. Acid ionization is

$$Zn(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Zn(H_2O)_5(OH)^+(aq) + H_3O^+(aq)$$

16.58. Acid ionization is

$$Cu(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Cu(H_2O)_5(OH)^+(aq) + H_3O^+(aq)$$

16.59.

a. $Fe(NO_3)_3$ is a salt of a weak base, $Fe(OH)_3$, and a strong acid, HNO_3, so it would be expected to be acidic. Fe^{3+} is not in Group IA or IIA, so it would be expected to form a metal hydrate ion that would hydrolyze to form an acidic solution.

b. Na_2CO_3 is a salt of a strong base, NaOH, and the anion of a weak acid, HCO_3^-, so it would be expected to be basic.

c. $Ca(CN)_2$ is a salt of a strong base, $Ca(OH)_2$, and a weak acid, HCN, so it would be expected to be basic.

d. NH_4ClO_4 is a salt of a weak base, NH_3, and a strong acid, $HClO_4$, so it would be expected to be acidic.

16.60.

a. Na_2S is a salt of a strong base, NaOH, and the anion of a weak acid, HS^-, so it would be expected to be basic.

b. $Cu(NO_3)_2$ is a salt of a weak base, $Cu(OH)_2$, and a strong acid, HNO_3, so it would be expected to be acidic. Cu^{2+} is not in Group IA or IIA, so it would be expected to form a metal hydrate ion that would hydrolyze to form an acidic solution.

c. $KClO_4$ is a salt of a strong base, KOH, and a strong acid, $HClO_4$, so no reaction would occur to change the neutral pH (7.00) of water.

d. C_3NH_3Cl is a salt of a weak base, CH_3NH_2, and a strong acid, HCl, so it would be expected to be acidic.

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16.61.

a. Both ions hydrolyze:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Calculate the K_a and K_b constants of the two to compare them:

$$NH_4^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}5 \times 10^{-10}$$

$$C_2H_3O_2^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.\underline{8}8 \times 10^{-10}$$

Because the K_b for the hydrolysis of $C_2H_3O_2^-$ is slightly larger than the constant, K_a, for the hydrolysis of NH_4^+, the solution will be slightly basic but close to pH 7.0.

b. Both ions hydrolyze:

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Calculate the K_a and K_b constants of the two to compare them:

$$C_6H_5NH_3^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.\underline{3}8 \times 10^{-5}$$

$$C_2H_3O_2^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.\underline{8}8 \times 10^{-10}$$

Because the constant, K_a, for the hydrolysis of $C_6H_5NH_3^+$ is larger than the hydrolysis constant, K_b, for the hydrolysis of $C_2H_3O_2^-$, the solution will be acidic and significantly less than pH 7.0.

16.62.

a. Both ions hydrolyze:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$CNO^- + H_2O \rightleftharpoons HCNO + OH^-$$

Calculate the K_a and K_b constants of the two to compare them:

$$NH_4^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}5 \times 10^{-10}$$

$$CNO^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.\underline{8}6 \times 10^{-11}$$

Because the constant, K_a, for the hydrolysis of NH_4^+ is larger than the hydrolysis constant, K_b, for the hydrolysis of CNO^-, the solution will be acidic and significantly less than pH 7.0.

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b. Both ions hydrolyze:

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

$$CNO^- + H_2O \rightleftharpoons HCNO + OH^-$$

Calculate the K_a and K_b constants of the two to compare them:

$$C_6H_5NH_3^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.\underline{3}8 \times 10^{-5}$$

$$CNO^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.\underline{8}6 \times 10^{-11}$$

Because the constant, K_a, for the hydrolysis of $C_6H_5NH_3^+$ is larger than the hydrolysis constant, K_b, for the hydrolysis of CNO^-, the solution will be acidic and significantly less than pH 7.0.

16.63.

a. The reaction is

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$$

The constant, K_b, is obtained by dividing K_w by the K_a of the conjugate acid, HNO_2:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.\underline{2}2 \times 10^{-11} = 2.2 \times 10^{-11}$$

b. The reaction is

$$C_5H_5NH^+ + H_2OC_5H_5N + H_3O^+$$

The constant, K_a, is obtained by dividing K_w by the K_b of the conjugate base, C_5H_5N:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.\underline{1}4 \times 10^{-6} = 7.1 \times 10^{-6}$$

16.64.

a. The reaction is

$$ClO^- + H_2O \rightleftharpoons HClO + OH^-$$

The constant, K_b, is obtained by dividing K_w by the K_a of the conjugate acid, HClO:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.\underline{8}57 \times 10^{-7} = 2.9 \times 10^{-7}$$

b. The reaction is

$$NH_3OH^+ + H_2O \quad H_3O^+ + NH_2OH$$

The constant, K_a, is obtained by dividing K_w by the K_b of the conjugate base, NH_2OH:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.\underline{0}9 \times 10^{-7} = 9.1 \times 10^{-7}$$

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16.65. Assemble the usual table, letting [Pr^-] equal the equilibrium concentration of the propionate anion (the only ion that hydrolyzes). Then calculate the K_b of the Pr^- ion from the K_a of its conjugate acid, HPr. Assume x is much smaller than the 0.025 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. Finally, calculate pOH from the [OH^-] and pH from the pOH.

Conc. (M)	$Pr^- + H_2O \rightleftharpoons$	HPr +	OH^-
Starting	0.025	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.025 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.\underline{6}9 \times 10^{-10}$$

Substitute into the equilibrium-constant expression.

$$K_b = \frac{[HPr]\,[OH^-]}{[Pr^-]} = \frac{(x)^2}{(0.025 - x)} \cong \frac{(x)^2}{(0.025)} = 7.\underline{6}9 \times 10^{-10}$$

$$x = [OH^-] = [HPr] \cong 4.\underline{3}8 \times 10^{-6} = 4.4 \times 10^{-6}\ M$$

$$pOH = -\log [OH^-] = -\log (4.38 \times 10^{-6}) = 5.3\underline{5}8$$

$$pH = 14.00 - 5.358 = 8.6\underline{4}2 = 8.64$$

16.66. Assemble the usual table, letting [CN^-] equal the equilibrium concentration of the cyanide anion (the only ion that hydrolyzes). Then, calculate the K_b of the CN^- ion from the K_a of its conjugate acid, HCN. Assume x is much smaller than the 0.020 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. (This is a borderline case, but the quadratic equation gives a value of 4.415×10^{-4} M for x, not much different from the approximation.) Finally, calculate pOH from the [OH^-] and pH from the pOH.

Conc. (M)	$CN^- + H_2O \rightleftharpoons$	HCN +	OH^-
Starting	0.0020	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0020 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.\underline{0}40 \times 10^{-5}$$

Substitute into the equilibrium-constant equation.

$$K_b = \frac{[HCN]\,[OH^-]}{[CN^-]} = \frac{(x)^2}{(0.0020 - x)} = 2.040 \times 10^{-5}$$

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In this case, x cannot be ignored compared to 0.0020 M. (If it is ignored, subtracting the calculated $[OH^-]$ from 0.0020 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (2.040 \times 10^{-5})x - 4.081 \times 10^{-8} = 0$$

$$x = \frac{-2.040 \times 10^{-5} \pm \sqrt{(2.040 \times 10^{-5})^2 - 4(-4.081 \times 10^{-8})}}{2}$$

$$x = \frac{-2.040 \times 10^{-5} \pm 4.045 \times 10^{-4}}{2}$$

Use the positive root.

$$x = [OH^-] = 1.\underline{9}20 \times 10^{-4}\ M$$

Now calculate pOH and pH:

$$pOH = -\log [OH^-] = -\log (1.920 \times 10^{-4}) = 3.7\underline{1}6$$

$$pH = 14.00 - 3.716 = 10.283 = 10.28$$

The cyanide ion concentration is

$$[CN^-] = 0.0020 - x = 0.0020 - 1.920 \times 10^{-4} = 0.001\underline{8}08 = 0.0018\ M$$

16.67. Assemble the usual table, letting $[PyNH^+]$ equal the equilibrium concentration of the pyridinium cation (the only ion that hydrolyzes). Then calculate the K_a of the $PyNH^+$ ion from the K_b of its conjugate base, PyN. Assume x is much smaller than the 0.15 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. Finally, calculate pH from the $[H_3O^+]$.

Conc. (M)	$PyNH^+ + H_2O$ ⇌	$H_3O^+ +$	PyN
Starting	0.15	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.15 - x$	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.\underline{1}4 \times 10^{-6}$$

Write the equilibrium-constant expression in terms of chemical symbols and then substitute the terms and solve for K_a:

$$K_a = \frac{[PyN]\,[H_3O^+]}{[PyNH^+]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 7.\underline{1}4 \times 10^{-6}$$

$$x = [H_3O^+] = [PyN] \cong 1.\underline{0}3 \times 10^{-3} = 0.0010 = 1.0 \times 10^{-3}\ M$$

$$pH = -\log [H^+] = -\log (1.03 \times 10^{-3}) = 2.9\underline{8}7 = 2.99$$

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16.68. Assemble the usual table, letting [$MeNH_3^+$] equal the equilibrium concentration of the methylammonium cation (the only ion that hydrolyzes). Then calculate the K_a of the $MeNH_3^+$ ion from the K_b of its conjugate base, $MeNH_2$. Assume x is much smaller than the 0.35 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. Finally, calculate pH from the [H_3O^+].

Conc. (M)	$MeNH_3^+ + H_2O \rightleftharpoons$	$H_3O^+ +$	$MeNH_2$
Starting	0.35	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.35 - x$	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.\underline{2}7 \times 10^{-11}$$

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and solve for K_a:

$$K_a = \frac{[MeNH_2]\,[H_3O^+]}{[MeNH_3^+]} = \frac{(x)^2}{(0.35 - x)} \cong \frac{(x)^2}{(0.35)} = 2.\underline{2}7 \times 10^{-11}$$

$$x = [H_3O^+] = [MeNH_2] \cong 2.\underline{8}2 \times 10^{-6} = 2.8 \times 10^{-6}\ M$$

$$pH = -\log [H_3O^+] = -\log (2.82 \times 10^{-6}) = 5.5\underline{4}9 = 5.55$$

16.69. To solve, assemble a table of starting, change, and equilibrium concentrations for each part. For each part, assume x is much smaller than the 0.75 M starting concentration of HF. Then solve for x in the numerator of each equilibrium-constant expression by using the product of 6.8×10^{-4} and other terms.

a. 0.75 M Hydrofluoric acid, HF:

Conc. (M)	$HF + H_2O \rightleftharpoons$	$H_3O^+ +$	F^-
Starting	0.75	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.75 - x$	x	x

$$K_a = \frac{[H_3O^+]\,[F^-]}{[HF]} = \frac{(x)^2}{(0.75 - x)} \cong \frac{(x)^2}{(0.75)} = 6.8 \times 10^{-4}$$

$$x^2 = 6.8 \times 10^{-4} \times (0.75)$$

$$x = [H_3O^+] = 0.02\underline{2}58\ M$$

Check to see whether the assumption is valid.

$$0.75 - (0.02258) = 0.7\underline{2}7 = 0.73$$

This is a borderline case; the quadratic equation gives [H_3O^+] = 0.02224 M, not much different. The degree of ionization is

$$\text{Degree of ionization} = \frac{0.02258}{0.75} = 0.03\underline{0}1 = 0.030$$

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b. 0.75 *M* HF with 0.12 *M* HCl:

Conc. (*M*)	$HF + H_2O$	$\rightleftharpoons$	H_3O^+	+	F^-
Starting	0.75		0.12		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.75 - x$		$0.12 + x$		x

Assuming x is negligible compared to 0.12 and to 0.75, substitute into the equilibrium-constant expression 0.12 for $[H_3O^+]$ from 0.12 *M* HCl and 0.75 from the HF:

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(0.12 + x)(x)}{(0.75 - x)} \cong \frac{(0.12)(x)}{(0.75)} = 6.8 \times 10^{-4}$$

$$x = [F^-] = \frac{(0.75)(6.8 \times 10^{-4})}{(0.12)} \cong 4.\underline{2}50 \times 10^{-3}\ M$$

Check to see whether the assumptions are valid:

$$0.75 - (4.250 \times 10^{-3}) = 0.7\underline{4}57 = 0.75$$

$$0.12 + (4.250 \times 10^{-3}) = 0.1\underline{2}42 = 0.12$$

$$\text{Degree of ionization} = \frac{4.25 \times 10^{-3}}{0.75} = 0.005\underline{6}6 = 0.0057$$

16.70. To solve, assemble a table of starting, change, and equilibrium concentrations for each part. For each part, assume x is much smaller than the 0.22 *M* starting concentration of $HCHO_2$. Then solve for x in each equilibrium-constant expression by using the product of 1.7×10^{-4} and each starting molarity of formic acid.

a. 0.22 *M* $HCHO_2$

Conc. (*M*)	$HCHO_2 + H_2O$	$\rightleftharpoons$	H_3O^+	+	CHO_2^-
Starting	0.22		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.22 - x$		x		x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and solve for K_a:

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = \frac{(x)^2}{(0.22 - x)} \cong \frac{(x)^2}{(0.22)} = 1.7 \times 10^{-4}$$

$$x^2 = 1.7 \times 10^{-4} \times (0.22\ M)$$

$$x = [H_3O^+] \cong 6.\underline{1}1 \times 10^{-3}\ M$$

Check to see whether the assumption is valid:

$$0.22 - (6.11 \times 10^{-3}) = 0.2\underline{1}3 = 0.21$$

The degree of ionization is

$$\text{Degree of ionization} = (6.11 \times 10^{-3}) \div 0.22 = 0.02\underline{7}7 = 0.028$$

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b. 0.22 *M* $HCHO_2$ with 0.12 *M* HCl:

Conc. (*M*)	$HCHO_2 + H_2O$	$\rightleftharpoons$	H_3O^+	+	CHO_2^-
Starting	0.22		0.12		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.22 - x$		$0.12 + x$		x

Assuming x is negligible compared to 0.12 and to 0.22, substitute into the equilibrium-constant expression 0.12 for $[H_3O^+]$ from 0.12 *M* HCl and 0.22 from the $HCHO_2$:

$$K_a = \frac{[H_3O^+]\,[CHO_2^-]}{[HCHO_2]} = \frac{(0.12 + x)(x)}{(0.22 - x)} \cong \frac{(0.12)(x)}{(0.22)} = 1.7 \times 10^{-4}$$

$$x = [CHO_2^-] = \frac{(0.22)(1.7 \times 10^{-4})}{(0.12)} \cong 3.\underline{1}1 \times 10^{-4}\ M$$

Check to see whether the assumptions are valid:

$$0.12 + 3.11 \times 10^{-4} = 0.1\underline{2}03 = 0.12$$

$$0.22 - (3.11 \times 10^{-4}) = 0.2\underline{1}9 = 0.22$$

The degree of ionization is

$$\text{Degree of ionization} = (3.11 \times 10^{-4}) \div 0.22 = 0.001\underline{4}1 = 0.0014$$

16.71. Assemble the usual table, using a starting NO_2^- of 0.10 *M*, from 0.10 *M* KNO_2, and a starting HNO_2 of 0.15 *M*. Assume x is negligible compared to 0.10 *M* and 0.15 *M*, and solve for the x in the numerator.

Conc. (*M*)	$HNO_2 + H_2O$	$\rightleftharpoons$	H_3O^+	+	NO_2^-
Starting	0.15		0		0.10
Change	$-x$		$+x$		$+x$
Equilibrium	$0.15 - x$		$0.12 + x$		$0.10 + x$

$$K_a = \frac{[H_3O^+]\,[NO_2^-]}{[HNO_2]} = \frac{(0.10 + x)(x)}{(0.15 - x)} \cong \frac{(0.10)(x)}{(0.15)} = 4.5 \times 10^{-4}$$

$$x = [H_3O^+] = 6.\underline{7}5 \times 10^{-4}\ M$$

$$\text{pH} = -\log [H_3O^+] = -\log (6.75 \times 10^{-4}) = 3.1\underline{7}0 = 3.17$$

16.72. Use a starting OCN^- of 0.20 *M* and a starting HOCN of 0.10 *M*. Assume x is negligible compared to 0.20 *M* and 0.10 *M*.

Conc. (*M*)	$HOCN + H_2O$	$\rightleftharpoons$	H_3O^+	+	OCN^-
Starting	0.10		0		0.20
Change	$-x$		$+x$		$+x$
Equilibrium	$0.10 - x$		x		$0.20 + x$

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$$K_a = \frac{[H_3O^+]\,[OCN^-]}{[HOCN]} = \frac{(0.20 + x)(x)}{(0.10 - x)} \cong \frac{(0.20)(x)}{(0.10)} = 3.5 \times 10^{-4}$$

$$x = [H_3O^+] = 1.\underline{7}5 \times 10^{-4}\ M$$

$$\text{pH} = -\log [H_3O^+] = -\log (1.75 \times 10^{-4}) = 3.7\underline{5}6 = 3.76$$

16.73. Assemble the usual table, using a starting $CH_3NH_3^+$ of 0.15 *M*, from 0.15 *M* CH_3NH_3Cl, and a starting CH_3NH_2 of 0.10 *M*. Assume *x* is negligible compared to 0.15 *M* and 0.10 *M*, and solve for the *x* in the numerator.

Conc. (*M*)	$CH_3NH_2 + H_2O$ ⇌	OH^- +	$CH_3NH_3^+$
Starting	0.10	0	0.15
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	$0.15 + x$

$$K_b = \frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]} = \frac{(0.15 + x)(x)}{(0.10 - x)} \cong \frac{(0.15)(x)}{(0.10)} = 4.4 \times 10^{-4}$$

$$x = [OH^-] = 2.\underline{9}3 \times 10^{-4}\ M$$

$$\text{pOH} = -\log [OH^-] = -\log (2.93 \times 10^{-4}) = 3.5\underline{3}2$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.532 = 10.4\underline{6}8 = 10.47$$

16.74. Assemble the usual table, using a starting $C_2H_5NH_3^+$ of 0.10 *M*, from 0.10 *M* $C_2H_5NH_3Br$, and a starting $C_2H_5NH_2$ of 0.15 *M*. Assume *x* is negligible compared to 0.10 *M* and 0.15 *M*, and solve for the *x* in the numerator.

Conc. (*M*)	$C_2H_5NH_2 + H_2O$ ⇌	OH^- +	$C_2H_5NH_3^+$
Starting	0.15	0	0.10
Change	$-x$	$+x$	$+x$
Equilibrium	$0.15 - x$	x	$0.10 + x$

$$K_b = \frac{[C_2H_5NH_3^+]\,[OH^-]}{[C_2H_5NH_2]} = \frac{(0.10 + x)(x)}{(0.15 - x)} \cong \frac{(0.10)(x)}{(0.15)} = 4.7 \times 10^{-4}$$

$$x = [OH^-] = 7.\underline{0}5 \times 10^{-4}\ M$$

$$\text{pOH} = -\log [OH^-] = -\log (7.05 \times 10^{-4}) = 3.1\underline{5}1$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.1518 = 10.8\underline{4}8 = 10.85$$

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16.75. Find the mol/L of HF and the mol/L of F^-, and assemble the usual table. Substitute the equilibrium concentrations into the equilibrium-constant expression; then, assume x is negligible compared to the starting concentrations of both HF and F^-. Solve for x in the numerator of the equilibrium-constant expression, and calculate the pH from this value.

Total volume = 0.045 L + 0.035 L = 0.080 L

(0.10 mol HF/L) x 0.035 L = 0.0035 mol HF (÷ 0.080 L total volume = 0.04375 *M*)

(0.15 mol F^-/L) x 0.045 L = 0.00675 mol F^- (÷ 0.080 L total volume = 0.084375 *M*)

Now, substitute these starting concentrations into the usual table:

Conc. (*M*)	$HF + H_2O \rightleftharpoons$	$H_3O^+ +$	F^-
Starting	0.04375	0	0.084375
Change	$-x$	$+x$	$+x$
Equilibrium	$0.04375 - x$	x	$0.084375 + x$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.084375 + x)}{(0.04375 - x)} \cong \frac{(x)(0.084375)}{(0.04375)} = 6.8 \times 10^{-4}$$

$x = [H_3O^+] = 3.\underline{5}2 \times 10^{-4}\ M$

$pH = -\log [H_3O^+] = -\log (3.52 \times 10^{-4}) = 3.4\underline{5}3 = 3.45$

16.76. Find the mol/L of NH_3 and the mol/L of NH_4^+, and assemble the usual table. Substitute the equilibrium concentrations into the equilibrium-constant expression; then, assume x is negligible compared to the starting concentrations of both NH_3 and NH_4^+. Solve for x in the numerator of the equilibrium-constant expression, and calculate the pH from this value.

Total volume = 0.115 L + 0.145 L = 0.260 L

(0.30 mol NH_3/L) x 0.115 L = 0.0345 mol NH_3 (÷ 0.260 L total vol = 0.1327 *M*)

(0.15 mol NH_4^+/L) x 0.145 L = 0.02175 mol NH_4^+ (÷ 0.260 L total vol = 0.08365 *M*)

Now, substitute these starting concentrations into the usual table:

Conc. (*M*)	$NH_3 + H_2O \rightleftharpoons$	$NH_4^+ +$	F^-
Starting	0.1327	00.8365	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.1327 - x$	$0.08365 + x$	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.08365 + x)(x)}{(0.1327 - x)} \cong \frac{(0.08365)(x)}{(0.1327)} = 1.8 \times 10^{-5}$$

$x = [OH^-] = 2.\underline{8}55 \times 10^{-5}\ M$

$pOH = -\log [OH^-] = -\log (2.855 \times 10^{-5}) = 4.5\underline{4}4$

$pH = 14.00 - 4.544 = 9.4\underline{5}6 = 9.46$

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16.77. First, use the 0.10 *M* NH_3 and 0.10 *M* NH_4^+ to calculate the $[OH^-]$ and pH before HCl is added. Assemble a table of starting, change, and equilibrium concentrations. Assume x is negligible compared to 0.10 *M*, and substitute the approximate concentrations into the equilibrium-constant expression.

Conc. (*M*)	$NH_3 + H_2O$ ⇌	NH_4^+	+	OH^-
Starting	0.10	0.10		0
Change	$-x$	$+x$		$+x$
Equilibrium	$0.10 - x$	$0.10 + x$		x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.10 + x)(x)}{(0.10 - x)} \cong \frac{(0.10)(x)}{(0.10)} = 1.8 \times 10^{-5}$$

$x = [OH^-] = 1\ 8 \times 10^{-5}\ M$

$pOH = -\log [OH^-] = -\log (1.8 \times 10^{-5}) = 4.744$

$pH = 14.00 - pOH = 14.00 - 4.744 = 9.2552 = 9.26$ (before HCl added)

Now, calculate the pH after the 0.012 L (12 mL) of 0.20 *M* HCl is added by noting that the H_3O^+ ion reacts with the NH_3 to form additional NH_4^+. Calculate the stoichiometric amount of HCl; then subtract the moles of HCl from the moles of NH_3. Add the resulting moles of NH_4^+ to the 0.0125 starting moles of NH_4^+ in the 0.125 L of buffer.

(0.20 mol HCl/L) x 0.012 L = 0.0024 mol HCl (reacts with 0.0024 mol NH_3)

mol NH_3 left = (0.0125 − 0.0024) mol = 0.0101 mol

mol NH_4^+ present = (0.0125 + 0.0024) mol = 0.0149 mol

The concentrations of NH_3 and NH_4^+ are

$$[NH_3] = \frac{0.0101\ \text{mol}\ NH_3}{0.137\ \text{L}} = 0.0737\ M$$

$$[NH_4^+] = \frac{0.0149\ \text{mol}\ NH_3}{0.137\ \text{L}} = 0.108\ M$$

Now, account for the ionization of NH_3 to NH_4^+ and OH^- at equilibrium by assembling the usual table. Assume x is negligible compared to 0.0737 *M* and 0.108 *M*, and solve the equilibrium-constant expression for x in the numerator. Calculate the pH from x, the $[OH^-]$.

Conc. (*M*)	$NH_3 + H_2O$ ⇌	NH_4^+	+	OH^-
Starting	0.0737	0.108		0
Change	$-x$	$+x$		$+x$
Equilibrium	$0.0737 - x$	$0.108 + x$		x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.108 + x)(x)}{(0.0737 - x)} \cong \frac{(0.108)(x)}{(0.0737)} = 1.8 \times 10^{-5}$$

$x = [OH^-] \cong 1.22 \times 10^{-5}\ M$

$pOH = -\log [OH^-] = -\log (1.22 \times 10^{-5}) = 4.913$

$pH = 14.00 - pOH = 14.00 - 4.913 = 9.086 = 9.09$ (after HCl added)

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16.78. First, use the 0.525 L of 0.50 *M* $HCHO_2$ (HFo) and 0.475 L of 0.50 *M* $NaCHO_2$ (Na^+Fo^-) to calculate the $[H_3O^+]$ and pH before HCl is added. Assemble a table of starting, change, and equilibrium concentrations. Assume *x* is negligible compared to both concentrations; substitute into the K_a expression.

0.50 *M* HFo x 0.525 L = 0.263 mol HFo (÷ 1.00 L = 0.2<u>6</u>3 *M*)

0.50 *M* Fo^- x 0.475 L = 0.238 mol Fo^- (÷ 1.00 L = 0.2<u>3</u>8 *M*)

Set up the table:

Conc. (*M*)	HFo + H_2O ⇌	H_3O^+ +	Fo^-
Starting	0.263	0	0.238
Change	$-x$	$+x$	$+x$
Equilibrium	$0.263 - x$	x	$0.238 + x$

$$K_a = \frac{[H_3O^+][Fo^-]}{[HFo]} = \frac{(x)(0.238 + x)}{(0.263 - x)} \cong \frac{(x)(0.238)}{(0.263)} = 1.7 \times 10^{-4}$$

$x = [H_3O^+] = 1.\underline{8}8 \times 10^{-4}$ *M*

pH = − log $[H_3O^+]$ = − log (1.88×10^{-4}) = 3.7<u>2</u>6 = 3.73 (before HCl added)

Now, calculate the pH after the 0.0086 L (8.6 mL) of 0.15 *M* HCl is added by noting that the H_3O^+ ion reacts with the Fo^- to form additional HFo. Calculate the stoichiometric amount of HCl; then subtract the moles of HCl from the moles of Fo^-. Add the resulting moles of HFo to the 0.02227 starting moles of HFo in the 0.086 L of buffer.

(0.15 mol HCl/L) x 0.0086 L = 0.00129 mol HCl (reacts with 0.00129 mol Fo^-)

mol Fo^- left = (0.02023 − 0.00129) mol = 0.01894 mol Fo^-

mol HFo present = (0.02227 + 0.00129) = 0.02356 mol HFo

The concentrations of HFo and Fo^- are

$$[HFo] = \frac{0.02356 \text{ mol HFo}}{0.0936 \text{ L}} = 0.2\underline{5}17 \text{ } M$$

$$[Fo^-] = \frac{0.01894 \text{ mol } Fo^-}{0.0936 \text{ L}} = 0.2\underline{0}25 \text{ } M$$

Now, account for the ionization of HFo to H_3O^+ and Fo^- at equilibrium by assembling the usual table. Assume *x* is negligible compared to 0.2517 *M* and 0.2025M, and solve the equilibrium-constant expression for *x* in the numerator. Calculate the pH from *x*, the $[H_3O^+]$.

Conc. (*M*)	HFo + H_2O ⇌	H_3O^+ +	Fo^-
Starting	0.2517	0	0.2025
Change	$-x$	$+x$	$+x$
Equilibrium	$0.2517 - x$	x	$0.2025 + x$

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Substitute into the equilibrium-constant equation to get

$$K_a = \frac{[H_3O^+]\,[Fo^-]}{[HFo]} = \frac{(x)(0.2025 + x)}{(0.2517 - x)} \cong \frac{(x)(0.2025)}{(0.2517)} = 1.7 \times 10^{-4}$$

$$x = [H_3O^+] = 2.\underline{1}1 \times 10^{-4}\ M$$

$$\text{pH} = -\log [H_3O^+] = -\log (2.11 \times 10^{-4}) = 3.6\underline{7}57 = 3.68 \text{ (after HCl added)}$$

16.79. Use the Henderson-Hasselbalch equation, where $pK_a = -\log K_a$.

$$\text{pH} = -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]}$$

$$= -\log (1.3 \times 10^{-3}) + \log \frac{(0.10\ M)}{(0.15\ M)} = 2.7\underline{1}0 = 2.71$$

16.80. Use the Henderson-Hasselbalch equation ($pK_a = -\log K_a$), and do the calculations in one step.

$$\text{pH} = -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]}$$

$$= -\log (1.3 \times 10^{-5}) + \log \frac{(0.20\ M)}{(0.10\ M)} = 5.1\underline{8}7 = 5.19$$

16.81. Calculate the K_a of the pyridinium ion from the K_b of pyridine, and then use the Henderson-Hasselbalch equation, where $pK_a = -\log K_a$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.\underline{1}4 \times 10^{-6}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]}$$

$$= -\log (7.14 \times 10^{-6}) + \log \frac{(0.15\ M)}{(0.10\ M)} = 5.3\underline{2}2 = 5.32$$

16.82. Calculate the K_a of the methylammonium ion from the K_b of methylamine, and then use the Henderson-Hasselbalch equation, where $pK_a = -\log K_a$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.\underline{2}7 \times 10^{-11}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]}$$

$$= -\log (2.27 \times 10^{-11}) + \log \frac{(0.15\ M)}{(0.20\ M)} = 10.5\underline{1}8 = 10.5$$

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16.83. Symbolize acetic acid as HOAc and sodium acetate as Na^+OAc^-. Use the Henderson-Hasselbalch equation to find the log of $[OAc^-]/[HOAc]$. Then solve for $[OAc^-]$ and for moles of NaOAc in the 2.0 L of solution.

$$pH = -\log K_a + \log \frac{[OAc^-]}{[HOAc]} = 5.00$$

$$5.00 = -\log (1.7 \times 10^{-5}) + \log \frac{[OAc^-]}{(0.10\ M)}$$

$$5.00 = 4.770 + \log [OAc^-] - \log (0.10)$$

$$\log[OAc^-] = 5.00 - 4.770 - 1.00 = -0.770$$

$$[OAc^-] = 0.1698\ M$$

$$\text{mol NaOAc} = 0.1698 \text{ mol/L} \times 2.0 \text{ L} = 0.3396 = 0.34 \text{ mol}$$

16.84. Use the Henderson-Hasselbalch equation to find the log of $[F^-]/[HF]$. Then solve for [HF] and for moles of HF in the 0.5000 L of solution.

$$pH = -\log K_a + \log \frac{[F^-]}{[HF]} = 3.50$$

$$3.50 = -\log (6.8 \times 10^{-4}) + \log \frac{(0.25\ M)}{[HF]}$$

$$3.50 = 3.167 + \log [0.25] - \log [HF]$$

$$\log [HF] = 3.167 - 0.602 - 3.50 = -0.9345$$

$$[HF] = 0.1162\ M$$

$$\text{mol HF} = 0.1162 \text{ mol/L} \times 0.5000 \text{ L} = 0.0581 = 0.058 \text{ mol HF}$$

16.85. All the OH^- (from the NaOH) reacts with the H_3O^+ from HCl. Calculate the stoichiometric amounts of OH^- and H_3O^+, and subtract the moles of OH^- from the moles of H_3O^+. Next, divide the remaining H_3O^+ by the total volume of 0.015 L + 0.025 L, or 0.040 L, to find the $[H_3O^+]$. Then calculate the pH.

$$\text{mol } H_3O^+ = (0.10 \text{ mol HCl/L}) \times 0.025 \text{ L HCl} = 0.0025 \text{ mol } H_3O^+$$

$$\text{mol } OH^- = (0.10 \text{ mol NaOH/L}) \times 0.015 \text{ L NaOH} = 0.0015 \text{ mol } OH^-$$

$$\text{mol } H_3O^+ \text{ left} = (0.0025 - 0.0015) \text{ mol } H_3O^+ = 0.0010 \text{ mol } H_3O^+$$

$$[H_3O^+] = 0.0010 \text{ mol } H_3O^+ \div 0.040 \text{ L total volume} = 0.0250\ M$$

$$pH = -\log [H_3O^+] = -\log (0.0250) = 1.602 = 1.60$$

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16.86. All the H^+ (from the HCl) reacts with the OH^- from NaOH. Calculate the stoichiometric amounts of OH^- and H_3O^+, and subtract the moles of H_3O^+ from the moles of OH^-. Next, divide the remaining OH^- by the total volume of 0.040 L + 0.025 L, or 0.065 L, to find the $[OH^-]$. Then calculate the pOH and pH.

mol OH^- = (0.10 mol NaOH/L) x 0.040 L NaOH = 0.0040 mol OH^-

mol H_3O^+ = (0.10 mol HCl/L) x 0.025 L HCl = 0.0025 mol H_3O^+

mol OH^- left = (0.0040 − 0.0025) mol OH^- = 0.0015 mol OH^-

$[OH^-]$ = 0.0015 mol OH^- ÷ 0.065 L total volume = 0.02<u>3</u>0 *M*

pOH = − log $[OH^-]$ = − log (0.0230) = 1.6<u>3</u>6

pH = 14.00 − pH = 14.00 − 1.636 = 12.3<u>6</u>3 = 12.37

16.87. Use HBen to symbolize benzoic acid and Ben^- to symbolize the benzoate anion. At the equivalence point, equal molar amounts of HBen and NaOH react to form a solution of NaBen. Start by calculating the moles of HBen. Use this to calculate the volume of NaOH needed to neutralize all of the HBen (and use the moles of HBen as the moles of Ben^- formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

mol HBen = 1.24 g HBen ÷ (122.1 g HBen/mol HBen) = 0.01016 mol HBen

Volume NaOH = 0.01016 mol NaOH ÷ (0.180 mol NaOH/L) = 0.056<u>4</u>4 L

Total volume = 0.05644 L + 0.050 L HBen soln = 0.10644 L

$[Ben^-]$ = (0.01016 mol Ben^- from HBen) ÷ 0.10644 L = 0.09545 *M*

Because the Ben^- hydrolyzes to OH^- and HBen, use this to calculate the $[OH^-]$. Start by calculating the K_b constant of Ben^- from the K_a of its conjugate acid, HBen. Then, assemble the usual table of concentrations, assume *x* is negligible, and calculate $[OH^-]$ and pH.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.\underline{5}9 \times 10^{-10}$$

Conc. (*M*)	Ben^- + H_2O $\rightleftharpoons$	HBen +	OH^-
Starting	0.09545	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	0.09545 $-x$	x	x

$$K_b = \frac{[HBen]\,[OH^-]}{[Ben^-]} = \frac{(x)^2}{(0.09545 - x)} \cong \frac{(x)^2}{(0.09545)} = 1.59 \times 10^{-10}$$

$x = [OH^-] = 3.\underline{8}95 \times 10^{-6}\ M$

pOH = − log $[OH^-]$ = − log (3.895×10^{-6}) = 5.4<u>0</u>94

pH = 14.00 − 5.4094 = 8.5<u>9</u>05 = 8.59

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16.88. Use HPr to symbolize propionic acid and Pr^- to symbolize the propionate anion. At the equivalence point, equal molar amounts of HPr and NaOH react to form a solution of NaPr. Start by calculating the moles of HPr. Use this to calculate the volume of NaOH needed to neutralize all of the HPr (and use the moles of HPr as the moles of Pr^- formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

mol HPr = 0.400 g HPr ÷ (74.08 g HPr/mol HPr) = 0.00540 mol HPr

Volume NaOH = 0.00540 mol NaOH ÷ (0.150 mol NaOH/L) = 0.03600 L

Total volume = 0.03600 L + 0.050 L HPr soln = 0.08600 L

$[Pr^-]$ = (0.00540 mol Pr^- from HPr) ÷ 0.08600 L = 0.06279 *M*

Because the Pr^- hydrolyzes to OH^- and HPr, use this to calculate the $[OH^-]$. Start by calculating the K_b constant of Pr^- from the K_a of its conjugate acid, HPr. Then assemble the usual table of concentrations, assume *x* is negligible, and calculate $[OH^-]$ and pH.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10}$$

Conc. (*M*)	$Pr^- + H_2O$ ⇌	HPr +	OH^-
Starting	0.06279	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.06279 - x$	x	x

$$K_b = \frac{[HPr]\,[OH^-]}{[Pr^-]} = \frac{(x)^2}{(0.06279 - x)} \cong \frac{(x)^2}{(0.06279)} = 7.69 \times 10^{-10}$$

$x = [OH^-] = 6.948 \times 10^{-6}\ M$

$pOH = -\log [OH^-] = -\log (6.948 \times 10^{-6}) = 5.158$

$pH = 14.00 - 5.158 = 8.841 = 8.84$

16.89. Use EtN to symbolize ethylamine and $EtNH^+$ to symbolize the ethylammonium cation. At the equivalence point, equal molar amounts of EtN and HCl react to form a solution of EtNHCl. Start by calculating the moles of EtN. Use this to calculate the volume of HCl needed to neutralize all of the EtN (and use the moles of EtN as the moles of $EtNH^+$ formed at the equivalence point). Add the volume of HCl to the original 0.032 L to find the total volume of solution.

(0.087 mol EtN/L) x 0.032 L = 0.00278 mol EtN

Volume HCl = 0.00278 mol HCl ÷ (0.15 mol HCl/L) = 0.0185 L

Total volume = 0.0185 L + 0.032 L EtN soln = 0.0505 L

$[EtNH^+]$ = (0.00278 mol $EtNH^+$ from EtN) ÷ 0.0505 L = 0.0550 *M*

Because the $EtNH^+$ hydrolyzes to H_3O^+ and EtN, use this to calculate the $[H_3O^+]$. Start by calculating the K_a constant of $EtNH^+$ from the K_b of its conjugate base, EtN. Then assemble the usual table of concentrations, assume *x* is negligible, and calculate $[H_3O^+]$ and pH.

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$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-4}} = 2.\underline{1}3 \times 10^{-11}$$

Conc. (M)	$EtNH^+ + H_2O$	$\rightleftharpoons$	$EtN + H_3O^+$
Starting	0.0550		0 0
Change	$-x$		$+x$ $+x$
Equilibrium	$0.0550 - x$		x x

$$K_a = \frac{[EtN]\,[H_3O^+]}{[EtNH^+]} = \frac{(x)^2}{(0.0550 - x)} \cong \frac{(x)^2}{(0.0550)} = 2.13 \times 10^{-11}$$

$x = [H_3O^+] = 1.\underline{0}8 \times 10^{-6}\ M$

$pH = -\log [H_3O^+] = -\log (1.08 \times 10^{-6}) = 5.9\underline{6}56 = 5.97$

16.90. Use HyN to symbolize hydroxylamine and $HyNH^+$ to symbolize the hydroxylammonium cation. At the equivalence point, equal molar amounts of HyN and HCl react to form a solution of HyNHCl. Start by calculating the moles of HyN. Use this to calculate the volume of HCl needed to neutralize all of the HyN (and use the moles of HyN as the moles of $HyNH^+$ formed at the equivalence point). Add volumes.

(0.20 mol HyN/L) x 0.022 L = 0.00440 mol HyN

Volume HCl = 0.00440 mol HCl ÷ (0.15 mol HCl/L) = 0.0293 L

Total volume = 0.0293 L + 0.022 L HyN soln = 0.0513 L

$[HyNH^+]$ = (0.00440 mol $HyNH^+$ from HyN) ÷ 0.0513 L = 0.0858 M

Use $HyNH^+$ hydrolysis to calculate the $[H_3O^+]$. Calculate the K_a constant of $HyNH^+$ from the K_b of HyN. Assemble the concentration table, assume x is negligible, and calculate $[H_3O^+]$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.\underline{0}9 \times 10^{-7}$$

Conc. (M)	$HyNH^+ + H_2O$	$\rightleftharpoons$	$HyN + H_3O^+$
Starting	0.0858		0 0
Change	$-x$		$+x$ $+x$
Equilibrium	$0.0858 - x$		x x

$$K_a = \frac{[HyN]\,[H_3O^+]}{[HyNH^+]} = \frac{(x)^2}{(0.0858 - x)} \cong \frac{(x)^2}{(0.0858)} = 9.09 \times 10^{-7}$$

$x = [H_3O^+] = 2.\underline{7}9 \times 10^{-4}\ M$

$pH = -\log [H_3O^+] = -\log (2.79 \times 10^{-4}) = 3.5\underline{5}4 = 3.55$

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16.91.

a. Assemble the usual table of concentrations.

Conc. (M)	$CN^- + H_2O \rightleftharpoons$	$HCN + OH^-$
Starting	0.100	0
Change	$-x$	$+x$
Equilibrium	$0.100 - x$	x

Now substitute into the equilibrium expression, assume x is negligible compared to 0.100 M, and calculate $[OH^-]$.

$$K_b = \frac{(x)^2}{(0.100 - x)} = \frac{(x)^2}{(0.100)} = 2.0 \times 10^{-5}$$

$$x = [OH^-] = 1.\underline{4}14 \times 10^{-3}\ M$$

Finally, calculate the pOH and then the pH.

$$pOH = -\log [OH^-] = -\log (1.414 \times 10^{-3}) = 2.8\underline{9}4$$

$$pH = 14.00 - 2.894 = 11.1\underline{5}0 = 11.15$$

b. After 15.0 mL of 0.200 M HCl is added. The reaction is

$$CN^- + H_3O^+ \rightarrow HCN + H_2O$$

The total volume at this point is 50.0 mL + 15.0 mL = 65.0 mL.

The moles of CN^- present at the start and the moles of HCl added are

$$\text{mol } CN^- = M \times V = 0.100\ M \times 50.0 \times 10^{-3}\ \text{L} = 5.0\underline{0}0 \times 10^{-3}\ \text{mol}$$

$$\text{mol HCl} = M \times V = 0.200\ M \times 15.0 \times 10^{-3}\ \text{L} = 3.0\underline{0}0 \times 10^{-3}\ \text{mol}$$

After reaction the moles of HCN equal the moles of added HCl. The moles of CN^- present are

$$\text{mol } CN^- = 5.000 \times 10^{-3}\ \text{mol} - 3.000 \times 10^{-3} = 2.0\underline{0}0 \times 10^{-3}\ \text{mol}$$

Now calculate the concentrations.

$$[CN^-] = \frac{2.000 \times 10^{-3}\ \text{mol } CN^-}{65.0 \times 10^{-3}\ \text{L}} = 0.030\underline{7}6\ M$$

$$[HCN] = \frac{3.000 \times 10^{-3}\ \text{mol HCN}}{65.0 \times 10^{-3}\ \text{L}} = 0.046\underline{1}5\ M$$

Substitute into the K_b expression and solve for $x = [OH^-]$.

$$K_b = 2.0 \times 10^{-5} = \frac{[HCN]\,[OH^-]}{[CN^-]} = \frac{(0.04615 + x)(x)}{(0.03076 - x)} \cong \frac{(0.04615)(x)}{(0.03076)}$$

$$x = [OH^-] = \frac{(0.03076)(2.0 \times 10^{-5})}{(0.04615)} = 1.\underline{3}3 \times 10^{-5}\ M$$

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Now calculate the pOH and finally the pH.

$$\text{pOH} = -\log (1.33 \times 10^{-5}) = 4.875$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.875 = 9.124 = 9.12$$

c. First calculate the volume of HCl added to reach the equivalence point.

$$V_2 = \frac{M_1 V_1}{M_2} = \frac{(0.100\ M)(50.0\ \text{mL})}{(0.200\ M)} = 25.00\ \text{mL}$$

The total volume at this point is 50.0 mL + 25.0 mL = 75.0 mL. The equilibrium is now

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

The moles of HCN present are the same as the moles of CN^- present initially, 5.00×10^{-3} mol. The concentration is

$$[HCN] = \frac{5.000 \times 10^{-3}\ \text{mol HCN}}{75.0 \times 10^{-3}\ \text{L}} = 0.0666\ M$$

Calculate the value of K_a from K_b, set up the equilibrium expression, and solve.

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{2.0 \times 10^{-5}} = 5.00 \times 10^{-10}$$

$$K_a = 5.00 \times 10^{-10} = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{x^2}{(0.0666 - x)}$$

$$x = [H_3O^+] = 5.773 \times 10^{-6}\ M$$

$$\text{pH} = -\log (5.773 \times 10^{-6}) = 5.238 = 5.24$$

d. After the addition of 30.0 mL HCl. The volume at this point is 50.0 mL + 30.0 mL = 80.0 mL. Now calculate the molarity of the excess H_3O^+.

$$\text{mol HCl added} = M \times V = (0.200\ M)(30.0 \times 10^{-3}\ \text{L}) = 6.000 \times 10^{-3}\ \text{mol}$$

$$\text{Excess mol HCl} = 6.000 \times 10^{-3}\ \text{mol} - 5.000 \times 10^{-3}\ \text{mol} = 1.000 \times 10^{-3}\ \text{mol}$$

$$[H_3O^+] = \frac{1.000 \times 10^{-3}\ \text{mol HCl}}{80.0 \times 10^{-3}\ \text{L}} = 0.012500\ M$$

Finally, calculate the pH

$$\text{pH} = -\log (0.01250) = 1.903 = 1.90$$

16.92.

a. Assemble the usual table of concentrations.

Conc. (M)	$C_7H_5O_2^-$ + H_2O $\rightleftharpoons$	$HC_7H_5O_2$ +	OH^-
Starting	0.250	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.250 - x$	x	x

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Now substitute into the equilibrium expression, assume x is negligible compared to 0.250 M, and calculate $[OH^-]$.

$$K_b = \frac{(x)^2}{(0.250 - x)} = \frac{(x)^2}{(0.250)} = 1.6 \times 10^{-10}$$

$$x = [OH^-] = 6.\underline{3}24 \times 10^{-6}\ M$$

Finally, calculate the pOH and then the pH.

$$pOH = -\log [OH^-] = -\log (6.324 \times 10^{-6}) = 5.1\underline{9}8$$

$$pH = 14.00 - 5.198 = 8.8\underline{0}1 = 8.80$$

b. After 50.0 mL of 0.200 M HBr is added. The reaction is

$$C_7H_5O_2^- + H_3O^+ \rightarrow HC_7H_5O_2 + H_2O$$

The total volume at this point is 50.0 mL + 50.0 mL = 100.0 mL.

The moles of $C_7H_5O_2^-$ present at the start and the moles of HBr added are

$$\text{mol } C_7H_5O_2^- = M \times V = 0.250\ M \times 50.0 \times 10^{-3}\ \text{L} = 0.012\underline{5}0 \text{ mol}$$

$$\text{mol HBr} = M \times V = 0.200\ M \times 50.0 \times 10^{-3}\ \text{L} = 0.010\underline{0}0 \text{ mol}$$

After reaction, the moles of $HC_7H_5O_2$ equal the moles of added HBr. The moles of $C_7H_5O_2^-$ present are

$$\text{mol } C_7H_5O_2^- = 0.01250 \text{ mol} - 0.01000 = 2.5\underline{0}0 \times 10^{-3} \text{ mol}$$

Now calculate the concentrations.

$$[C_7H_5O_2^-] = \frac{2.500 \times 10^{-3} \text{ mol}}{0.1000 \text{ L}} = 0.025\underline{0}0\ M$$

$$[HC_7H_5O_2] = \frac{0.01000 \text{ mol}}{0.1000 \text{ L}} = 0.10\underline{0}0\ M$$

Substitute into the K_b expression and solve for $x = [OH^-]$.

$$K_b = 1.6 \times 10^{-10} = \frac{(0.1000 + x)(x)}{(0.02500 - x)} \cong \frac{(0.1000)(x)}{(0.02500)}$$

$$x = [OH^-] = \frac{(0.02500)(1.6 \times 10^{-10})}{(0.1000)} = 4.\underline{0}0 \times 10^{-11}\ M$$

Now calculate the pOH and finally the pH.

$$pOH = -\log (4.00 \times 10^{-11}) = 10.3\underline{9}7$$

$$pH = 14.00 - pOH = 14.00 - 4.875 = 10.397 = 3.6\underline{0}2 = 3.60$$

c. First calculate the volume of HBr added to reach the equivalence point.

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(0.250\ M)(50.0 \text{ mL})}{(0.200\ M)} = 62.\underline{5}0 \text{ mL}$$

The total volume at this point is 50.0 mL + 62.50 mL = 112.5 mL. The equilibrium is now

$$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$$

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The moles of $HC_7H_5O_2$ present are the same as the moles of $C_7H_5O_2^-$ present initially, 0.01250 mol. The concentration is

$$[HC_7H_5O_2] = \frac{0.01250 \text{ mol}}{0.1125 \text{ L}} = 0.1111\ M$$

Calculate the value of K_a from K_b, set up the equilibrium expression, and solve.

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.6 \times 10^{-10}} = 6.25 \times 10^{-5}$$

$$K_a = 6.25 \times 10^{-5} = \frac{[C_7H_5O_2^-][H_3O^+]}{[HC_7H_5O_2]} = \frac{x^2}{(0.1111 - x)}$$

$$x = [H_3O^+] = 2.635 \times 10^{-3}\ M$$

$$\text{pH} = -\log (2.635 \times 10^{-6}) = 2.579 = 2.58$$

d. After the addition of 75.00 mL HBr. The volume at this point is 50.0 mL + 75.00 mL = 125.00 mL. Now calculate the molarity of the excess H_3O^+.

$$\text{mol HBr added} = M \times V = (0.200\ M)(75.00 \times 10^{-3}\ \text{L}) = 0.01500 \text{ mol}$$

$$\text{Excess mol HCl} = 0.01500 \text{ mol} - 0.01250 \text{ mol} = 2.500 \times 10^{-3} \text{ mol}$$

$$[H_3O^+] = \frac{2.500 \times 10^{-3} \text{ mol}}{0.1250 \text{ L}} = 0.0200\ M$$

Finally, calculate the pH.

$$\text{pH} = -\log (0.02000) = 1.698 = 1.70$$

16.93. Calculate the stoichiometric amounts of NH_3 and HCl, which forms NH_4^+. Then divide NH_3 and NH_4^+ by the total volume of 0.500 L + 0.200 L = 0.700 L to find the starting concentrations. Calculate the $[OH^-]$, the pOH, and the pH.

$$\text{mol } NH_3 = (0.10 \text{ mol } NH_3/\text{L}) \times 0.500 \text{ L} = 0.0500 \text{ mol } NH_3$$

$$\text{mol HCl} = (0.15 \text{ mol HCl/L}) \times 0.200 \text{ L} = 0.0300 \text{ mol HCl } (0.0300 \text{ mol } NH_4^+)$$

$$\text{mol } NH_3 \text{ left} = 0.0500 \text{ mol} - 0.0300 \text{ mol HCl} = 0.0200 \text{ mol } NH_3$$

$$0.0200 \text{ mol } NH_3 \div 0.700 \text{ L} = 0.0286\ M\ NH_3$$

$$0.0300 \text{ mol } NH_4^+ \div 0.700 \text{ L} = 0.0429\ M\ NH_4^+$$

Conc. (M)	$NH_3 + H_2O$ $\rightleftharpoons$	NH_4^+ +	OH^-
Starting	0.0286	0.0429	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0286 - x$	$0.0429 + x$	x

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$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = \frac{(0.0429 + x)(x)}{(0.0286 - x)} \cong \frac{(0.0429)(x)}{(0.0286)} = 1.8 \times 10^{-5}$$

$x = [OH^-] = 1.\underline{2}0 \times 10^{-5}\ M$

$pOH = -\log [OH^-] = -\log (1.20 \times 10^{-5}) = 4.9\underline{2}0$

$pH = 14.00 - pOH = 14.00 - 4.920 = 9.0\underline{7}9 = 9.08$

16.94. Use the symbols HAc for acetic acid and Ac^- for the acetate ion from sodium acetate. Calculate the stoichiometric amounts of HAc and Ac^-. Then divide the HAc and Ac^- by the total volume of 0.035 L + 0.025 L, or 0.060 L, to find the starting concentrations. Calculate the $[H_3O^+]$ and pH.

mol HAc = (0.15 mol HAc/L) x 0.035 L HAc = 0.00525 mol HAc

mol Ac^- = (0.10 mol NaAc/L) x 0.025 L NaAc = 0.00250 mol Ac^-

0.00525 mol HAc ÷ 0.060 L = 0.0875 *M* HAc

0.00250 mol Ac^- ÷ 0.060 L = 0.0417 *M* Ac^-

Set up a table.

Conc. (*M*)	HAc + H_2O	$\rightleftharpoons$	H_3O^+ +	Ac^-
Starting	0.0875		0	0.0417
Change	$-x$		$+x$	$+x$
Equilibrium	$0.0875 - x$		x	$0.0417 + x$

$$K_a = \frac{[H_3O^+]\,[Ac^-]}{[HAc]} = \frac{(0.0417 + x)(x)}{(0.0875 - x)} \cong \frac{(0.0417)(x)}{(0.0875)} = 1.7 \times 10^{-5}$$

$[H_3O^+] \cong 3.\underline{5}7 \times 10^{-5}\ M$

$pH = -\log [H_3O^+] = -\log (3.57 \times 10^{-5}) = 4.4\underline{4}7 = 4.45$

■ SOLUTIONS TO GENERAL PROBLEMS

16.95. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HSal to symbolize salicylic acid, and use Sal^- for the anion. Begin by converting pH to $[H_3O^+]$:

$[H_3O^+]$ = antilog (−pH) = antilog (−2.43) = $3.72 \times 10^{-3}\ M$

Starting *M* of HSal = (2.2 g ÷ 138 g/mol) ÷ 1.00 L = 0.01$\underline{5}$9 *M*

Conc. (*M*)	HSal + H_2O	$\rightleftharpoons$	H_3O^+ +	Sal^-
Starting	0.0159		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.0159 - x$		x	x

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The value of x equals the value of the molarity of the H_3O^+ ion, which is 3.72×10^{-3} M. Substitute into the equilibrium-constant expression to find K_a:

$$K_a = \frac{(x)^2}{(0.0159 - x)} = \frac{(3.72 \times 10^{-3})^2}{(0.0159 - 3.72 \times 10^{-3})} = 1.\underline{1}3 \times 10^{-3} = 1.1 \times 10^{-3}$$

16.96. To solve, assemble a table of starting, change, and equilibrium concentrations. Use HCyn to symbolize cyanoacetic acid, and use Cyn^- for the anion. Begin by converting pH to $[H_3O^+]$:

$[H_3O^+]$ = antilog (−pH) = antilog (−1.89) = $1.\underline{2}9 \times 10^{-2}$ M

Starting M of HCyn = (5.0g ÷ 85.1 g/mol) ÷ 1.00 L = 0.0588 M

Conc. (M)	HCyn + H_2O ⇌	H_3O^+ +	Cyn^-
Starting	0.0588	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0588 - x$	x	x

The value of x equals the value of the molarity of the H_3O^+ ion, which is 1.29×10^{-2} M. Substitute into the equilibrium-constant expression to find K_a:

$$K_a = \frac{(x)^2}{(0.0588 - x)} = \frac{(1.29 \times 10^{-2})^2}{(0.0588 - 1.29 \times 10^{-2})} = 3.\underline{6}2 \times 10^{-3} = 3.6 \times 10^{-3}$$

16.97. To solve, assemble a table of starting, change, and equilibrium concentrations. Begin by converting pH to $[H_3O^+]$:

$[H_3O^+]$ = antilog (−pH) = antilog (−1.73) = 1.86×10^{-2} M

Starting M of HSO_4^- = 0.050 M

Conc. (M)	HSO_4^- + H_2O ⇌	H_3O^+ +	SO_4^{2-}
Starting	0.050	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.050 - x$	x	x

The value of x equals the value of the molarity of the H_3O^+ ion, which is 1.86×10^{-2} M. Substitute into the equilibrium-constant expression to find K_{a_2}:

$$K_{a_2} = \frac{(x)^2}{(0.050 - x)} = \frac{(1.86 \times 10^{-2})^2}{(0.050 - 1.86 \times 10^{-2})} = 1.\underline{1}0 \times 10^{-2} = 1.1 \times 10^{-2}$$

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16.98. To solve, assemble a table of starting, change, and equilibrium concentrations. Begin by converting pH to $[H_3O^+]$:

$$[H_3O^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-4.10) = 7.94 \times 10^{-5}\ M$$

Starting M of $H_2PO_4^-$ = 0.10 M

Conc. (M)	$H_2PO_4^-$ + H_2O ⇌	H_3O^+ +	HPO_4^{2-}
Starting	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

The value of x equals the value of the molarity of the H_3O^+ ion, which is $7.94 \times 10^{-5}\ M$. Substitute into the equilibrium-constant expression to find K_{a_2}:

$$K_{a_2} = \frac{(x)^2}{(0.10 - x)} = \frac{(7.94 \times 10^{-5})^2}{(0.10 - 7.94 \times 10^{-5})} = 6.\underline{3}04 \times 10^{-8} = 6.3 \times 10^{-8}$$

16.99. For the base ionization (hydrolysis) of CN^- to HCN + OH^-, the base-ionization constant is

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.\underline{0}4 \times 10^{-5} = 2.0 \times 10^{-5}$$

For the base ionization (hydrolysis) of CO_3^{2-} to HCO_3^- + OH^-, the base-ionization constant is calculated from the ionization constant (K_{a_2}) of HCO_3^-, the conjugate acid of CO_3^{2-}.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.\underline{0}8 \times 10^{-4} = 2.1 \times 10^{-4}$$

Because the constant of CO_3^{2-} is larger, it is the stronger base.

16.100. For the base ionization (hydrolysis) of PO_4^{3-} to HPO_4^{2-} + OH^-, the base-ionization constant is calculated from the ionization constant (K_{a_3}) of HPO_4^{2-}, the conjugate acid of PO_4^{3-}.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 2.\underline{0}8 \times 10^{-2} = 2.1 \times 10^{-2}$$

For the base ionization (hydrolysis) of SO_4^{2-} to HSO_4^- + OH^-, the base-ionization constant is calculated from the ionization constant (K_{a_2}) of HSO_4^-, the conjugate acid of SO_4^{2-}.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.\underline{0}9 \times 10^{-13} = 9.1 \times 10^{-13}$$

Because the constant of PO_4^{3-} is larger, it is the stronger base.

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16.101. Assume Al^{3+} is $Al(H_2O)_6^{3+}$. Assemble the usual table to calculate the $[H_3O^+]$ and pH. Use the usual equilibrium-constant expression.

Conc. (*M*)	$Al(H_2O)_6^{3+}$ + H_2O ⇌	H_3O^+ +	$Al(H_2O)_5(OH)^{2+}$
Starting	0.15	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.15 - x$	x	x

$$K_a = \frac{[Al(H_2O)_5(OH)^{2+}][H_3O^+]}{[Al(H_2O)_6^{3+}]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 1.4 \times 10^{-5}$$

$$x = [H_3O^+] = 1.\underline{4}49 \times 10^{-3}\ M$$

$$pH = -\log [H_3O^+] = -\log (1.449 \times 10^{-3}) = 2.8\underline{3}8 = 2.84$$

16.102. Assume Zn^{2+} is $Zn(H_2O)_6^{2+}$. Assemble the usual table to calculate the $[H_3O^+]$ and pH.

Conc. (*M*)	$Zn(H_2O)_6^{2+}$ + H_2O ⇌	H_3O^+ +	$Zn(H_2O)_5(OH)^+$
Starting	0.15	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.15 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols and substitute.

$$K_a = \frac{[Zn(H_2O)_5(OH)^+][H_3O^+]}{[Zn(H_2O)_6^{2+}]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 2.5 \times 10^{-10}$$

$$x = [H_3O^+] = 6.\underline{1}2 \times 10^{-6}\ M$$

$$pH = -\log [H_3O^+] = -\log (6.12 \times 10^{-6}) = 5.2\underline{1}3 = 5.21$$

16.103. Calculate the concentrations of the tartaric acid (H_2Tar) and the hydrogen tartrate ion ($HTar^-$).

$$(11.0\ g\ H_2Tar \div 150.1\ g/mol) \div 1.00\ L = 0.07328\ M\ H_2Tar$$

$$(20.0\ g\ KHTar^- \div 188.2\ g/mol) \div 1.00\ L = 0.1063\ M\ [HTar^-]$$

Conc. (*M*)	H_2Tar + H_2O ⇌	H_3O^+ +	$HTar^-$
Starting	0.07328	0	0.1063
Change	$-x$	$+x$	$+x$
Equilibrium	$0.07328 - x$	x	$0.1063 + x$

Ignoring x compared to 0.07328 and 0.1063 and substituting into the K_{a_1} expression give

$$K_{a_1} = \frac{[H_3O^+]\,[HTar^-]}{[H_2Tar]} = \frac{(0.1063 + x)(x)}{(0.07328 - x)} \cong \frac{(0.1063)(x)}{(0.07328)} = 1.0 \times 10^{-3}$$

$$x = [H_3O^+] = 6.\underline{8}9 \times 10^{-4}\ M$$

$$pH = -\log [H_3O^+] = -\log (6.89 \times 10^{-4}) = 3.1\underline{6}1 = 3.16$$

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16.104. Calculate the concentrations of the dihydrogen phosphate ion ($H_2PO_4^-$) and the hydrogen phosphate ion (HPO_4^{2-}).

(13.0 g NaH_2PO_4 ÷ 120.0 g/mol) ÷ 1.00 L = 0.1082 *M* $H_2PO_4^-$

(15.0 g Na_2HPO_4 ÷ 142.0 g/mol) ÷ 1.00 L = 0.1056 *M* HPO_4^{2-}

Conc. (*M*)	$H_2PO_4^-$ + H_2O ⇌	H_3O^+ +	HPO_4^{2-}
Starting	0.1082	0	0.1056
Change	$-x$	$+x$	$+x$
Equilibrium	$0.1082 - x$	x	$0.1056 + x$

Ignoring *x* compared to 0.1082 and 0.1056 and substituting into the K_{a_1} expression give

$$K_{a_1} = \frac{[H_3O^+]\,[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(0.1056 + x)(x)}{(0.1082 - x)} \cong \frac{(0.1056)(x)}{(0.1082)} = 6.2 \times 10^{-8}$$

$x = [H_3O^+] = 6.\underline{3}5 \times 10^{-8}\ M$

$pH = -\log [H_3O^+] = -\log (6.353 \times 10^{-8}) = 7.1\underline{9}7 = 7.20$

16.105. Use the Henderson-Hasselbalch equation, where $[H_2CO_3]$ = the buffer acid, $[HCO_3^-]$ = the buffer base, and K_{a_1} of carbonic acid is the ionization constant.

$$pH = -\log K_a + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 7.40$$

$$7.40 = -\log (4.3 \times 10^{-7}) + \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\log \frac{[HCO_3^-]}{[H_2CO_3]} = 7.40 - 6.366 = 1.0\underline{3}4$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{10.81}{1} = \frac{11}{1}$$

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16.106. Use the Henderson-Hasselbalch equation, where $[C_{18}H_{21}NO_3]$ = [Cod] = the buffer base, and $[HC_{18}H_{21}NO_3^+]$ = $[HCod^+]$ = the buffer acid. The ionization constant is calculated as follows:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-9}} = 1.\underline{6}1 \times 10^{-6}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{Cod}]}{[HCod^+]} = 4.60$$

$$4.60 = -\log (1.61 \times 10^{-6}) + \log \frac{[\text{Cod}]}{[HCod^+]}$$

$$\log \frac{[\text{Cod}]}{[HCod^+]} = 4.60 - 5.793 = -1.1\underline{9}3$$

$$\log \frac{[HCod^+]}{[\text{Cod}]} = 1.193$$

$$\frac{[HCod^+]}{[\text{Cod}]} = \frac{15.6}{1} = \frac{16}{1}$$

16.107. All the OH^- (from the NaOH) reacts with the H_3O^+ from HCl. Calculate the stoichiometric amounts of OH^- and H_3O^+, and subtract the moles of OH^- from the moles of H_3O^+. Next, divide the remaining H_3O^+ by the total volume of 0.456 L + 0.285 L, or 0.741 L, to find the $[H_3O^+]$. Then calculate the pH.

mol H_3O^+ = (0.10 mol HCl/L) x 0.456 L HCl = 0.0456 mol H_3O^+

mol OH^- = (0.15 mol NaOH/L) x 0.285 L NaOH = 0.0428 mol OH^-

mol H_3O^+ left = (0.0456 − 0.0428) mol H_3O^+ = 0.0028 mol H_3O^+

$[H_3O^+]$ = 0.0028 mol H_3O^+ ÷ 0.741 L total volume = 0.00$\underline{3}$8 *M*

pH = − log $[H_3O^+]$ = − log (0.0038) = 2.$\underline{4}$2 = 2.4

16.108. All the H_3O^+ (from the $HClO_4$) reacts with the OH^- from KOH. Calculate the stoichiometric amounts of OH^- and H_3O^+, and subtract the moles of H_3O^+ from the moles of OH^-. Next, divide the remaining OH^- by the volume of 0.115 L to find the $[OH^-]$. Then calculate the pOH and pH.

mol OH^- = 2.0 g KOH ÷ (56.1 g KOH/mol KOH) = 0.03$\underline{5}$7 mol OH^-

mol H_3O^+ = (0.19 mol $HClO_4$/L) x 0.115 L HCl = 0.02$\underline{1}$9 mol H_3O^+

mol OH^- left = (0.0357 − 0.0219) mol OH^- = 0.01$\underline{3}$8 mol OH^-

$[OH^-]$ = 0.0138 mol OH^- ÷ 0.115 L volume = 0.1$\underline{2}$0 *M*

pOH = − log $[OH^-]$ = − log (0.120) = 0.9$\underline{2}$08

pH = 14.00 − pOH = 14.00 − 0.9208 = 13.0$\underline{7}$9 = 13.08

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16.109. Use BzN to symbolize benzylamine and $BzNH^+$ to symbolize the benzylammonium cation. At the equivalence point, equal molar amounts of BzN and HCl react to form a solution of BzNHCl. Start by calculating the moles of BzN. Use this number to calculate the volume of HCl needed to neutralize all the BzN (and use the moles of BzN as the moles of $BzNH^+$ formed at the equivalence point). Add the volume of HCl to the original 0.025 L to find the total volume of solution.

(0.025 mol BzN/L) x 0.065 L = 0.00162 mol BzN

Volume HCl = 0.00162 mol HCl ÷ (0.050 mol HCl/L) = 0.0324 L

Total volume = 0.025 L + 0.0324 L = 0.0574 L

$[BzNH^+]$ = (0.00162 mol $BzNH^+$ from BzN) ÷ 0.0574 L = 0.0282 *M*

Because the $BzNH^+$ hydrolyzes to H_3O^+ and BzN, use this to calculate the $[H_3O^+]$. Start by calculating the K_a constant of $BzNH^+$ from the K_b of its conjugate base, BzN. Then assemble the usual table of concentrations, assume x is negligible, and calculate $[H_3O^+]$ and pH.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-10}} = 2.13 \times 10^{-5}$$

Conc. (*M*)	$BzNH^+$ + H_2O ⇌	H_3O^+ +	BzN
Starting	0.0282	0	0.1056
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0282 - x$	x	$0.1056 + x$

Substitute into the equilibrium-constant equation.

$$K_a = \frac{[H_3O^+][BzN]}{[BzNH^+]} = \frac{(x)^2}{(0.0282 - x)} \cong \frac{(x)^2}{(0.0282)} = 2.13 \times 10^{-5}$$

$x = [H_3O^+] = 7.7502 \times 10^{-4}$ *M*

pH = − log $[H_3O^+]$ = − log (7.7502×10^{-4}) = 3.1106 = 3.11

16.110. At the equivalence point, equal molar amounts of HSO_4^- and NaOH react to form a solution of Na_2SO_4. Start by calculating the moles of HSO_4^-. Use this number to calculate the volume of NaOH needed to neutralize all the HSO_4^- (and use the moles of HSO_4^- as the moles of SO_4^{2-} formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

mol HSO_4^- = 1.24 g $NaHSO_4$ ÷ (120.1 g $NaHSO_4$/mol $NaHSO_4$) = 0.01032 mol HSO_4^-

Volume NaOH = 0.01032 mol NaOH ÷ (0.175 mol NaOH/L) = 0.05899 L

Total volume = 0.05899 L + 0.0500 L HSO_4^- soln = 0.1089 L

$[SO_4^{2-}]$ = (0.01032 mol SO_4^{2-} from HSO_4^-) ÷ 0.1089 L = 0.09468 *M*

Because the SO_4^{2-} hydrolyzes to OH^- and HSO_4^-, use this number to calculate the $[OH^-]$. Start by calculating the K_a constant of SO_4^{2-} from the K_a of its conjugate acid, HSO_4^-. Assemble the usual table of concentrations, assume x is negligible, and calculate $[OH^-]$ and pH.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.09 \times 10^{-13}$$

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Conc. (M)	SO_4^{2-} + H_2O	⇌	HSO_4^-	+	OH^-
Starting	0.09468		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	0.09468 − x		x		0

Substitute into the equilibrium-constant equation.

$$K_b = \frac{[HSO_4^-][OH^-]}{[SO_4^{2-}]} = \frac{(x)^2}{(0.09468 - x)} \cong \frac{(x)^2}{(0.09468)} = 9.09 \times 10^{-13}$$

$$x = [OH^-] = 2.\underline{9}3 \times 10^{-7}\ M$$

$$pOH = -\log\ [OH^-] = -\log (2.93 \times 10^{-7}) = 6.5\underline{3}2$$

$$pH = 14.00 - 6.532 = 7.4\underline{6}7 = 7.47$$

16.111.

a. $[H_3O^+] \cong 0.100\ M$

b. The 0.100 M H_2SO_4 ionizes to 0.100 M H_3O^+ and 0.100 M HSO_4^-. Assemble the usual table, and substitute into the K_{a_2} equilibrium-constant expression for H_2SO_4. Solve the resulting quadratic equation.

Conc. (M)	HSO_4^- + H_2O	⇌	H_3O^+	+	SO_4^{2-}
Starting	0.100		0.100		0
Change	$-x$		$+x$		$+x$
Equilibrium	0.100 − x		0.100 + x		0

$$x^2 + 0.111\,x - (1.10 \times 10^{-3}) = 0$$

$$x = \frac{-0.111 \pm \sqrt{(0.111)^2 + 4(1.10 \times 10^{-3})}}{2}$$

$$x = \frac{-0.111 \pm 0.1293}{2}$$

$$x = 9.\underline{1}54 \times 10^{-3}\ M$$

$$[H_3O^+] = 0.100 + x = 0.10\underline{0} + 0.009\underline{1}54 = 0.1\underline{0}9 = 0.11\ M$$

16.112.

a. $[H_3O^+] \cong 0.150\ M$

b. The 0.150 M H_2SeO_4 ionizes to 0.150 M H_3O^+ and 0.150 M $HSeO_4^-$. Assemble the usual table, and substitute into the K_{a_2} equilibrium-constant expression for H_2SeO_4. Solve the resulting quadratic equation.

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Set up the table.

Conc. (*M*)	$HSeO_4^-$ + H_2O	⇌	H_3O^+	+	SeO_4^{2-}
Starting	0.150		0.150		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.150 - x$		$0.150 + x$		0

$$x^2 + 0.162\,x - (1.80 \times 10^{-3}) = 0$$

$$x = \frac{-0.162 \pm \sqrt{(0.162)^2 + 4(1.8 \times 10^{-3})}}{2}$$

$$x = \frac{-0.162 \pm 0.1828}{2}$$

$$x = 1.\underline{0}4 \times 10^{-2}$$

$$[H_3O^+] = 0.150 + 0.0104 = 0.1\underline{6}04 = 0.16\ M$$

16.113.

a. From the pH, calculate the H_3O^+ ion concentration:

$$[H_3O^+] = 10^{-pH} = 10^{-5.82} = 1.\underline{5}1 \times 10^{-6}\ M$$

Use the table approach, giving the starting, change, and equilibrium concentrations.

Conc. (*M*)	$CH_3NH_3^+$ + H_2O	⇌	CH_3NH_2	+	H_3O^+
Starting	0.10		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.10 - x$		x		0

From the hydronium-ion concentration, $x = 1.51 \times 10^{-6}$. Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = \frac{(x)^2}{(0.10 - x)} \cong \frac{(1.51 \times 10^{-6})^2}{(0.10)} = 2.\underline{2}8 \times 10^{-11}$$

$$= 2.3 \times 10^{-11}$$

b. Now, use K_w to calculate the value of K_b:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.28 \times 10^{-11}} = 4.\underline{3}8 \times 10^{-4} = 4.4 \times 10^{-4}$$

c. The equilibrium concentration of $CH_3NH_3^+$ is approximately 0.450 mol/1.00 L = 0.450 *M*. Use $[CH_3NH_2] \cong 0.250\ M$. For K_a, we get

$$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} \cong \frac{(0.250)\,[H_3O^+]}{(0.450)} = 2.\underline{2}8 \times 10^{-11}$$

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Solving for $[H_3O^+]$ gives

$$[H_3O^+] \cong \frac{(2.28 \times 10^{-11})(0.450)}{(0.250)} = 4.\underline{1}0 \times 10^{-11}\ M$$

Thus, the pH is

$$pH = -\log (4.10 \times 10^{-11}) = 10.3\underline{8}7 = 10.39$$

16.114.

a. From the pOH, calculate the OH^- ion concentration:

$$[OH^-] = 10^{-pOH} = 10^{-5.31} = 4.\underline{9}0 \times 10^{-6}\ M$$

Use the table approach, giving the starting, change, and equilibrium concentrations.

Conc. (*M*)	$C_6H_5COO^-$ + H_2O ⇌	C_6H_5COOH +	OH^-
Starting	0.15	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.15 - x$	x	0

From the hydroxide-ion concentration, $x = 4.90 \times 10^{-6}$. Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[C_6H_5COOH]\,[OH^-]}{[C_6H_5COO^-]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(4.90 \times 10^{-6})^2}{(0.15)} = 1.\underline{6}0 \times 10^{-10}$$

$$= 1.6 \times 10^{-10}$$

b. Now, use K_w to calculate the value of K_a:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.60 \times 10^{-10}} = 6.\underline{2}5 \times 10^{-5} = 6.3 \times 10^{-5}$$

c. The reaction is

$$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$$

From the pH, calculate the H_3O^+ and $C_6H_5COO^-$ ion concentrations:

$$[C_6H_5COO^-] = [H_3O^+] = 10^{-pH} = 10^{-2.83} = 1.\underline{4}8 \times 10^{-3}\ M$$

Use the value of K_a to calculate the solubility of $C_6H_5COOH = y$.

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} = \frac{(1.48 \times 10^{-3})^2}{y} = 6.\underline{2}5 \times 10^{-5}$$

$$y = \frac{(1.48 \times 10^{-3})^2}{(6.25 \times 10^{-5})} = 0.03\underline{5}0\ M$$

The molar solubility will be the total dissolved benzoic acid, molecular and dissociated:

$$0.0350 + 0.00148 = 0.03\underline{6}48 = 0.036\ M$$

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16.115.

a. True. Weak acids have small K_a values, so most of the solute is present as undissociated molecules.

b. True. Weak acids have small K_a values, so most of the solute is present as the molecule.

c. False. The hydroxide concentration equals the hydronium concentration only in neutral solutions.

d. False. If HA were a strong acid, the pH would be equal to 2.

e. False. The H_3O^+ would be 0.010 *M* if HA were a strong acid.

f. True. For every HA molecule that dissociates, one H_3O^+ is generated along with one A^-.

16.116.

a. True. Approximately 1% or less of most weak bases reacts with water.

b. True. Very little base has reacted with water. For weak bases, most of the base is present as the molecule.

c. False. This is a basic solution, so there will be very little H_3O^+.

d. False. If B were a strong base, the $[OH^-]$ would be equal to 0.10 *M*.

e. True. $B + H_2O \rightleftharpoons BH^+ + OH^-$

f. False. Most B is present as B, so little OH^- is produced upon addition of the base to water.

16.117.

a. At the equivalence point, moles of acid equal moles of base. Thus,

$$\text{Moles of acid} = 0.115 \text{ mol/L} \times 0.03383 \text{ L} = 3.8\underline{9}0 \times 10^{-3}$$

The molar mass is

$$\text{Molar mass} = \frac{0.288 \text{ g}}{3.890 \times 10^{-3} \text{ mol}} = 74.\underline{0}4 = 74.0 \text{ g/mol}$$

b. At the 50% titration point, $pH = pK_a$. Since the pH measurement wasn't made, it is necessary to obtain an $[A^-]/[HA]$ ratio. The ratio can be in terms of moles, percent, mL, or *M* because the units end up canceling out. First, use the pH to obtain the H_3O^+ ion concentration. Express the other concentrations in milliliters for convenience.

$$[H_3O^+] = 10^{-4.92} = 1.\underline{2}0 \times 10^{-5} \, M$$

$$HA_0 \cong 33.83 \text{ mL}$$

$$[HA] \cong 33.83 - 17.54 = 16.29 \text{ mL}$$

$$[A^-] \cong [OH^-] = 17.54 \text{ mL}$$

$$K_a = [H_3O^+] \times \frac{[A^-]}{[HA]} = 1.20 \times 10^{-5} \, M \times \frac{17.54 \text{ mL}}{16.29 \text{ mL}} = 1.\underline{2}9 \times 10^{-5} = 1.3 \times 10^{-5}$$

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16.118.

a. At the equivalence point, moles of base equal moles of acid. Thus

Moles of base = 0.135 mol/L x 0.03924 L = $5.2\underline{9}7 \times 10^{-3}$

The molar mass is

$$\text{Molar mass} = \frac{0.239 \text{ g}}{5.297 \times 10^{-3} \text{ mol}} = 45.\underline{1}1 = 45.1 \text{ g/mol}$$

b. At the 50% titration point, pK_b = pOH. Since the pH measurement wasn't made, it is necessary to obtain a $[HB^+]/[B]$ ratio. The ratio can be in terms of moles, percent, mL, or *M* because the units end up canceling out. First, use the pH to obtain the OH^- ion concentration. Express the other concentrations in milliliters for convenience.

pOH = 14.00 − 10.73 = 3.27

$[OH^-] = 10^{-3.27} = 5.3\underline{7}0 \times 10^{-4}$

$B_0 \cong 39.24$ mL

$[B] \cong 39.24 - 18.35 = 20.89$ mL

$[HB^+] \cong [H_3O^+] = 18.35$ mL

$$K_b = [OH^-] \times \frac{[HB^+]}{[B]} = 5.370 \times 10^{-4}\, M \times \frac{18.35 \text{ mL}}{20.89 \text{ mL}} = 4.\underline{7}2 \times 10^{-4} = 4.7 \times 10^{-4}$$

16.119.

a. Initial pH: Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (*M*)	$NH_3 + H_2O$	⇌	NH_4^+	+	OH^-
Starting	0.10		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.10 - x$		x		0

Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[NH_4^+][OH^-]}{[OH^-]} = \frac{(x)^2}{(0.10 - x)} \cong \frac{(x)^2}{(0.10)} = 1.8 \times 10^{-5}$$

Rearranging and solving for *x* give

$$x = [OH^-] = \sqrt{(0.10)(1.8 \times 10^{-5})} = 1.\underline{3}4 \times 10^{-3}\, M$$

$\text{pOH} = -\log(1.34 \times 10^{-3}) = 2.8\underline{7}3$

$\text{pH} = 14 - \text{pOH} = 14 - 2.873 = 11.1\underline{2}7 = 11.13$

30% titration point: Express the concentrations as percents for convenience.

$[NH_3] \approx 70\%$ and $[NH_4^+] \approx 30\%$

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Plug into the equilibrium-constant expression.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(30\%)(x)}{(70\%)} = 1.8 \times 10^{-5}$$

Solving for x gives

$$x = [OH^-] = 1.8 \times 10^{-5} \times \frac{70\%}{30\%} = 4.\underline{2}0 \times 10^{-5}\ M$$

$$pOH = -\log (4.20 \times 10^{-5}) = 4.3\underline{7}7$$

$$pH = 14 - pOH = 14 - 4.377 = 9.6\underline{2}3 = 9.62$$

50% titration point:

$$[NH_4^+] = [NH_3]$$

$$K_b = [OH^-] = 1.8 \times 10^{-5}\ M$$

$$pOH = -\log (1.8 \times 10^{-5}) = 4.7\underline{4}4$$

$$pH = 14 - pOH = 14 - 4.744 = 9.2\underline{5}6 = 9.26$$

100% titration point:

The NH_4Cl that is produced has undergone a twofold dilution.

$$[NH_4^+] = 0.05\underline{0}0\ M$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$NH_3 + H_2O$ $\rightleftharpoons$	NH_3	+	H_3O^+
Starting	0.0500	0		0
Change	$-x$	$+x$		$+x$
Equilibrium	$0.0500 - x$	x		x

Now, use K_w to calculate the value of K_a:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}5 \times 10^{-10}$$

Plug into the equilibrium-constant expression.

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(x)^2}{(0.0500 - x)} \cong \frac{(x)^2}{(0.0500)} = 5.55 \times 10^{-10}$$

Solving for x gives

$$x = [H_3O^+] = \sqrt{0.0500 \times \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 5.\underline{2}7 \times 10^{-6}\ M$$

$$pH = -\log (5.27 \times 10^{-6}) = 5.2\underline{7}8 = 5.28$$

b. The solution is acidic because the NH_4^+ ion reacts with water to produce acid. Ammonium chloride is the salt of a weak base and a strong acid.

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16.120.

a. Initial pH: Use the table approach, and give the starting, change, and equilibrium concentrations. Here, A = $CH_3CH_2COO^-$.

Conc. (*M*)	HA + H_2O	⇌	H_3O^+	+	A^-
Starting	0.15		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.15 - x$		x		x

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 1.3 \times 10^{-5}$$

Rearranging and solving for x give

$$x = [H_3O^+] = \sqrt{(0.15)(1.3 \times 10^{-5})} = 1.\underline{4}0 \times 10^{-3}\ M$$

$$pH = -\log(1.40 \times 10^{-3}) = 2.8\underline{5}3 = 2.85$$

50% titration point:

$$[H_3O^+] = [A^-] = K_a = 1.3 \times 10^{-5}\ M$$

$$pH = -\log(1.3 \times 10^{-5}) = 4.8\underline{8}6 = 4.89$$

60% titration point: Express the concentrations as percents for convenience.

$$[HA] \approx 40\% \text{ and } [A^-] \approx 60\%$$

Plug into the equilibrium-constant expression.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \cong \frac{(60\%)(x)}{(40\%)} = 1.3 \times 10^{-5}$$

Solving for x gives

$$x = [H_3O^+] = 1.3 \times 10^{-5} \times \frac{40\%}{60\%} = 8.\underline{6}7 \times 10^{-6}\ M$$

$$pH = -\log(8.67 \times 10^{-6}) = 5.0\underline{6}2 = 5.06$$

100% titration point:

The salt produced has undergone a twofold dilution.

$$[A^-] = 0.07\underline{5}0\ M$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (*M*)	A^- + H_2O	⇌	HA	+	OH^-
Starting	0.0750		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.0750 - x$		x		x

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Now, use K_w to calculate the value of K_b:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.\underline{6}9 \times 10^{-10}$$

Plug into the equilibrium-constant expression.

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{0.0750 - x} \cong \frac{x^2}{0.0750} = 7.69 \times 10^{-10}$$

Solving for x gives

$$x = [OH^-] = \sqrt{0.0750 \times 7.69 \times 10^{-10}} = 7.\underline{5}9 \times 10^{-6}\ M$$

$$pOH = -\log (7.59 \times 10^{-6}) = 5.1\underline{2}0$$

$$pH = 14 - pOH = 14 - 5.1\underline{2}0 = 8.8\underline{8}0 = 8.88$$

b. The solution is basic because the propionate ion reacts with water to produce OH^-. Potassium propionate is the salt of a weak acid and a strong base.

16.121.

a. Select the conjugate pair that has a pK_a value closest to a pH of 2.88.

pK_a ($H_2C_2O_4$) = 1.25

pK_a (H_3PO_4) = 2.16

pK_a (HCOOH) = 3.77

Therefore, the best pair is H_3PO_4 and $H_2PO_4^-$.

b. Using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$2.88 = 2.16 + \log \frac{[A^-]}{[HA]}$$

$$\log \frac{[A^-]}{[HA]} = 0.72$$

$$\frac{[A^-]}{[HA]} = 10^{0.72} = 5.\underline{2}4$$

Therefore, 5.24 times more conjugate base is needed than acid. Since the starting concentrations of H_3PO_4 (HA) and $H_2PO_4^-$ (A^-) are the same, the volume of A^- needed is 5.24 times the volume of HA needed. For 50 mL of buffer, this is

$$50\ mL = vol\ HA + vol\ A^- = vol\ HA + 5.24\ vol\ HA = 6.24\ vol\ HA$$

Therefore, the volume of 0.10 M H_3PO_4 required is

$$\text{Volume of } H_3PO_4 = \frac{50\ mL}{6.24} = \underline{8}.01\ mL = 8\ mL$$

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The volume of 0.10 *M* $H_2PO_4^-$ required is

50 mL − 8.01 mL = 42.0 mL = 42 mL

16.122.

a. Select the conjugate pair that has a pK_a value closest to a pH of 6.96.

pK_a (NH_4^+) = 9.25

pK_a (H_2CO_3) = 6.37

pK_a ($H_2PO_4^-$) = 7.21

Therefore, the best pair is $H_2PO_4^-$ and HPO_4^{2-}.

b. Using the Henderson-Hasselbalch equation,

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

$$6.96 = 7.21 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = -0.25$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{0.25} = 0.562$$

Therefore, 0.562 times more conjugate base is needed than acid. Since the starting concentrations of $H_2PO_4^-$ (HA) and HPO_4^{2-} (A^-) are the same, the volume of A^- needed is 0.562 times the volume of HA needed. For 100 mL of buffer, this is

100 mL = vol HA + vol A^- = vol HA + 0.562 vol HA = 1.562 vol HA

Therefore, the volume of 0.10 *M* $H_2PO_4^-$ required is

$$\text{Volume of } H_2PO_4^- = \frac{100 \text{ mL}}{1.562} = 64.02 \text{ mL} = 64 \text{ mL}$$

The volume of 0.10 *M* HPO_4^{2-} required is

100 mL − 64.02 mL = 35.98 mL = 36 mL

16.123.

a. At the equivalence point, moles of base equal moles of acid. Therefore,

$$M_{NH_2OH} \times 25.0 \text{ mL} = 0.150\ M \times 35.8 \text{ mL}$$

$$M_{NH_2OH} = \frac{0.150\ M \times 35.8 \text{ mL}}{25.0 \text{ mL}} = 0.2148 = 0.215$$

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b. Concentration of NH_3OH^+ at the equivalence point is

$$[NH_3OH^+] = \frac{(25.0\text{ mL})(0.215\ M)}{25.0\text{ mL} + 35.8\text{ mL}} = 0.088\underline{4}0\ M$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.\underline{0}9 \times 10^{-7}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$NH_3OH^+ + H_2O$ ⇌	NH_2OH +	H_3O^+
Starting	0.088$\underline{4}$0	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	0.088$\underline{4}$0 $- x$	x	x

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[NH_2OH]\,[H_3O^+]}{[NH_3OH^+]} = \frac{(x)^2}{(0.08840 - x)} \cong \frac{(x)^2}{(0.08840)} = 9.\underline{0}9 \times 10^{-7}$$

Rearranging and solving for x give

$$x = [H_3O^+] = \sqrt{(0.08840)(9.\underline{0}9 \times 10^{-7})} = 2.\underline{8}3 \times 10^{-4}\ M$$

$$\text{pH} = -\log(2.\underline{8}4 \times 10^{-4}) = 3.5\underline{4}7 = 3.55$$

c. You need an indicator to change color around a pH of 3 to 4. Therefore, the appropriate indicator is bromophenol blue. Select an indicator that changes color around the equivalence point.

16.124.

a. At the equivalence point, moles of base equal moles of acid. The molar mass of $NaHCO_3$ is 84.01 g/mol. Therefore,

$$\text{mol base} = \text{mol acid} = 0.562\text{ g } NaHCO_3 \times \frac{1\text{ mol } NaHCO_3}{84.01\text{ g } NaHCO_3} = 6.6\underline{9}0 \times 10^{-3}\text{ mol}$$

The molarity of the base is

$$M_{NaOH} = \frac{6.6\underline{9}0 \times 10^{-3}\text{ mol}}{0.04236\text{ L}} = 0.15\underline{7}9 = 0.158\ M$$

b. The concentration of CO_3^{2-} at the equivalence point is

$$[CO_3^{2-}] = \frac{6.6\underline{9}0 \times 10^{-3}\text{ mol}}{0.02500\text{ L} + 0.04236\text{ L}} = 0.099\underline{3}2\ M$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.\underline{0}8 \times 10^{-4}$$

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Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (*M*)	$CO_3^{2-} + H_2O$	$\rightleftharpoons$	HCO_3^-	+	OH^-
Starting	0.09932		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.09932 - x$		x		x

Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.09932 - x} \cong \frac{x^2}{0.09932} = 2.08 \times 10^{-4}$$

Rearranging and solving for x give

$$x = [OH^-] = \sqrt{(0.09932)(2.08 \times 10^{-4})} = 4.55 \times 10^{-3}\ M$$

$$pOH = -\log(4.55 \times 10^{-3}) = 2.342$$

$$pH = 14 - pOH = 14 - 2.342 = 11.658 = 11.66$$

c. Alizarin yellow R. It changes color around the equivalence point.

16.125.

a. $H_3O^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + H_2O(l)$

b. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$

c. Initial:

$$\text{mol } NH_3 = 1.0 \text{ mol/L} \times 0.100 \text{ L} = 0.100 = 0.10 \text{ mol}$$

$$\text{mol } NH_4^+ = 0.50 \text{ mol/L} \times 0.100 \text{ L} \times \frac{2 \text{ mol } NH_4^+}{1 \text{ mol } (NH_4)_2SO_4} = 0.100 = 0.10 \text{ mol}$$

After addition of HCl: The HCl is completely consumed by producing 0.0100 mol of NH_4^+. The amount of NH_3 is decreased by 0.0100 mol.

$$\text{mol HCl added} = 1.00 \text{ mol/L} \times 0.0100 \text{ L} = 0.01000 \text{ mol}$$

$$\text{mol } NH_3 = 0.100 - 0.01000 = 0.090 = 0.090 \text{ mol}$$

$$\text{mol } NH_4^+ = 0.100 + 0.01000 = 0.110 = 0.11 \text{ mol}$$

The reaction is

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

Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.110)[OH^-]}{(0.090)} = 1.8 \times 10^{-5}$$

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Rearranging and solving for $[OH^-]$ give

$$[OH^-] = 1.8 \times 10^{-5} \times \frac{0.090}{0.110} = 1.47 \times 10^{-5}\ M$$

$$pOH = -\log (1.47 \times 10^{-5}) = 4.83$$

$$pH = 14 - pOH = 14 - 4.83 = 9.17 = 9.2$$

d. This is a buffer system, so the ratio of NH_4^+/NH_3 has not changed very much.

16.126.

a. Use the table approach, and give the starting, change, and equilibrium concentrations. The initial concentration of formic acid (HCOOH) is 0.150 mol/0.425 L = 0.3529 *M*.

Conc. (*M*)	$HCOOH + H_2O$ ⇌	H_3O^+ +	$HCOO^-$
Starting	0.3529	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.3529 - x$	x	x

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[HCOO^-]\,[H_3O^+]}{[HCOOH]} = \frac{(x)^2}{(0.3529 - x)} \cong \frac{(x)^2}{(0.3529)} = 1.7 \times 10^{-4}$$

Rearranging and solving for x give

$$x = [H_3O^+] = [HCOO^-] = \sqrt{(0.3529)(1.7 \times 10^{-4})} = 7.74 \times 10^{-3} = 7.7 \times 10^{-3}\ M$$

b. To decrease the $HCOO^-$ concentration by a factor of 10, the concentration must be reduced to 7.74×10^{-4} *M*. The change in equilibrium is

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

Assume the changes in concentration are small, so $[HCOOH] \cong 0.3529\ M$. Substitute into the rearranged equilibrium-constant equation.

$$[H_3O^+] = \frac{[HCOOH]K_a}{[HCOO^-]} = \frac{(0.3529)(1.7 \times 10^{-4})}{7.74 \times 10^{-4}} = 0.0775 = 0.078\ M$$

$0.0775\ M \times 425\ mL = 2.00\ M \times V$

$V = 16.4 = 16\ mL$

c. This is the common-ion effect. An increase in the H_3O^+ concentration shifts the equilibrium so the percent dissociation of HCOOH is decreased.

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16.127.

a. From the pH, $[H_3O^+] = 10^{-7.44} = 3.\underline{6}3 \times 10^{-8}\ M$. The reaction is

$$H_2PO_4^-(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \quad K_{a_2} = 6.2 \times 10^{-8}$$

$$K_{a_2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$$

Rearranging gives

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{[H_3O^+]}{K_{a_2}} = \frac{3.63 \times 10^{-8}}{6.2 \times 10^{-8}} = \frac{0.5\underline{8}55}{1} = 0.59 \text{ to } 1$$

Or, using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

$$7.44 = 7.21 + \log \frac{[base]}{[acid]}$$

$$\log \frac{[base]}{[acid]} = 0.23$$

$$\frac{[base]}{[acid]} = 10^{0.23} = 1.\underline{7}1$$

You must invert each side. The result is

$$\frac{[acid]}{[base]} = \frac{1}{1.71} = \frac{0.5\underline{8}57}{1} = 0.59 \text{ to } 1$$

b. $[H_3O^+] = K_{a_2} = \dfrac{[H_2PO_4^-]}{[HPO_4^{2-}]}$

If $HPO_4^{2-} = 1.00$ mol, then when 25% of it is converted into $H_2PO_4^-$, 0.75 mol remains, and $H_2PO_4^-$ becomes $0.5\underline{8}6 + 0.25 = 0.8\underline{3}6$ mol. Therefore,

$$[H_3O^+] = 6.2 \times 10^{-8} \times \frac{0.836}{0.75} = 6.\underline{9}1 \times 10^{-8}$$

$$pH = -\log (6.\underline{9}1 \times 10^{-8}) = 7.1\underline{6}1 = 7.16$$

c. Assume $H_2PO_4^- = 0.5\underline{8}6$ mol. Then, the numbers of moles of $H_2PO_4^-$ remaining is

$0.5\underline{8}6 - (0.15 \times 0.5\underline{8}6) = 0.85 \times 0.5\underline{8}6 = 0.4\underline{9}8$ mol left

The moles of $HPO_4^{2-} = 1.00 + (0.15 \times 0.5\underline{8}6) = 1.0\underline{8}8$ mol

$$[H_3O^+] = 6.2 \times 10^{-8} \times \frac{0.498}{1.088} = 2.\underline{8}4 \times 10^{-8}\ M$$

$$pH = -\log (2.84 \times 10^{-8}) = 7.5\underline{4}7 = 7.55$$

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16.128.

a. From the pH, $[H_3O^+] = 10^{-7.42} = 3.\underline{8}0 \times 10^{-8}\ M$. The reaction is

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = 4.3 \times 10^{-7}$$

$$K_{a_1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$$

Rearranging gives

$$\frac{[H_2CO_3]}{[HCO_3^-]} = \frac{[H_3O^+]}{K_{a_1}} = \frac{3.80 \times 10^{-8}}{4.3 \times 10^{-7}} = \frac{0.08\underline{8}4}{1} = 0.088 \text{ to } 1$$

Or, using the Henderson-Hasselbalch equation,

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

$$7.42 = 6.3\underline{6}7 + \log \frac{[base]}{[acid]}$$

$$\log \frac{[base]}{[acid]} = 1.0\underline{5}3$$

$$\frac{[base]}{[acid]} = 10^{1.053} = 1\underline{1}.30$$

You must invert each side. The result is

$$\frac{[acid]}{[base]} = \frac{1}{1\underline{1}.30} = \frac{0.08\underline{8}5}{1} = 0.089 \text{ to } 1$$

b. If HCO_3^- = 1.00 mol, then when 15% of it is converted into H_2CO_3, 0.85 mol remains, and H_2CO_3 becomes $0.08\underline{8}4 + 0.15 = 0.2\underline{3}8$ mol. Therefore,

$$[H_3O^+] = 4.3 \times 10^{-7} \times \frac{0.238}{0.85} = 1.\underline{2}0 \times 10^{-7}\ M$$

$$pH = -\log (1.\underline{2}0 \times 10^{-7}) = 6.9\underline{2}0 = 6.92$$

c. Assume $H_2CO_3 = 0.08\underline{8}4$ mol. Then, the moles of HCO_3^- left are

$0.08\underline{8}4 - 0.25 \times 0.08\underline{8}4 = 0.75 \times 0.08\underline{8}4 = 0.06\underline{6}3$ mol left

Moles of $HCO_3^- = 1.000 + 0.25 \times 0.08\underline{8}4 = 1.02\underline{2}1$ mol

$$[H_3O^+] = 4.3 \times 10^{-7} \times \frac{0.0663}{1.0221} = 2.\underline{7}9 \times 10^{-8}\ M$$

$$pH = -\log (2.\underline{7}9 \times 10^{-8}) = 7.5\underline{4}7 = 7.55$$

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16.129.

a. $H_2A + H_2O \rightleftharpoons H_3O^+ + HA \quad K_{a_1}$

$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-} \quad K_{a_2}$

$H_2A + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + A^{2-}, \; K = K_{a_1} \times K_{a_2}$

b. $H_2A >> H_3O^+ = HA^- >> A^{2-}$

c.

$$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^- \qquad K_{a_1} = 1.0 \times 10^{-3}$$

$0.0250 - x \qquad\qquad x \qquad\qquad x$

$$K_{a_1} = \frac{[HA^-][H_3O^+]}{[H_2A]} = \frac{(x)^2}{(0.0250 - x)} = 1.0 \times 10^{-3}$$

Rearranging into a quadratic equation and solving for x give

$$x^2 + (1.0 \times 10^{-3})\,x + (-2.50 \times 10^{-5}) = 0$$

$$x = \frac{-(1.0 \times 10^{-3}) \pm \sqrt{(1.0 \times 10^{-3})^2 - (4)(1)(-2.50 \times 10^{-5})}}{2}$$

$x = [H_3O^+] = [HA^-] = 4.\underline{5}2 \times 10^{-3} = 4.5 \times 10^{-3}\,M$

$pH = -\log(4.\underline{5}2 \times 10^{-3}) = 2.3\underline{4}4 = 2.34$

$[H_2A] = 0.0250 - x = 0.0250 - 4.52 \times 10^{-3} = 0.020\underline{4}8 = 0.0205\,M$

d.

$$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-} \qquad Ka_2 = 4.6 \times 10^{-5}$$

$4.52 \times 10^{-3} + y \qquad\qquad 4.52 \times 10^{-3} + y \qquad y$

Assume y is small compared to $4.52 \times 10^{-3}\,M$. Substitute into the rearranged equilibrium-constant equation to get

$$[A^{2-}] = \frac{[HA^-]K_{a_2}}{[H_3O^+]} = \frac{(4.52 \times 10^{-3})(4.6 \times 10^{-5})}{(4.52 \times 10^{-3})} = 4.6 \times 10^{-5}\,M$$

16.130.

a. $H_2A + H_2O \rightleftharpoons H_3O^+ + HA \quad K_{a_1}$

$HA^- + H_2O \rightleftharpoons H_3O^+ + A^2 \quad K_{a_2}$

$H_2A + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + A^{2-}, \; K = K_{a_1} \times K_{a_2}$

b. $H_2A >> H_3O^+ = HA^- >> A^{2-}$

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c.

$$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^- \qquad Ka_1 = 4.0 \times 10^{-4}$$

$$0.0150 - x \qquad x \qquad x$$

Substitute into the equilibrium-constant equation to get

$$K_{a_1} = \frac{[HA^-][H_3O^+]}{[H_2A]} = \frac{(x)^2}{(0.0150 - x)} = 4.0 \text{ x } 10^{-4}$$

Rearranging into a quadratic equation and solving for x give

$$x^2 + (4.0 \text{ x } 10^{-4})\,x + (-6.00 \text{ x } 10^{-6}) = 0$$

$$x = \frac{-(4.0 \text{ x } 10^{-4}) \pm \sqrt{(4.0 \text{ x } 10^{-4})^2 - (4)(1)(-6.00 \text{ x } 10^{-6})}}{2}$$

$$x = [H_3O^+] = [HA^-] = 2.257 \text{ x } 10^{-3} = 2.3 \text{ x } 10^{-3}\ M$$

$$\text{pH} = -\log(2.257 \text{ x } 10^{-3}) = 2.646 = 2.65$$

$$[H_2A] = 0.0150 - x = 0.0150 - 2.257 \text{ x } 10^{-3} = 0.0127 = 0.013\ M$$

d.

$$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-} \qquad Ka_2 = 9.0 \text{ x } 10^{-6}$$

$$1.81 \text{ x } 10^{-3} - y \qquad 1.81 \text{ x } 10^{3} + y \qquad y$$

Assume y is small compared to $1.81 \text{ x } 10^{-3}\ M$. Substitute into the rearranged equilibrium-constant equation to get

$$[A^{2-}] = \frac{[HA^-]K_{a_2}}{[H_3O^+]} = \frac{(1.81 \text{ x } 10^{-3})(9.0 \text{ x } 10^{-6})}{(1.81 \text{ x } 10^{-3})} = 9.0 \text{ x } 10^{-6}\ M$$

16.131.

a. From the pH, $[H_3O^+] = 10^{-4.45} = 3.55 \text{ x } 10^{-5}\ M$. The $NaCH_3COO$ is generated by the acid-base reaction, resulting in the formation of a buffer solution. The reaction is

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \qquad K_a = 1.7 \text{ X } 10^{-5}$$

$$0.15 - x \qquad x \qquad x$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Rearranging gives

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H_3O^+]}$$

$$\frac{x}{0.15 - x} = \frac{1.7 \text{ x } 10^{-5}}{3.55 \text{ x } 10^{-5}}$$

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Solving for x gives $x = 0.04\underline{8}6$ mol. Therefore, the molar concentration is

$[CH_3COO^-] = 0.04\underline{8}6 \text{ mol}/0.375 \text{ L} = 0.1\underline{2}96 = 0.13\ M$

b. mol OH^- = mol CH_3COO^-

$0.04\underline{8}6 \text{ mol} = 0.25\ M \times V_{NaOH}$

$V_{NaOH} = 0.0486 \text{ mol}/0.25\ M = 0.1\underline{9}4 = 0.19 \text{ L}\ (1.9 \times 10^2 \text{ mL})$

c. The volume of the original acid is $V = 0.375 \text{ L} - 0.1\underline{9}4 \text{ L} = 0.1\underline{8}1$ L. Therefore, the concentration of the original acid is

$[CH_3COOH] = 0.15 \text{ mol}/0.181 \text{ L} = 0.8\underline{2}9 = 0.83\ M$

16.132.

a. From the pH, $[H_3O^+] = 10^{-4.56} = 2.\underline{7}5 \times 10^{-5}\ M$. The CH_3COOH is generated by the acid-base reaction, resulting in the formation of a buffer solution. The reaction is

$$\underset{0.10 - x}{CH_3COO^-} + H_3O^+ \rightleftharpoons \underset{x}{H_2O} + \underset{x}{CH_3COOH} \qquad K_a = 1.7 \times 10^{-5}$$

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

Rearranging gives

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H_3O^+]}$$

$$\frac{0.10 - x}{x} = \frac{1.7 \times 10^{-5}}{2.75 \times 10^{-5}}$$

Solving for x gives $x = 0.06\underline{1}8$ mol. Therefore, the molar concentration is

$[CH_3COOH] = 0.06\underline{1}8 \text{ mol}/0.650 \text{ L} = 0.09\underline{5}1 = 0.095\ M$

b. Moles of HCl equal moles of CH_3COOH.

$0.06\underline{1}8 \text{ mol} = 0.15\ M \times V_{NaOH}$

$V_{NaOH} = 0.0618 \text{ mol}/0.15\ M = 0.4\underline{1}2 = 0.41$ L

c. The volume of the original salt is $V = 0.650 \text{ L} - 0.4\underline{1}2 \text{ L} = 0.2\underline{3}8$ L. Therefore, the concentration of the original salt is

$[CH_3COONa] = 0.10 \text{ mol}/0.238 \text{ L} = 0.4\underline{2}0 = 0.42\ M$

16.133. Natural rain dissolves carbon dioxide from the atmosphere to give a slightly acidic solution.

16.134. Acid rain is rain that has a pH lower than natural rain (pH 5.6). The acidity is primarily the result of the dissolving in rainwater of sulfur oxides and nitrogen oxides from human activities. The sulfuric acid in acid rain has been traced to the burning of fossil fuels and to the burning of sulfide ores in the production of metals, such as zinc and copper.

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■ SOLUTIONS TO STRATEGY PROBLEMS

16.135.

a. Assemble the usual table of concentrations.

Conc. (M)	$HClO + H_2O$	$\rightleftharpoons$	H_3O^+	+	ClO^-
Starting	0.05		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.05 - x$		x		x

Now substitute into the equilibrium expression, assume x is negligible compared to 0.05 M, and calculate $[H_3O^+]$.

$$K_a = \frac{(x)^2}{(0.05 - x)} = \frac{(x)^2}{(0.05)} = 3.5 \times 10^{-8}$$

$$x = [H_3O^+] = \underline{4}.18 \times 10^{-5}\ M$$

Finally, calculate the pH.

$$pH = -\log [H_3O^+] = -\log (4.18 \times 10^{-5}) = 4.\underline{3}7 = 4.4$$

b. After 30.00 mL of 0.0250 M KOH is added, the reaction is

$$HClO + OH^- \rightarrow ClO^- + H_2O$$

The total volume at this point is 30.0 mL + 30.00 mL = 60.$\underline{0}$0 mL.

The moles of HClO present at the start and the moles of OH^- added are

$$\text{mol HClO} = M \times V = 0.05\ M \times 30.0 \times 10^{-3}\ \text{L} = \underline{1}.50 \times 10^{-3}\ \text{mol}$$

$$\text{mol } OH^- = M \times V = 0.0250\ M \times 30.0 \times 10^{-3}\ \text{L} = 0.750\underline{0} \times 10^{-3}\ \text{mol}$$

After reaction the moles of ClO^- equal the moles of added OH^-. The moles of HClO present are

$$\text{mol HClO} = 1.50 \times 10^{-3}\ \text{mol} - 0.7500 \times 10^{-3} = \underline{0}.7500 \times 10^{-3}\ \text{mol}$$

Now calculate the concentrations.

$$[HClO] = \frac{0.7500 \times 10^{-3}\ \text{mol}}{60.00 \times 10^{-3}\ \text{L}} = 0.0\underline{1}25\ M$$

$$[ClO^-] = \frac{0.7500 \times 10^{-3}\ \text{mol}}{60.00 \times 10^{-3}\ \text{L}} = 0.0\underline{1}25\ M$$

Substitute into the K_a expression and solve for $x = [H_3O^+]$.

$$K_a = 3.5 \times 10^{-8} = \frac{[H_3O^+]\,[ClO^-]}{[HClO]} = \frac{(x)(0.0125 + x)}{(0.00125 - x)} \cong x$$

$$x = [H_3O^+] = 3.5 \times 10^{-8}\ M$$

$$pH = -\log (3.5 \times 10^{-8}) = 7.4\underline{5}5 = 7.46$$

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c. First calculate the volume of KOH added to reach the equivalence point.

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(0.05\ \text{M})(30.0\ \text{mL})}{(0.0250\ \text{M})} = \underline{6}0.0\ \text{mL}$$

The total volume at this point is 30.0 mL + 60.0 mL = $\underline{9}$0.0 mL.. The equilibrium is now

$$ClO^- + H_2O \rightleftharpoons HClO + OH^-$$

The moles of ClO^- present are the same as the moles of HClO present initially, 1.50×10^{-3} mol. The concentration is

$$[ClO^-] = \frac{1.50 \times 10^{-3}\ \text{mol}}{90.0 \times 10^{-3}\ \text{L}} = 0.0\underline{1}66\ M$$

Calculate the value of K_b from K_a, set up the equilibrium expression, and solve.

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.\underline{8}5 \times 10^{-7}$$

$$K_b = 2.85 \times 10^{-7} = \frac{[HClO]\,[OH^-]}{[ClO^-]} = \frac{x^2}{(0.0166 - x)}$$

$$x = [OH^-] = \underline{6}.90 \times 10^{-5}\ M$$

$$pOH = -\log(6.90 \times 10^{-5}) = 4.\underline{1}61$$

$$pH = 14.00 - pOH = 14.00 - 4.161 = 9.\underline{8}3 = 9.8$$

d. The volume at this point is 90.0 mL + 4.0 mL = 94.0 mL. Now calculate the molarity of the excess KOH.

$$\text{mol KOH added} = M \times V = (0.0250\ M)(64.0 \times 10^{-3}\ \text{L}) = \underline{1}.60 \times 10^{-3}\ \text{mol}$$

$$\text{Excess mol KOH} = 1.60 \times 10^{-3}\ \text{mol} - 1.5 \times 10^{-3}\ \text{mol} = \underline{0}.10 \times 10^{-3}\ \text{mol}$$

$$[OH^-] = \frac{0.10 \times 10^{-3}\ \text{mol}}{94.0 \times 10^{-3}\ \text{L}} = 0.00\underline{1}06\ M$$

Finally, calculate the pOH and pH.

$$pOH = -\log(0.00106) = 2.\underline{9}73$$

$$pH = 14.00 - pOH = 14.00 - 2.973 = 11.\underline{0}2 = 11.0$$

16.136. The percent dissociation of a weak acid HA is

$$\text{Percent dissociation} = \frac{[H_3O^+]}{[HA]_o} \times 100\%$$

Rearrange this equation and solve for $[H_3O^+]$.

$$[H_3O^+] = \frac{\text{Percent dissociation}}{100\%} \times [HA]_o = (0.0416)(0.108\ M) = 4.\underline{4}92 \times 10^{-3}\ M$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{4.492 \times 10^{-3}} = 2.2\underline{2}5 \times 10^{-12} = 2.23 \times 10^{-12}\ M$$

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16.137. The reaction is

$$B^- + H_2O \rightleftharpoons HB + OH^-$$

Calculate K_b from K_a and [OH^- from the pH 10.10.

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.99 \times 10^{-9}} = 5.025 \times 10^{-6}$$

$$pOH = 14.00 - pH = 14.00 - 10.10 = 3.90$$

$$[OH^-] = 10^{-pOH} = 10^{-3.90} = 1.258 \times 10^{-4}\ M$$

Now set up the equilibrium expression with $x = [OH^-]$ and solve for the initial concentration.

$$K_b = 5.025 \times 10^{-6} = \frac{x^2}{[B^-]_0 - x} = \frac{(1.258 \times 10^{-4})^2}{[B^-]_0 - 1.258 \times 10^{-4}}$$

$$[B^-]_0 = 1.258 \times 10^{-4} + \frac{(1.258 \times 10^{-4})^2}{5.025 \times 10^{-6}} = 0.00327 = 0.0033\ M$$

16.138. The total volume at this point is 0.60 L + 0.50 L = 1.10 L. The concentration of NH_4^+ is now

$$[NH_4^+] = \frac{(\text{mol } NH_4^+ \text{ at start}) - (\text{mol } OH^- \text{ added})}{\text{total volume}}$$

$$[NH_4^+] = \frac{(0.10\ M)(0.60\ L) - (0.10\ M)(0.50\ L)}{1.10\ L} = 9.090 \times 10^{-3}\ M$$

The moles of NH_3 formed are equal to the moles of OH^- added, so the concentration of OH^- is

$$[NH_3] = \frac{(\text{mol } OH^- \text{ added})}{\text{total volume}} = \frac{(0.10\ M)(0.50\ L)}{1.10\ L} = 0.04545\ M$$

Calculate K_a from K_b.

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

The reaction is

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Set up the equilibrium expression and solve for $x = [H_3O^+]$.

$$K_a = 5.55 \times 10^{-10} = \frac{(x)(0.04545 + x)}{(0.009090 - x)}$$

$$x = [H_3O^+] = \frac{(5.55 \times 10^{-10})(0.009090 - x)}{(0.04545 + x)} \cong \frac{(5.55 \times 10^{-10})(0.009090)}{(0.04545)} = 1.11 \times 10^{-10}$$

Finally, calculate the pH.

$$pH = -\log (1.11 \times 10^{-10}) = 9.954 = 9.95$$

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16.139. The equilibrium is

$$HOCN + H_2O \rightleftharpoons H_3O^+ + OCN^-$$

Set up the equilibrium expression and solve for $x = [H_3O^+]$.

$$K_a = 3.5 \times 10^{-4} = \frac{(x)(0.0419 + x)}{(0.293 - x)}$$

$$x = [H_3O^+] = \frac{(3.5 \times 10^{-4})(0.293 - x)}{(0.0419 + x)} \cong \frac{(3.5 \times 10^{-4})(0.293)}{(0.0419)} = 2.\underline{4}47 \times 10^{-3}$$

Finally, calculate the degree of ionization.

$$\text{Degree of ionization} = \frac{[H_3O^+]}{[HOCN]_o} = \frac{2.447 \times 10^{-3}}{0.293} = 8.\underline{3}5 \times 10^{-3} = 8.4 \times 10^{-3}$$

16.140. The total volume at this point is 65.1 mL + 39.2 mL = 104.3 mL. Calculate the concentrations of NH_3 and NH_4^+ after mixing together.

$$[NH_3] = \frac{M_1V_1}{V_2} = \frac{(0.142\ M)(65.1\ \text{mL})}{(104.3\ \text{mL})} = 0.088\underline{6}3\ M$$

$$[NH_4^+] = \frac{M_1V_1}{V_2} = \frac{(0.172\ M)(39.2\ \text{mL})}{(104.3\ \text{mL})} = 0.064\underline{6}4\ M$$

The equilibrium is

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

Calculate K_a from K_b.

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}55 \times 10^{-10}$$

Now use the Hendersen-Hasselbalch equation to calculate the pH.

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = -\log (5.55 \times 10^{-10}) + \log \left(\frac{0.08863}{0.06464}\right)$$

$$= 9.2\underline{5}5 + 0.013\underline{7}07 = 9.3\underline{9}2 = 9.39$$

16.141. Before any HCl is added:

The total volume at this point is 529 mL+ 494 mL = 1023 mL. Calculate the concentration of $HCHO_2$ and CHO_2^- after mixing together.

$$[HCHO_2] = \frac{M_1V_1}{V_2} = \frac{(0.465\ M)(529\ \text{mL})}{(1023\ \text{mL})} = 0.240\underline{4}5\ M$$

$$[CHO_2^-] = \frac{M_1V_1}{V_2} = \frac{(0.524\ M)(494\ \text{mL})}{(1023\ \text{mL})} = 0.253\underline{0}3\ M$$

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The equilibrium is

$$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$$

Now use the Hendersen-Hasselbalch equation to calculate the pH.

$$pH = pK_a + \log \frac{[base]}{[acid]} = -\log (1.7 \times 10^{-4}) + \log \left(\frac{0.25303}{0.24045} \right)$$

$$= 3.76\underline{9}5 + 0.022\underline{1}4 = 3.79\underline{1} = 3.79$$

After adding 110. mL of 0.152 *M* HCl:

The total volume is 529 mL + 494 mL = 1023 mL. The concentration of $HCHO_2$ at this point is

$$[HCHO_2] = \frac{(\text{mol } HCHO_2 \text{ at start}) + (\text{mol HCl added})}{\text{total volume}}$$

$$[HCHO_2] = \frac{(0.465\ M)(529\ \text{mL}) + (0.152\ M)(110.\ \text{mL})}{1133\ \text{mL}} = 0.23\underline{1}86\ M$$

The concentration of CHO_2^- at this point is

$$[CHO_2^-] = \frac{(\text{mol } CHO_2^- \text{ at start}) - (\text{mol HCl added})}{\text{total volume}}$$

$$[CHO_2^-] = \frac{(0.524\ M)(494\ \text{mL}) - (0.152\ M)(110.\ \text{mL})}{1133\ \text{mL}} = 0.21\underline{3}71\ M$$

Now use the Hendersen-Hasselbalch equation to calculate the pH.

$$pH = pK_a + \log \frac{[base]}{[acid]} = -\log (1.7 \times 10^{-4}) + \log \left(\frac{0.21371}{0.23186} \right)$$

$$= 3.76\underline{9}5 - 0.035\underline{4}0 = 3.73\underline{4} = 3.73$$

16.142. Before any HCl is added:

The total volume at this point is 52.1 mL+ 46.1 mL = 98.2 mL. Calculate the concentration of $HC_2H_3O_2$ and $C_2H_3O_2^-$ after mixing together.

$$[HC_2H_3O_2] = \frac{M_1V_1}{V_2} = \frac{(0.122\ M)(52.1\ \text{mL})}{(98.2\ \text{mL})} = 0.064\underline{7}27\ M$$

$$[C_2H_3O_2^-] = \frac{M_1V_1}{V_2} = \frac{(0.182\ M)(46.1\ \text{mL})}{(98.2\ \text{mL})} = 0.085\underline{4}39\ M$$

The equilibrium is

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

Now use the Hendersen-Hasselbalch equation to calculate the pH.

$$pH = pK_a + \log \frac{[base]}{[acid]} = -\log (1.7 \times 10^{-5}) + \log \left(\frac{0.085439}{0.064727} \right)$$

$$= 4.76\underline{9}5 + 0.12\underline{0}5 = 4.89\underline{0} = 4.89$$

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After adding 5.82 mL of 0.125 *M* NaOH:

The volume at this point is 98.2 + 5.82 = 104.02 mL The concentration of $HCHO_2$ at this point is

$$[HCHO_2] = \frac{(\text{mol } HCHO_2 \text{ at start}) - (\text{mol NaOH added})}{\text{total volume}}$$

$$[HCHO_2] = \frac{(0.122\ M)(52.1\text{ mL}) - (0.125\ M)(5.82\text{ mL})}{104.02\text{ mL}} = 0.054111\ M$$

The concentration of $C_2H_3O_2^-$ at this point is

$$[C_2H_3O_2^-] = \frac{(\text{mol } C_2H_3O_2^- \text{ at start}) + (\text{mol NaOH added})}{\text{total volume}}$$

$$[C_2H_3O_2^-] = \frac{(0.182\ M)(46.1\text{ mL}) + (0.125\ M)(5.82\text{ mL})}{104.02\text{ mL}} = 0.087653\ M$$

Now use the Hendersen-Hasselbalch equation to calculate the pH.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = -\log(1.7 \times 10^{-5}) + \log\left(\frac{0.087653}{0.054111}\right)$$

$$= 4.7695 + 0.2094 = 4.9789 = 4.98$$

16.143. In this system, HCl is in excess. The reaction is

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$

The total volume after mixing is 7.52 mL + 22.5 mL = 30.02 mL. Note that for each mole of $Ca(OH)_2$, two moles of HCl are reacted. Thus, the concentration of H_3O^+ after mixing is

$$[H_3O^+] = \frac{(\text{mol HCl at start}) - (2)(\text{mol } Ca(OH)_2 \text{ added})}{\text{total volume}}$$

$$[H_3O^+] = \frac{(0.11\ M)(22.5\text{ mL}) - (2)(0.049\ M)(7.52\text{ mL})}{30.02\text{ mL}} = 0.05789\ M$$

Now, calculate the pH.

$$\text{pH} = -\log(0.05789) = 1.237 = 1.24$$

16.144.

a. Assemble the usual table of concentrations.

Conc. (*M*)	$ClO^- + H_2O$	$\rightleftharpoons$	HClO	+	OH^-
Starting	0.15	→	0	→	0
Change	$-x$	→	$+x$	→	$+x$
Equilibrium	$0.15 - x$	→	x	→	x

Calculate K_b using K_a.

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.85 \times 10^{-7}$$

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Now substitute into the equilibrium expression, assume x is negligible compared to 0.100 M, and calculate $[OH^-]$.

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = \frac{(x)^2}{(0.15 - x)} = \frac{(x)^2}{(0.15)} = 2.85 \times 10^{-7}$$

$$x = [OH^-] = 2.\underline{0}70 \times 10^{-4}\ M$$

Finally, calculate the pOH and then the pH.

$$pOH = -\log [OH^-] = -\log (2.070 \times 10^{-4}) = 3.6\underline{8}3$$

$$pH = 14.00 - 3.683 = 10.3\underline{1}6 = 10.32$$

b. At the half-way point, $[ClO^-] = [HClO]$. This gives

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = [OH^-] = 2.85 \times 10^{-7}\ M$$

Now calculate the pOH and PH.

$$pOH = -\log (2.85 \times 10^{-7}) = 6.5\underline{4}4$$

$$pH = 14.00 - pOH = 14.00 - 6.544 = 7.4\underline{5}5 = 7.46$$

c. First calculate the volume of HCl added to reach the equivalence point.

$$V_2 = \frac{M_1V_1}{M_2} = \frac{(0.150\ M)(50.0\ mL)}{(0.100\ M)} = 75.\underline{0}0\ mL$$

The total volume at this point is 50.0 mL + 75.00 mL = 125.00 mL. The equilibrium is now

$$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$$

The moles of HClO present are the same as the moles of ClO^- present initially. The concentration is

$$[HClO] = \frac{M_1V_1}{V_2} = \frac{(0.150\ M)(50.0\ mL)}{(125.00\ mL)} = 0.0600\underline{0}\ M$$

Set up the equilibrium expression, and solve.

$$K_a = 3.5 \times 10^{-8} = \frac{[H_3O^+]\,[ClO^-]}{[HClO]} = \frac{x^2}{(0.06000 - x)} \cong \frac{x^2}{(0.06000)}$$

$$x = [H_3O^+] = 4.\underline{5}8 \times 10^{-5}\ M$$

$$pH = -\log (4.58 \times 10^{-5}) = 4.3\underline{3}8 = 4.34$$

d. The volume at this point is 125.00 mL + 5.00 mL = 130.00 mL. Now calculate the molarity of the excess H_3O^+.

$$[H_3O^+] = \frac{(\text{mol HCl added}) - (\text{mol } ClO^- \text{ at start})}{\text{total volume}}$$

$$[H_3O^+] = \frac{(0.100\ M)(80.00\ mL) - (0.150\ M)(50.0\ mL)}{130.00\ mL} = 3.8\underline{4}6 \times 10^{-3}\ M$$

Finally, calculate the pH.

$$pH = -\log (3.846 \times 10^{-3}) = 2.41\underline{4}9 = 2.415$$

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SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

16.145. Use the pH to calculate $[H_3O^+]$, and then use the K_a of 1.7 x 10^{-5} and the K_a expression to calculate the molarity of acetic acid (HAc), assuming ionization is negligible. Convert molarity to mass percentage using the formula mass of 60.05 g/mol of HAc.

$[H_3O^+]$ = antilog (−2.45) = 3.5̲48 x 10^{-3} *M*

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the *x* and the (0.003548 *M*) terms into the expression:

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} \cong \frac{(0.003548)^2}{(x)}$$

Solve the equation for *x*, assuming 0.003548 is much smaller than *x*.

$x = (0.003548)^2 \div (1.7 \times 10^{-5}) \cong [HAc] \cong 0.7\underline{4}04\ M$

(0.7404 mol HAc/L) x (60.05 g/mol) x (1 L/1090 g)(100%) = 4.0̲78 = 4.1% HAc

16.146. Use the pH to calculate $[OH^-]$, and then use the K_b of 1.8 x 10^{-5} and the K_b expression to calculate the molarity of ammonia (NH_3), assuming ionization is negligible. Convert molarity to mass percentage using the formula mass of 17.03 g/mol of NH_3.

$[OH^-]$ = antilog [− (14.00 − 11.87)] = 7.4̲13 x 10^{-3} *M*

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the *x* and the (0.007413 *M*) terms into the expression:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \cong \frac{(0.007413)^2}{(x)} = 1.8 \times 10^{-5}$$

Solve the equation for *x*, assuming 0.007413 is much smaller than *x*.

$x = (0.007413)^2 \div (1.8 \times 10^{-5}) \cong [NH_3] = 3.053\ M$

(3.053 mol NH_3/L) x (17.03 g/mol) x (1 L/1000 g) x 100% = 5.1̲99 = 5.2% NH_3

16.147. Find $[H_3O^+]$ and $[C_2H_3O_2^-]$ by solving for the approximate $[H_3O^+]$, noting that *x* is much smaller than the starting 0.92 *M* of acetic acid. The usual table is used but is not shown; only the final setup for $[H_3O^+]$ is shown. Use K_f = 1.858 °C/m for the constant for water.

$[H_3O^+] = [C_2H_3O_2^-] = (1.7 \times 10^{-5} \times 0.92)^{1/2} = 0.003\underline{9}54\ M$

Total molarity of acid + ions = 0.92 + 0.003954 = 0.9̲239

The mass of water in 1 L of solution is

1000 mL x 1.008 g/mL − 0.92 mol x 60.05 g/mol = 9̲52.8 g = 0.9̲528 kg

Molality = *m* = 0.9239 mol ÷ (1.000 L x 0.9528 kg H_2O/L) = 0.9695 *m*

Freezing point = $-\Delta T_f = -K_f c_m$ = (−1.858 °C/*m*) x 0.9695 *m* = −1.801 = −1.8°C

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16.148. Find the $[NH_4^+]$ and $[OH^-]$ by solving for the approximate $[OH^-]$, noting that x is much smaller than the starting 0.87 M of ammonia. The usual table is used but is not shown; only the final setup for $[OH^-]$ is shown. Use $K_f = 1.858$ °C/m for the constant for water.

$[NH_4^+] = [OH^-] = (1.8 \times 10^{-5} \times 0.87)^{1/2} = 0.003957\ M$

Total molarity of base and ions $= 0.87 + 0.003957 = 0.8739\ M$

kg NH_3/L $= 0.87$ mol/L $\times$ 0.017 kg/mol $= 0.0148$ kg NH_3/L

kg H_2O/L $= 0.992$ kg soln/L $- 0.0148$ kg NH_3/L $= 0.977$ kg H_2O/L

Molality $= m = 0.8739$ mol $\div$ (1.000 L $\times$ 0.977 kg solv/L) $= 0.8944\ m$

Freezing point $= -\Delta T_f = -K_f c_m = (-1.858\ °C/m) \times 0.8944\ m = -1.662 = -1.7°C$

16.149. The $[H_3O^+] = -\text{antilog}(-4.35) = 4.46 \times 10^{-5}\ M$. Note that 0.465 L of 0.0941 M NaOH will produce 0.043756 mol of acetate, Ac^-, ion. Rearranging the K_a expression for acetic acid (HAc) and Ac^- and canceling the volume in the mol/L of each, you obtain

$$\frac{[\text{HAc}]}{[\text{Ac}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{4.46 \times 10^{-5}}{1.7 \times 10^{-5}} = \frac{2.63}{1.00} \cong \frac{x\ \text{mol HAc}}{0.043756\ \text{mol Ac}^-}$$

$x = 0.1149$ mol HAc

Total moles of HAc added $= 0.1149 + 0.043756 = 0.1587$ mol HAc

mol/L of pure HAc $= 1049$ g HAc/L $\times$ (1 mol HAc/60.05 g) $= 17.467$ mol/L

L of pure HAc needed $= 0.1587$ mol HAc $\times$ (L/17.467 mol) $= 0.00908$ L (9.1 mL)

16.150. The $[H_3O^+] = -\text{antilog}(-3.50) = 3.16 \times 10^{-4}\ M$. Note that 0.325 L of 0.0857 M NaOH will produce 0.027852 mol of formate, Fo^-, ion. Rearranging the K_a expression for formic acid (HFo) and Fo^- and canceling the volume in the mol/L of each, you obtain

$$\frac{[\text{HFo}]}{[\text{Fo}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{3.16 \times 10^{-4}}{1.7 \times 10^{-4}} = \frac{1.858}{1.00} \cong \frac{x\ \text{mol HFo}}{0.027852\ \text{mol Fo}^-}$$

$x = 0.05175$ mol HF

Total moles of HFo added $= 0.05175 + 0.027852 = 0.079602$ mol HFo

mol/L of pure HFo $= 1220$ g HFo/L $\times$ (1 mol HFo/46.027 g) $= 26.506$ mol/L

L of pure HFo needed $= 0.079602$ mol HAc $\times$ (L/26.506 mol) $= 0.00300$ L (3.0 mL)

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CHAPTER 17

Solubility and Complex-Ion Equilibria

■ SOLUTIONS TO EXERCISES

Note on significant figures If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

17.1.

a. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ $\quad K_{sp} = [Ba^{2+}][SO_4^{2-}]$

b. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ $\quad K_{sp} = [Fe^{3+}][OH^-]^3$

c. $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ $\quad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

17.2. Calculate the molar solubility. Then assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. (Because no concentrations can be given for solid AgCl, dashes are written. In later problems, similar spaces will be left blank.)

$$\frac{1.9 \times 10^{-3}\ \text{g}}{1\ \text{L}} \times \frac{1\ \text{mol}}{143\ \text{g}} = 1.\underline{3}3 \times 10^{-5}\ M$$

Set up the table as usual.

Conc. (M)	$AgCl(s)$	$\rightleftharpoons$	Ag^+	+	Cl^-
Starting	—		0		0
Change	—		$+1.33 \times 10^{-5}$		$+1.33 \times 10^{-5}$
Equilibrium	—		1.33×10^{-5}		1.33×10^{-5}

$$K_{sp} = [Ag^+][Cl^-] = (1.33 \times 10^{-5})(1.33 \times 10^{-5}) = 1.\underline{7}68 \times 10^{-10} = 1.8 \times 10^{-10}$$

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17.3. Calculate the molar solubility. Then assemble the usual concentration table, and substitute from it into the equilibrium-constant expression. (Because no concentrations can be given for solid $Pb_3(AsO_4)_2$, spaces are left blank.)

$$\frac{3.0 \times 10^{-5}\ \text{g}}{1\ \text{L}} \times \frac{1\ \text{mol}}{899\ \text{g}} = 3.\underline{3}4 \times 10^{-8}\ M$$

Conc. (M)	$Pb_3(AsO_4)_2(s)$	$\rightleftharpoons$	$3Pb^{2+}$	+	$2AsO_4^{3-}$
Starting			0		0
Change			$+3(3.34 \times 10^{-8})$		$+2(3.34 \times 10^{-8})$
Equilibrium			$3(3.34 \times 10^{-8})$		$2(3.34 \times 10^{-8})$

$$K_{sp} = [Pb^{2+}]^3[AsO_4^{3-}]^2 = [3 \times (3.34 \times 10^{-8})]^3(2 \times 3.34 \times 10^{-8})^2 = 4.\underline{4}89 \times 10^{-36}$$
$$= 4.5 \times 10^{-36}$$

17.4. Assemble the usual concentration table. Let x equal the molar solubility of $CaSO_4$. When x mol $CaSO_4$ dissolves in 1 L of solution, x mol Ca^{2+} and x mol SO_4^{2-} form.

Conc. (M)	$CaSO_4(s)$	$\rightleftharpoons$	Ca^{2+}	+	SO_4^{2-}
Starting			0		0
Change			$+x$		$+x$
Equilibrium			x		x

Substitute the equilibrium concentrations into the equilibrium-constant expression, and solve for x. Then convert to g $CaSO_4$ per liter.

$$[Ca^{2+}][SO_4^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 2.4 \times 10^{-5}$$

$$x = \sqrt{(2.4 \times 10^{-5})} = 4.\underline{8}9 \times 10^{-3}\ M$$

$$\frac{4.89 \times 10^{-3}\ \text{mol}}{\text{L}} \times \frac{136\ \text{g}}{1\ \text{mol}} = 0.6\underline{6}64 = 0.67\ \text{g/L}$$

17.5.

a. Let x equal the molar solubility of BaF_2. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$BaF_2(s)$	$\rightleftharpoons$	Ba^{2+}	+	$2F^-$
Starting			0		0
Change			$+x$		$+2x$
Equilibrium			x		$2x$

$$[Ba^{2+}][F^-]^2 = K_{sp}$$

$$(x)(2x)^2 = 4x^3 = 1.0 \times 10^{-6}$$

$$x = \sqrt[3]{\frac{1.0 \times 10^{-6}}{4}} = 6.\underline{2}99 \times 10^{-3} = 6.3 \times 10^{-3}\ M$$

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b. At the start, before any BaF_2 dissolves, the solution contains 0.15 *M* F^-. At equilibrium, *x* mol of solid BaF_2 dissolves to yield *x* mol Ba^{2+} and 2*x* mol F^-. Assemble the usual concentration table, and substitute the equilibrium concentrations into the equilibrium-constant expression. As an approximation, assume *x* is negligible compared to 0.15 *M* F^-.

Conc. (*M*)	$BaF_2(s)$ ⇌	Ba^{2+} +	$2F^-$
Starting		0	0.15
Change		+*x*	+2*x*
Equilibrium		*x*	0.15 + 2*x*

$$[Ba^{2+}][F^-]^2 = K_{sp}$$

$$(x)(0.15 + 2x)^2 \cong (x)(0.15)^2 \cong 1.0 \times 10^{-6}$$

$$x \cong \frac{1.0 \times 10^{-6}}{(0.15)^2} = 4.\underline{4}44 \times 10^{-5} = 4.4 \times 10^{-5}\ M$$

Note that adding 2*x* to 0.15 *M* will not change it (to two significant figures), so 2*x* is negligible compared to 0.15 *M*. The solubility of 4.4×10^{-5} *M* in 0.15 *M* NaF is lower than the solubility of 6.3×10^{-3} *M* in pure water.

17.6. Calculate the ion product, Q_c, after evaporation, assuming no precipitation has occurred. Compare it with the K_{sp}.

$$Q_c = [Ca^{2+}][SO_4^{2-}]$$

$$Q_c = (2 \times 0.0052)(2 \times 0.0041) = 8.528 \times 10^{-5}$$

Since $Q_c > K_{sp}$ (2.4×10^{-5}), precipitation occurs.

17.7. Calculate the concentrations of Pb^{2+} and SO_4^{2-}, assuming no precipitation. Use a total volume of 0.456 L + 0.255 L, or 0.711 L.

$$[Pb^{2+}] = \frac{\frac{0.00016\ \text{mol}}{\text{L}} \times 0.255\ \text{L}}{0.711\ \text{L}} = 5.\underline{7}4 \times 10^{-5}\ M$$

$$[SO_4^{2-}] = \frac{\frac{0.00023\ \text{mol}}{\text{L}} \times 0.456\ \text{L}}{0.711\ \text{L}} = 1.\underline{4}8 \times 10^{-4}\ M$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = [Pb^{2+}][SO_4^{2-}] = (5.74 \times 10^{-5})(1.48 \times 10^{-4}) = 8.\underline{4}9 \times 10^{-9}$$

Because Q_c is less than the K_{sp} of 1.7×10^{-8}, no precipitation occurs, and the solution is unsaturated.

17.8. The solubility of AgCN would increase as the pH decreases, because the increasing concentration of H_3O^+ would react with the CN^- to form the weakly ionized acid HCN. As CN^- is removed, more AgCN dissolves to replace the cyanide:

$$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq) \quad [+ H_3O^+ \rightarrow HCN + H_2O]$$

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In the case of AgCl, the chloride ion is the conjugate base of a strong acid and would, therefore, not be affected by any amount of hydrogen ion.

17.9. Because $K_f = 4.8 \times 10^{12}$ and because the starting concentration of NH_3 is much larger than that of the Cu^{2+} ion, you can make a rough assumption that most of the copper(II) is converted to $Cu(NH_3)_4^{2+}$ ion. This ion then dissociates slightly to give a small concentration of Cu^{2+} and additional NH_3. The amount of NH_3 remaining at the start after reacting with 0.015 *M* Cu^{2+} is

$$[0.100\ M - (4 \times 0.015\ M)] = 0.040\ M \text{ starting } NH_3$$

Assemble the usual concentration table using this starting concentration for NH_3 and assuming the starting concentration of Cu^{2+} is zero.

Conc. (*M*)	$Cu(NH_3)_4^{2+}$	$\rightleftharpoons$	Cu^{2+}	+	$4NH_3$
Starting	0.015		0		0.040
Change	$-x$		$+x$		$+4x$
Equilibrium	$0.015 - x$		$+x$		$0.040 + 4x$

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming x is negligible compared to 0.015 and $4x$ is negligible compared to 0.040.

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{(0.015 - x)}{(x)(0.040 + 4x)^4} \cong \frac{(0.015)}{(x)(0.040)^4} \cong 4.8 \times 10^{12}$$

Rearrange and solve for x:

$$x = [Cu^{2+}] \cong (0.015) \div [(4.8 \times 10^{12})(0.040)^4] \cong 1.22 \times 10^{-9} = 1.2 \times 10^{-9}\ M$$

17.10. Start by calculating the $[Ag^+]$ in equilibrium with the $Ag(CN)_2^-$ formed from Ag^+ and CN^-. Then use the $[Ag^+]$ to decide whether or not AgI will precipitate by calculating the ion product and comparing it with the K_{sp} of 8.3×10^{-17} for AgI. Assume all the 0.0045 *M* Ag^+ reacts with CN^- to form 0.0045 *M* $Ag(CN)_2^-$, and calculate the remaining CN^-. Use these as starting concentrations for the usual concentration table.

$$[0.20\ M \text{ KCN} - (2 \times 0.0045\ M)] = 0.191\ M \text{ starting } CN^-$$

Conc. (*M*)	$Ag(CN)_2^-$	$\rightleftharpoons$	Ag^+	+	$2CN^-$
Starting	0.0045		0		0.191
Change	$-x$		$+x$		$+2x$
Equilibrium	$0.0045 - x$		x		$0.191 + 2x$

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming x is negligible compared to 0.0045 and $2x$ is negligible compared to 0.191.

$$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{(0.0045 - x)}{(x)(0.191 + 2x)^2} \cong \frac{(0.0045)}{(x)(0.191)^2} \cong 5.6 \times 10^{18}$$

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Rearrange and solve for x:

$$x = [Ag^+] \cong (0.0045) \div [(5.6 \times 10^{18})(0.191)^2] \cong 2.\underline{2}02 \times 10^{-20}\ M$$

Now, calculate the ion product for AgI:

$$Q_c = [Ag^+][I^-] = (2.20 \times 10^{-20})(0.15) = 3.\underline{3}0 \times 10^{-21} = 3.3 \times 10^{-21}$$

Because Q_c is less than the K_{sp} of 8.3×10^{-17}, no precipitate will form, and the solution is unsaturated.

17.11. Obtain the overall equilibrium constant for this reaction from the product of the individual equilibrium constants of the two individual equations whose sum gives this equation:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$$
$$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) \qquad K_f = 2.9 \times 10^{13}$$
$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq) \qquad K_c = K_{sp} \times K_f = 14.5$$

Assemble the usual table using 1.0 M as the starting concentration of $S_2O_3^{2-}$ and x as the unknown concentration of $Ag(S_2O_3)_2^{3-}$ formed.

Conc. (M)	$AgBr(s)$ +	$2S_2O_3^{2-}$ ⇌	$Ag(S_2O_3)_2^{3-}$ +	Br^-
Starting		1.0	0	0
Change				
Change		$-2x$	$+x$	$+x$
Equilibrium		$1.0 - 2x$	x	x

The equilibrium-constant expression can now be used. Simply substitute all exact equilibrium concentrations into the equilibrium-constant expression. The solution can be obtained without using the quadratic equation.

$$K_c = \frac{[Ag(S_2O_3)_2^{3-}][Br^-]}{[S_2O_3^{2-}]^2} = \frac{(x)^2}{(1.0 - 2x)^2} = 14.5$$

Take the square root of both sides of the two right-hand terms, and solve for x:

$$\frac{x}{(1.0 - 2x)} = 3.\underline{8}08$$

$$x = 3.808\,(1.0 - 2x)$$

$$7.62x + x = 3.808$$

$$x = 0.4\underline{4}17 = 0.44\ M \quad \text{(molar solubility of AgBr in 1.0 } M\ Na_2S_2O_3\text{)}$$

■ ANSWERS TO CONCEPT CHECKS

17.1. Solubility and K_{sp} are related, although not directly. You can compare K_{sp}'s for a series of salts, however, if they have the same number of cations and anions in each of their formulas. (In that case, K_{sp} and solubility are related in the same way for each salt.) In this problem, each of the lead(II) compounds has one Pb^{2+} cation and one anion, so you can compare the K_{sp}'s directly. Lead(II) sulfate has the largest K_{sp} and, therefore, is the most soluble of these lead(II) compounds.

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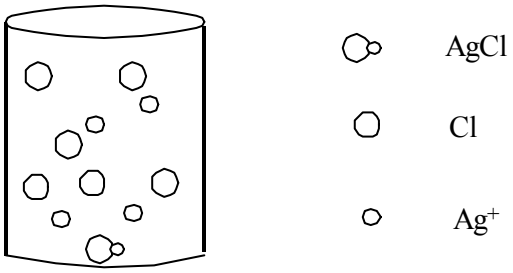
17.2. Let's look at each compound in turn. $NaNO_3$ has no ion in common with $PbSO_4$, so it should have little effect on its solubility. Na_2SO_4 is a soluble compound and provides the common ion SO_4^{2-}, which would repress the solubility of $PbSO_4$. PbS has an ion in common with $PbSO_4$ (Pb^{2+}), but the compound is so insoluble that very little of the Pb^{2+} ion is available. Because of this, the solubility of $PbSO_4$ is little affected by the PbS. Therefore, the $NaNO_3$ solution will dissolve the most $PbSO_4$.

17.3. If NaCl were added to a saturated AgCl solution, the equilibrium would shift to consume the added chloride ion, and some AgCl would precipitate. After the addition of two Cl^- ions, there would be six Cl^- ions, four Ag^+ ions, and one AgCl molecule. The solution would look like the following (For clarity, Na^+ is not shown).



17.4. If you compare K_{sp}'s for magnesium oxalate (8.5×10^{-5}) and calcium oxalate (2.3×10^{-9}), you can see magnesium oxalate is much more soluble in water solution than the calcium salt (the K_{sp} is larger). This means it provides a greater concentration of oxalate ion. In water solution, some of the magnesium oxalate dissolves, giving an oxalate ion concentration that tends to repress the dissolution of calcium oxalate (common-ion effect). The addition of acid tends to remove oxalate ion, but this is replenished by the dissolution of more magnesium oxalate. Therefore, you would expect the magnesium oxalate to be more likely to dissolve.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

17.1. The solubility equation is $Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$. If the molar solubility of $Ni(OH)_2 = x$ molar, the concentrations of the ions in the solution must be $x\ M\ Ni^{2+}$ and $2x\ M\ OH^-$. Substituting into the equilibrium-constant expression gives

$$K_{sp} = [Ni^{2+}][OH^-]^2 = (x)(2x)^2 = 4x^3$$

17.2. Calcium sulfate is less soluble in a solution containing sodium sulfate because the increase in sulfate from the sodium sulfate causes the equilibrium composition in the equation below to shift to the left:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

The result is a decrease in the calcium ion concentration and a decrease in the solubility of calcium sulfate.

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17.3. Substitute the 0.10 *M* concentration of chloride into the solubility product expression and solve for $[Ag^+]$:

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.10} = 1.\underline{8}0 \times 10^{-9} = 1.8 \times 10^{-9}\ M$$

17.4. In order to predict whether or not PbI_2 will precipitate when lead nitrate and potassium iodide are mixed, the concentrations of Pb^{2+} and I^- after mixing would have to be calculated first (if the concentrations are not known or are not given). Then, the value of Q_c, the ion product, would have to be calculated for PbI_2. Finally, Q_c would have to be compared with the value of K_{sp}. If $Q_c > K_{sp}$, then a precipitate will form at equilibrium. If $Q_c \leq K_{sp}$, no precipitate will form.

17.5. Barium fluoride, normally insoluble in water, dissolves in dilute hydrochloric acid because the fluoride ion, once it forms, reacts with the hydronium ion to form weakly ionized HF:

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)\ [+ 2H_3O^+ \rightarrow 2HF + 2H_2O]$$

17.6. Metal ions such as Pb^{2+} and Zn^{2+} are separated by controlling the $[S^{2-}]$ in a solution of saturated H_2S by means of adjusting the pH correctly. Because the K_{sp} of 2.5×10^{-27} for PbS is smaller than the K_{sp} of 1.1×10^{-21} for ZnS, the pH can be adjusted to make the $[S^{2-}]$ just high enough to precipitate PbS without precipitating ZnS.

17.7. When NaCl is first added to a solution of $Pb(NO_3)_2$, a precipitate of $PbCl_2$ forms. As more NaCl is added, the excess chloride reacts further with the insoluble $PbCl_2$, forming soluble complex ions of $PbCl_3^-$ and $PbCl_4^{2-}$:

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$$

$$PbCl_2(s) + Cl^-(aq) \rightleftharpoons PbCl_3^-(aq)$$

$$PbCl_3^-(aq) + Cl^-(aq) \rightleftharpoons PbCl_4^{2-}(aq)$$

17.8. When a small amount of NaOH is added to a solution of $Al_2(SO_4)_3$, a precipitate of $Al(OH)_3$ forms at first. As more NaOH is added, the excess hydroxide ion reacts further with the insoluble $Al(OH)_3$, forming a soluble complex ion of $Al(OH)_4^-$.

17.9. The Ag^+, Cu^{2+}, and Ni^{2+} ions can be separated in two steps: (1) Add HCl to precipitate just the Ag^+ as AgCl, leaving the others in solution. (2) After pouring the solution away from the precipitate, add 0.3 *M* HCl and H_2S to precipitate only the CuS away from the Ni^{2+} ion, whose sulfide is soluble under these conditions.

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17.10. By controlling the pH through the appropriate buffer, one can control the $[CO_3^{2-}]$ using the equilibrium reaction:

$$H_3O^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$$

Calcium carbonate is much less soluble than magnesium carbonate and thus will precipitate in weakly basic solution, whereas magnesium carbonate will not. Magnesium carbonate will precipitate only in highly basic solution. (There is the possibility that $Mg(OH)_2$ might precipitate, but the $[OH^-]$ is too low for this to occur.)

17.11. The answer is c, 9.1×10^{-40}.

17.12. The answer is e, $K_{sp} = [Ag^+]^3[PO_4^{3-}]$.

17.13. The answer is d, 1.1×10^{-8} *M*.

17.14. The answer is a, AX.

■ ANSWERS TO CONCEPT EXPLORATIONS

17.15.

a. Yes, the beakers with MnS, AgCl, and $BaSO_4$ would still have an observable solid present. These salts are insoluble in water.

b. Yes, the potassium ion concentration can be calculated for the solutions of KNO_3 and K_2S. Each salt has a concentration of 0.10 *M* and dissociates completely in water. For KNO_3, there is one K^+ ion per formula unit, so the concentration of K^+ is 0.10 *M* for this solution. For K_2S, there are two K^+ ions per formula unit, so the K^+ ion concentration is $2 \times 0.10\ M = 0.20\ M$. The K^+ ion concentration in K_2S is double the K^+ ion concentration in KNO_3.

c. Since $(NH_4)_2S$ and K_2S are soluble in water, and since each has one S^{2-} ion per formula unit, these two solutions have the same S^{2-} concentration. MnS is insoluble in water, so the S^{2-} concentration is this solution is much less than for the other two. Thus the order is $(NH_4)_2S = K_2S >> MnS$.

d. Yes, you need additional information to calculate the sulfide-ion concentration in the solution of MnS. The additional information needed is the value of K_{sp} for this compound.

e. More information is required to determine the ion concentrations present in the solutions of MnS, AgCl, and $BaSO_4$. You can find the K_{sp} values from the table in the text or from some other source.

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f. The solubility of an ionic compound is related to the concentrations of the ions through the solubility product constant expression for that compound. Consider the hypothetical compound A_xB_y. The reaction for its dissociation in water, and the related solubility product constant expression, are

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

17.16.

a. The chemical equations are

$$AX \rightleftharpoons A^+ + X^-$$

$$AX_2 \rightleftharpoons A^{2+} + 2X^-$$

$$AX_3 \rightleftharpoons A^{3+} + 3X^-$$

b. The concentration of each solution in the compound is 0.25 *M*. This is because 0.25 mol of the compound was dissolved in 1.0 L of water in each case. Also, when considering the compounds, it is not necessary to consider how each may dissolve in water to form ions.

c. In each of these solutions, the concentration of A^+ ion will be different. Just knowing the stoichiometry of the reaction is not enough. You will need the values of the solubility product constant for each compound. Since the solubility product constant is the same for all the compounds, but each compound dissociates into a different number of ions, the solubilities of the compounds will be different.

d. The greatest molar solubility will be for the compound that dissociates into the most ions per formula unit. In this case AX_3 will have the greatest molar solubility.

e. The molar solubilities of the compounds are as follows. First, for AX,

$$K_{sp} = [A^+][X^-] = s^2 = 5.5 \times 10^{-7}.$$

$$s = = \sqrt{5.5 \times 10^{-7}} = 7.\underline{4}1 \times 10^{-4} = 7.4 \times 10^{-4}\ M$$

For AX_2,

$$K_{sp} = [A^{2+}][X^-]^2 = 4s^3 = 5.5 \times 10^{-7}.$$

$$s = \sqrt[3]{\frac{5.5 \times 10^{-7}}{4}} = 5.\underline{1}6 \times 10^{-3} = 5.2 \times 10^{-3}\ M$$

For AX_3,

$$K_{sp} = [A^{3+}][X^-]^3 = 27s^4 = 5.5 \times 10^{-7}.$$

$$s = \sqrt[4]{\frac{5.5 \times 10^{-7}}{27}} = 1.\underline{1}9 \times 10^{-2} = 1.2 \times 10^{-2} M$$

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■ ANSWERS TO CONCEPTUAL PROBLEMS

17.17.

a. Since both compounds contain the same number of ions, the salt with the larger K_{sp} value will be more soluble. The K_{sp} for AgCl is 1.8×10^{-10} and for AgI is 8.3×10^{-17}. Therefore, silver chloride (AgCl) is more soluble.

b. Since both compounds contain the same number of ions, the salt with the larger K_{sp} value will be more soluble. The K_{sp} for $Mg(OH)_2$ is 1.8×10^{-11} and for $Cu(OH)_2$ is 2.6×10^{-19}. Therefore, magnesium hydroxide ($Mg(OH)_2$) is more soluble.

17.18. Dissolve a sample of each mineral in water in a separate container. NaCl is soluble in water, and CaF_2 is insoluble in water ($K_{sp} = 3.4 \times 10^{-11}$), so the sample that dissolves is NaCl, and the sample that doesn't dissolve is CaF_2.

17.19. 0.1 *M* NaCl will be most effective in causing a precipitate from a saturated solution of $PbCl_2$, since it is completely soluble and contains the common ion Cl^-. Therefore, the answer is a.

17.20. The beaker on the left depicts all the AgCl as individual formula units in solution. This implies AgCl is a soluble nonelectrolye, which is not the case since AgCl as a slightly soluble ionic compound. The center beaker depicts AgCl as a soluble ionic compound that completely dissolves in solution, leaving no AgCl(*s*). Once again, this cannot be correct since AgCl is slightly soluble. The beaker on the right indicates there are ions of Ag^+ and Cl^- present in the solution along with solid AgCl. This is consistent with AgCl being a slightly soluble ionic compound.

17.21. The beaker on the left depicts all the NaCl as individual formula units in solution. This implies NaCl is a soluble nonelectrolye, which is not the case since NaCl is a very soluble ionic compound that produces ions in solution. The center beaker depicts NaCl as a soluble ionic compound that completely dissolves in solution, producing only $Na^+(aq)$ and $Cl^-(aq)$. This must be correct since NaCl is a very soluble ionic compound. The beaker on the right indicates that there are ions of Na^+ and Cl^- present in the solution, along with solid NaCl. The presence of solid is not consistent with NaCl being an unsaturated solution as stated in the problem.

17.22. When first added to a solution of copper(II) nitrate, the ammonia causes a pale blue precipitate of $Cu(OH)_2$ to form ($K_{sp} = 2.6 \times 10^{-19}$). After enough ammonia has been added, however, the complex ion $Cu(NH_3)_4^{2+}$ forms ($K_f = 4.8 \times 10^{12}$), and the precipitate dissolves.

17.23. Add just enough Na_2SO_4 to precipitate all the Ba^{2+}; filter off the $BaSO_4$; add more Na_2SO_4 to precipitate all the Ca^{2+}; filter off the $CaSO_4$; Mg^{2+} remains in the solution.

17.24. When a precipitate fails to form when HCl is added to the solution, this indicates that no silver ion is present. When a precipitate fails to form when the solution is acidified and H_2S is added, this indicates that no copper(II) ion is present in the solution.

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SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

17.25.

a. NaBr is soluble (Group IA salts are soluble).

b. PbI_2 is insoluble (PbI_2 is an insoluble iodide).

c. $BaCO_3$ is insoluble (carbonates are generally insoluble).

d. $(NH_4)_2SO_4$ is soluble (all ammonium salts are soluble).

17.26.

a. $Ca(NO_3)_2$ is soluble (nitrate salts are soluble).

b. AgBr is insoluble (AgBr is an insoluble bromide salt).

c. MgI_2 is soluble (iodide salts are generally soluble).

d. $PbSO_4$ is insoluble ($PbSO_4$ is an insoluble sulfate salt).

17.27.

a. $K_{sp} = [Mg^{2+}][OH^-]^2$

b. $K_{sp} = [Sr^{2+}][CO_3^{2-}]$

c. $K_{sp} = [Ca^{2+}]^3[AsO_4^{3-}]^2$

d. $K_{sp} = [Fe^{3+}][OH^-]^3$

17.28.

a. $K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2$

b. $K_{sp} = [Fe^{3+}][PO_4^{3-}]$

c. $K_{sp} = [Pb^{2+}][I^-]^2$

d. $K_{sp} = [Ag^+]^2[S^{2-}]$

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17.29. Calculate molar solubility, assemble the usual table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. (Dashes are given for $AgBrO_3(s)$. In later problems, the dashes are omitted.)

$$\frac{7.2 \times 10^{-3}\ \text{g}}{\text{L}} \times \frac{1\ \text{mol}}{236\ \text{g}} = 3.\underline{0}5 \times 10^{-5}\ M$$

Conc. (M)	$AgBrO_3(s)$	$\rightleftharpoons$	Ag^+	+	BrO_3^-
Starting	—		0		0
Change	—		$+3.05 \times 10^{-5}$		$+3.05 \times 10^{-5}$
Equilibrium	—		3.05×10^{-5}		3.05×10^{-5}

$$K_{sp} = [Ag^+][BrO_3^-] = (3.05 \times 10^{-5})(3.05 \times 10^{-5}) = 9.\underline{3}02 \times 10^{-10} = 9.3 \times 10^{-10}$$

17.30. Assemble the usual concentration table, and substitute from it the equilibrium concentrations into the equilibrium-constant expression.

Conc. (M)	$MgC_2O_4(s)$	$\rightleftharpoons$	Mg^{2+}	+	$C_2O_4^{2-}$
Starting	—		0		0
Change	—		$+9.3 \times 10^{-3}$		$+9.3 \times 10^{-3}$
Equilibrium	—		9.3×10^{-3}		9.3×10^{-3}

$$K_{sp} = [Mg^{2+}][C_2O_4^{2-}] = (9.3 \times 10^{-3})(9.3 \times 10^{-3}) = 8.\underline{6}49 \times 10^{-5} = 8.6 \times 10^{-5}$$

17.31. Calculate the molar solubility. Then assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$$\frac{0.13\ \text{g}}{0.100\ \text{L}} \times \frac{1\ \text{mol}}{413\ \text{g}} = 3.\underline{1}47 \times 10^{-3}\ M$$

Conc. (M)	$Cu(IO_3)_2(s)$	$\rightleftharpoons$	Cu^{2+}	+	$2IO_3^-$
Starting			0		0
Change			$+3.147 \times 10^{-3}$		$+2 \times 3.147 \times 10^{-3}$
Equilibrium			3.147×10^{-3}		$2 \times 3.147 \times 10^{-3}$

$$K_{sp} = [Cu^{2+}][IO_3^-]^2 = (3.147 \times 10^{-3})[2(3.147 \times 10^{-3})]^2 = 1.\underline{2}47 \times 10^{-7} = 1.2 \times 10^{-7}$$

17.32. Calculate the molar solubility. Then assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$$\frac{1.59\ \text{g}}{\text{L}} \times \frac{1\ \text{mol}}{431.74\ \text{g}} = 3.6\underline{8}2 \times 10^{-3}\ M$$

Conc. (M)	$Ag_2Cr_2O_7(s)$	$\rightleftharpoons$	$2Ag^+$	+	$Cr_2O_7^{2-}$
Starting			0		0
Change			$+2(3.6\underline{8}2 \times 10^{-3})$		$3.6\underline{8}2 \times 10^{-3}$
Equilibrium			$2(3.6\underline{8}2 \times 10^{-3})$		$3.6\underline{8}2 \times 10^{-3}$

$$K_{sp} = [Ag^+]^2[Cr_2O_7^{2-}] = [2(3.6\underline{8}2 \times 10^{-3})]^2(3.6\underline{8}2 \times 10^{-3}) = 1.9\underline{9}7 \times 10^{-7} = 2.00 \times 10^{-7}$$

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17.33. Calculate the pOH from the pH, and then convert pOH to $[OH^-]$. Then assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

$$pOH = 14.00 - 10.52 = 3.48$$

$$[OH^-] = \text{antilog}(-pOH) = \text{antilog}(-3.48) = 3.\underline{3}11 \times 10^{-4}\ M$$

$$[Mg^{2+}] = [OH^-] \div 2 = (3.311 \times 10^{-4}) \div 2 = 1.655 \times 10^{-4}\ M$$

Conc. (M)	$Mg(OH)_2(s)$ ⇌	Mg^{2+}	+ $2OH^-$
Starting		0	0
Change		$+1.655 \times 10^{-4}$	$+3.311 \times 10^{-4}$
Equilibrium		1.655×10^{-4}	3.311×10^{-4}

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (1.655 \times 10^{-4})(3.311 \times 10^{-4})^2 = 1.\underline{8}1 \times 10^{-11} = 1.8 \times 10^{-11}$$

17.34. Calculate the pOH from the pH, and then convert pOH to $[OH^-]$.

$$pOH = 14.00 - 12.35 = 1.65$$

$$[OH^-] = \text{antilog}(-pOH) = \text{antilog}(-1.65) = 2.\underline{2}38 \times 10^{-2}\ M$$

$$[Ca^{2+}] = [OH^-] \div 2 = (2.238 \times 10^{-2}) \div 2 = 1.119 \times 10^{-2}\ M$$

Assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

Conc. (M)	$Ca(OH)_2(s)$ ⇌	Ca^{2+}	+ $2OH^-$
Starting		0	0
Change		$+1.119 \times 10^{-2}$	$+2.238 \times 10^{-2}$
Equilibrium		1.119×10^{-2}	2.238×10^{-2}

$$K_{sp} = [Ca^{2+}][OH^-]^2 = (1.119 \times 10^{-2})(2.238 \times 10^{-2})^2 = 5.\underline{6}0 \times 10^{-6} = 5.6 \times 10^{-6}$$

17.35. Assemble the usual concentration table. Let x equal the molar solubility of $SrCO_3$. When x mol $SrCO_3$ dissolves in 1 L of solution, x mol Sr^{2+} and x mol CO_3^{2-} form.

Conc. (M)	$SrCO_3(s)$ ⇌	Sr^{2+}	+ CO_3^{2-}
Starting		0	0
Change		$+x$	$+x$
Equilibrium		x	x

Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x. Then convert to grams $SrCO_3$ per liter.

$$[Sr^{2+}][CO_3^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 9.3 \times 10^{-10}$$

$$x = \sqrt{(9.3 \times 10^{-10})} = 3.\underline{0}4 \times 10^{-5}\ M$$

$$\frac{3.04 \times 10^{-5}\ \text{mol}}{\text{L}} \times \frac{147.63\ \text{g}}{1\ \text{mol}\ SrCO_3} = 4.\underline{5}0 \times 10^{-3} = 0.0045\ \text{g/L}$$

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17.36. Assemble the usual concentration table. Let x equal the molar solubility of $MgCO_3$. When x mol $MgCO_3$ dissolves in 1 L of solution, x mol Mg^{2+} and x mol CO_3^{2-} form.

Conc. (M)	$MgCO_3(s)$ ⇌	Mg^{2+}	+	CO_3^{2-}
Starting		0		0
Change		$+x$		$+x$
Equilibrium		x		x

Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x. Then convert to grams $MgCO_3$ per liter.

$$[Mg^{2+}][CO_3^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 1.0 \times 10^{-5}$$

$$x = \sqrt{(1.0 \times 10^{-5})} = 3.162 \times 10^{-3}\ M$$

$$\frac{3.162 \times 10^{-3}\ \text{mol}}{\text{L}} \times \frac{84.32\ \text{g}}{1\ \text{mol}\ MgCO_3} = 0.2666 = 0.27\ \text{g/L}$$

17.37. Let x equal the molar solubility of PbF_2. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$PbF_2(s)$ ⇌	Pb^{2+}	+	$2F^-$
Starting		0		0
Change		$+x$		$+2x$
Equilibrium		x		$2x$

$$[Pb^{2+}][F^-]^2 = K_{sp}$$

$$(x)(2x)^2 = 4x^3 = 2.7 \times 10^{-8}$$

$$x = \sqrt[3]{\frac{2.7 \times 10^{-8}}{4}} = 1.88 \times 10^{-3} = 1.9 \times 10^{-3}\ M$$

17.38. Let x equal the molar solubility of MgF_2. Assemble the usual concentration table.

Conc. (M)	$MgF_2(s)$ ⇌	Mg^{2+}	+	$2F^-$
Starting		0		0
Change		x		$+2x$
Equilibrium		x		$2x$

Substitute from the table into the equilibrium-constant expression.

$$[Mg^{2+}][F^-]^2 = K_{sp}$$

$$(x)(2x)^2 = 4x^3 = 7.4 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{7.4 \times 10^{-11}}{4}} = 2.644 \times 10^{-4} = 2.6 \times 10^{-4}\ M$$

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17.39. At the start, before any $SrSO_4$ dissolves, the solution contains 0.23 *M* SO_4^{2-}. At equilibrium, *x* mol of solid $SrSO_4$ dissolves to yield *x* mol Sr^{2+} and *x* mol SO_4^{2-}. Assemble the usual concentration table, and substitute the equilibrium concentrations into the equilibrium-constant expression. As an approximation, assume *x* is negligible compared to 0.23 *M* SO_4^{2-}.

Conc. (*M*)	$SrSO_4(s)$ ⇌	Sr^{2+} +	SO_4^{2-}
Starting		0	0.23
Change		$+x$	$+x$
Equilibrium		X	$0.23 + x$

$$[Sr^{2+}][SO_4^{2-}] = K_{sp}$$

$$(x)(0.23 + x) \cong (x)(0.23) \cong 2.5 \times 10^{-7}$$

$$x \cong \frac{2.5 \times 10^{-7}}{0.23} = 1.\underline{0}86 \times 10^{-6}\ M$$

$$\frac{1.086 \times 10^{-6}\ \text{mol}}{\text{L}} \times \frac{183.69\ \text{g}}{1\ \text{mol}\ SrSO_4} = 1.\underline{9}9 \times 10^{-4} = 2.0 \times 10^{-4}\ \text{g/L}$$

Note that adding x to 0.23 *M* will not change it (to two significant figures), so *x* is negligible compared to 0.23 *M*.

17.40. Let *x* = the molar solubility of $PbCrO_4$. At the start, before any $PbCrO_4$ dissolves, the solution contains 0.13 *M* CrO_4^{2-}. At equilibrium, *x* mol of solid $PbCrO_4$ dissolves to yield x mol Pb^{2+} and *x* mol CrO_4^{2-}. Assemble the usual concentration table, and substitute the equilibrium concentrations into the equilibrium-constant expression. As an approximation, assume *x* is negligible compared to 0.13 *M* CrO_4^{2-}.

Conc. (*M*)	$PbCrO_4(s)$ ⇌	Pb^{2+} +	CrO_4^{2-}
Starting		0	0.13
Change		$+x$	$+x$
Equilibrium		x	$0.13 + x$

$$[Pb^{2+}][CrO_4^{2-}] = K_{sp}$$

$$(x)(0.13 + x) \cong (x)(0.13) \cong 1.8 \times 10^{-14}$$

$$x \cong \frac{1.8 \times 10^{-14}}{0.13} = 1.\underline{3}8 \times 10^{-13}\ M$$

$$\frac{1.38 \times 10^{-13}\ \text{mol}}{\text{L}} \times \frac{323.2\ \text{g}}{1\ \text{mol}\ PbCrO_4} = 4.\underline{4}7 \times 10^{-11} = 4.5 \times 10^{-11}\ \text{g/L}$$

Note that adding *x* to 0.13 *M* will not change it (to two significant figures), so *x* is negligible compared to 0.13 *M*.

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17.41. Calculate the value of K_{sp} from the solubility using the concentration table. Then, using the common-ion calculation, assemble another concentration table. Use 0.020 *M* NaF as the starting concentration of F^- ion. Substitute the equilibrium concentrations from the table into the equilibrium-constant expression. As an approximation, assume $2x$ is negligible compared to 0.020 *M* F^- ion.

$$\frac{0.016\ \text{g}}{\text{L}} \times \frac{1\ \text{mol}\ MgF_2}{62.31\ \text{g}} = 2.\underline{5}67 \times 10^{-4}\ M$$

Conc. (*M*)	$MgF_2(s)$	$\rightleftharpoons$	Mg^{2+}	+	$2F^-$
Starting			0		0.13
Change			$+2.\underline{5}67 \times 10^{-4}$		$+2 \times 2.\underline{5}67 \times 10^{-4}$
Equilibrium			$2.\underline{5}67 \times 10^{-4}$		$2 \times 2.\underline{5}67 \times 10^{-4}$

$$K_{sp} = [Mg^{2+}][F^-]^2 = (2.\underline{5}67 \times 10^{-4})[2(2.\underline{5}67 \times 10^{-4})]^2 = 6.\underline{7}72 \times 10^{-11}$$

Now, use K_{sp} to calculate the molar solubility of MgF_2.

Conc. (*M*)	$MgF_2(s)$	$\rightleftharpoons$	Mg^{2+}	+	$2F^-$
Starting			0		0.020
Change			$+x$		$+2x$
Equilibrium			x		$0.020 + 2x$

$$[Mg^{2+}][F^-]^2 = K_{sp}$$

$$(x)(0.020 + 2x)^2 \cong (x)(0.020)^2 = 6.\underline{7}72 \times 10^{-11}$$

$$x \cong \frac{6.772 \times 10^{-11}}{(0.020)^2} = 1.\underline{6}93 \times 10^{-7}\ M$$

$$\frac{1.693 \times 10^{-7}\ \text{mol}}{\text{L}} \times \frac{62.31\ \text{g}}{1\ \text{mol}\ MgF_2} = 1.\underline{0}54 \times 10^{-5} = 1.1 \times 10^{-5}\ \text{g/L}$$

17.42. Calculate the value of K_{sp} from the solubility using the concentration table. Then, using the common-ion calculation, assemble another concentration table. Use 0.45 *M* Na_2SO_4 as the starting concentration of SO_4^{2-} ion. Substitute the equilibrium concentrations from the table into the equilibrium-constant expression. As an approximation, assume x is negligible compared to 0.45 *M* SO_4^{2-} ion.

$$\frac{8.0\ \text{g}}{\text{L}} \times \frac{1\ \text{mol}\ Ag_2SO_4}{311.81\ \text{g}} = 0.02\underline{5}65\ M$$

Conc. (*M*)	$Ag_2SO_4(s)$	$\rightleftharpoons$	$2Ag^+$	+	SO_4^{2-}
Starting			0		0
Change			$+2 \times 0.02565$		$+0.02565$
Equilibrium			2×0.02565		0.02565

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2 \times 0.02565)^2(0.02565) = 6.\underline{7}55 \times 10^{-5}$$

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Now, use K_{sp} to calculate the molar solubility of Ag_2SO_4.

Conc. (M)	$Ag_2SO_4(s)$ ⇌	$2Ag^+$ +	SO_4^{2-}
Starting		0	0.45
Change		$+2x$	$+x$
Equilibrium		$2x$	$0.45 + x$

$$[Ag^+]^2[SO_4^{2-}] = K_{sp}$$

$$(2x)^2(0.45 + x) \cong (2x)^2(0.45) = 6.755 \times 10^{-5}$$

$$x \cong \sqrt{\frac{(6.755 \times 10^{-5})}{4 \times 0.45}} = 6.\underline{1}25 \times 10^{-3}\ M$$

$$\frac{6.125 \times 10^{-3}\ \text{mol}}{\text{L}} \times \frac{311.81\ \text{g}}{1\ \text{mol}\ Ag_2SO_4} = 1.\underline{9}10 = 1.9\ \text{g/L}$$

17.43. The concentration table follows.

Conc. (M)	$MgC_2O_4(s)$ ⇌	Mg^{2+} +	$C_2O_4^{2-}$
Starting		0	0.020
Change		$+x$	$+x$
Equilibrium		x	$0.020 + x$

The equilibrium-constant expression is

$$K_{sp} = [Mg^{2+}][C_2O_4^{2-}]$$

$$8.5 \times 10^{-5} = (x)(0.020 + x)$$

$$x^2 + 0.020x - (8.5 \times 10^{-5}) = 0$$

Solving the quadratic equation gives

$$x = \frac{-0.020 \pm \sqrt{(0.020)^2 + 4(8.5 \times 10^{-5})}}{2} = 0.00\underline{3}6\ M$$

The solubility in grams per liter is

$$\frac{0.0036\ \text{mol}}{\text{L}} \times \frac{112\ \text{g}}{1\ \text{mol}} = 0.\underline{4}03 = 0.4\ \text{g/L}$$

17.44. The concentration table follows.

Conc. (M)	$SrSO_4(s)$ ⇌	Sr^{2+} +	SO_4^{2-}
Starting		0	0.0015
Change		$+x$	$+x$
Equilibrium		x	$0.0015 + x$

$$K_{sp} = 2.5 \times 10^{-7} = (x)(0.0015 + x)$$

$$x^2 + 0.0015x - (2.5 \times 10^{-7}) = 0$$

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Solving the quadratic equation gives

$$x = \frac{-0.0015 \pm \sqrt{(0.0015)^2 + 4(2.5 \times 10^{-7})}}{2} = 1.\underline{5}1 \times 10^{-4}\ M$$

The solubility in grams per liter is

$$\frac{1.51 \times 10^{-4}\ \text{mol}}{\text{L}} \times \frac{183.69\ \text{g}}{1\ \text{mol}\ SrSO_4} = 0.02\underline{7}7 = 0.030\ \text{g/L}$$

17.45.

a. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then use parentheses for the concentrations.

$$Q_c = [Ba^{2+}][F^-]^2$$

$$Q_c = (0.020)(0.015)^2 = 4.\underline{5}0 \times 10^{-6}$$

Since $Q_c > K_{sp}$ (1.0×10^{-6}), precipitation will occur.

b. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then use parentheses for the concentrations.

$$Q_c = [Pb^{2+}][Cl^-]^2$$

$$Q_c = (0.035)(0.15)^2 = 7.\underline{8}7 \times 10^{-4}$$

Since $Q_c > K_{sp}$ (1.6×10^{-5}), precipitation will occur.

17.46.

a. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then use parentheses for the concentrations.

$$Q_c = [Sr^{2+}][CO_3^{2-}]$$

$$Q_c = (0.012)(0.0015) = 1.\underline{8}0 \times 10^{-5}$$

Since $Q_c > K_{sp}$ (9.3×10^{-10}), precipitation will occur.

b. Calculate Q_c, the ion product of the solution, using the concentrations in the problem as the concentrations present after mixing and assuming no precipitation. Then compare Q_c with K_{sp} to determine whether precipitation has occurred. Start by defining the ion product with brackets as used for the definition of K_{sp}; then use parentheses for the concentrations.

$$Q_c = [Pb^{2+}][Cl^-]^2$$

$$Q_c = (0.0012)(0.041)^2 = 2.\underline{0}1 \times 10^{-6}$$

Since $Q_c > K_{sp}$ (1.6×10^{-9}), precipitation will occur.

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17.47. Calculate the ion product, Q_c, after preparation of the solution, assuming no precipitation has occurred. Compare it with the K_{sp}.

$$Q_c = [Pb^{2+}][CrO_4^{2-}]$$

$$Q_c = (5.0 \times 10^{-4})(5.0 \times 10^{-5}) = 2.\underline{5}0 \times 10^{-8}\ M^2 \quad (> K_{sp} \text{ of } 1.8 \times 10^{-14})$$

The solution is supersaturated before equilibrium is reached. At equilibrium, precipitation occurs, and the solution is saturated.

17.48. Calculate the ion product, Q_c, after preparation of the solution and assuming no precipitation has occurred. Compare it with the K_{sp}.

$$Q_c = [Pb^{2+}][SO_4^{2-}]$$

$$Q_c = (5.0 \times 10^{-4})(1.0 \times 10^{-5}) = 5.\underline{0}0 \times 10^{-9}\ M^2 \quad (< K_{sp} \text{ of } 1.7 \times 10^{-8})$$

At equilibrium, no precipitation occurs, and the solution is unsaturated.

17.49. Calculate the concentrations of Mg^{2+} and OH^-, assuming no precipitation. Use a total volume of 1.0 L + 1.0 L, or 2.0 L. (Note that the concentrations are halved when the volume is doubled.)

$$[Mg^{2+}] = \frac{\dfrac{0.0020 \text{ mol}}{\text{L}} \times 1.0 \text{ L}}{2.0 \text{ L}} = 1.\underline{0}0 \times 10^{-3}\ M$$

$$[OH^-] = \frac{\dfrac{0.00010 \text{ mol}}{\text{L}} \times 1.0 \text{ L}}{2.0 \text{ L}} = 5.\underline{0}0 \times 10^{-5}\ M$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = [Mg^{2+}][OH^-]^2 = (1.00 \times 10^{-3})(5.00 \times 10^{-5})^2 = 2.\underline{5}0 \times 10^{-12}$$

Because Q_c is less than the K_{sp} of 1.8×10^{-11}, no precipitation occurs, and the solution is unsaturated.

17.50. Calculate the concentrations of Ca^{2+} and SO_4^{2-}, assuming no precipitation. Use a total volume of 0.045 L + 0.055 L, or 0.100 L.

$$[Ca^{2+}] = \frac{\dfrac{0.015 \text{ mol}}{\text{L}} \times 0.045 \text{ L}}{0.100 \text{ L}} = 0.006\underline{7}5\ M$$

$$[SO_4^{2-}] = \frac{\dfrac{0.010 \text{ mol}}{\text{L}} \times 0.055 \text{ L}}{0.100 \text{ L}} = 0.005\underline{5}0\ M$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = [Ca^{2+}][SO_4^{2-}] = (0.00675)(0.00550) = 3.\underline{7}1 \times 10^{-5}$$

Because Q_c is greater than the K_{sp} of 2.4×10^{-5}, the solution is supersaturated before equilibrium is reached. At equilibrium, precipitation occurs, and the solution is saturated.

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17.51. Calculate the concentrations of Ba^{2+} and F^-, assuming no precipitation. Use a total volume of 0.045 L + 0.075 L, or 0.120 L.

$$[Ba^{2+}] = \frac{\frac{0.0015 \text{ mol}}{\text{L}} \times 0.045 \text{ L}}{0.120 \text{ L}} = 5.\underline{6}25 \times 10^{-4}\ M$$

$$[F^-] = \frac{\frac{0.0025 \text{ mol}}{\text{L}} \times 0.075 \text{ L}}{0.120 \text{ L}} = 1.\underline{5}6 \times 10^{-3}\ M$$

Calculate the ion product and compare it to K_{sp}.

$$Q_c = [Ba^{2+}][F^-]^2 = (5.625 \times 10^{-4})(1.56 \times 10^{-3})^2 = 1.\underline{3}6 \times 10^{-9}$$

Because Q_c is less than the K_{sp} of 1.0×10^{-6}, no precipitation occurs, and the solution is unsaturated.

17.52. Calculate the concentrations of Pb^{2+} and Cl^-, assuming no precipitation. Use a total volume of 0.040 L + 0.065 L, or 0.105 L.

$$[Pb^{2+}] = \frac{\frac{0.010 \text{ mol}}{\text{L}} \times 0.065 \text{ L}}{0.105 \text{ L}} = 6.\underline{1}9 \times 10^{-3}\ M$$

$$[Cl^-] = \frac{\frac{0.035 \text{ mol}}{\text{L}} \times 0.040 \text{ L}}{0.105 \text{ L}} = 1.\underline{3}3 \times 10^{-2}\ M$$

Calculate the ion product and compare it to K_{sp}.

$$Q_c = [Pb^{2+}][Cl^-]^2 = (6.19 \times 10^{-3})(1.33 \times 10^{-2})^2 = 1.\underline{0}9 \times 10^{-6}$$

Because Q_c is less than the K_{sp} of 1.6×10^{-5}, no precipitation occurs, and the solution is unsaturated.

17.53. A mixture of $CaCl_2$ and K_2SO_4 can precipitate only $CaSO_4$ because KCl is soluble. Use the K_{sp} expression to calculate the $[Ca^{2+}]$ needed to just begin precipitating the 0.020 M SO_4^{2-} (in essentially a saturated solution). Then convert to moles.

$$[Ca^{2+}][SO_4^{2-}] = K_{sp} = 2.4 \times 10^{-5}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{2.4 \times 10^{-5}}{2.0 \times 10^{-2}} = 1.\underline{2}0 \times 10^{-3}\ M$$

The number of moles in 1.5 L of this calcium-containing solution is (mol $CaCl_2$ = mol Ca^{2+}):

$$1.5 \text{ L} \times (1.20 \times 10^{-3}) \text{ mol/L} = 1.\underline{8}0 \times 10^{-3} = 0.0018 \text{ mol } CaCl_2$$

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17.54. A mixture of $MgSO_4$ and NaOH can precipitate only $Mg(OH)_2$ because Na_2SO_4 is soluble. Use the K_{sp} expression to calculate the $[Mg^{2+}]$ needed to just begin precipitating the 0.040 *M* OH^- (in essentially a saturated solution). Then convert to moles and finally to grams.

$$[Mg^{2+}][OH^-]^2 = K_{sp} = 1.8 \times 10^{-11}$$

$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(0.040)^2} = 1.\underline{1}25 \times 10^{-8}\ M$$

The number of moles, and grams, in 0.456 L (456 mL) of this magnesium-containing solution is (mol $MgSO_4$ = mol Mg^{2+}).

$$0.456\ L \times (1.125 \times 10^{-8}\ mol/L) = 5.\underline{1}3 \times 10^{-9}\ mol\ MgSO_4$$

$$(5.13 \times 10^{-9}\ mol\ MgSO_4) \times (120\ g\ MgSO_4/1\ mol\ MgSO_4)$$

$$= 6.\underline{1}56 \times 10^{-7} = 6.2 \times 10^{-7}\ g\ MgSO_4$$

17.55. Because the $AgNO_3$ solution is relatively concentrated, ignore the dilution of the solution of Cl^- and I^- from the addition of $AgNO_3$. The $[Ag^+]$ just as the AgCl begins to precipitate can be calculated from the K_{sp} expression for AgCl using $[Cl^-] = 0.015\ M$. Therefore, for AgCl,

$$[Ag^+][Cl^-] = K_{sp}$$

$$[Ag^+][0.015] = 1.8 \times 10^{-10}$$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.015} = 1.\underline{2}0 \times 10^{-8}\ M$$

The $[I^-]$ at this point can be obtained by substituting the $[Ag^+]$ into the K_{sp} expression for AgI. Therefore, for AgI,

$$[Ag^+][I^-] = K_{sp}$$

$$[1.20 \times 10^{-8}][I^-] = 8.3 \times 10^{-17}$$

$$[I^-] = \frac{8.3 \times 10^{-17}}{1.2 \times 10^{-8}} = 6.\underline{9}1 \times 10^{-9} = 6.9 \times 10^{-9}\ M$$

17.56. Because the problem asks you to find $[Cl^-]$ at the point when Ag_2CrO_4 just begins to precipitate, you start with the K_{sp} expression for Ag_2CrO_4 and ignore temporarily what may have happened to the Cl^- ion. Also, because the $AgNO_3$ solution is relatively concentrated, ignore the dilution of the solution of Cl^- and CrO_4^{2-} from the addition of $AgNO_3$. The $[Ag^+]$ just as the Ag_2CrO_4 begins to precipitate can be calculated from the K_{sp} expression for Ag_2CrO_4 using $[CrO_4^{2-}] = 0.015\ M$. Thus, for Ag_2CrO_4,

$$[Ag^+]^2[CrO_4^{2-}] = K_{sp}$$

$$[Ag^+]^2[0.015] = 1.1 \times 10^{-12}$$

$$[Ag^+] = \sqrt{\frac{1.1 \times 10^{-12}}{0.015}} = 8.\underline{5}6 \times 10^{-6}\ M$$

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The $[Cl^-]$ at this point can be obtained by substituting the $[Ag^+]$ into the K_{sp} expression for AgCl. Therefore, for AgCl,

$$[Ag^+][Cl^-] = K_{sp}$$

$$[8.56 \times 10^{-6}][Cl^-] = 1.8 \times 10^{-10}$$

$$[Cl^-] = \frac{1.8 \times 10^{-10}}{8.56 \times 10^{-6}} = 2.\underline{1}02 \times 10^{-5} = 2.1 \times 10^{-5}\ M$$

Because this Cl^- concentration is extremely small compared to the initial 0.015 *M* concentration, you can also deduce that essentially all the chloride ion precipitates before the Ag_2CrO_4 begins to precipitate.

17.57. The net ionic equation is

$$BaF_2(s) + 2H_3O^+(aq) \rightleftharpoons Ba^{2+}(aq) + 2HF(aq) + 2H_2O(l)$$

17.58. The net ionic equation is

$$PbCO_3(s) + 2H_3O^+(aq) \rightleftharpoons Pb^{2+}(aq) + CO_2(g) + 3H_2O(l)$$

17.59. Calculate the value of *K* for the reaction of H_3O^+ with both the SO_4^{2-} and F^- anions as they form by the slight dissolving of the insoluble salts. These constants are the reciprocals of the K_a values of the conjugate acids of these anions.

$$F^-(aq) + H_3O^+(aq) \rightleftharpoons HF(aq) + H_2O(l)$$

$$K = \frac{1}{K_a} = \frac{1}{6.8 \times 10^{-4}} = 1.\underline{4}7 \times 10^3$$

$$SO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HSO_4^-(aq) + H_2O(l)$$

$$K = \frac{1}{K_{a_2}} = \frac{1}{1.1 \times 10^{-2}} = 9\underline{0}.9$$

Because *K* for the fluoride ion is relatively larger, more BaF_2 than $BaSO_4$ will dissolve in acid.

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17.60. Calculate the value of K for the reaction of H_3O^+ with both the SO_4^{2-} and PO_4^{3-} anions as they form by the slight dissolving of the insoluble salts. These constants are the reciprocals of the K_a values of the conjugate acids of these anions.

$$PO_4^{3-}(aq) + H_3O^+(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$$

$$K = \frac{1}{K_{a_3}} = \frac{1}{4.8 \times 10^{-13}} = 2.\underline{0}8 \times 10^{12}$$

$$SO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HSO_4^-(aq) + H_2O(l)$$

$$K = \frac{1}{K_{a_2}} = \frac{1}{1.1 \times 10^{-2}} = 9\underline{0}.9$$

Because K for the phosphate ion is relatively larger, more $Ca_3(PO_4)_2$ than $CaSO_4$ will dissolve in acid.

17.61. The equation is

$$Cu^+(aq) + 2\,CN^-(aq) \rightleftharpoons Cu(CN)_2^-(aq)$$

The K_f expression is

$$K_f = \frac{[Cu(CN)_2^-]}{[Cu^+]\,[CN^-]^2} = 1.0 \times 10^{16}$$

17.62. The equation is

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$$

The K_f expression is

$$K_f = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}]\,[NH_3]^6} = 5.6 \times 10^8$$

17.63. Assume the only $[Ag^+]$ is that in equilibrium with the $Ag(CN)_2^-$ formed from Ag^+ and CN^-. (In other words, assume all the 0.015 M Ag^+ reacts with CN^- to form 0.015 M $Ag(CN)_2^-$.) Subtract the CN^- that forms the 0.015 M $Ag(CN)_2^-$ from the initial 0.100 M CN^-. Use this as the starting concentration of CN^- for the usual concentration table.

[0.100 M NaCN − (2 x 0.015 M)] = 0.070 M starting CN^-

Conc. (M)	$Ag(CN)_2^-$	$\rightleftharpoons$	Ag^+	+	$2CN^-$
Starting	0.015		0		0.070
Change	$-x$		$+x$		$+2x$
Equilibrium	$0.015 - x$		x		$0.070 + 2x$

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all the exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming x is negligible compared to 0.015 and $2x$ is negligible compared to 0.070.

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$$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{(0.015 - x)}{(x)(0.070 + 2x)^2} \cong \frac{(0.015)}{(x)(0.070)^2} \cong 5.6 \times 10^{18}$$

Rearrange and solve for x = $[Ag^+]$:

$$x \cong (0.015) \div [(5.6 \times 10^{18})(0.070)^2] \cong 5.\underline{4}6 \times 10^{-19} = 5.5 \times 10^{-19}\ M$$

17.64. You can make a rough assumption that most of the $Zn(OH)_4^{2-}$ that dissociates forms Zn^{2+} and OH^- ions. Assemble the usual concentration table, using 0.20 *M* as the starting concentration for $Zn(OH)_4^{2-}$ and assuming the starting concentrations of Zn^{2+} and OH^- ions are zero.

Conc. (*M*)	$Zn(OH)_4^{2-}$ ⇌	Zn^{2+}	+	$4OH^-$
Starting	0.20	0		0
Change	$-x$	$+x$		$+4x$
Equilibrium	$0.20 - x$	x		$4x$

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all the exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming *x* is negligible compared to 0.20.

$$K_f = \frac{[Zn(OH)_4^{2-}]}{[Zn^{2+}][OH^-]^4} = \frac{(0.20 - x)}{(x)(4x)^4} \cong \frac{(0.20)}{(x)(4x)^4} \cong 2.8 \times 10^{15}$$

Rearrange and solve for $x = [Zn^{2+}]$:

$$x \cong \sqrt[5]{\frac{(0.20)}{256 \times (2.8 \times 10^{15})}} = 1.\underline{9}4 \times 10^{-4} = 1.9 \times 10^{-4}\ M$$

17.65. Start by calculating the $[Cd^{2+}]$ in equilibrium with the $Cd(NH_3)_4^{2+}$ formed from Cd^{2+} and NH_3. Then use the $[Cd^{2+}]$ to decide whether or not CdC_2O_4 will precipitate by calculating the ion product and comparing it with the K_{sp} of 1.5×10^{-8} for CdC_2O_4. Assume all the 0.0020 *M* Cd^{2+} reacts with NH_3 to form 0.0020 *M* $Cd(NH_3)_4^{2+}$, and calculate the remaining NH_3. Use these as the starting concentrations for the usual concentration table.

$[0.10\ M\ NH_3 - (4 \times 0.0020\ M)] = 0.0\underline{9}2\ M$ starting NH_3

Conc. (*M*)	$Cd(NH_3)_4^{2+}$ ⇌	Cd^{2+}	+	$4NH_3$
Starting	0.0020	0		0.092
Change	$-x$	$+x$		$+4x$
Equilibrium	$0.0020 - x$	x		$0.092 + 4x$

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all the exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming *x* is negligible compared to 0.0020 and $4x$ is negligible compared to 0.092.

$$K_f = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = \frac{(0.0020 - x)}{(x)(0.092 + 4x)^4} \cong \frac{(0.0020)}{(x)(0.092)^4} \cong 1.0 \times 10^7$$

Rearrange and solve for *x*:

$$x \cong (0.0020) \div [(1.0 \times 10^7)(0.092)^4] \cong \underline{2}.79 \times 10^{-6}\ M \cong [Cd^{2+}]$$

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Now, calculate the ion product for CdC_2O_4:

$$Q_c = [Cd^{2+}][C_2O_4^{2-}] = (2.79 \times 10^{-6})(0.010) = 2.\underline{7}9 \times 10^{-8}$$

Because Q_c is greater than the K_{sp} of 1.5×10^{-8}, the solution is supersaturated before equilibrium. At equilibrium, a precipitate will form, and the solution will be saturated.

17.66. Start by calculating the $[Ni^{2+}]$ in equilibrium with the $Ni(NH_3)_6^{2+}$ formed from Ni^{2+} and NH_3. Then use the $[Ni^{2+}]$ to decide whether or not $Ni(OH)_2$ will precipitate by calculating the ion product and comparing it with the K_{sp} of 2.0×10^{-15} for $Ni(OH)_2$. Assume all the 0.0020 *M* Ni^{2+} reacts with NH_3 to form 0.0020 *M* $Ni(NH_3)_6^{2+}$, and calculate the remaining NH_3. Use these as starting concentrations for the usual concentration table.

$$[0.10\ M\ NH_3 - (6 \times 0.0020\ M)] = 0.0\underline{8}8\ M \text{ starting } NH_3$$

Conc. (*M*)	$Ni(NH_3)_6^{2+}$	$\rightleftharpoons$	Ni^{2+} +	$6NH_3$
Starting	0.0020		0	0.088
Change	$-x$		$+x$	$+6x$
Equilibrium	$0.0020 - x$		x	$0.088 + 6x$

Even though this reaction is the opposite of the equation for the formation constant, the formation-constant expression can be used. Simply substitute all the exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming that x is negligible compared to 0.0020 and $6x$ is negligible compared to 0.088.

$$K_f = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = \frac{(0.0020 - x)}{(x)(0.088 + 6x)^6} \cong \frac{(0.0020)}{(x)(0.088)^6} \cong 5.60 \times 10^8$$

Rearrange and solve for x:

$$x \cong (0.0020) \div [5.6 \times 10^8 \times (0.088)^6] \cong \underline{7}.69 \times 10^{-6}\ M \cong [Ni^{2+}]$$

Now, calculate the ion product for $Ni(OH)_2$:

$$Q_c = [Ni^{2+}][OH^-]^2 = (7.69 \times 10^{-6})(0.010)^2 = \underline{7}.69 \times 10^{-10}$$

Because Q_c is greater than the K_{sp} of 2.0×10^{-15}, the solution is supersaturated before equilibrium. At equilibrium, a precipitate will form, and the solution will be saturated.

17.67. Using the rule from Chapter 14, obtain the overall equilibrium constant for this reaction from the product of the individual equilibrium constants of the two individual equations whose sum gives this equation.

$CdC_2O_4(s)$	$\rightleftharpoons$	$Cd^{2+}(aq) + C_2O_4^{2-}(aq)$	$K_{sp} = 1.5 \times 10^{-8}$
$Cd^{2+}(aq) + 4NH_3(aq)$	$\rightleftharpoons$	$Cd(NH_3)_4^{2+}(aq)$	$K_f = 1.0 \times 10^7$
$CdC_2O_4(s) + 4NH_3(aq)$	$\rightleftharpoons$	$Cd(NH_3)_4^{2+}(aq) + C_2O_4^{2-}(aq)$	$K_c = K_{sp} \times K_f = 0.15$

Assemble the usual table using 0.10 *M* as the starting concentration of NH_3 and x as the unknown concentration of $Cd(NH_3)_4^{2+}$ formed.

Conc. (*M*)	$CdC_2O_4(s)$ +	$4NH_3$	$\rightleftharpoons$	$Cd(NH_3)_4^{2+}$ +	$C_2O_4^{2-}$
Starting		0.10		0	0
Change		$-4x$		$+x$	$+x$
Equilibrium		$0.10 - 4x$		x	x

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The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression.

$$K_c = \frac{[Cd(NH_3)_4^{2+}][C_2O_4^{2-}]}{[NH_3]^4} = \frac{(x)^2}{(0.10 - 4x)^4} = 0.15$$

Take the square root of both sides of the two right-hand terms, rearrange into a quadratic equation, and solve for x:

$$\frac{x}{(0.10 - 4x)^2} = 0.3\underline{8}7$$

$$16x^2 - 3.38x + 0.010 = 0$$

$$x = \frac{3.38 \pm \sqrt{(-3.38)^2 - 4(16)(0.010)}}{2(16)} = 0.208 \text{ (too large) and } 3.\underline{0}01 \times 10^{-3}$$

Using the smaller root, $x = 3.\underline{0}01 \times 10^{-3} = 3.0 \times 10^{-3}\ M$ (molar solubility of CdC_2O_4).

17.68. Using the rule from Chapter 14, obtain the overall equilibrium constant for this reaction from the product of the individual equilibrium constants of the two individual equations whose sum gives this equation.

$NiS(s)$	$\rightleftharpoons$	$Ni^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = 3 \times 10^{-19}$
$Ni^{2+}(aq) + 6NH_3(aq)$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}(aq)$	$K_f = 5.6 \times 10^{8}$
$NiS(s) + 6NH_3(aq)$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}(aq) + S^{2-}(aq)$	$K_c = K_{sp} \times K_f = \underline{1}.7 \times 10^{-10}$

Assemble the usual table using 0.10 M as the starting concentration of NH_3 and x as the unknown concentration of $Ni(NH_3)_6^{2+}$ formed.

Conc. (M)	$NiS(s)$ +	$6NH_3$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}$ +	S^{2-}
Starting		0.10		0	0
Change		$-6x$		$+x$	$+x$
Equilibrium		$0.10 - 6x$		x	x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression. It will be necessary to simplify the exact equation to obtain a solution without using a higher-order equation.

$$K_c = \frac{[Ni(NH_3)_6^{2+}][S^{2-}]}{[NH_3]^6} = \frac{(x)^2}{(0.10 - 6x)^6} = 1.7 \times 10^{-10}$$

Take the square root of both sides of the two right-hand terms. Note that the resulting equation contains an x^3 term and an x term.

$$\frac{x}{(0.10 - 6x)^3} = \underline{1}.3 \times 10^{-5}$$

Assume $6x$ is negligible compared to 0.10 M, and solve the above equation for x:

$$\frac{x}{(0.10)^3} = \underline{1}.3 \times 10^{-5}$$

$$x = \underline{1}.3 \times 10^{-8} = 1 \times 10^{-8}\ M \text{ (molar solubility of NiS in 0.10 } M\ NH_3)$$

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17.69. The Pb^{2+}, Cd^{2+}, and Sr^{2+} ions can be separated in two steps: (1) Add HCl to precipitate only the Pb^{2+} as $PbCl_2$, leaving the others in solution. (2) After pouring the solution away from the precipitate, add 0.3 *M* HCl and H_2S to precipitate only the CdS away from the Sr^{2+} ion, whose sulfide is soluble under these conditions.

17.70. The Hg^{2+}, Ca^{2+}, and Na^{+} ions can be separated in two steps: (1) Add 0.3 *M* HCl and H_2S to precipitate only the HgS, leaving the others in solution. (2) After pouring the solution away from the precipitate, add NH_3 and $(NH_4)_2HPO_4$ to precipitate only the $Ca_3(PO_4)_2$ away from the Na^{+} ion, whose phosphate is soluble under these conditions.

17.71.

a. Ag^{+} is not possible because no precipitate formed with HCl.

b. Ca^{2+} is not possible if the compound contains only one cation because Mn^{2+} is indicated by the evidence. However, if the compound consists of two or more cations, Ca^{2+} is possible because no reactions were described involving Ca^{2+}.

c. Mn^{2+} is possible because a precipitate was obtained with basic sulfide ion.

d. Cd^{2+} is not possible because no precipitate was obtained with acidic sulfide solution.

17.72. Since no precipitate formed on addition of hydrochloric acid, the compound cannot contain an Analytical Group I cation. Thus, the precipitate cannot be $PbCl_2$, PbS, or Ag_2S. CdS could be the precipitate since it is an Analytical Group II cation and precipitates in acidic sulfide solution. Therefore, the answer is b, CdS.

■ SOLUTIONS TO GENERAL PROBLEMS

17.73. Assemble the usual concentration table. Let x equal the molar solubility of $PbSO_4$. When *x* mol $PbSO_4$ dissolves in 1 L of solution, *x* mol Pb^{2+} and *x* mol SO_4^{2-} form.

Conc. (*M*)	$PbSO_4(s)$	$\rightleftharpoons$	Pb^{2+}	+	SO_4^{2-}
Starting			0		0
Change			$+x$		$+x$
Equilibrium			x		x

Substitute the equilibrium concentrations into the equilibrium-constant expression, and solve for *x*.

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 1.7 \times 10^{-8}$$

$$x = \sqrt{(1.7 \times 10^{-8})} = 1.3\underline{0}3 \times 10^{-4} = 1.3 \times 10^{-4}\ M$$

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17.74. Assemble the usual concentration table. Let x equal the molar solubility of HgS. When x mol HgS dissolves in 1 L of solution, x mol Hg^{2+} and x mol S^{2-} form.

Conc. (M)	$HgS(s)$ ⇌	Hg^{2+}	+	S^{2-}
Starting		0		0
Change		$+x$		$+x$
Equilibrium		x		x

Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x.

$$[Hg^{2+}][S^{2-}] = K_{sp}$$

$$(x)(x) = x^2 = 1.6 \times 10^{-52}$$

$$x = \sqrt{(1.6 \times 10^{-52})} = 1.\underline{2}6 \times 10^{-26} = 1.3 \times 10^{-26}\ M$$

17.75. Let x equal the molar solubility of Hg_2Cl_2. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$Hg_2Cl_2(s)$ ⇌	Hg_2^{2+}	+	$2Cl^-$
Starting		0		0
Change		$+x$		$+2x$
Equilibrium		x		2x

$$[Hg_2^{2+}][Cl^-]^2 = K_{sp}$$

$$(x)(2x)^2 = 4x^3 = 1.3 \times 10^{-18}$$

$$x = \sqrt[3]{\frac{1.3 \times 10^{-18}}{4}} = 6.\underline{8}7 \times 10^{-7}\ M$$

a. Molar solubility $= 6.\underline{8}7 \times 10^{-7} = 6.9 \times 10^{-7}\ M$

b. $$\frac{6.87 \times 10^{-7}\ \text{mol}}{\text{L}} \times \frac{472.1\ \text{g}\ Hg_2Cl_2}{1\ \text{mol}} = 3.\underline{2}4 \times 10^{-4} = 3.2 \times 10^{-4}\ \text{g/L}$$

17.76. Let x equal the molar solubility of $MgNH_4PO_4$. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$MgNH_4PO_4(s)$ ⇌	Mg^{2+}	+	NH_4	+	PO_4^{3-}
Starting		0		0		0
Change		$+x$		$+x$		$+x$
Equilibrium		x		x		x

$$[Mg^{2+}][NH_4^+][PO_4^{3-}] = K_{sp}$$

$$(x)(x)(x) = x^3 = 2.5 \times 10^{-13}$$

$$x = \sqrt[3]{2.5 \times 10^{-13}} = 6.\underline{2}99 \times 10^{-5}\ M$$

a. Molar solubility $= 6.\underline{2}99 \times 10^{-5} = 6.3 \times 10^{-5}\ M$

b. $$\frac{6.299 \times 10^{-5}\ \text{mol}}{\text{L}} \times \frac{137.3\ \text{g}\ MgNH_4PO_4}{1\ \text{mol}} = 8.\underline{6}48 \times 10^{-3} = 8.6 \times 10^{-3}\ \text{g/L}$$

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17.77. Let x equal the molar solubility of $Ce(OH)_3$. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$Ce(OH)_3(s)$ ⇌	Ce^{3+} +	$3OH^-$
Starting		0	0
Change		$+x$	$+3x$
Equilibrium		x	$3x$

$[Ce^{3+}][OH^-]^3 = K_{sp}$

$(x)(3x)^3 = 27x^4 = 2.0 \times 10^{-20}$

$$x = \sqrt[4]{\frac{2.0 \times 10^{-20}}{27}} = 5.\underline{2}16 \times 10^{-6}\ M$$

a. Molar solubility $= 5.\underline{2}16 \times 10^{-6} = 5.2 \times 10^{-6}\ M$

b. $[OH^-] = 3x = 1.\underline{5}6 \times 10^{-5}\ M$

pOH $= 4.8\underline{0}54 = 4.81$

17.78. Let x equal the molar solubility of $Cu_2Fe(CN)_6$. Assemble the usual concentration table, and substitute from the table into the equilibrium-constant expression.

Conc. (M)	$Cu_2Fe(CN)_6$ (s) ⇌	$2Cu^{2+}$ +	$Fe(CN)_6^{4-}$
Starting		0	0
Change		$+2x$	$+x$
Equilibrium		$2x$	x

$[Cu^{2+}]^2[Fe(CN)_6^{4-}] = K_{sp}$

$(2x)^2(x) = 4x^3 = 1.3 \times 10^{-16}$

$$x = \sqrt[3]{\frac{1.3 \times 10^{-16}}{4}} = 3.\underline{1}9 \times 10^{-6}\ M$$

a. Molar solubility $= 3.\underline{1}9 \times 10^{-6} = 3.2 \times 10^{-6}\ M$

b. $$\frac{3.19 \times 10^{-6}\ \text{mol}}{\text{L}} \times \frac{339.0\ \text{g}\ Cu_2Fe(CN)_6}{1\ \text{mol}} = 1.\underline{0}8 \times 10^{-3} = 1.1 \times 10^{-3}\ \text{g/L}$$

17.79. Calculate the pOH from the pH, and then convert pOH to $[OH^-]$. Next, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression.

pOH $= 14.00 - 8.80 = 5.20$

$[OH^-] = \text{antilog}(-\text{pOH}) = \text{antilog}(-5.20) = 6.\underline{3}09 \times 10^{-6}\ M$

Conc. (M)	$Mg(OH)_2(s)$ ⇌	Mg^{2+} +	$2OH^-$
Starting		0	0
Change		$+x$	0
Equilibrium		x	6.309×10^{-6}

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$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(6.309 \times 10^{-6})^2 = 1.8 \times 10^{-11}$$

$$x = \frac{1.8 \times 10^{-11}}{(6.309 \times 10^{-6})^2} = 0.4\underline{5}2 = 0.45\ M$$

$$\frac{0.452\ \text{mol}}{\text{L}} \times \frac{58.3\ \text{g}\ Mg(OH)_2}{1\ \text{mol}} = 2\underline{6}.3 = 26\ \text{g/L}$$

17.80. Calculate the pOH from the pH, and then convert pOH to $[OH^-]$. Next, assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. Let $2x$ equal the molar solubility of the Ag^+ ion because you are seeking x, the molar solubility of Ag_2O.

$$pOH = 14.00 - 10.50 = 3.50$$

$$[OH^-] = \text{antilog}\,(-pOH) = \text{antilog}\,(-3.50) = 3.\underline{1}6 \times 10^{-4}\ M$$

Conc. (M)	$Ag_2O(s)$ + $2H_2O$ $\rightleftharpoons$	$2Ag^+$ +	$2OH^-$
Starting		0	0
Change	x	$+2x$	0
Equilibrium		$2x$	3.16×10^{-4}

$$K_c = [Ag^+]^2[OH^-]^2 = (2x)^2(3.16 \times 10^{-4})^2 = 2.0 \times 10^{-8}$$

$$x = \sqrt{\frac{2.0 \times 10^{-8}}{4 \times (3.16 \times 10^{-4})^2}} = 0.2\underline{2}4 = 0.22\ M$$

$$\frac{0.224\ \text{mol}}{\text{L}} \times \frac{231.7\ \text{g}\ Ag_2O}{1\ \text{mol}} = 5\underline{1}.9 = 52\ \text{g/L}$$

17.81. Let x equal the change in M of Mg^{2+} and 0.10 M equal the starting OH^- concentration. Then assemble the usual concentration table, and let substitute the equilibrium concentrations from it into the equilibrium-constant expression. Assume $2x$ is negligible compared to 0.10 M, and perform an approximate calculation.

Conc. (M)	$Mg(OH)_2(s)$ $\rightleftharpoons$	Mg^{2+} +	$2OH^-$
Starting		0	0.10
Change		$+x$	$+2x$
Equilibrium		x	$0.10 + 2x$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(0.10 + 2x)^2 \cong (x)(0.10)^2 \cong 1.8 \times 10^{-11}$$

$$x = \frac{1.8 \times 10^{-11}}{(0.10)^2} = 1.\underline{8}0 \times 10^{-9} = 1.8 \times 10^{-9}\ M$$

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17.82. Let x equal the change in M of Al^{3+} and let 0.0010 M equal the starting OH^- concentration. Then assemble the usual concentration table, and substitute the equilibrium concentrations from it into the equilibrium-constant expression. Assume $3x$ is negligible compared to 0.0010 M, and perform an approximate calculation.

Conc. (M)	$Al(OH)_3(s)$ ⇌	Al^{3+}	+	$3OH^-$
Starting		0		0.0010
Change		$+x$		$+3x$
Equilibrium		x		$0.0010 + 3x$

$$K_{sp} = [Al^{3+}][OH^-]^3 = (x)(0.0010 + 3x)^3 \cong (x)(0.0010)^3 \cong 4.6 \times 10^{-33}$$

$$x = \frac{4.6 \times 10^{-33}}{(0.0010)^3} = 4.\underline{6}0 \times 10^{-24} = 4.6 \times 10^{-24}\ M$$

17.83. To begin precipitation, you must add just slightly more sulfate ion than that required to give a saturated solution. Use the K_{sp} expression to calculate the $[SO_4^{2-}]$ needed to just begin precipitating the 0.0030 M Ca^{2+}.

$$[Ca^{2+}][SO_4^{2-}] = K_{sp} = 2.4 \times 10^{-5}$$

$$[SO_4^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{2.4 \times 10^{-5}}{3.0 \times 10^{-3}} = 8.\underline{0}0 \times 10^{-3}\ M$$

When the sulfate ion concentration slightly exceeds 8.0×10^{-3} M, precipitation begins.

17.84. To begin precipitation, you must add just slightly more chromate ion than that required to give a saturated solution. Use the K_{sp} expression to calculate the $[CrO_4^{2-}]$ needed to just begin precipitating the 0.0025 M Sr^{2+}.

$$[Sr^{2+}][CrO_4^{2-}] = K_{sp} = 3.5 \times 10^{-5}$$

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Sr^{2+}]} = \frac{3.5 \times 10^{-5}}{2.5 \times 10^{-3}} = 1.\underline{4}0 \times 10^{-2}\ M$$

When the chromate ion concentration slightly exceeds 1.4×10^{-2} M, precipitation begins.

17.85. Calculate the concentrations of Pb^{2+} and Cl^-. Use a total volume of 3.20 L + 0.80 L, or 4.00 L.

$$[Pb^{2+}] = \frac{\frac{1.25 \times 10^{-3}\ \text{mol}}{\text{L}} \times 3.20\ \text{L}}{4.00\ \text{L}} = 1.\underline{0}0 \times 10^{-3}\ M$$

$$[Cl^-] = \frac{\frac{5.0 \times 10^{-1}\ \text{mol}}{\text{L}} \times 0.80\ \text{L}}{4.00\ \text{L}} = 1.\underline{0}0 \times 10^{-1}\ M$$

Calculate the ion product, and compare it to K_{sp}.

$$Q_c = [Pb^{2+}][Cl^-]^2 = (1.00 \times 10^{-3})(1.00 \times 10^{-1})^2 = 1.\underline{0}0 \times 10^{-5}\ M^3$$

Because the Q_c is less than the K_{sp} of 1.6×10^{-5}, no precipitation occurs, and the solution is not saturated.

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17.86. Rounded answer: Q_c equals 1.8×10^{-11} (equals K_{sp}, so the solution is saturated). Calculate the concentrations of Mg^{2+} and OH^-. Use a total volume of 0.150 L + 0.050 L, or 0.200 L.

$$[Mg^{2+}] = \frac{\frac{2.4 \times 10^{-5}\ \text{mol}}{\text{L}} \times 0.150\ \text{L}}{0.200\ \text{L}} = 1.\underline{8}0 \times 10^{-5}\ M$$

$$[OH^-] = \frac{\frac{4.0 \times 10^{-3}\ \text{mol}}{\text{L}} \times 0.050\ \text{L}}{0.200\ \text{L}} = 1.\underline{0}0 \times 10^{-3}\ M$$

Calculate the ion product and compare it to K_{sp}.

$$Q_c = [Mg^{2+}][OH^-]^2 = (1.80 \times 10^{-5})(1.00 \times 10^{-3})^2 = 1.\underline{8}0 \times 10^{-11}$$

Because Q_c equals the K_{sp} of 1.8×10^{-11}, no precipitation occurs, and the solution is saturated.

17.87. A mixture of $AgNO_3$ and NaCl can precipitate only AgCl because $NaNO_3$ is soluble. Use the K_{sp} expression to calculate the $[Cl^-]$ needed to prepare a saturated solution (just before precipitating the 0.0015 M Ag^+). Then convert to moles and finally to grams.

$$[Ag^+][Cl^-] = K_{sp} = 1.8 \times 10^{-10}$$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.5 \times 10^{-3}} = 1.\underline{2}0 \times 10^{-7}\ M$$

The numbers of moles and grams in 0.785 L (785 mL) of this chloride-containing solution are

$$0.785\ \text{L} \times (1.20 \times 10^{-7}\ \text{mol/L}) = 9.\underline{4}2 \times 10^{-8}\ \text{mol } Cl^- = 9.\underline{4}2 \times 10^{-8}\ \text{mol NaCl}$$

$$(9.42 \times 10^{-8}\ \text{mol NaCl}) \times (58.5\ \text{g NaCl/1mol}) = 5.\underline{5}1 \times 10^{-6} = 5.5 \times 10^{-6}\ \text{g NaCl}$$

This amount of NaCl is too small to weigh on a balance.

17.88. A mixture of $BaCl_2$ and Na_2SO_4 can precipitate only $BaSO_4$ because NaCl is soluble. Use the K_{sp} expression to calculate the $[SO_4^{2-}]$ needed to prepare a saturated solution (just before precipitating the 0.0028 M Ba^{2+}). Then convert to moles and finally to grams.

$$[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.1 \times 10^{-10}$$

$$[SO_4^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.1 \times 10^{-10}}{2.8 \times 10^{-3}} = 3.\underline{9}3 \times 10^{-8}\ M$$

The numbers of moles and grams in 0.435 L of this sulfate-containing solution are

$$(0.435\ \text{L} \times 3.93 \times 10^{-8}\ \text{mol/L}) = 1.\underline{7}09 \times 10^{-8}\ \text{mol } SO_4^{2-} = 1.\underline{7}09 \times 10^{-8}\ \text{mol } Na_2SO_4$$

$$(1.709 \times 10^{-8}\ \text{mol } Na_2SO_4) \times (142\ \text{g/1 mol } Na_2SO_4) = 2.\underline{4}2 \times 10^{-6} = 2.4 \times 10^{-6}\ \text{g } Na_2SO_4$$

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17.89. From the magnitude of K_f, assume Fe^{3+} and SCN^- react essentially completely to form 2.00 *M* $Fe(SCN)^{2+}$ at equilibrium. Use 2.00 *M* as the starting concentration of $Fe(SCN)^{2+}$ for the usual concentration table.

Conc. (*M*)	Fe^{3+}	+	SCN^-	⇌	$FeSCN^{2+}$
Starting	0		0		2.00
Change	$+x$		$+x$		$-x$
Equilibrium	x		x		$2.00 - x$

Substitute all the exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming x is negligible compared to 2.00 *M*.

$$K_f = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(2.00 - x)}{(x)(x)} \cong \frac{(2.00)}{x^2} \cong 9.0 \times 10^2$$

Rearrange and solve for x:

$$x = \sqrt{\frac{2.00}{9.0 \times 10^2}} = 4.\underline{7}1 \times 10^{-2} = 4.7 \times 10^{-2}\ M$$

Fraction dissociated = $[(4.\underline{7}1 \times 10^{-2}) \div (2.00)] \times 100\% = 0.02\underline{3}5$ (< 0.03, so acceptable)

17.90. From the magnitude of K_f, assume Co^{2+} and SCN^- react essentially completely to form 2.00 *M* $Co(SCN)^+$ at equilibrium. Use 2.00 *M* as the starting concentration of $Co(SCN)^+$ for the usual concentration table.

Conc. (*M*)	Co^{2+}	+	SCN^-	⇌	$CoSCN^+$
Starting	0		0		2.00
Change	$+x$		$+x$		$-x$
Equilibrium	X		X		$2.00 - x$

Substitute all the exact equilibrium concentrations into the formation-constant expression; then simplify the exact equation by assuming x is negligible compared to 2.00 *M*.

$$K_f = \frac{[CoSCN^+]}{[Co^{2+}][SCN^-]} = \frac{(2.00 - x)}{(x)(x)} \cong \frac{(2.00)}{x^2} \cong 1.0 \times 10^2$$

Rearrange and solve for x:

$$x = \sqrt{\frac{2.00}{1.0 \times 10^2}} = 0.1\underline{4}1 = 0.14\ M$$

The value of $x = 0.14$ affects the term $2.00 - x$ slightly in the second significant figure. From the quadratic formula, you obtain $x = 0.1\underline{3}7$, which also rounds to 0.14.

17.91. Obtain the overall equilibrium constant for this reaction from the product of the individual equilibrium constants of the two individual equations whose sum gives this equation:

$AgBr(s)$	⇌	$Ag^+(aq) + Br^-(aq)$	$K_{sp} = 5.0 \times 10^{-13}$
$Ag^+(aq) + 2NH_3(aq)$	⇌	$Ag(NH_3)_2^+(aq)$	$K_f = 1.7 \times 10^7$
$AgBr(s) + 2NH_3(aq)$	⇌	$Ag(NH_3)_2^+(aq) + Br^-(aq)$	$K_c = K_{sp} \times K_f = 8.\underline{5}0 \times 10^{-6}$

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Assemble the usual table using 5.0 *M* as the starting concentration of NH_3 and *x* as the unknown concentration of $Ag(NH_3)_2^+$ formed.

Conc. (*M*)	$AgBr(s)$ +	$2NH_3$ ⇌	$Ag(NH_3)_2^+$ +	Br^-
Starting		5.0	0	0
Change		$-2x$	$+x$	$+x$
Equilibrium		$5.0 - 2x$	x	x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression; it will not be necessary to simplify the equation, because taking the square root of both sides removes the x^2 term.

$$K_c = \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2} = \frac{x^2}{(5.0 - 2x)^2} = 8.\underline{5}0 \times 10^{-6}$$

Take the square root of both sides of the two right-hand terms and solve for *x*.

$$\frac{x}{(5.0 - 2x)} = 2.\underline{9}15 \times 10^{-3}$$

$$x + (5.8 \times 10^{-3})x = 1.\underline{4}575 \times 10^{-2}$$

$$x = 1.\underline{4}49 \times 10^{-2} = 1.4 \times 10^{-2}\ M \text{ (the molar solubility of AgBr in 5.0 } M\ NH_3)$$

17.92. Obtain the overall equilibrium constant for this reaction from the product of the individual equilibrium constants of the two individual equations whose sum gives this equation:

$AgI(s)$	⇌	$Ag^+(aq) + I^-(aq)$	$K_{sp} = 8.3 \times 10^{-17}$
$Ag^+(aq) + 2NH_3(aq)$	⇌	$Ag(NH_3)_2^+(aq)$	$K_f = 1.7 \times 10^7$
$AgCl(s) + 2NH_3(aq)$	⇌	$Ag(NH_3)_2^+(aq) + I^-(aq)$	$K_c = K_{sp} \times K_f = 1.\underline{4}1 \times 10^{-9}$

Assemble the usual table using 2.0 *M* as the starting concentration of NH_3 and *x* as the unknown concentration of $Ag(NH_3)_2^+$ formed.

Conc. (*M*)	$AgI(s)$ +	$2NH_3$ ⇌	$Ag(NH_3)_2^+$ +	I^-
Starting		2.0	0	0
Change		$-2x$	$+x$	$+x$
Equilibrium		$2.0 - 2x$	x	x

The equilibrium-constant expression can now be used. Simply substitute all the exact equilibrium concentrations into the equilibrium-constant expression; it will not be necessary to simplify the equation, because taking the square root of both sides removes the x^2 term.

$$K_c = \frac{[Ag(NH_3)_2^+][I^-]}{[NH_3]^2} = \frac{x^2}{(2.0 - 2x)^2} = 1.\underline{4}1 \times 10^{-9}$$

Take the square root of both sides of the two right-hand terms and solve for *x*.

$$\frac{x}{(2.0 - 2x)} = 3.\underline{7}5 \times 10^{-5}$$

$$x + (7.5 \times 10^{-5})x = 7.\underline{5}0 \times 10^{-5}$$

$$x = 7.\underline{4}99 \times 10^{-5} = 7.5 \times 10^{-5}\ M \text{ (the molar solubility of AgI in 2.0 } M\ NH_3)$$

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17.93. Start by recognizing that because each zinc oxalate produces one oxalate ion, the solubility of zinc oxalate equals the oxalate concentration:

$$ZnC_2O_4(s) + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + C_2O_4^{2-}$$

Thus, the $[C_2O_4^{2-}] = 3.6 \times 10^{-4}\ M$. Now, calculate the $[Zn^{2+}]$ in equilibrium with the oxalate ion using the K_{sp} expression for zinc oxalate.

$$K_{sp} = [Zn^{2+}][C_2O_4^{2-}] = 1.5 \times 10^{-9}$$

$$[Zn^{2+}] = \frac{1.5 \times 10^{-9}}{3.6 \times 10^{-4}} = 4.\underline{1}6 \times 10^{-6} = 4.2 \times 10^{-6}\ M$$

To calculate K_f, the $[Zn(NH_3)_4^{2+}]$ term must be calculated. This can be done by recognizing that the molar solubility of ZnC_2O_4 is the sum of the concentration of Zn^{2+} and $Zn(NH_3)_4^{2+}$ ions:

$$\text{Molar solubility of } ZnC_2O_4 = [Zn^{2+}] + [Zn(NH_3)_4^{2+}]$$

$$3.6 \times 10^{-4} = (4.16 \times 10^{-6}) + [Zn(NH_3)_4^{2+}]$$

$$[Zn(NH_3)_4^{2+}] = (3.6 \times 10^{-4}) - (4.16 \times 10^{-6}) = 3.\underline{5}58 \times 10^{-4}\ M$$

Now, the $[NH_3]$ term must be calculated by subtracting the ammonia in $[Zn(NH_3)_4^{2+}]$ from the starting NH_3 of 0.0150 *M*.

$$[NH_3] = 0.0150 - 4\,[Zn(NH_3)_4^{2+}] = 0.0150 - 4(3.558 \times 10^{-4}) = 0.013\underline{5}7\ M$$

Solve for K_f by substituting the known concentrations into the K_f expression:

$$K_f = \frac{[Zn(NH_3)_4^{2+}]}{[Zn^{2+}][NH_3]^4} = \frac{3.558 \times 10^{-4}}{(4.16 \times 10^{-6})(0.01357)^4} = 2.\underline{5}2 \times 10^{9} = 2.5 \times 10^{9}$$

17.94. Start by recognizing that because each cadmium oxalate produces one oxalate ion, the solubility of cadmium oxalate equals the oxalate concentration:

$$CdC_2O_4(s) + 4NH_3 \rightleftharpoons Cd(NH_3)_4^{2+} + C_2O_4^{2-}$$

Thus, the $[C_2O_4^{2-}] = 6.1 \times 10^{-3}\ M$. Now, calculate the $[Cd^{2+}]$ in equilibrium with the oxalate ion using the K_{sp} expression for cadmium oxalate.

$$K_{sp} = [Cd^{2+}][C_2O_4^{2-}] = 1.5 \times 10^{-8}$$

$$[Cd^{2+}] = \frac{1.5 \times 10^{-8}}{6.1 \times 10^{-3}} = 2.\underline{4}6 \times 10^{-6} = 2.5 \times 10^{-6}\ M$$

To calculate K_f, the $[Cd(NH_3)_4^{2+}]$ term must be calculated. This can be done by recognizing that the molar solubility of CdC_2O_4 is the sum of the concentration of Cd^{2+} and $Cd(NH_3)_4^{2+}$ ions:

$$\text{Molar solubility of } CdC_2O_4 = [Cd^{2+}] + [Cd(NH_3)_4^{2+}]$$

$$6.1 \times 10^{-3} = (2.46 \times 10^{-6}) + [Cd(NH_3)_4^{2+}]$$

$$[Cd(NH_3)_4^{2+}] = (6.1 \times 10^{-3}) - (2.46 \times 10^{-6}) \cong 6.1 \times 10^{-3}\ M$$

Now the $[NH_3]$ term must be calculated by subtracting the ammonia in $[Cd(NH_3)_4^{2+}]$ from the starting NH_3 of 0.0150 *M*.

$$[NH_3] = 0.150 - 4[Cd(NH_3)_4^{2+}] = 0.150 - 4(6.1 \times 10^{-3}) = 0.12\underline{5}6\ M$$

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Solve for K_f by substituting the known concentrations into the K_f expression:

$$K_f = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = \frac{6.1 \times 10^{-3}}{(2.46 \times 10^{-6})(0.1256)^4} = 9.\underline{9}6 \times 10^6 = 1.0 \times 10^7$$

17.95. The OH^- formed by ionization of NH_3 (to NH_4^+ and OH^-) is a common ion that will precipitate Mg^{2+} as the slightly soluble $Mg(OH)_2$ salt. The simplest way to treat the problem is to calculate the $[OH^-]$ of 0.10 *M* NH_3 before the soluble Mg^{2+} salt is added. As the soluble Mg^{2+} salt is added, the $[Mg^{2+}]$ will increase until the solution is saturated with respect to $Mg(OH)_2$ (the next Mg^{2+} ions to be added will precipitate). Calculate the $[Mg^{2+}]$ at the point at which precipitation begins.

To calculate the $[OH^-]$ of 0.10 *M* NH_3, let *x* equal the moles per liter of NH_3 that ionize, forming *x* mol/L of NH_4^+ and *x* mol/L of OH^- and leaving $(0.10 - x)$ *M* NH_3 in solution. We can summarize the situation in tabular form:

Conc. (*M*)	NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-
Starting	0.10				~0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.10 - x$				x		x

The equilibrium-constant equation is:

$$K_c = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{(0.10 - x)} \cong \frac{x^2}{(0.10)}$$

The value of *x* can be obtained by rearranging and taking the square root:

$$[OH^-] \cong \sqrt{1.8 \times 10^{-5} \times 0.10} = 1.\underline{3}4 \times 10^{-3}\ M$$

Note that $(0.10 - x)$ is not significantly different from 0.10, so *x* can be ignored in the $(0.10 - x)$ term. Now, use the K_{sp} of $Mg(OH)_2$ to calculate the $[Mg^{2+}]$ of a saturated solution of $Mg(OH)_2$, which essentially will be the Mg^{2+} ion concentration when $Mg(OH)_2$ begins to precipitate.

$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(1.34 \times 10^{-3})^2} = 1.\underline{0}0 \times 10^{-5} = 1.0 \times 10^{-5}\ M$$

17.96. The OH^- formed by ionization of N_2H_4 (to $N_2H_5^+$ and OH^-) is a common ion that will precipitate Mg^{2+} as the slightly soluble $Mg(OH)_2$ salt. The simplest way to treat the problem is to calculate the $[OH^-]$ of 0.20 *M* N_2H_4 before the soluble Mg^{2+} salt is added. As the soluble Mg^{2+} salt is added, the $[Mg^{2+}]$ will increase until the solution is saturated with respect to $Mg(OH)_2$ (the next Mg^{2+} ions to be added will precipitate). Calculate the $[Mg^{2+}]$ at the point at which precipitation begins.

To calculate the $[OH^-]$ of 0.20 *M* N_2H_4, let *x* equal the moles per liter of N_2H_4 that ionize, forming *x* mol/L of $N_2H_5^+$ and *x* mol/L of OH^- and leaving $(0.20 - x)$ *M* N_2H_4 in solution. We can summarize the situation in tabular form:

Conc. (*M*)	N_2H_4	+	H_2O	$\rightleftharpoons$	$N_2H_5^+$	+	OH^-
Starting	0.20				~0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.20 - x$				x		x

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The equilibrium-constant equation is

$$K_c = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = \frac{x^2}{(0.20 - x)} \cong \frac{x^2}{(0.20)}$$

The value of x can be obtained by rearranging and taking the square root:

$$[OH^-] \cong \sqrt{1.7 \times 10^{-6} \times 0.20} = 5.\underline{8}3 \times 10^{-4}\ M$$

Note that $(0.20 - x)$ is not significantly different from 0.20, so x can be ignored in the $(0.20 - x)$ term.

Now, use the K_{sp} of $Mg(OH)_2$ to calculate the $[Mg^{2+}]$ of a saturated solution of $Mg(OH)_2$, which essentially will be the Mg^{2+} ion concentration when $Mg(OH)_2$ begins to precipitate.

$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(5.83 \times 10^{-4})^2} = 5.\underline{2}9 \times 10^{-5} = 5.3 \times 10^{-5}\ M$$

17.97.

a. Use the solubility information to calculate K_{sp}. The reaction is

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

$$2.7 \times 10^{-3} \qquad 2 \times (2.7 \times 10^{-3})$$

$$K_{sp} = [Cu^{2+}][IO_3^-]^2 = [2.7 \times 10^{-3}][2 \times (2.7 \times 10^{-3})]^2 = 7.\underline{8}7 \times 10^{-8}$$

Set up an equilibrium. The reaction is

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

$$y \qquad 0.35 + 2y \approx 0.35$$

$$K_{sp} = [y][0.35]^2 = 7.87 \times 10^{-8}$$

$$\text{Molar solubility} = y = 6.\underline{4}2 \times 10^{-7} = 6.4 \times 10^{-7}\ M$$

b. Set up an equilibrium. The reaction is

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

$$y + 0.35 \approx 0.35 \qquad 2y$$

$$K_{sp} = [0.35][2y]^2 = 7.87 \times 10^{-8}$$

$$\text{Molar solubility} = y = 2.\underline{3}7 \times 10^{-4} = 2.4 \times 10^{-4}\ M$$

c. Yes, $Cu(IO_3)_2$ is a 1:2 electrolyte. It takes two IO_3^- ions to combine with one Cu^{2+} ion. The IO_3^- ion is involved as a square term in the K_{sp} expression.

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17.98.

a. Use the solubility information to calculate K_{sp}. The reaction is

$$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2IO_3^-(aq)$$

$$4.0 \times 10^{-5}\ M \qquad 2 \times (4.0 \times 10^{-5})\ M$$

$K_{sp} = [Pb^{2+}][IO_3^-]^2 = [4.0 \times 10^{-5}][2 \times (4.0 \times 10^{-5})]^2 = 2.56 \times 10^{-13}$

Set up an equilibrium. The reaction is

$$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2IO_3^-(aq)$$

$$y + 0.15 \approx 0.15 \qquad 2y$$

$K_{sp} = [0.15][2y]^2 = 2.56 \times 10^{-13}$

Molar solubility $= y = 6.53 \times 10^{-7} = 6.5 \times 10^{-7}\ M$

b. Because of the common-ion effect or a consideration of Le Châtelier's principle, the molar solubility would be less.

17.99.

a. Set up an equilibrium. The reaction and equilibrium-constant expression are

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \quad K_{sp} = [Pb^{2+}][I^-]^2 = 6.5 \times 10^{-9}$$

The Pb^{2+} ion concentration is 0.0150 *M*. Plug this in, and solve for the iodine-ion concentration.

$$[I^-] = \sqrt{\frac{6.5 \times 10^{-9}}{0.0150}} = 6.58 \times 10^{-4} = 6.6 \times 10^{-4}\ M$$

b. Solve the equilibrium-constant expression for the lead-ion concentration.

$$[Pb^{2+}] = \frac{6.5 \times 10^{-9}}{(2.0 \times 10^{-3})^2} = 1.63 \times 10^{-3} = 1.6 \times 10^{-3}\ M$$

The percent of the lead(II) ion remaining in solution is

$$\text{Percent } Pb^{2+} \text{ remaining} = \frac{1.63 \times 10^{-3}}{0.0150} \times 100\% = 10.9 = 11\%$$

17.100.

a. Set up an equilibrium. The reaction and equilibrium-constant expression are

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Ca^{2+}][F^-]^2 = 3.4 \times 10^{-11}$$

Solve the equilibrium-constant expression for the fluoride-ion concentration. The calcium-ion concentration is 0.00750 *M*.

$$[F^-] = \sqrt{\frac{3.4 \times 10^{-11}}{0.00750}} = 6.73 \times 10^{-5} = 6.7 \times 10^{-5}\ M$$

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b. Solve the equilibrium-constant expression for the calcium ion concentration. The fluoride-ion concentration is 9.5×10^{-4} *M*.

$$[Ca^{2+}] = \frac{3.4 \times 10^{-11}}{(9.5 \times 10^{-4})^2} = 3.\underline{7}7 \times 10^{-5}\ M$$

The percent of the calcium ion precipitated is

$$\text{Percent } Ca^{2+} \text{ precipitated} = \frac{0.00750 - 3.77 \times 10^{-5}}{0.00750} \times 100\% = 99.4 = 99\%$$

17.101.

a. The reaction and equilibrium-constant expression are

$$Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2OH^-(aq) \quad K_{sp} = [Co^{2+}][OH^-]^2$$

From the molar solubility, $[Co^{2+}] = 5.4 \times 10^{-6}\ M$ and $[OH^-] = 2 \times (5.4 \times 10^{-6})\ M$. Therefore,

$$K_{sp} = [5.4 \times 10^{-6}][2 \times (5.4 \times 10^{-6})]^2 = 6.\underline{3}0 \times 10^{-16} = 6.3 \times 10^{-16}$$

b. From the pOH (14 − pH), the $[OH^-] = 10^{-3.57} = 2.\underline{6}9 \times 10^{-4}\ M$. The molar solubility is equal to the cobalt-ion concentration at equilibrium.

$$[Co^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{6.3 \times 10^{-16}}{(2.69 \times 10^{-4})^2} = 8.\underline{7}1 \times 10^{-9} = 8.7 \times 10^{-9}\ M$$

c. The common-ion effect (OH^-) in part b decreases the solubility of Co^{2+}.

17.102.

a. The reaction and equilibrium-constant expression are

$$Be(OH)_2(s) \rightleftharpoons Be^{2+}(aq) + 2OH^-(aq) \quad K_{sp} = [Be^{2+}][OH^-]^2$$

From the molar solubility, $[Be^{2+}] = 8.6 \times 10^{-7}\ M$ and $[OH^-] = 2 \times (8.6 \times 10^{-7})\ M$. Therefore,

$$K_{sp} = [8.6 \times 10^{-7}][2 \times (8.6 \times 10^{-7})]^2 = 2.\underline{5}4 \times 10^{-18} = 2.5 \times 10^{-18}$$

b. This is a buffer system. The reaction is

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b = 1.8 \times 10^{-5}$$

Set up the equilibrium, and calculate the OH^- ion concentration.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.25)[OH^-]}{(1.50)} = 1.8 \times 10^{-5}$$

$$[OH^-] = 1.\underline{0}8 \times 10^{-4}\ M$$

The molar solubility is equal to the beryllium-ion concentration at equilibrium.

$$[Be^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{2.5 \times 10^{-18}}{(1.08 \times 10^{-4})^2} = 2.\underline{1}4 \times 10^{-10} = 2.1 \times 10^{-10}\ M$$

c. The common-ion effect (a Le Châtelier stress) decreases the solubility of Be^{2+}.

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17.103.

a.

$$\begin{array}{lll} AgCl(s) & \rightleftharpoons & Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.8 \times 10^{-10} \\ Ag^+(aq) + 2NH_3(aq) & \rightleftharpoons & Ag(NH_3)_2^+(aq) \quad K_f = 1.7 \times 10^7 \\ \hline AgCl(s) + 2NH_3(aq) & \rightleftharpoons & Ag(NH_3)_2^+(aq) + Cl^-(aq) \end{array}$$

$K = K_{sp} \times K_f = (1.8 \times 10^{-10})(1.7 \times 10^7) = 3.\underline{0}6 \times 10^{-3} = 3.1 \times 10^{-3}$

b. The equilibrium-constant expression is

$$\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \frac{y^2}{(0.80)^2} = 3.06 \times 10^{-3}$$

$y = [Ag(NH_3)_2^+] = 0.04\underline{4}3 = 0.044\ M$

mol AgCl dissolved = mol $Ag(NH_3)_2^+$ = 0.044 mol/L x 1.00 L = 0.044 mol

$$\text{mol } NH_3 \text{ reacted} = 0.0443 \text{ mol } Ag(NH_3)_2^+ \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } Ag(NH_3)_2^+} = 0.08\underline{8}6 \text{ mol}$$

Total moles of NH_3 added = 0.80 M x 1.00 L + 0.08$\underline{8}$6 = 0.8$\underline{8}$9 = 0.89 mol

17.104.

a.

$$\begin{array}{lll} AgBr(s) & \rightleftharpoons & Ag^+(aq) + Br^-(aq) \quad K_{sp} = 5.0 \times 10^{-13} \\ Ag^+(aq) + 2S_2O_3^{2-}(aq) & \rightleftharpoons & Ag(S_2O_3)_2^{3-} \quad K_f = 2.9 \times 10^{13} \\ \hline AgBr(s) + 2S_2O_3^{2-}(aq) & \rightleftharpoons & Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq) \end{array}$$

$K = K_{sp} \times K_f = (5.0 \times 10^{-13})(2.9 \times 10^{13}) = 1\underline{4}.5 = 15$

$$\text{mol AgBr} = 2.5 \text{ g AgBr} \times \frac{1 \text{ mol AgBr}}{187.77 \text{ g AgBr}} = 0.01\underline{3}3 \text{ mol}$$

mol $Ag(S_2O_3)_2^{3-}$ = mol AgBr = 0.0133 mol

$$\frac{[Ag(S_2O_3)_2^{2-}][Br^-]}{[S_2O_3^{2-}]^2} = \frac{(0.0133)^2}{[S_2O_3^{2-}]^2} = 14.5$$

Take the square root of both sides to obtain the moles of $S_2O_3^{2-}$ at equilibrium.

$$\frac{0.0133}{[S_2O_3^{2-}]} = \sqrt{14.5}$$

$[S_2O_3^{2-}] = 0.00\underline{3}49$ mol/L

Moles of $S_2O_3^{2-}$ in $Ag(S_2O_3)_2^{3-}$ = 2 x 0.0133 = 0.02$\underline{6}$6 mol

Total moles of $S_2O_3^{2-}$ = 0.02$\underline{6}$6 + 0.00349 = 0.03$\underline{0}$1 = 0.030 mol

Moles of $Na_2S_2O_3$ added = moles of $S_2O_3^{2-}$ = 0.030 mol

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17.105.

a. The moles of NH_4Cl (molar mass 53.49 g/mol) are given by

$$\text{mol } NH_4Cl = 26.7 \text{ g} \times \frac{1 \text{ mol } NH_4Cl}{53.49 \text{ g } NH_4Cl} = 0.499\underline{2} \text{ mol}$$

The reaction and equilibrium-constant expression are

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Solve the equilibrium-constant expression for $[OH^-]$. The molarity of the NH_4Cl is 0.499$\underline{2}$ mol/1.0 L = 0.4$\underline{9}$92 *M*.

$$[OH^-] = \frac{(1.8 \times 10^{-5})(4.2)}{(0.4992)} = 1.\underline{5}1 \times 10^{-4} = 1.5 \times 10^{-4} \, M$$

b. The reaction and equilibrium-constant expression are

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^- \quad K_{sp} = [Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$$

Solving for $[Mg^{2+}]$ gives

$$[Mg^{2+}] = \frac{(1.8 \times 10^{-11})}{(1.51 \times 10^{-4})^2} = 7.\underline{8}9 \times 10^{-4} = 7.9 \times 10^{-4} \, M$$

The percent Mg^{2+} that has been removed is given by

$$\text{Percent } Mg^{2+} \text{ removed} = \frac{0.075 - 7.89 \times 10^{-4}}{0.075} \times 100\% = 9\underline{8}.9 = 99\%$$

17.106.

a. The moles of $(NH_4)_2SO_4$ (molar mass 132.15 g/mol) are given by

$$\text{mol } (NH_4)_2SO_4 = 75.8 \text{ g} \times \frac{1 \text{ mol } (NH_4)_2SO_4}{132.15 \text{ g } (NH_4)_2SO_4} = 0.573\underline{6} \text{ mol}$$

The moles of $NH_4^+ = 2 \times 0.5736 = 1.1\underline{4}7$ mol. The reaction and equilibrium-constant expression are

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Solve the equilibrium-constant expression for $[OH^-]$. The molarity of the NH_4Cl is 1.1$\underline{4}$7 mol/1.0 L = 1.1$\underline{4}$7 *M*.

$$[OH^-] = \frac{(1.8 \times 10^{-5})(1.6)}{(1.147)} = 2.\underline{5}1 \times 10^{-5} = 2.5 \times 10^{-5} \, M$$

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b. The reaction and equilibrium-constant expression are

$$Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2OH^- \quad K_{sp} = [Mn^{2+}][OH^-]^2 = 4.6 \times 10^{-14}$$

Solving for $[Mn^{2+}]$ gives

$$[Mn^{2+}] = \frac{(4.6 \times 10^{-14})}{(2.51 \times 10^{-5})^2} = 7.\underline{3}0 \times 10^{-5} = 7.3 \times 10^{-5}\ M$$

The percent Mn^{2+} that has been removed is given by

$$\text{Percent } Mn^{2+} \text{ removed} = \frac{0.058 - 7.30 \times 10^{-5}}{0.058} \times 100\% = 9\underline{9}.9\%$$

Nearly 100% of the Mn^{2+} has been removed.

17.107. Water that has filtered through decomposing vegetation contains carbonic acid, as well as other acids. When such an acidic solution comes in contact with limestone, it carves out caverns. The water is now a solution of calcium hydrogen carbonate.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

17.108. The formation of stalactites and stalagmites is the reverse of the reaction in the previous problem. As the calcium hydrogen carbonate solution percolates through holes in the limestone and drips into caverns, water evaporates and carbon dioxide gas escapes; calcium carbonate precipitates onto icicle-shaped stalactites.

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$$

Excess solution drips onto the cavern floor, where calcium carbonate precipitates on upward-growing stalagmites.

■ SOLUTIONS TO STRATEGY PROBLEMS

17.109. When the solutions are mixed together, the combined volume is 100.0 mL. Since the volume doubled, the concentrations are reduced by one-half. Thus, after mixing, the solution is initially 0.0500 *M* HCl and 0.0500 *M* $AgNO_3$. HCl is a strong acid, so the concentration of H_3O^+ is also 0.0500 *M*. Silver chloride precipitates. The solubility product constant is

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = (0.0500 - x)^2$$

where *x* is the concentration of ion precipitated. Solve for the chloride-ion concentration.

$$[Cl^-] = (0.0500 - x) = \sqrt{1.8 \times 10^{-10}} = 1.\underline{3}4 \times 10^{-5} = 1.3 \times 10^{-5}\ M$$

17.110. After mixing, the final volume is 2.00 L. Since the volume doubled, the concentrations are reduced by one-half. Thus, after mixing, the initial concentration of Na_2CO_3 is 0.0500 *M*, and the concentration of $CaCl_2$ is 0.100 *M*. Calcium chloride precipitates. First, assume that CO_3^{2-} reacts completely. After the reaction $[Ca^{2+}] = 0.0500\ M$. Now, find the carbonate ion concentration in this solution. The solubility product constant is

$$K_{sp} = 3.8 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] = (0.0500 - x)(x)$$

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Assume x is negligible compared to 0.0500 and solve for x.

$$x = [CO_3^{2-}] = \frac{3.8 \times 10^{-9}}{0.0500} = 7.\underline{6}0 \times 10^{-8} = 7.6 \times 10^{-8}\ M$$

17.111. First, convert the solubility to molarity using the molar mass of $PbBr_2$.

$$\frac{1.31\ g}{1\ L} \times \frac{1\ mol\ PbBr_2}{367.01\ g} = 3.5\underline{6}9 \times 10^{-3}\ M$$

In a solution of 0.100 M NaBr, the concentrations of Pb^{2+} and Br^- are

$$[Pb^{2+}] = 3.569 \times 10^{-3}\ M$$

$$[Br^-] = 0.100\ M + 2(3.569 \times 10^{-3}\ M) = 0.10\underline{7}1\ M$$

Now calculate the solubility product constant for $PbBr_2$.

$$K_{sp} = [Pb^{2+}][Br^-]^2 = (3.569 \times 10^{-3})(0.1071)^2 = 4.0\underline{9}7 \times 10^{-5} = 4.10 \times 10^{-5}$$

17.112. First, convert the solubilities to molarities using the molar masses.

$$[Na^+] = \frac{3.2\ g}{1\ L} \times \frac{1\ mol\ Na^+}{22.99\ g} = 0.1\underline{3}91\ M$$

$$[NaC_5H_3N_4O_3] = \frac{7.0\ mg}{100\ mL} \times \frac{1000\ mL}{1\ L} \times \frac{1\ g}{1000\ mg} \times \frac{1\ mol\ NaC_5H_3N_4O_3}{190.10\ g}$$

$$= 3.\underline{6}82 \times 10^{-4}\ M$$

K_{sp} can be calculated from the molar solubility of $NaC_5H_3N_4O_3$ in aqueous solution.

$$K_{sp} = [Na^+][C_5H_3N_4O_3^-] = (3.682 \times 10^{-4})^2 = 1.\underline{3}55 \times 10^{-7}$$

Now calculate the concentration of urate ion in blood plasma, assuming x is negligible compared to 0.1391 M.

$$K_{sp} = 1.\underline{3}55 \times 10^{-7} = [Na^+][C_5H_3N_4O_3^-] = (0.1391 + x)(x)$$

$$x = \frac{1.355 \times 10^{-7}}{0.1391} = 9.\underline{7}4 \times 10^{-7} = 9.7 \times 10^{-7}\ M$$

17.113. Assume all the chloride-ion reacts when the $AgNO_3$ is added. The initial moles of chloride present are equal to the moles of added silver-ion. From the titration, the volume of silver nitrate added is 60.3 mL − 50.0 mL = 10.3 mL.

$$\text{mol } Cl^- = \text{mol } Ag^+ = (0.100\ M) \times (10.3 \times 10^{-3}\ L) = 1.0\underline{3}0 \times 10^{-3} = 1.03 \times 10^{-3}\ \text{mol}$$

Next, determine the silver ion concentration when Ag_2CrO_4 begins to precipitate. The concentration of CrO_4^{2-} at this point is

$$[CrO_4^{2-}] = 1.00\ g \times \frac{1\ mol\ K_2CrO_4}{194.190\ g} \times \frac{1}{0.0603\ L} = 0.085\underline{3}9\ M$$

$$[Ag^+] = \sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}} = \sqrt{\frac{1.1 \times 10^{-12}}{0.08539}} = 3.\underline{5}88 \times 10^{-6}\ M$$

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Next, use K_{sp} for AgCl to determine the chloride-ion concentration.

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{3.588 \times 10^{-6}} = 5.\underline{0}15 \times 10^{-5}\ M$$

The final volume in the titration is 60.3 mL, so the moles of chloride-ion at this point are

$$5.015 \times 10^{-5}\ M \times 60.3 \times 10^{-3}\ \text{L} = 3.\underline{0}29 \times 10^{-6} = 3.0 \times 10^{-6}\ \text{mol}$$

17.114. The solubility of calcium fluoride will be reduced in the presence of fluoride ion from another source. In a saturated solution of barium fluoride, the concentration of fluoride ion is calculated using K_{sp}.

$$K_{sp} = 1.0 \times 10^{-6} = [Ba^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3$$

$$x = \sqrt[3]{\frac{1.0 \times 10^{-6}}{4}} = 6.\underline{2}9 \times 10^{-3}\ M$$

$$[F^-] = 2x = 2(6.29 \times 10^{-3}) = 0.01\underline{2}59\ M$$

Now calculate the solubility of calcium fluoride using the K_{sp} value. Assume $2x$ is negligible compared to 0.01259.

$$K_{sp} = 3.4 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (x)(0.01259 + 2x)^2$$

$$Ca^{2+}] = x = \frac{3.4 \times 10^{-11}}{(0.01259)^2} = 2.\underline{1}4 \times 10^{-7} = 2.1 \times 10^{-7}\ M$$

The solubility of CaF_2 in water is calculated in Example 17.4 to be $2.0 \times 10^{-4}\ M$. Therefore, the solubility of CaF_2 in a solution saturated with BaF_2 is about 1000 times smaller, which is what you would expect.

17.115. First calculate the OH^- ion concentration using the pOH, which is 14.00 − 4.50 = 9.50.

$$[OH^-] = 10^{-pOH} = 10^{-9.50} = 3.\underline{1}6 \times 10^{-10}\ M$$

Now calculate the solubility of $Fe(OH)_3$ in the solution using K_{sp}. Because the solution is a buffer, the OH^- concentration remains around $3.16 \times 10^{-10}\ M$.

$$K_{sp} = 2.5 \times 10^{-39} = [Fe^{3+}][OH^-]^3 = (x)(3.16 \times 10^{-10})^3$$

$$[Fe^{3+}] = x = \frac{2.5 \times 10^{-39}}{(3.162 \times 10^{-10})^3} = 7.\underline{9}0 \times 10^{-11}\ M$$

The nanograms of iron in 1.00 L can now be calculated.

$$\frac{7.905 \times 10^{-11}\ \text{mol}}{1\ \text{L}} \times \frac{55.845\ \text{g}}{1\ \text{mol Fe}} \times \frac{10^9\ \text{ng}}{1\ \text{g}} = 4.\underline{4}1 = 4.4\ \text{ng}$$

17.116. $CaSO_4$ has a larger K_{sp} value (2.4×10^{-5}) than $BaSO_4$ (1.1×10^{-10}), so first calculate the concentration of Ca^{2+} and SO_4^{2-} in a saturated solution of $CaSO_4$.

$$K_{sp} = 2.4 \times 10^{-5} = [Ca^{2+}][SO_4^{2-}] = x^2$$

$$[Ca^{2+}] = [SO_4^{2-}] = x = \sqrt{2.4 \times 10^{-5}} = 4.\underline{8}9 \times 10^{-3}\ M$$

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Now calculate the solubility of $BaSO_4$ in the solution using the K_{sp} value. Assume y is negligible compared to 4.89×10^{-3}.

$$K_{sp} = 1.1 \times 10^{-10} = [Ba^{2+}][SO_4^{2-}] = (y)(4.89 \times 10^{-3} + y)$$

$$y = \frac{1.1 \times 10^{-10}}{4.89 \times 10^{-3}} = 2.\underline{2}4 \times 10^{-8}\ M$$

The concentrations of the ions are

$$[Ca^{2+}] = x = 4.9 \times 10^{-3}\ M$$

$$[Ba^{2+}] = y = 2.2 \times 10^{-8}\ M$$

$$[SO_4^{2-}] = x + y = 4.89 \times 10^{-3} + 2.24 \times 10^{-8} = 4.\underline{8}9 \times 10^{-3} = 4.9 \times 10^{-3}\ M$$

17.117. The HF comes from the reaction of the conjugate base F^- with water. Its formation should increase the solubility of CaF_2 slightly. To determine the concentration of HF in the solution, consider the hydrolysis of the fluoride ion and calculate the value of K_b for the base using K_w.

$$F^-(aq) + H_2O(l) \rightarrow HF(aq) + OH^-(aq)$$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.\underline{4}7 \times 10^{-11}$$

Now write out the expression for the equilibrium constant. From Example 17.4, the initial fluoride-ion concentration is $4.0 \times 10^{-4}\ M$.

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{4.0 \times 10^{-4} - x} = 1.47 \times 10^{-11}$$

Assume x is negligible with respect to 4.0×10^{-4} and solve for the concentration of HF in the solution.

$$[HF] = x = \sqrt{(1.47 \times 10^{-11})(4.0 \times 10^{-4})} = 7.\underline{6}6 \times 10^{-8} = 7.7 \times 10^{-8}\ M$$

Therefore, the fluoride-ion concentration did not change significantly, and the formation of HF has a negligible effect on the solubility of calcium fluoride.

For $CaCO_3$, the acid-dissociation constant for HCO_3^- is 4.8×10^{-11}. This gives 2.08×10^{-4} for the value of K_b for CO_3^{2-}. Since K_b is much larger, the concentration of HCO_3^- is significant, and the reaction of CO_3^{2-} with water is important in determining the solubility of calcium carbonate.

17.118. First, set up the equilibrium equations and determine K for the overall reaction.

$Ni(IO_3)_2(s)$	$\rightleftharpoons$	$Ni^{2+}(aq) + 2IO_3^-(aq)$	$K_{sp} = 1.4 \times 10^{-8}$
$Ni^{2+}(aq) + 6NH_3(aq)$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}(aq)$	$K_f = 5.6 \times 10^8$
$Ni(IO_3)_2(s) + 6NH_3(aq)$	$\rightleftharpoons$	$Ni(NH_3)_6^{2+}(aq) + 2IO_3^-(aq)$	$K_c = K_{sp}/(K_a)^2$

Now calculate the moles of $Ni(IO_3)_2$ present in the 1 L of solution.

$$\text{mol } Ni(IO_3)_2 = 5.00 \text{ g } Ni(IO_3)_2 \times \frac{1 \text{ mol } Ni(IO_3)_2}{408.49 \text{ g}} = 0.0122\underline{4} \text{ mol}$$

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Since the $Ni(IO_3)_2$ is completely dissolved, this gives a solution with $[Ni^{2+}] = 0.01224\ M$ and $[IO_3^-] = 2 \times 0.01224\ M = 0.02448\ M$. Assume $[Ni(NH_3)_6^{2+}] = [Ni^{2+}]$ Now use K for the reaction above to determine the NH_3 concentration remaining in solution.

$$K = \frac{[Ni(NH_3)_6^{2+}][IO_3^-]^2}{[NH_3]^6}$$

Rearrange and solve for the ammonia concentration remaining in solution.

$$[NH_3] = \sqrt[6]{\frac{[Ni(NH_3)_6^{2+}][IO_3^-]^2}{K}} = \sqrt[6]{\frac{(0.01224)(0.02448)^2}{7.84}} = 0.09\underline{8}90\ M$$

The total moles of ammonia can now be determined.

Moles of $NH_3 = 6 \times 0.01224 + 0.09890 = 0.17\underline{2}3 = 0.172$ mol

Therefore, to just dissolve the nickel, add 0.172 moles of ammonia.

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

17.119. Using the K_{sp} of 1.1×10^{-21} for ZnS, calculate the $[S^{2-}]$ needed to maintain a saturated solution (without precipitation):

$$[S^{2-}] = \frac{1.1 \times 10^{-21}}{1.5 \times 10^{-4}\ M\ Zn^{2+}} = 7.\underline{3}3 \times 10^{-18}\ M$$

Next, use the overall H_2S ionization expression to calculate the $[H_3O^+]$ needed to achieve this $[S^{2-}]$ level:

$$[H_3O^+] = \sqrt{\frac{1.1 \times 10^{-20}\ (0.10\ M)}{7.33 \times 10^{-18}\ M}} = 1.\underline{2}25 \times 10^{-2}\ M$$

Finally, calculate the buffer ratio of $[SO_4^{2-}]/[HSO_4^-]$ from the H_2SO_4 K_{a_2} expression where K_{a_2} has the value 1.1×10^{-2}:

$$\frac{[SO_4^{2-}]}{[HSO_4^-]} = \frac{K_{a_2}}{[H_3O^+]} = \frac{1.1 \times 10^{-2}}{1.225 \times 10^{-2}} = \frac{0.8979}{1.000}$$

If $[HSO_4^-] = 0.20\ M$, then

$$[SO_4^{2-}] = 0.8979 \times 0.20\ M = 0.1\underline{7}95 = 0.18\ M$$

17.120. Using the K_{sp} of 4×10^{-21} for CoS, calculate the $[S^{2-}]$ needed to maintain a saturated solution (without precipitation):

$$[S^{2-}] = \frac{4 \times 10^{-21}}{1.8 \times 10^{-4}\ M\ Co^{2+}} = \underline{2}.22 \times 10^{-17}\ M$$

Next, use the overall H_2S ionization expression to calculate the $[H_3O^+]$ needed to achieve this $[S^{2-}]$ level:

$$[H_3O^+] = \sqrt{\frac{1.1 \times 10^{-20}\ (0.10\ M)}{2.22 \times 10^{-17}\ M}} = 7.\underline{0}4 \times 10^{-3}\ M$$

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Finally, calculate the buffer ratio of $[SO_4^{2-}]/[HSO_4^-]$ from the H_2SO_4 K_{a_2} expression where K_{a_2} has the value 1.1×10^{-2}:

$$\frac{[SO_4^{2-}]}{[HSO_4^-]} = \frac{K_{a_2}}{[H_3O^+]} = \frac{1.1 \times 10^{-2}}{7.04 \times 10^{-3}} = \frac{1.56}{1.000}$$

If $[HSO_4^-] = 0.20\ M$, then

$$[SO_4^{2-}] = 1.56 \times 0.20\ M = 0.312 = 0.3\ M$$

17.121. Begin by solving for $[H_3O^+]$ in the buffer. Ignoring changes in $[HCHO_2]$ as a result of ionization in the buffer, you obtain

$$[H_3O^+] \cong 1.7 \times 10^{-4} \times \frac{0.45\ M}{0.20\ M} = 3.825 \times 10^{-4}\ M$$

You should verify that this approximation is valid (you obtain the same result from the Henderson-Hasselbalch equation). The equilibrium for the dissolution of CaF_2 in acidic solution is obtained by subtracting twice the acid ionization of HF from the solubility equilibrium of CaF_2.

$CaF_2(s)$			$\rightleftharpoons$	$Ca^{2+}(aq) + 2F^-(aq)$	K_{sp}
$2H_3O^+(aq)$	+	$2F^-(aq)$	$\rightleftharpoons$	$2HF(aq) + 2\ H_2O(l)$	$1/(K_a)^2$
$2H_3O^+(aq)$	+	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq) + 2HF(aq) + 2\ H_2O(l)$	$K_c = K_{sp}/(K_a)^2$

Therefore, $K_c = (3.4 \times 10^{-11}) \div (6.8 \times 10^{-4})^2 = 7.35 \times 10^{-5}$. In order to solve the equilibrium-constant equation, you require the concentration of HF, which you obtain from the acid-ionization constant for HF.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$6.8 \times 10^{-4} = 3.825 \times 10^{-4} \times \frac{[F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = 1.778, \text{ or } [F^-] = 1.778\,[HF]$$

Let x be the solubility of CaF_2 in the buffer. Then $[Ca^{2+}] = x$ and $[F^-] + [HF] = 2x$. Substituting from the previous equation, you obtain

$$2x = 1.778[HF] + [HF] = 2.778[HF], \text{ or } [HF] = 2x/2.778$$

You can now substitute for $[H_3O^+]$ and [HF] into the equation for K_c.

$$K_c = \frac{[Ca^{2+}][HF]^2}{[H_3O^+]^2} = \frac{(x)(2x/2.778)^2}{(3.825 \times 10^{-4})^2} = 7.35 \times 10^{-5}$$

$$7.35 \times 10^{-5} = (3.543 \times 10^6)x^3$$

$$x^3 = 2.075 \times 10^{-11}$$

$$x = 2.748 \times 10^{-4} = 2.7 \times 10^{-4}\ M$$

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17.122. Begin by solving for $[H_3O^+]$ in the buffer. Ignoring changes in $[HC_2H_3O_2]$ as a result of ionization in the buffer, you obtain

$$[H_3O^+] \cong 1.7 \times 10^{-5} \times \frac{0.45\ M}{0.20\ M} = 3.\underline{8}25 \times 10^{-5}\ M$$

You should verify that this approximation is valid (you obtain the same result from the Henderson-Hasselbalch equation). The equilibrium for the dissolution of MgF_2 in acidic solution is obtained by subtracting twice the acid ionization of HF from the solubility equilibrium of MgF_2.

$MgF_2(s)$			$\rightleftharpoons$	$Mg^{2+}(aq) + 2F^-(aq)$	K_{sp}
$2H_3O^+(aq)$	+	$2F^-(aq)$	$\rightleftharpoons$	$2HF(aq) + 2\ H_2O(l)$	$1/(K_a)^2$
$2H_3O^+(aq)$	+	$MgF_2(s)$	$\rightleftharpoons$	$Mg^{2+}(aq) + 2HF(aq) + 2\ H_2O(l)$	$K_c = K_{sp}/(K_a)^2$

Therefore, $K_c = (6.5 \times 10^{-9}) \div (6.8 \times 10^{-4})^2 = 1.\underline{4}06 \times 10^{-2}$. In order to solve the equilibrium-constant equation, you require the concentration of HF, which you obtain from the acid-ionization constant for HF.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$6.8 \times 10^{-4} = 3.825 \times 10^{-5} \times \frac{[F^-]}{[HF]}$$

$$\frac{[F^-]}{[HF]} = 17.78, \text{ or } [F^-] = 1\underline{7}.78\ [HF]$$

Let x be the solubility of MgF_2 in the buffer. Then $[Mg^{2+}] = x$ and $[F^-] + [HF] = 2x$. Substituting from the previous equation, you obtain

$$2x = 17.78[HF] + [HF] = 18.78[HF], \text{ or } [HF] = 2x/1\underline{8}.78$$

You can now substitute for $[H_3O^+]$ and $[HF]$ into the equation for K_c.

$$K_c = \frac{[Mg^{2+}][HF]^2}{[H_3O^+]^2} = \frac{x(2x/18.78)^2}{(3.825 \times 10^{-5})^2} = 1.406 \times 10^{-2}$$

$$1.406 \times 10^{-2} = (7.752 \times 10^6)x^3$$

$$x^3 = 1.812 \times 10^{-9}$$

$$x = 1.\underline{2}19 \times 10^{-3} = 1.2 \times 10^{-3}\ M$$

17.123. The net ionic equation is

$$Ba^{2+}(aq) + 2OH^-(aq) + Mg^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons BaSO_4(s) + Mg(OH)_2(s)$$

Start by calculating the moles per liter of each ion after mixing and before precipitation. Use a total volume of 0.0450 + 0.0670 L = 0.112 L.

M of SO_4^{2-} and Mg^{2+} = (0.350 mol/L x 0.0670 L) ÷ 0.112 L = 0.20$\underline{9}$4 M

M of Ba^{2+} = (0.250 mol/L x 0.0450 L) ÷ 0.112 L = 0.10$\underline{0}$4 M

M of OH^- = (2 x 0.250 mol/L x 0.0450 L) ÷ 0.112 L = 0.20$\underline{0}$89 M

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Assemble a table showing the precipitation of $BaSO_4$ and $Mg(OH)_2$.

Conc. (M)	Ba^{2+}	+ SO_4^{2-}	+ Mg^{2+} + $2OH^-$ ⇌	$BaSO_4(s)$ + $Mg(OH)_2(s)$
Starting	0.1004	0.2094	0.2094	0.20089
Change	−0.1004	−0.1004	−0.1004	−0.20089
Equilibrium	0.0000	0.1090	0.1090	0.0000

To calculate $[Ba^{2+}]$, use the K_{sp} expression for $BaSO_4$.

$$[Ba^{2+}] = \frac{1.1 \times 10^{-10}}{0.1090\ M\ SO_4^{2-}} = 1.009 \times 10^{-9} = 1.0 \times 10^{-9}\ M$$

$$[SO_4^{2-}] = 0.1090 = 0.109\ M$$

Calculate the $[OH^-]$ using the K_{sp} expression for $Mg(OH)_2$:

$$[OH^-] = \sqrt{\frac{1.8 \times 10^{-11}}{0.1090\ M\ Mg^{2+}}} = 1.28 \times 10^{-5} = 1.3 \times 10^{-5}\ M$$

$$[Mg^{2+}] = 0.1090 = 0.109\ M$$

17.124. The net ionic equation is

$$Pb^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2AgCl(s)$$

Start by calculating the moles per liter of each ion after mixing and before precipitation. Use a total volume of 0.0250 + 0.0500 L = 0.0750 L.

M of SO_4^{2-} = (0.0150 mol/L x 0.0500 L) ÷ 0.0750 L = 0.01000 M

M of Pb^{2+} = (0.0100 mol/L x 0.0250 L) ÷ 0.0750 L = 0.003333 M

M of Ag^+ = (2 x 0.0150 mol/L x 0.0500 L) ÷ 0.0750 L = 0.02000 M

M of Cl^- = (2 x 0.0100 mol/L x 0.0250 L) ÷ 0.07500 = 0.006666 M

Assemble a table showing the precipitation of $PbSO_4$ and AgCl.

Conc. (M)	Pb^{2+}	+ SO_4^{2-}	+ Ag^+ + Cl^- ⇌	$PbSO_4(s)$ + $AgCl(s)$
Starting	0.003333	0.01000	0.02000	0.006667
Change	−0.003333	−0.003333	−0.006667	−0.006667
Equilibrium	0.000000	0.006667	0.013333	0.000000

To calculate $[Pb^{2+}]$, use the K_{sp} expression for $PbSO_4$.

$$[Pb^{2+}] = \frac{1.7 \times 10^{-8}}{0.006667\ M\ SO_4^{2-}} = 2.549 \times 10^{-6} = 2.50 \times 10^{-6}\ M$$

$$[SO_4^{2-}] = 0.006667 = 0.0067\ M$$

Calculate the $[Cl^-]$ using the K_{sp} expression for AgCl:

$$[Cl^-] = \frac{1.8 \times 10^{-10}}{0.01333\ M\ Ag^+} = 1.3503 \times 10^{-8} = 1.4 \times 10^{-8}\ M$$

$$[Ag^+] = 0.01333 = 0.0133\ M$$

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CHAPTER 18

Thermodynamics and Equilibrium

■ SOLUTIONS TO EXERCISES

Note on units and significant figures: The mole unit is omitted from all thermodynamic parameters such as $S°$, $\Delta S°$, etc. If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

18.1. Calculate the work, w, done using $w = F \times d = (mg) \times d$. Then use w to calculate ΔE.

$$w = (mg) \times d = (2.20 \text{ kg} \times 9.80 \text{ m/s}^2) \times 0.250 \text{ m} = 5.39\underline{0} \text{ kg•m}^2/\text{s}^2 = 5.39 \text{ J}$$

$$\Delta U = q + w = (-1.50 \text{ J}) + (5.39\underline{0} \text{ J}) = 3.89\underline{0} = 3.89 \text{ J}$$

18.2. At 1.00 atm and 25°C, the volume occupied by 1.00 mol of any of the gases in the equation is 22.41 L x (298/273) = 24.46 L. Find the change in volume:

$$CH_4(24.46 \text{ L}) + 2O_2(2 \times 24.46 \text{ L}) \rightarrow CO_2(24.46 \text{ L}) + 2H_2O(l)$$

$$\Delta V = 24.46 \text{ L} - (3 \times 24.46 \text{ L}) = -48.\underline{9}2 \text{ L}$$

Next, calculate the work, w, done on the system (its value decreases) using 1.00 atm = 1.013×10^5 Pa and 1.00 L = 1.00×10^{-3} m^3. Add this to the heat, q_p, at constant P:

$$w = -P\Delta V = -(1.013 \times 10^5 \text{ Pa}) \times (-48.92 \times 10^{-3} \text{ m}^3) = 4.9\underline{5}56 \times 10^3 \text{ J} = 4.96 \text{ kJ}$$

$$\Delta U = q_p + w = (-890.\underline{2} \text{ kJ}) + (+4.9\underline{5}56 \text{ kJ}) = -885.\underline{2}4 = -885.2 \text{ kJ}$$

18.3. When the liquid evaporates, it absorbs heat: $\Delta H_{vap} = 42.6$ kJ/mol (42.6×10^3 J/mol) at 25°C, or 298 K. The entropy change, ΔS, is

$$\Delta S = \frac{\Delta H_{vap}}{T} = \frac{42.6 \times 10^3 \text{ J/mol}}{298 \text{ K}} = 14\underline{2}.9 \text{ J/(mol•K)}$$

The entropy of one mole of the vapor equals the entropy of one mole of liquid (161 J/K) plus 142.9 J/K.

$$S° = (161 + 142.9) \text{ J/(mol•K)} = 30\underline{3}.9 = 304 \text{ J/(mol•K)}$$

18.4.

a. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +1$) from a solid reactant forming a mole of gas. (Entropy increases.)

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b. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +1$) from a liquid reactant forming a mole of gas. (Entropy increases.)

c. $\Delta S°$ is negative because there is a decrease in moles of gas ($\Delta n_{gas} = -1$) from liquid and gaseous reactants forming two moles of solid. (Entropy decreases.)

d. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +1$) from solid and liquid reactants forming a mole of gas and four moles of an ionic compound. (Entropy increases.)

18.5. The reaction and standard entropies are given below. Multiply the $S°$ values by their stoichiometric coefficients, and subtract the entropy of the reactant from the sum of the product entropies.

	$C_6H_{12}O_6$	$\rightarrow$	$2C_2H_5OH(l)$	+	$2CO_2(g)$
$S°$:	212.1		2 x 160.7		2 x 213.7 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(2 \times 160.7 + 2 \times 213.7) - 212.1]\ \text{J/K} = 536.7\ \text{J/K}$

18.6. The reaction, standard enthalpy changes, and standard entropies are as follows:

	$CH_4(g)$	+	$2O_2(g)$	$\rightarrow$	$CO_2(g)$	+	$2H_2O(g)$
$\Delta H_f°$:	-74.87		0		-393.5		$2 \times (-285.8)$ kJ
$S°$:	186.1		2 x 205.0		213.7		2×188.7 J/K

Calculate $\Delta H°$ and $\Delta S°$ for the reaction by taking the values for products and subtracting the values for reactants.

$\Delta H° = \Sigma n\Delta H_f°(\text{products}) - \Sigma m\Delta H_f°(\text{reactants}) =$

$[(-393.5 + 2 \times -285.8) - (-74.87)]\ \text{kJ} = -890.23\ \text{kJ}$

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(213.7 + 2 \times 188.7) - (186.1 + 2 \times 205.0)]\ \text{J/K} = -5.0\ \text{J/K}$

Now, substitute into the equation for $\Delta G°$ in terms of $\Delta H°$ and $\Delta S°$ ($= -5.0 \times 10^{-3}$ kJ/K):

$\Delta G° = \Delta H° - T\Delta S° = -890.23\ \text{kJ} - (298\ \text{K})(-5.0 \times 10^{-3}\ \text{kJ/K}) = -888.74 = -888.7\ \text{kJ}$

18.7. Write the values of $\Delta G_f°$ multiplied by their stoichiometric coefficients below each formula:

	$CaCO_3(s)$	$\rightarrow$	$CaO(s)$	+	$CO_2(g)$
$\Delta G_f°$:	-1128.8		-603.5		-394.4 kJ

The calculation is

$\Delta G° = \Sigma nG_f°(\text{products}) - \Sigma mG_f°(\text{reactants}) =$

$[(-603.5) + (-394.4) - (-1128.8)]\ \text{kJ} = 130.9\ \text{kJ}$

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18.8.

a.

	$C(\text{graphite})$	+	$2H_2(g)$	→	$CH_4(g)$
$\Delta G_f°$:	0		0		-50.80 kJ

$\Delta G° = [(-50.80) - (0)]$ kJ = -50.80 kJ (spontaneous reaction)

b.

	$2H_2(g)$	+	$O_2(g)$	→	$2H_2O(l)$
$\Delta G_f°$:	0		0		2 x (-237.1) kJ

$\Delta G° = [(2 \times -237.1) - (0)]$ kJ = -474.2 kJ (spontaneous reaction)

c.

	$4HCN(g)$	+	$5O_2(g)$	→	$2H_2O(l)$	+	$4CO_2(g)$	+	$2N_2(g)$
$\Delta G_f°$:	4 x 124.7		0		2 x (-237.1)		4 x (-394.4)		0 kJ

$\Delta G° = [(2 \times -237.1) + 4 \times (-394.4) - (4 \times 124.7)]$ kJ = -2550.6 kJ (spontaneous reaction)

d.

	$Ag^+(aq)$	+	$I^-(aq)$	→	$AgI(s)$
$\Delta G_f°$:	77.12		-51.59		-66.19 kJ

$\Delta G° = [(-66.19) - (77.12 - 51.59)]$ kJ = -91.72 kJ (spontaneous reaction)

18.9.

a. $K = K_p = P_{CO_2}$

b. $K = K_{sp} = [Pb^{2+}][I^-]^2$

c. $K = \dfrac{P_{CO_2}}{[H^+][HCO_3^-]}$

18.10. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Table 18.2.

	$CaCO_3(s)$	⇌	$CaO(s)$	+	$CO_2(g)$
$\Delta G_f°$:	-1128.8		-603.5		-394.4 kJ

Subtract $\Delta G_f°$ of reactants from that of the products:

$$\Delta G_f° = \Sigma n \Delta G_f°(\text{products}) - \Sigma m \Delta G_f°(\text{reactants}) =$$
$$[(-603.5) + (-394.4) - (-1128.8)] \text{ kJ} = 130.9 \text{ kJ}$$

Use the rearranged form of the equation, $\Delta G° = -RT \ln K$, to solve for $\ln K$. To get compatible units, express $\Delta G°$ in joules, and set R equal to 8.31 J/(mol•K). Substituting the numerical values into the expression gives

$$\ln K = \frac{-\Delta G°}{RT} = \frac{130.9 \times 10^3}{-8.31 \times 298} = -52.859$$

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$$K = K_p = e^{-52.859} = \underline{1}.10 \times 10^{-23} = 1 \times 10^{-23}$$

18.11. First, calculate $\Delta G°$ using the $\Delta G_f°$ values in the exercise.

	$Mg(OH)_2(s)$	$\rightarrow$	$Mg^{2+}(aq)$	+	$2OH^-(aq)$
$\Delta G_f°$:	-833.7		-454.8		2 x (-157.3) kJ

Hence, $\Delta G°$ for the reaction is

$$\Delta G° = [2 \times (-157.3) + (-454.8) - (-833.7)] \text{ kJ} = 64.\underline{3} \text{ kJ}$$

Now, substitute numerical values into the equation relating ln K and $\Delta G°$.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{64.3 \times 10^3}{-8.31 \times 298} = -25.\underline{9}65$$

$$K = K_{sp} = e^{-25.965} = \underline{5}.289 \times 10^{-12} = 5 \times 10^{-12}$$

18.12. From Appendix C, you have

	$H_2O(l)$	$\rightleftharpoons$	$H_2O(g)$
$\Delta H_f°$:	-285.8		-241.8 kJ
$S°$:	69.95		188.7 J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$$\Delta H° = [-241.8 - (-285.8)] \text{ kJ} = 44.\underline{0} \text{ kJ}$$

$$\Delta S° = [188.7 - 69.95] \text{ J/K} = 118.\underline{7}5 \text{ J/K}$$

Substitute $\Delta H°$, $\Delta S°$ (= 0.11875 kJ/K), and T (= 318 K) into the equation for $\Delta G_T°$:

$$\Delta G_T° = \Delta H° - T\Delta S° = 44.0 \text{ kJ} - (318 \text{ K})(0.11875 \text{ kJ/K}) = 6.\underline{2}3 \text{ kJ}$$

Substitute the value of $\Delta G°$ (6.23×10^3 J) at 318 K into the equation relating ln K and $\Delta G°$.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{6.23 \times 10^3}{-8.31 \times 318} = -2.\underline{3}60$$

$$K = K_p = e^{-2.360} = 0.0\underline{9}43 = 0.09$$

$K_p = P_{H_2O}$, so the vapor pressure of H_2O is 0.09 atm (71.7 mmHg).

The value is 71.9 mmHg in Appendix B.

18.13. First, calculate $\Delta H°$ and $\Delta S°$ using the given $\Delta H_f°$ and $S°$ values.

	$MgCO_3(s)$	$\rightleftharpoons$	$MgO(s)$	+	$CO_2(g)$
$\Delta H_f°$:	-1111.7		-601.2		-393.5 kJ
$\Delta S°$:	65.85		26.92		213.7 J/K

$$\Delta H° = [-601.2 + (-393.5) - (-1111.7)] \text{ kJ} = 117.\underline{0} \text{ kJ}$$

$$\Delta S° = [(26.92 + 213.7) - 65.85] \text{ J/K} = 174.\underline{7}7 \text{ J/K}$$

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Substitute these values into the expression relating T, $\Delta H°$, and $\Delta S°$ (= 0.17477 kJ/K).

$$T = \frac{\Delta H°}{\Delta S°} = \frac{117.0 \text{ kJ}}{0.17477 \text{ kJ/K}} = 669.45 \text{ K (lower than that for } CaCO_3)$$

ANSWERS TO CONCEPT CHECKS

18.1. The process is $I_2(s) \rightarrow I_2(g)$. The iodine atoms have gone from a state of some order (crystalline iodine) to one that is more disordered (gas). The entropy will have increased.

18.2. The standard free energy of formation for NO(g) is 86.60 kJ/mol. This rather large positive value means the equilibrium constant is small. At equilibrium, the NO concentration is low.

18.3.

a. The standard free-energy change, $\Delta G°$, is independent of concentration, so it will not change.

b. The relationship between ΔG and $\Delta G°$ is given by $\Delta G = \Delta G° + RT \ln Q$, where Q is the reaction quotient. If the concentration of C is increased, it will cause the value of Q to increase and, in turn, ΔG to increase.

18.4. You must break a chemical bond when N_2O_4 goes to $2NO_2$. It will take energy to do that, so you expect ΔH to be positive (the reaction is endothermic). Also, when you break a molecule in two, you generally increase the entropy (ΔS is positive). According to Table 18.3, the reaction should be nonspontaneous at relatively low temperature, but spontaneous at some higher temperature. That is, the concentration of NO_2 increases with temperature.

ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

18.1. A spontaneous process is a chemical and/or a physical change that occurs by itself without the continuing intervention of an outside agency. Three examples are (1) a rock on a hilltop rolls down, (2) heat flows from a hot object to a cold one, and (3) iron rusts in moist air. Three examples of nonspontaneous processes are (1) a rock rolls uphill by itself, (2) heat flows from a cold object to a hot one, and (3) rust is converted to iron and oxygen.

18.2. Because the energy is more dispersed in liquids than in solids, liquid benzene contains more entropy than does the same quantity of frozen benzene.

18.3. The second law of thermodynamics states that for a spontaneous process, the total entropy of a system and its surroundings always increases. As stated in Section 18.2, a spontaneous process actually creates energy dispersal, or entropy.

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18.4. The relationship between entropy and enthalpy can be expressed in terms of the following equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

At equilibrium, ΔG equals 0, so the equation reduces to $\Delta H/T$, whereas, when not at equilibrium, $\Delta G \neq 0$, so this is not the case. In contrast to a phase change at equilibrium, the entropy change for a spontaneous chemical reaction (at constant pressure) does not equal $\Delta H/T$ because entropy is created by the spontaneous reaction. This can be an increase in the entropy of the surroundings or of the system. An example of the latter is the reaction $N_2O_4(g) \rightarrow 2NO_2(g)$, where one reactant molecule forms two product molecules, thus increasing the randomness.

18.5. The standard entropy of hydrogen gas at 25°C can be obtained by starting near 0.0 K as a reference point, where the entropy of perfect crystals of hydrogen is almost zero. Then, warm to room temperature in small increments, and calculate $\Delta S°$ for each incremental temperature change (say, 2 K) by dividing the heat absorbed by the average temperature (1 K is used as the average for 0 K to 2 K), and also take into account the entropy increases that accompany a phase change.

18.6. To predict the sign of $\Delta S°$, look for a change, Δn_{gas}, in the number of moles of gas. If there is an increase in moles of gas in the products (Δn_{gas} is positive), then $\Delta S°$ should be positive. A decrease in moles of gas in the products suggests $\Delta S°$ should be negative.

18.7. Free energy, G, equals $H - TS$; that is, it is the difference between the enthalpy of a system and the product of temperature and entropy. The free-energy change, ΔG, equals $\Delta H - T\Delta S$.

18.8. The standard free-energy change, $\Delta G°$, equals $\Delta H° - T\Delta S°$; that is, it is the difference between the standard enthalpy change of a system and the product of temperature and the standard entropy change of a system. The standard free-energy change of formation is the free-energy change when 1 mole of a substance is formed from its elements in their stable states at 1 atm and at a standard temperature, usually 25°C.

18.9. If $\Delta G°$ for a reaction is negative, the equation for the reaction is spontaneous in the direction written; that is, the reactants form the products as written. If it is positive, then the equation as written is nonspontaneous.

18.10. In principle, if a reaction is carried out so that no entropy is produced, the useful work obtained is the maximum useful work, w_{max}, and is equal to ΔG of the reaction.

18.11. When gasoline burns in an automobile engine, the change in free energy shows up as useful work. Gasoline, a mixture of hydrocarbons such as C_8H_{18} or octane, burns to yield energy, gaseous CO_2, and gaseous H_2O.

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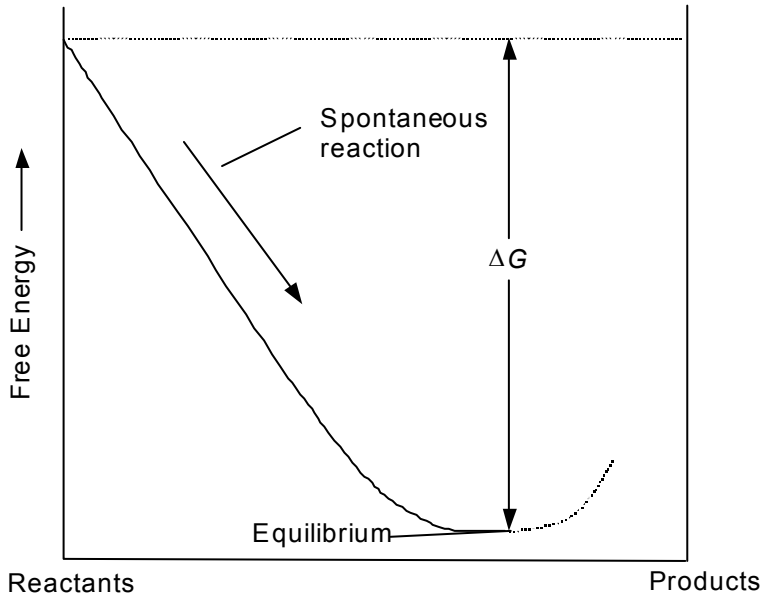
18.12. A nonspontaneous reaction can be made to occur by coupling it with a spontaneous reaction having a sufficiently negative $\Delta G°$ to furnish the required energy. (The net $\Delta G°$ of the coupled reactions must be negative.)

18.13. As a spontaneous reaction proceeds, the free energy decreases until equilibrium is reached at a minimum ΔG. See the diagram below.



18.14. Because the equilibrium constant is related to $\Delta H°$ and $\Delta S°$ by $-RT \ln K = \Delta H° - T\Delta S°$, heat measurements alone can be used to obtain it. The standard enthalpy, $\Delta H°$, is the heat of reaction measured at constant pressure. The standard entropy change, $\Delta S°$, can be calculated from standard entropies, which are obtained from heat-capacity data.

18.15. The four combinations are as follows: (1) A negative $\Delta H°$ and a positive $\Delta S°$ always give a negative $\Delta G°$ and a spontaneous reaction. (2) A positive $\Delta H°$ and a negative $\Delta S°$ always give a positive $\Delta G°$ and a nonspontaneous reaction. (3) A negative $\Delta H°$ and a negative $\Delta S°$ may give a negative or a positive $\Delta G°$. At low temperatures, $\Delta G°$ will usually be negative and the reaction spontaneous; at high temperatures, $\Delta G°$ will usually be positive and the reaction nonspontaneous. (4) A positive $\Delta H°$ and a positive $\Delta S°$ may give a negative or a positive $\Delta G°$. At low temperatures, $\Delta G°$ will usually be positive and the reaction nonspontaneous; at high temperatures, $\Delta G°$ will usually be negative and the reaction spontaneous.

18.16. You can estimate the temperature at which a nonspontaneous reaction becomes spontaneous by substituting zero for $\Delta G°$ into the equation $\Delta G° = \Delta H° - T\Delta S°$ and then solving for T using the form $T = \Delta H°/\Delta S°$.

18.17. The answer is e, $\Delta G < 0$, $\Delta H > 0$, and $\Delta S > 0$.

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18.18. The answer is c, III only.

18.19. The answer is d, 5.49 K

18.20. The answer is a, −956 kJ.

ANSWERS TO CONCEPT EXPLORATIONS

18.21.

a. The temperature of the water sample will gradually increase, and water will evaporate into the room. This would be a spontaneous process.

b. The change in enthalpy is positive since heat is absorbed when water evaporates, and heat is absorbed as the water sample increases temperature. The change in entropy is positive since water molecules are escaping into the gas phase.

c. The entropy change of the water is positive because the water molecules are at a higher temperature and are moving faster. Also, since the enthalpy change is positive, the only way to have a spontaneous process is when the entropy change is also positive.

d. The change in free energy for the water sample is negative since the process is spontaneous.

e. The temperature of the water sample will gradually decrease, and water will evaporate into the room. This would be a spontaneous process.

f. The enthalpy change of the water sample is negative since heat is released as the water sample decreases in temperature. As the water evaporates it will also remove heat from the water sample. The change in entropy is positive since water molecules are escaping into the gas phase.

g. The entropy change of the water is negative because the water molecules are at a lower temperature and are moving slower. However, some water evaporates and becomes vapor, leading to an increase in entropy.

h. The change in free energy for the water sample is negative since the process is spontaneous.

i. The temperature of the water sample will remain constant, and water will evaporate into the room. This would be a spontaneous process.

j. The change in enthalpy is positive since heat is absorbed when water evaporates. The change in entropy is positive since water molecules are escaping into the gas phase.

k. Since the enthalpy change is positive, the only way to have a spontaneous process is when the entropy change is also positive.

l. The free energy change of the water is negative because this is a spontaneous process.

18.22.

a. Since $\Delta G^\circ = -RT \ln K$, as long as the temperature remains constant, the value of ΔG° also remains constant.

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b. In this case, $\Delta G = \Delta G° + RT \ln Q$. Since the reaction quotient Q changes as the reaction proceeds, the value of ΔG will also change.

c. Since the value of K is large, the reaction is spontaneous.

d. No, the statement is not true. At equilibrium, ΔG is zero, but the value of $\Delta G°$ is constant, so it is not zero.

e. Since the value of K is large, at equilibrium the composition will be mostly B(g).

f. For the reverse reaction, $K_r = 1/K_f$, so $\Delta G°$ will have the same numerical value with the opposite sign and will be a constant. At equilibrium, ΔG will be zero, and the reaction mixture will still be mostly B(g). The reaction will not be spontaneous in this direction.

■ ANSWERS TO CONCEPTUAL PROBLEMS

18.23.

a. False. The enthalpy change (heat of reaction) has no direct relation to spontaneity.

b. False. The rate of a reaction has nothing to do with the spontaneity (thermodynamics) of a reaction.

c. False. The entropy may increase or decrease during a spontaneous reaction.

d. True. The entropy of the system plus its surroundings always increases during a spontaneous change.

e. False. The energy may increase or decrease during a spontaneous reaction.

18.24.

a. Spontaneous. Sugar dissolves spontaneously in hot water.

b. Nonspontaneous. Rust does not spontaneously change to iron; rather, iron spontaneously rusts in air.

c. Spontaneous. The burning of butane in air is a spontaneous reaction.

d. Nonspontaneous. A pendulum, once stopped, will not spontaneously begin to move again.

e. Nonspontaneous. Water will not spontaneously decompose into its elements.

18.25.

a. The 2.0 mol of CO_2 at 20°C and 1 atm has a greater entropy; two moles of substance have more entropy than one mole.

b. The 1.0 mol of butane gas at 20°C and 10 atm has the higher entropy; the gaseous state has more entropy than the liquid state of the same substance under the same conditions.

c. The 1.0 mol of $CO_2(s)$ at −80°C and 1 atm has the higher entropy; a solid substance has more entropy at the higher temperature.

d. The 25 grams of bromine vapor at −7°C and 1 atm has the higher entropy; the gaseous (vapor) state has more entropy than the liquid state of the same substance under the same conditions.

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18.26.

a. Entropy increases; ΔS is positive; energy dispersal increases when the food coloring disperses throughout the water.

b. Entropy decreases; ΔS is negative; as a tree leafs out, energy dispersal decreases, and entropy decreases.

c. Entropy increases; ΔS is positive; as flowers wilt and stems decompose, energy dispersal increases and entropy increases.

d. Entropy decreases; ΔS is negative; as a liquid changes to a solid, there is a decrease in energy dispersal and a decrease of entropy.

e. Entropy increases; ΔS is positive; as a liquid changes to a vapor, energy dispersal increases and entropy increases.

18.27.

a. Since this is a gas-phase reaction, calculate the change in the number of moles of gas molecules, $\Delta n = 1 - 3 = -2$. This corresponds to a decrease in entropy, so ΔS is negative for this reaction.

b. Since this is an equilibrium state, $\Delta G = 0$, so $\Delta H - T\Delta S = 0$ also. This gives $\Delta H = T\Delta S$, and since ΔS is negative, so is ΔH.

c. The reaction spontaneously re-establishes equilibrium, so ΔG is negative prior to equilibrium.

d. At equilibrium, $\Delta G = 0$.

18.28. The process is not spontaneous; you have to stretch the rubber band (the opposite process, a stretched rubber band snapping to its normal shorter shape, is spontaneous). Thus, ΔG is positive. The fact that the stretched rubber band feels warm means that ΔH is negative (exothermic). Note that $\Delta G = \Delta H - T\Delta S$; so $\Delta S = -(\Delta G - \Delta H)/T$. This implies that ΔS is negative, which is consistent with an increase in order.

18.29.

a. Changes in volume will affect the position of the equilibrium but will not change the value of the equilibrium constant for a reaction.

b. The increase in volume of the container corresponds to a decrease in the pressure. According to Le Châtelier's principle, the reaction will shift toward the side with more gas molecules to re-establish the pressure. This means the reaction will shift toward the left side, $X(g) + Y(g)$. A reaction that shifts to the left has a Q value larger than the equilibrium constant.

c. Immediately after the volume change, the value of ΔS for the forward reaction will still be the same, negative. Since the reaction is now spontaneous in the reverse reaction, ΔG for the forward reaction must be positive.

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18.30.

a. $\Delta H°$ is positive for this reaction (you need energy to break bonds), and $\Delta S°$ is also positive (breaking a molecule into two increases energy dispersal and entropy). Referring to Table 18.3, you see the reaction is nonspontaneous at low T and spontaneous at high T. Therefore, the spontaneity ($\Delta G°$) of the reaction increases with temperature.

b. $\Delta S°$ for this reaction is negative (two molecules form one, so there is a decrease in energy dispersal and a decrease in entropy), and $\Delta H°$ is also negative (energy is released when bonds form). Referring to Table 18.3, you see the reaction is spontaneous at low T and nonspontaneous at high T. Therefore, the spontaneity ($\Delta G°$) of the reaction decreases with temperature.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: The mole unit is omitted from all thermodynamic parameters such as $S°$, $\Delta S°$, etc. If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

18.31. The values of q and w are −82 J and 29 J, respectively.

$$\Delta U = q + w = (-82\text{ J}) + 29\text{ J} = -53\text{ J}$$

18.32. $\Delta U = 0 = q + w$

$$0 = (-76\text{ J}) + w$$

$$w = 76\text{ J}$$

18.33. At 100°C (373 K) and 1 atm (1.013×10^5 Pa), 1.00 mol of $H_2O(g)$ occupies

$$22.41\text{ L} \times \frac{373\text{ K}}{273\text{ K}} = 30.\underline{6}19\text{ L}\ (30.\underline{6}19 \times 10^{-3}\text{ m}^3)$$

The work done by the chemical system in pushing back the atmosphere is

$$w = -P\Delta V = -(1.013 \times 10^5\text{ Pa}) \times (30.619 \times 10^{-3}\text{ m}^3) = -3.10\underline{1}7 \times 10^3\text{ J} = -3.10\underline{1}7\text{ kJ}$$

$$\Delta U = q_p + w = (40.6\underline{6}\text{ kJ}) + (-3.1017\text{ kJ}) = 37.5\underline{5}83 = 37.56\text{ kJ}$$

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18.34. At 25°C (298 K) and 1 atm (1.013×10^5 Pa), the decrease in volume going from three moles to zero mol of gas is

$$-3 \text{ x } 22.41 \text{ L x } \frac{298 \text{ K}}{273 \text{ K}} = -73.\underline{3}86 \text{ L } (-73.\underline{3}86 \times 10^{-3} \text{ m}^3)$$

The enthalpy change for this reaction is two times the enthalpy of formation of $H_2O(l)$, which is −571.6 kJ. The work done on the chemical system by the atmosphere is

$$w = -P\Delta V = -(1.013 \times 10^5 \text{ Pa}) \text{ x } (-73.386 \times 10^{-3} \text{ m}^3) = 7.4\underline{3}4 \times 10^3 \text{ J} = 7.4\underline{3}4 \text{ kJ}$$

$$\Delta U = q_p + w = (-571.6 \text{ kJ}) + 7.434 \text{ kJ} = -564.\underline{1}6 = -564.2 \text{ kJ}$$

18.35. First, determine the enthalpy change for the reaction of 1.20 mol of $CHCl_3$.

$$\Delta H = 1.20 \text{ mol x } \frac{29.6 \text{ kJ}}{1 \text{ mol}} = 35.\underline{5}2 \text{ kJ} = 3.5\underline{5}2 \times 10^4 \text{ J}$$

Use the equilibrium relation between ΔS and ΔH_{vap} at the boiling point (61.2°C = 334.4 K):

$$\Delta S = \frac{\Delta H}{T} = \frac{3.552 \times 10^4 \text{J}}{334.4 \text{ K}} = 10\underline{6}.2 = 106 \text{ J/K}$$

18.36. First, determine the enthalpy change for 1.34 mol of $(C_2H_5)_2O$.

$$\Delta H = 1.34 \text{ mol x } \frac{26.7 \text{ kJ}}{1 \text{ mol}} = 35.\underline{7}78 \text{ kJ} = 3.5\underline{7}78 \times 10^4 \text{ J}$$

Use the equilibrium relation between ΔS and ΔH_{vap} at the boiling point (35.6°C = 308.8 K):

$$\Delta S = \frac{\Delta H}{T} = \frac{3.5778 \times 10^4 \text{J}}{308.8 \text{ K}} = 11\underline{5}.86 = 116 \text{ J/K}$$

18.37. First, determine the enthalpy change for the condensation of 1.00 mol of $CH_3OH(l)$. $\Delta H_{cond} = -\Delta H_{vap} = -38.0$ kJ/mol.

The entropy change for this condensation at 25°C (298 K) is

$$\Delta S = \frac{\Delta H_{cond}}{T} = \frac{-3.80 \times 10^4 \text{J}}{298 \text{ K}} = -12\underline{7}.51 \text{ J/K}$$

The entropy of one mole of liquid is calculated using the entropy of one mole of vapor, 255 J/(mol•K).

$$S_{liq} = S_{vap} + \Delta S_{cond} = 255 \text{ J/K} + (-127.51 \text{ J/K}) = 12\underline{7}.48 = 127 \text{ J/K}$$

18.38. First, determine the enthalpy change for the vaporization of 1.00 mol of $CS_2(l)$.

$$\Delta H_{cond} = -\Delta H_{vap} = -27.2 \text{ kJ/mol}$$

The entropy change for this condensation at 25°C (298 K) is

$$\Delta S = \frac{\Delta H_{cond}}{T} = \frac{-2.72 \times 10^4 \text{J}}{298 \text{ K}} = -91.\underline{2}7 \text{ J/K}$$

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The entropy of one mole of liquid is calculated using the entropy of one mole of vapor, 243 J/(mol•K).

$$S_{liq} = S_{vap} + \Delta S_{cond} = 243 \text{ J/K} + (-91.27 \text{ J/K}) = 151.7 = 152 \text{ J/K}$$

18.39.

a. $\Delta S°$ is negative because there is a decrease in moles of gas ($\Delta n_{gas} = -2$) from three moles of gaseous reactants forming one mole of gaseous product. (Entropy decreases.)

b. $\Delta S°$ is not predictable from the rules given. The molecules N_2, O_2 and NO are of similar size and present in equal numbers. There is no change in moles of gas ($\Delta n_{gas} = 0$), since two moles of gaseous reactants form two moles of gaseous products. Also, there is no phase change occurring.

c. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +1$) from five moles of gaseous reactants forming six moles of gaseous products. (Entropy increases.)

d. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +1$) from a solid reactant and one mole of gaseous reactant forming two moles of gaseous products. (Entropy increases.)

18.40.

a. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +3$) from one mole of liquid reactant forming three moles of gaseous products. (Entropy increases.)

b. $\Delta S°$ is negative because there is a decrease in moles of gas ($\Delta n_{gas} = -1$) from a liquid reactant and three moles of gaseous reactant forming two moles of gaseous product and liquid product. (Entropy decreases.)

c. $\Delta S°$ is negative because there is a decrease in moles of gas ($\Delta n_{gas} = -5$) from five moles of gaseous reactant and one mole of solid reactant forming one mole of solid product. (Entropy decreases.)

d. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +2$) from a solid reactant forming two moles of gaseous product plus solid product. (Entropy increases.)

18.41. The reaction and standard entropies are given below. Multiply the $S°$ values by their stoichiometric coefficients, and subtract the entropy of the reactant from the sum of the product entropies.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

a. $S°$: 2 x 51.46 223.0 2 x 72.12 J/K

$$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$$

$$[(2 \times 72.12) - (2 \times 51.46 + 223.0)] \text{ J/K} = -181.68 = -181.7 \text{ J/K}$$

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b.

	$Ag(s)$	+	$1/2\ Cl_2(g)$	→	$AgCl(s)$
$S°$:	42.55		1/2 x 223.0		96.2 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(96.2) - (42.55 + 1/2 \times 223.0)]\ J/K = -57.\underline{8}5 = -57.9\ J/K$

c.

	$CS_2(l)$	+	$3O_2(g)$	→	$CO_2(g)$	+	$2SO_2(g)$
$S°$:	151.3		3 x 205.0		213.7		2 x 248.1 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(213.7 + 2 \times 248.1) - (151.3 + 3 \times 205.0)]\ J/K = -56.4\ J/K$

d.

	$2CH_3OH(l)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$4H_2O(g)$
$S°$:	2 x 126.8		3 x 205.0		2 x 213.7		4 x 188.7 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(2 \times 213.7 + 4 \times 188.7) - (2 \times 126.8 + 3 \times 205.0)]\ J/K = 31\underline{3}.6 = 314\ J/K$

18.42. In part d, note that aqueous $CaCl_2$ exists as $Ca^+(aq)$ and $2Cl^-(aq)$ ions.

a.

	$Pb(s)$	+	$1/2\ O_2(g)$	→	$PbO(s)$
$S°$:	64.78		1/2 x 205.0		66.32 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[66.32 - 64.78 - 1/2 \times 205.0]\ J/K = -100.\underline{9}6 = -101.0\ J/K$

b.

	$CS_2(g)$	+	$4H_2(g)$	→	$CH_4(g)$	+	$2H_2S(g)$
$S°$:	237.9		4 x 130.6		186.1		2 x 205.6 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(186.1 + 2 \times 205.6) - (237.9 + 4 \times 130.6)]\ J/K = -163.0\ J/K$

c.

	$C_2H_4(g)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$2H_2O(g)$
$S°$:	219.2		3 x 205.0		2 x 213.7		2 x 188.7 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(2 \times 213.7 + 2 \times 188.7) - (219.2 + 3 \times 205.0)]\ J/K = -29.4\ J/K$

d.

	$Ca(s)$	+	$2HCl(aq)$	→	$Ca^{2+}(aq)$	+	$2Cl^-(aq)$	+	$H_2(g)$
$S°$:	41.59		2 x 56.5		-53.1		2 x 56.5		130.6 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(-53.1) + (2 \times 56.5) + (130.6) - (41.59) - (2 \times 56.5)]\ J/K = 35.\underline{9}1 = 35.9\ J/K$

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18.43.

	$C_2H_4(g)$	+ $3O_2(g)$	→ $2CO_2(g)$	+ $2H_2O(l)$
$S°$:	219.2	3 x 205.0	2 x 213.7	2 x 69.95 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(2 \times 213.7 + 2 \times 69.95) - (219.2 + 3 \times 205.0)]\ \text{J/K} = -266.\underline{9}0\ \text{J/K}$

S decreases, as expected from the decrease in moles of gas.

18.44.

	$CaCO_3(s)$	+ $2H^+(aq)$	→ $Ca^{2+}(aq)$	+ $H_2O(l)$	+ $CO_2(g)$
$S°$:	92.9	0	-53.1	69.95	213.7 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(-53.1 + 69.95 + 213.7) - (92.9)]\ \text{J/K} = 137.\underline{6}5\ \text{J/K}$

S increases, as expected from the increase in moles of gas.

18.45. The reaction, with standard enthalpies of formation and standard entropies written underneath, is

	$2CH_3OH(l)$	+ $3O_2(g)$	→ $2CO_2(g)$	+ $4H_2O(l)$
$\Delta H_f°$:	2 x (-238.7)	0	2 x (-393.5)	4 x (-285.8) kJ
$S°$:	2 x 126.8	3 x 205.0	2 x 213.7	4 x 69.95 J/K

Calculate $\Delta H°$ and $\Delta S°$ for the reaction.

$\Delta H° = \Sigma n\Delta H_f°(\text{products}) - \Sigma m\Delta H_f°(\text{reactants}) =$

$[2 \times (-393.5) + 4 \times (-285.8) - 2 \times (-238.7)]\ \text{kJ} = -1452.8\ \text{kJ}$

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(2 \times 213.7 + 4 \times 69.95) - (2 \times 126.8 + 3 \times 205.0)]\ \text{J/K} = -161.\underline{4}0$
$= -161.4\ \text{J/K}$

Now, substitute into the equation for $\Delta G°$ in terms of $\Delta H°$ and $\Delta S°$ ($= -0.16\underline{1}40$ kJ/K).

$\Delta G° = \Delta H° - T\Delta S° = -1452.8\ \text{kJ} - (298\ \text{K}) \times (-0.16140\ \text{kJ/K}) = -1404.\underline{7}0$
$= -1404.7\ \text{kJ}$

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18.46. The reaction, standard enthalpy changes, and standard entropies are as follows:

	$C_3H_8(g)$	+	$5O_2(g)$	→	$3CO_2(g)$	+	$4H_2O(g)$
ΔH_f°:	-104.7		0		3 x (-393.5)		4 x (-241.8) kJ
S°:	270.2		5 x 205.0		3 x 213.7		4 x 188.7 J/K

Calculate $\Delta H°$ and $\Delta S°$ for the reaction.

$\Delta H° = \Sigma n\Delta H_f°(\text{products}) - \Sigma m\Delta H_f°(\text{reactants}) =$

$[3 \times (-393.5) + 4 \times (-241.8) - (-104.7)]\ \text{kJ} = -2043.\underline{0}\ \text{kJ}$

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(3 \times 213.7 + 4 \times 188.7) - (270.2 + 5 \times 205.0)]\ \text{J/K} = 100.\underline{7}\ (0.100\underline{7}\ \text{kJ/K})$

$\Delta G° = \Delta H° - T\Delta S° = -2043.0\ \text{kJ} - (298\ \text{K})(0.1007\ \text{kJ/K}) = -2073.\underline{0}0 = -2073.0\ \text{kJ}$

18.47.

a. $K(s) + 1/2Br_2(l) \rightarrow KBr(s)$

b. $3/2H_2(g) + C(\text{graphite}) + 1/2Cl_2(g) \rightarrow CH_3Cl(l)$

c. $1/8S_8(\text{rhombic}) + H_2(g) \rightarrow H_2S(g)$

d. $As(s) + 3/2H_2(g) \rightarrow AsH_3(g)$

18.48.

a. $Mg(s) + 1/2O_2(g) \rightarrow MgO(s)$

b. $C(\text{graphite}) + 1/2O_2(g) + Cl_2(g) \rightarrow COCl_2(g)$

c. $C(\text{graphite}) + 2F_2(g) \rightarrow CF_4(g)$

d. $P(\text{white}) + 5/2Cl_2(g) \rightarrow PCl_5(g)$

18.49. Write the values of $\Delta G_f°$ multiplied by their stoichiometric coefficients below each formula; then subtract $\Delta G_f°$ of the reactants from that of the products.

a.

	$C_2H_4(g)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$2H_2O(g)$
ΔG_f°:	68.39		0		-394.4		2 x (-228.6) kJ

$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants}) =$

$[2(-394.4) + 2(-228.6) - (68.39)]\ \text{kJ} = -1314.\underline{3}9 = -1314.4\ \text{kJ}$

b.

	$CaCO_3(s)$	+	$2H^+(aq)$	→	$Ca^{2+}(aq)$	+	$H_2O(l)$	+	$CO_2(g)$
ΔG_f°:	-1128.8		0		-553.5		-237.1		-394.4 kJ

$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants}) =$

$[(-553.5) + (-237.1) + (-394.4) - (-1128.8)]\ \text{kJ} = -56.2\ \text{kJ}$

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18.50. Write the values of $\Delta G_f°$ below each formula; then subtract $\Delta G_f°$ values.

a.

	$C_2H_4(g)$	+	$3O_2(g)$	→	$2CO_2(g)$	+	$2H_2O(g)$
$\Delta G_f°$:	68.39		0		2 x (-394.4)		2 x (-228.6) kJ

$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants}) =$

$[2(-394.4) + 2(-228.6) - (68.39)]\ \text{kJ} = -1314.\underline{3}9 = -1314.4\ \text{kJ}$

b.

	$Na_2CO_3(s)$	+	$H^+(aq)$	→	$2Na^+(aq)$	+	$HCO_3^-(aq)$
$\Delta G_f°$:	-1048.0		0		2 x (-261.9)		-586.8 kJ

$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants}) =$

$[2(-261.9) + (-586.8) - (-1048.0)]\ \text{kJ} = -62.6\ \text{kJ}$

18.51.

a. Spontaneous reaction
b. Spontaneous reaction
c. Nonspontaneous reaction
d. Equilibrium mixture; significant amounts of both
e. Nonspontaneous reaction

18.52.

a. Spontaneous reaction
b. Spontaneous reaction
c. Nonspontaneous reaction
d. Nonspontaneous reaction
e. Equilibrium mixture; significant amounts of both

18.53. Calculate $\Delta H°$ and $\Delta G°$ using the given $\Delta H_f°$ and $\Delta G_f°$ values.

a.

	$Al_2O_3(s)$	+	$2Fe(s)$	→	$Fe_2O_3(s)$	+	$2Al(s)$
$\Delta H_f°$:	-1675.7		0		-825.5		0 kJ
$\Delta G_f°$:	-1582.3		0		-743.5		0 kJ

$\Delta H° = [(-825.5) - (-1675.7)]\ \text{kJ} = 850.2\ \text{kJ}$

$\Delta G° = [(-743.5) - (-1582.3)]\ \text{kJ} = 838.8\ \text{kJ}$

The reaction is endothermic, absorbing 850.2 kJ of heat. The large positive value for $\Delta G°$ indicates that the equilibrium composition is mainly reactants.

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		$COCl_2(g)$	+	$H_2O(l)$	→	$CO_2(g)$	+	$2HCl(g)$
	ΔH_f°:	-220.1		-285.8		-393.5		2 x (-92.31) kJ
b.	ΔG_f°:	-205.9		-237.1		-394.4		2 x (-95.30) kJ

$\Delta H° = [-393.5 + (2)(-92.31) - (-220.1) - (-285.8)]$ kJ $= -72.\underline{2}2 = -72.2$ kJ

$\Delta G° = [-394.4 + (2)(-95.30) - (-205.9) - (-237.1)]$ kJ $= -142.\underline{0}0 = -142.0$ kJ

The reaction is exothermic; the $\Delta G°$ value indicates mainly products at equilibrium.

18.54. Calculate $\Delta H°$ and $\Delta G°$ using the given $\Delta H_f°$ and $\Delta G_f°$ values.

		$2PbO(s)$	+	$N_2(g)$	→	$2Pb(s)$	+	$2NO(g)$
	ΔH_f°:	2(-219.4)		0		0		2 x 90.29 kJ
a.	ΔG_f°:	2(-189.3)		0		0		2 x 86.60 kJ

$\Delta H° = [2(90.29) - 2(-219.4)]$ kJ $= 619.\underline{3}8 = 619.4$ kJ

$\Delta G° = [2(86.60) - 2(-189.3)]$ kJ $= 551.\underline{8}0 = 551.8$ kJ

The reaction is endothermic, absorbing 619.4 kJ of heat. The large positive value for $\Delta G°$ indicates that the equilibrium composition is mainly reactants.

		$CS_2(l)$	+	$2H_2O(l)$	→	$CO_2(g)$	+	$2H_2S(g)$
	ΔH_f°:	89.70		2 x (-285.8)		-393.5		2 x (-20.50) kJ
b.	ΔG_f°:	65.27		2 x (-237.1)		-394.4		2 x (-33.33) kJ

$\Delta H° = [-393.5 + 2(-20.50) - (89.70) - 2(-285.8)]$ kJ $= 47.\underline{4}0 = 47.4$ kJ

$\Delta G° = [(-394.4) + 2(-33.33) - (65.27) - 2(-237.1)]$ kJ $= -52.\underline{1}3 = -52.1$ kJ

The reaction is endothermic; $\Delta G°$ indicates that the equilibrium composition is mainly products.

18.55. Calculate $\Delta G°$ using the given $\Delta G_f°$ values.

	$2H_2(g)$	+	$O_2(g)$	→	$2H_2O(l)$
ΔG_f°:	0		0		2 x (-237.1) kJ

$\Delta G° = [2(-237.1) - 0]$ kJ $= -474.2$ kJ

Maximum work equals $\Delta G°$ equals −474.2 kJ. Because maximum work is stipulated, no entropy is produced.

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18.56. Calculate $\Delta G°$ using the given $\Delta G_f°$ values.

	$H_2(g)$	+	$Br_2(l)$	→	$2HBr(g)$
$\Delta G_f°$:	0		0		2 x (-53.50) kJ

$\Delta G° = 2(-53.50)\text{ kJ} = -107.0\text{ kJ}$

Maximum work equals $\Delta G°$ equals −110.16 kJ. Because maximum work is stipulated, no entropy is produced.

18.57. Calculate $\Delta G°$ per 1 mol Zn(s) using the given $\Delta G_f°$ values.

	$Zn(s)$	+	$Cu^{2+}(aq)$	→	$Zn^{2+}(aq)$	+	$Cu(s)$
$\Delta G_f°$:	0		65.52		-147.0		0 kJ

$\Delta G° = [(-147.0) - (65.52)]\text{ kJ} = -212.52\text{ kJ/mol Zn}$

$-212.52\text{ kJ/mol Zn} \times (4.85\text{ g} \div 65.39\text{ g/mol Zn}) = -15.76 = -15.8\text{ kJ}$

Maximum work equals $\Delta G°$ equals −15.8 kJ. Because maximum work is stipulated, no entropy is produced.

18.58. Calculate $\Delta G°$ per 1 mol Zn(s) using the given $\Delta G_f°$ values.

	$Zn(s)$	+	$2H^+(aq)$	→	$Zn^{2+}(aq)$	+	$H_2(g)$
$\Delta G_f°$:	0		0		-147.0		0 kJ

$\Delta G° = [(-147.0) - 0]\text{ kJ} = -147.0\text{ kJ/mol Zn}$

$-147.0\text{ kJ/mol Zn} \times (3.65\text{ g} \div 65.39\text{ g/mol Zn}) = -8.205 = -8.21\text{ kJ}$

Maximum work equals $\Delta G°$ equals −8.21 kJ. Because maximum work is stipulated, no entropy is produced.

18.59.

a. $K = K_p = \dfrac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$

b. $K = K_{sp} = [Mg^{2+}][OH^-]^2$

c. $K = [Li^+]^2[OH^-]^2\ P_{H_2}$

18.60.

a. $K = K_p = \dfrac{P_{CH_3OH}}{P_{CO} P_{H_2}^{\ 2}}$

b. $K = \dfrac{1}{K_{sp}} = \dfrac{1}{[Ag^+]^2[CrO_4^{2-}]}$

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c. $K = \dfrac{[Ca^{2+}]P_{CO_2}}{[H^+]^2}$

18.61. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$H_2(g)$	$Br_2(l)$	$\rightarrow$	$2HBr(g)$
$\Delta G_f°$:	0	0		2 x (-53.50) kJ

$\Delta G° = [2(-53.50) - 0]\ kJ = -107.00\ kJ$

Use the rearranged form of the equation, $\Delta G° = -RT \ln K$, to solve for ln K. To get compatible units, express $\Delta G°$ in joules, and set R equal to 8.31 J/(mol•K). Substituting the numerical values into the expression gives

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-107.00 \times 10^3}{-8.31 \times 298} = 43.\underline{2}08$$

$$K = e^{43.208} = \underline{5}.82 \times 10^{18} = 6 \times 10^{18}$$

18.62. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$H_2(g)$	+	S(rhombic)	$\rightarrow$	$H_2S(g)$
$\Delta G_f°$:	0		0		-33.33 kJ

$\Delta G° = [(-33.33) - 0]\ kJ = -33.33\ kJ$

Use the rearranged form of the equation, $\Delta G° = -RT \ln K$, to solve for ln K. To get compatible units, express $\Delta G°$ in joules, and set R equal to 8.31 J/(mol•K). Substituting the numerical values into the expression gives

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-33.33 \times 10^3}{-8.31 \times 298} = 13.\underline{4}59$$

$$K = e^{13.459} = \underline{7}.00 \times 10^5 = 7 \times 10^5$$

18.63. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$CO(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$CH_4(g)$	+	$H_2O(g)$
$\Delta G_f°$:	-137.2		0		-50.80		-228.6 kJ

Subtract $\Delta G_f°$ of the reactants from that of the products:

$\Delta G° = [(-50.80) + (-228.6) - (-137.2)]\ kJ = -142.20\ kJ$

Use the rearranged form of the equation, $\Delta G° = -RT \ln K$, to solve for ln K. To get compatible units, express $\Delta G°$ in joules, and set R equal to 8.31 J/(mol•K). Substituting the numerical values into the expression gives

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-142.20 \times 10^3}{-8.31 \times 298} = 57.\underline{4}22$$

$$K = K_p = e^{57.422} = \underline{8}.67 \times 10^{24} = 9 \times 10^{24}$$

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18.64. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$CO(g)$	+	$2H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$
$\Delta G_f°$:	-137.2		0		-162.0 kJ

Subtract $\Delta G_f°$ of the reactants from that of the product:

$$\Delta G° = [(-162.0) - (-137.2)]\ \text{kJ} = -24.8\ \text{kJ}$$

Use the rearranged form of the equation, $\Delta G° = -RT \ln K$, to solve for $\ln K$. To get compatible units, express $\Delta G°$ in joules, and set R equal to 8.31 J/(mol•K).

Substituting the numerical values into the expression gives

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-24.8 \times 10^3}{-8.31 \times 298} = 10.\underline{0}14$$

$$K = K_p = e^{10.014} = \underline{2}.23 \times 10^4 = 2 \times 10^4$$

18.65. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$Fe(s)$	+	$Cu^{2+}(aq)$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+	$Cu(s)$
$\Delta G_f°$:	0		65.52		-78.87		0 kJ

Hence

$$\Delta G° = [(-78.87) - 65.52]\ \text{kJ} = -144.39\ \text{kJ}$$

Now, substitute numerical values into the equation relating $\ln K$ and $\Delta G°$.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-144.39 \times 10^3}{-8.31 \times 298} = 58.\underline{3}06$$

Therefore,

$$K = K_c = e^{58.306} = \underline{2}.10 \times 10^{25} = 2 \times 10^{25}$$

18.66. First, calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$Zn(s)$	+	$2Ag^+(aq)$	$\rightleftharpoons$	$Zn^{2+}(aq)$	+	$2Ag(s)$
$\Delta G_f°$:	0		2 x (77.12)		-147.0		0 kJ

Hence,

$$\Delta G° = [(-147.0) - 2(77.12)]\ \text{kJ} = -301.\underline{2}4\ \text{kJ}$$

Now, substitute numerical values into the equation relating $\ln K$ and $\Delta G°$.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-301.24 \times 10^3}{-8.31 \times 298} = 12\underline{1}.645$$

Therefore,

$$K = K_c = e^{121.645} = 6.75 \times 10^{\underline{52}} = 7 \times 10^{52}$$

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18.67. From Appendix C, you have

	C(graphite) + $CO_2(g)$	⇌	$2CO(g)$
ΔH_f°:	0 + -393.5		2 x (-110.5) kJ
S°:	5.740 + 213.7		2 x (197.5) J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$\Delta H° = [2(-110.5) - (-393.5)]\ \text{kJ} = 172.5\ \text{kJ}$

$\Delta S° = [2(197.5) - (5.740 + 213.7)]\ \text{J/K} = 175.56\ \text{J/K}$

Substitute $\Delta H°$, $\Delta S°$ (= 0.17556 kJ/K), and T (= 1273 K) into the equation for $\Delta G_T°$.

$\Delta G_T° = \Delta H° - T\Delta S° = 172.5\ \text{kJ} - (1273\ \text{K})(0.17556\ \text{kJ/K}) = -50.987\ \text{kJ}$

Substitute the value of $\Delta G°$ (= -50.987×10^3 J) into the equation relating ln K and $\Delta G°$.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-50.987 \times 10^3}{-8.31 \times 1273} = 4.8198$$

$$K = K_p = e^{4.8198} = 123.9 = 1.2 \times 10^2$$

Because K_p is greater than 1, the data predict that combustion of carbon should form significant amounts of CO product at equilibrium.

18.68. From Appendix C, you have

	$N_2(g)$ + $O_2(g)$	⇌	$2NO(g)$
ΔH_f°:	0 + 0		2 x (90.29) kJ
S°:	191.6 + 205.0		2 x (210.6) J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$\Delta H° = [2(90.29) - (0)]\ \text{kJ} = 180.58\ \text{kJ}$

$\Delta S° = [2(210.6) - (191.6 + 205.0)]\ \text{J/K} = 24.6\ \text{J/K}$

Substitute $\Delta H°$, $\Delta S°$ (= 0.0246 kJ/K), and T (= 2373 K) into the equation for $\Delta G_T°$.

$\Delta G_T° = \Delta H° - T\Delta S° = 180.58\ \text{kJ} - (2373\ \text{K})(0.0246\ \text{kJ/K}) = 122.204\ \text{kJ}$

Substitute the value of $\Delta G°$ (= 122.204×10^3 J) into the equation relating ln K and $\Delta G°$.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{122.204 \times 10^3}{-8.31 \times 2373} = -6.1971$$

$$K = K_p = e^{-6.1971} = 2.0354 \times 10^{-3} = 2.0 \times 10^{-3}$$

Because K_p is slightly less than 1 but greater than 10^{-4}, the data predict that combustion of nitrogen and oxygen should form small (but significant) amounts of NO product at equilibrium.

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18.69. First, calculate $\Delta H°$ and $\Delta S°$ using the given $\Delta H_f°$ and $S°$ values.

	$2NaHCO_3(s)$	$\rightarrow$	$Na_2CO_3(s)$	+	$H_2O(g)$	+	$CO_2(g)$
$\Delta H_f°$:	2 x (-950.8)		-1130.8		-241.8		-393.5 kJ
$\Delta S°$:	2 x 101.7		138.8		188.7		213.7 J/K

$\Delta H° = [(-1130.8) + (-241.8) + (-393.5) - 2(-950.8)]$ kJ $= 135.5$ kJ

$\Delta S° = [(138.8 + 188.7 + 213.7) - 2(101.7)]$ J/K $= 337.8$ J/K $(0.3378$ kJ/K$)$

Substitute these values into $\Delta G° = \Delta H° - T\Delta S°$; let $\Delta G° = 0$, and rearrange to solve for T.

$$T = \frac{\Delta H°}{\Delta S°} = \frac{135.5 \text{ kJ}}{0.3378 \text{ kJ/K}} = 401 \text{ K}$$

18.70. First, calculate $\Delta H°$ and $\Delta S°$ using the given $\Delta H_f°$ and $S°$ values.

	$2HgO(s)$	$\rightarrow$	$2Hg(g)$	+	$O_2(g)$
$\Delta H_f°$:	2 x (-90.79)		2 x 61.38		0 kJ
$\Delta S°$:	2 x 70.27		2 x 174.9		205.0 J/K

$\Delta H° = [(2 \text{ x } 61.38) - 2(-90.79)]$ kJ $= 304.34$ kJ

$\Delta S° = [(2 \text{ x } 174.9 + 205.0) - 2(70.27)]$ J/K $= 414.\underline{2}6$ J/K $(0.41426$ kJ/K$)$

Substitute these values into $\Delta G° = \Delta H° - T\Delta S°$, let $\Delta G° = 0$, and rearrange to solve for T.

$$T = \frac{\Delta H°}{\Delta S°} = \frac{304.34 \text{ kJ}}{0.41426 \text{ kJ/K}} = 734.\underline{6}5 = 734.7 \text{ K}$$

■ SOLUTIONS TO GENERAL PROBLEMS

18.71. The sign of $\Delta S°$ should be positive because there is an increase in moles of gas ($\Delta n_{gas} = +5$) as the solid reactant forms five moles of gas. The reaction is endothermic, denoting a positive $\Delta H°$. The fact that the reaction is spontaneous implies that the product, $T\Delta S°$, is larger than $\Delta H°$, so $\Delta G°$ is negative, as required for a spontaneous reaction.

18.72. The sign of $\Delta S°$ should be negative because there is a decrease in moles of gas ($\Delta n_{gas} = -3$) as the seven moles of gaseous reactants form four moles of gaseous product plus liquid product. The reaction is exothermic, denoting a negative $\Delta H°$. The fact that the reaction is spontaneous implies that the negative $\Delta H°$ is larger than the positive value of $-T\Delta S°$, so $\Delta G°$ is negative, as required for a spontaneous reaction.

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18.73. The ΔH value $\cong$ BE(H−H) + BE(Cl−Cl) − BE(H−Cl) $\cong$ [432 + 240 − 2(428)] kJ ~ −184 kJ, and thus the reaction is exothermic. $\Delta S°$ should be positive because there is a increase in energy dispersal with the formation of unsymmetrical molecules from symmetrical H_2 and Cl_2. The reaction should be spontaneous because the contributions of both the ΔH term and the $-T\Delta S$ term are negative.

18.74. The ΔH value $\cong$ BE(HC) + BE(CN) + 2BE(HH) − 3BE(CH) − 3BE(CN) − 2BE(NH) $\cong$ [411 + 887 + 2(432) − 3(411) − 305 − 2(386)] kJ ~ −148 kJ. Thus, the reaction is exothermic. $\Delta S°$ should be negative because there is a decrease in moles of gas ($\Delta n_{gas} = -2$) with the formation of one mole of gas from three moles of gas. The reaction is spontaneous because the contributions of the ΔH term dominate the $-T\Delta S$ term.

18.75. When the liquid freezes, it releases heat: $\Delta H_{fus} = -69.0$ J/g at 16.6°C (289.8 K). The entropy change is

$$\Delta S = \frac{\Delta H_{fus}}{T} = \frac{-69.0 \text{ J/g}}{289.8 \text{ K}} \times \frac{60.05 \text{ g}}{1 \text{ mol}} = -14.\underline{3}0 = -14.3 \text{ J/(K•mol)}$$

18.76. When the liquid evaporates, it absorbs heat: ΔH_{vap} = 29.1 kJ/mol, or 2.91 x 10^4 J/mol, at 56°C (329 K). The entropy change is

$$\Delta S = \frac{\Delta H_{vap}}{T} = \frac{2.91 \times 10^4 \text{ J/g}}{329 \text{ K}} = 88.\underline{4}5 = 88.4 \text{ J/(K•mol)}$$

18.77.

a. $\Delta S°$ is negative because there is a decrease in moles of gas ($\Delta n_{gas} = -1$) from one mole of gaseous reactant forming aqueous and liquid products. (Entropy decreases.)

b. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +5$) from a solid reactant forming five moles of gas. (Entropy increases.)

c. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +3$) from two moles of gaseous reactant forming five moles of gaseous products. (Entropy increases.)

d. $\Delta S°$ is negative because there is a decrease in moles of gas ($\Delta n_{gas} = -1$) from three moles of gaseous reactants forming two moles of gaseous products. (Entropy decreases.)

18.78.

a. Entropy decreases; $\Delta S°$ is negative because there is a decrease in the moles of gas ($\Delta n_{gas} = -2$) from four moles of gaseous reactant forming two moles of gaseous products.

b. Entropy increases; $\Delta S°$ is certainly positive because there is an increase in the moles of gas ($\Delta n_{gas} = +2$) from a solid reactant forming two moles of gas.

c. Entropy decreases; $\Delta S°$ is negative because there is a decrease in the moles of gas ($\Delta n_{gas} = -3$) from three moles of gaseous reactant forming a liquid product.

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d. Entropy increases; $\Delta S°$ is certainly positive because there is an increase in moles of gas ($\Delta n_{gas} = +1$) from solid and liquid reactants forming one mole of gaseous product.

18.79. $\Delta S°$ is negative because there is a decrease in the moles of gas ($\Delta n_{gas} = -2$) from three moles of gaseous reactant forming one mole of gaseous product plus liquid product.

18.80. $\Delta S°$ is positive because there is an increase in moles of gas ($\Delta n_{gas} = +2$) from three moles of gaseous reactant forming five moles of gaseous products.

18.81. Calculate $\Delta S°$ from the individual $S°$ values:

	$C_2H_5OH(l)$	+	$O_2(g)$	→	$CH_3COOH(l)$	+	$H_2O(l)$
$S°$:	160.7		205.0		159.8		69.95 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(159.8 + 69.95) - (160.7 + 205.0)]$ J/K $= -135.\underline{9}5 = -136.0$ J/K

18.82. Calculate $\Delta S°$ from the individual $S°$ values:

	$CO(g)$	+	$2H_2(g)$	→	$CH_3OH(I)$
$S°$:	197.5		2 x 130.6		126.8 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[(126.8) - (197.5 + 2 \times 130.6)]$ J/K $= -331.9$ J/K

18.83. Calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$H_2(g)$	+	$SO_2(g)$	→	$H_2S(g)$	+	$O_2(g)$
$\Delta G_f°$:	0		-300.1		-33.33		0 kJ

$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants}) =$

$[(-33.33) - (-300.1)]$ kJ $= 266.\underline{7}7 = 266.8$ kJ

Because $\Delta G°$ is positive, the reaction is nonspontaneous as written, at 25°C.

18.84. Calculate $\Delta G°$ using the $\Delta G_f°$ values from Appendix C.

	$N_2(g)$	+	$CH_4(g)$	→	$HCN(g)$	+	$NH_3(g)$
$\Delta G_f°$:	0		-50.80		124.7		-16.40 kJ

$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants}) =$

$[(-16.40 + 124.7) - (-50.80)]$ kJ $= 159.\underline{1}0 = 159.1$ kJ

Because $\Delta G°$ is positive, the reaction is nonspontaneous as written, at 25°C.

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18.85. At low (room) temperature, $\Delta G°$ or $(\Delta H° - T\Delta S°)$ must be positive, but at higher temperatures, $\Delta G°$ or $(\Delta H° - T\Delta S°)$ must be negative. Thus, at the higher temperatures, the $-T\Delta S°$ term must become more negative than $\Delta H°$. Thus, $\Delta S°$ must be positive and so must $\Delta H°$. If either were negative, $\Delta G°$ would not become negative at higher temperatures.

18.86. At low (room) temperature, $\Delta G°$ or $(\Delta H° - T\Delta S°)$ must be negative, but at higher temperatures, $\Delta G°$or $(\Delta H° - T\Delta S°)$ must be positive. Thus, at the higher temperatures, the $-T\Delta S°$ term must become more positive than $\Delta H°$. Thus, $\Delta S°$ must be negative and so must $\Delta H°$. If either were positive, $\Delta G°$ would not become negative at lower temperatures.

18.87. First, calculate $\Delta G°$ using the values in Appendix C.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$\Delta G_f°$: -1173.5 -553.5 2 x (-278.8) kJ

Hence, $\Delta G°$ for the reaction is

$$\Delta G_f° = [-553.5 + 2(-278.8) - (-1173.5)]\ \text{kJ} = 62.4\ \text{kJ}$$

Now, substitute numerical values into the equation relating ln K and $\Delta G°$.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{62.4 \times 10^3}{-8.31 \times 298} = -25.\underline{1}98$$

$$K = K_{sp} = e^{-25.198} = \underline{1}.13 \times 10^{-11} = 1 \times 10^{-11}$$

18.88. First, calculate $\Delta G°$ using the values in Appendix C.

$$BaSO_4(s) \rightleftharpoons Ba_2^+(aq) + SO_4^{2-}(aq)$$

$\Delta G_f°$: -1362.3 -560.7 -744.6 kJ

Hence, $\Delta G°$ for the reaction is

$$\Delta G° = [-560.7 + (-744.6) - (-1362.3)]\ \text{kJ} = 57.0\ \text{kJ}$$

Now, substitute numerical values into the equation relating ln K and $\Delta G°$.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{57.0 \times 10^3}{-8.31 \times 298} = -23.\underline{0}17$$

$$K = K_{sp} = e^{-23.017} = \underline{1}.00 \times 10^{-10} = 1 \times 10^{-10}$$

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18.89. From Appendix C, you have

	$COCl_2(g)$	$\rightarrow$	$CO(g)$	+	$Cl_2(g)$
$\Delta H_f°$:	-220.1		-110.5		0 kJ
$S°$:	283.9		197.5		223.0 J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$\Delta H° = [(-110.5) - (-220.1)]$ kJ $= 109.6$ kJ

$\Delta S° = [197.5 + 223.0 - 283.9]$ J/K $= 136.6$ J/K $(0.1366$ kJ/K$)$

At 25°C: $\Delta G° = \Delta H° - T\Delta S° = 109.6$ kJ $-$ (298 K)(0.1366 kJ/K) $= 68.\underline{8}9 = 68.9$ kJ

At 800°C: $\Delta G_T° = \Delta H° - T\Delta S° = 109.6$ kJ $-$ (1073 K)(0.1366 kJ/K)

$= -36.\underline{9}7 = -37.0$ kJ

Thus, $\Delta G°$ changes from a positive value and a nonspontaneous reaction at 25°C to a negative value and a spontaneous reaction at 800°C.

18.90. From Appendix C, you have

	$CS_2(g)$	+	$4H_2(g)$	$\rightleftharpoons$	$CH_4(g)$	+	$2H_2S(g)$
$\Delta H_f°$:	116.9		0		-74.87		2 x (-20.50) kJ
$S°$:	237.9		4 x 130.6		186.1		2 x 205.6

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$\Delta H° = [(-74.87) + 2(-20.50) - (116.9)]$ kJ $= -232.\underline{7}7$ kJ

$\Delta S° = [186.1 + 2(205.6) - (237.9) - 4(130.6)]$ J/K $= -163.0$ J/K $(-0.1630$ kJ/K$)$

At 25°C: $\Delta G° = \Delta H° - T\Delta S° = -232.77$ kJ $-$ (298 K)(−0.1630 kJ/K) $= -184.\underline{1}9$

$= -184.2$ kJ

At 650°C: $\Delta G_T° = \Delta H° - T\Delta S° = -232.77$ kJ $-$ (923 K)(−0.1630 kJ/K) $= -82.\underline{3}2$

$= -82.3$ kJ

Thus, $\Delta G°$ has a negative value at both temperatures, and the reaction is spontaneous at both temperatures. However, $\Delta G°$ is more negative at 25°C than at 650°C, and so the relative proportion of the products is greater at 25°C.

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18.91

a.

			$\Delta H°$, kJ
$CO_2(g) + 2H_2(g)$	$\rightarrow$	$HCHO(g) + H_2O(g)$	35
$HCHO(g) + 2H_2(g)$	$\rightarrow$	$CH_4(g) + H_2O(g)$	−201
$C(s) + O_2(g)$	$\rightarrow$	$CO_2(g)$	−393
$2H_2O(g)$	$\rightarrow$	$2H_2(g) + O_2(g)$	484
$C(s) + 2H_2(g)$	$\rightarrow$	$CH_4(g)$	−75 kJ

b.

	$C(s)$	+ $2H_2(g)$	$\rightarrow$ $CH_4(g)$
$S°$:	5.740	2 x 130.6	186.1 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[186.1 - 5.740 - 2(130.6)]\ \text{J/K} = -80.\underline{8}4\ \text{J/K}\ (-0.08084\ \text{kJ/K})$

c. $\Delta G°$ for the reaction, which involves 1 mole of methane, is equal to $\Delta G_f°$ for methane and is obtained as follows:

$\Delta G_f° = \Delta G° = \Delta H° - T\Delta S°$

$= -75\ \text{kJ} - (298\ \text{K})(-0.08084\ \text{kJ/K})$

$= -5\underline{0}.90 = -51\ \text{kJ/mol}$

18.92.

a.

			$\Delta H°$, kJ
$CH_3CHO(g) + 2H_2(g)$	$\rightarrow$	$C_2H_6(g) + H_2O(l)$	−204
$C_2H_5OH(l) + 1/2O_2(g)$	$\rightarrow$	$CH_3CHO(g) + H_2O(l)$	1/2(−348)
$2C(s) + 3H_2(g) + 1/2O_2(g)$	$\rightarrow$	$C_2H_5OH(l)$	1/2(−555)
$2H_2O(g)$	$\rightarrow$	$2H_2(g) + O_2(g)$	484
$2H_2O(l)$	$\rightarrow$	$2H_2O(g)$	2(44)
$2C(s) + 3H_2(g)$	$\rightarrow$	$C_2H_6(g)$	$-8\underline{3}.5 = -84$ kJ

b.

	$2C(s)$	+ $3H_2(g)$	$\rightarrow$ $C_2H_6(g)$
$S°$:	2 x 5.740	3 x 130.6	229.5 J/K

$\Delta S° = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants}) =$

$[229.5 - 2(5.740) - 3(130.6)]\ \text{J/K} = -173.\underline{7}8\ \text{J/K}\ (-0.17378\ \text{kJ/K})$

c. $\Delta G°$ for the reaction, which involves 1 mol of ethane, is equal to $\Delta G_f°$ for ethane and is obtained as follows.

$\Delta G_f° = \Delta G° = \Delta H° - T\Delta S°$

$= -83.5\ \text{kJ} - (298\ \text{K})(-0.17378\ \text{kJ/K})$

$= -31.\underline{7}1 = -31.7\ \text{kJ/mol}$

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18.93. $\Delta H° = [-393.5 + 2(-285.8) - (-238.7)]$ kJ $= -726.4$ kJ

$\Delta G° = \Delta H° - T\Delta S°$

-702.2 kJ $= -726.4$ kJ $-$ (298 K)($\Delta S°$)

$$\Delta S° = -\frac{(-702.2 \text{ kJ}) - (-726.4 \text{ kJ})}{298 \text{ K}} = -0.081\underline{2}0 \text{ kJ/K} = -81.\underline{2}0 \text{ J/K}$$

$\Delta S° = -81.20$ J/K $= [2(70.0) + 213.7 - (126.8) -$ (3/2 mol) x $S°(O_2)]$ J/K

$S°(O_2) = 205.\underline{4}0 = 205.4$ J/mol•K

18.94. $\Delta H° = [-241.8 + (-393.5) - (-117.0) - 2/3(142.7)]$ kJ $= -613.\underline{4}3$ kJ

$\Delta G° = \Delta H° - T\Delta S°$

-618.8 kJ $= -613.43$ kJ $-$ (298 K)($\Delta S°$)

$$\Delta S° = -\frac{(-618.8 \text{ kJ}) - (-613.43 \text{ kJ})}{298 \text{ K}} = -0.018\underline{0}2 \text{ kJ/K} = 18.\underline{0}2 \text{ J/K}$$

$\Delta S° = 18.02$ J/K $= [188.7 + 213.7 - (219.0) -$ (2/3 mol) x $S°(O_3)]$ J/K

$S°(O_3) = 248.\underline{0}6 = 248.1$ J/mol•K

18.95.

a. The first reaction is

	$SnO_2(s)$	+	$2H_2(g)$	→	$Sn(s)$	+	$2H_2O(g)$
$\Delta H_f°$:	-580.7		0		0		-241.8 kJ
$S°$:	52.3		130.6		51.55		188.7 J/K

$\Delta H° = [2(-241.8) - (-580.7)]$ kJ $= 97.\underline{1}$ kJ $= 97.\underline{1} \times 10^3$ J

$\Delta S° = [2(188.7) + 51.55 - 2(130.6) - 52.3]$ J/K $= 115.\underline{4}5$ J/K

The second reaction is

	$SnO_2(s)$	+	$C(s)$	→	$Sn(s)$	+	$CO_2(g)$
$\Delta H_f°$:	-580.7		0		0		-393.5 kJ
$S°$:	52.3		5.740		51.55		213.7 J/K

$\Delta H° = [-393.5 - (-580.7)]$ kJ $= 187.\underline{2}$ kJ $= 18\underline{7}.2 \times 10^3$ J

$\Delta S° = [213.7 + 51.55 - 5.740 - 52.3]$ J/K $= 207.\underline{2}1$ J/K

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b. For H_2, at what temperature does $\Delta G = 0$?

$$0 = \Delta H° - T\Delta S°$$

$$T = \frac{\Delta H}{\Delta S} = \frac{97.1 \times 10^3 \text{ J}}{115.45 \text{ J/K}} = 841.0 = 841 \text{ K}$$

At temperatures greater than 841 K, the reaction will be spontaneous.

For C, at what temperature does $\Delta G = 0$?

$$T = \frac{\Delta H}{\Delta S} = \frac{187.2 \times 10^3 \text{ J}}{207.21 \text{ J/K}} = 903.4 = 903 \text{ K}$$

At temperatures greater than 904 K, the reaction will be spontaneous.

c. From a consideration of temperature, the process with hydrogen would be preferred. But hydrogen is very expensive and carbon is cheap. On this basis, carbon would be preferred. Tin is produced commercially using carbon as the reducing agent.

18.96.

a. $\Delta G° = [3(-228.6) - (-763.1)] \text{ kJ} = 77.3 \text{ kJ}$

Since $\Delta G°$ is positive, K will be less than 1.

b. $\Delta H° = [3(-241.8) - (-839.9)] \text{ kJ} = 114.5 \text{ kJ}$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$77.3 \text{ kJ} = 114.5 \text{ kJ} - (298 \text{ K})\,\Delta S°$$

$$\Delta S° = 0.1248 \text{ kJ/K} = 125 \text{ J/K}$$

c. $$T = \frac{\Delta H}{\Delta S} = \frac{114.5 \times 10^3 \text{ J}}{124.8 \text{ J/K}} = 917.4 = 917 \text{ K}$$

d. The driving force is the change in entropy. At high temperatures, the term $T\Delta S$ becomes very important.

18.97.

a. Formic acid is favored because it is of lower energy than CO and H_2O.

b. The change in entropy for the decomposition of formic acid is positive as a mole of gas is produced. Thus, the change in entropy would be the driving force for this reaction, favoring the formation of products.

18.98.

a. It depends on whether the products are of lower energy than the reactants (exothermic) or of higher energy than the reactants (endothermic). If the products have stronger bonds than the reactants, the reaction will be exothermic. If the reactants have stronger bonds than the products, the reaction will be endothermic.

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b.

(1) For a highly exothermic reaction, the driving force is the change in enthalpy. The $T\Delta S$ term under these conditions won't be of great significance.

(2) The driving force will be the entropy. The change in entropy must be positive, and the $T\Delta S$ must be greater than ΔH.

18.99.

a. If $\Delta G°$ is negative, then K must be greater than 1. Consequently, the products will predominate.

b. The molecules must have enough energy to react when they collide with each other. Thus, it depends upon the activation energy for the reaction. Usually it is necessary to heat solids for a reaction to occur, because it is difficult to have effective collisions.

18.100.

a. Since a gaseous product is produced, $\Delta S°$ for the reaction would be positive.

b. Since $\Delta H°$ is negative and $S°$ is positive, this would give a negative value for $\Delta G°$, and K would be greater than 1. Products would predominate.

c. Evidently the reaction doesn't take place at room temperature. Since the reaction requires a catalyst, we must conclude there is a high activation energy without the catalyst. Also, it is necessary to heat the mixture so that a greater fraction of the molecules will have enough energy to react.

18.101.

a. $C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

$$\Delta H° = \frac{-49.50 \text{ kJ}}{1.000 \text{ g}} \times \frac{58.12 \text{ g}}{1 \text{ mol}} = -2876.94 \text{ kJ/mol}$$

$$\Delta H° = \Sigma n\Delta H_f°(\text{products}) - \Sigma m\Delta H_f°(\text{reactants})$$

$$-2876.94 \text{ kJ} = [4(-393.5) + 5(-285.8) - (1 \text{ mol}) \times \Delta H_f°(C_4H_{10})] \text{ kJ}$$

$$\Delta H_f°(C_4H_{10}) = -126.06 = -126 \text{ kJ/mol}$$

b. $\Delta G° = [4(-394.4) + 5(-237.1) - (-17.2)] \text{ kJ} = -2745.9 \text{ kJ}$

c. $\Delta G° = \Delta H° - T\Delta S°$

$$-2745.9 \text{ kJ} = -2876.94 \text{ kJ} - (298 \text{ K}) \Delta S°$$

$$\Delta S° = -\frac{(-2745.9 \text{ kJ}) - (-2876.94 \text{ kJ})}{298 \text{ K}} = -0.4397 \text{ kJ/K} = -440. \text{ J/K} \text{ (for one mole)}$$

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18.102.

a. $C_2H_6O_2(l) + 5/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$$\Delta H^\circ = \frac{-19.18 \text{ kJ}}{1.000 \text{ g}} \times \frac{62.07 \text{ g}}{1 \text{ mol}} = -1190.4 \text{ kJ/mol}$$

$\Delta H^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants})$

$-1190.4 \text{ kJ} = [2(-393.5) + 3(-285.8) - (1 \text{ mol}) \times \Delta H_f^\circ(C_2H_6O_2)] \text{ kJ}$

$\Delta H_f^\circ[C_2H_6O_2] = -454.0 = -454 \text{ kJ/mol}$

b. $\Delta G^\circ = [2(-394.4) + 3(-237.1) - (-322.5)] \text{ kJ} = -1177.6 \text{ kJ}$

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

$-1177.6 \text{ kJ} = -1190.4 \text{ kJ} - (298 \text{ K})(\Delta S^\circ)$

$$\Delta S^\circ = -\frac{(-1177.6 \text{ kJ}) - (-1190.4 \text{ kJ})}{298 \text{ K}} = -0.04295 \text{ kJ/K} = -43.0 \text{ J/K} \text{ (for one mole)}$$

18.103.

a. $\Delta H^\circ = [-1285 - (-1288.3)] \text{ kJ} = 3.3 \text{ kJ} = 3.3 \times 10^3 \text{ J}$

$\Delta S^\circ = [89 - 158.2] \text{ J/K} = -69.2 \text{ J/K}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = 3.3 \times 10^3 \text{ J} - (298 \text{ K})(-69.2 \text{ J/K}) = 23.921 \times 10^3 \text{ J}$

Now, substitute numerical values into the equation relating ln K and ΔG°.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{23.921 \times 10^3}{-8.31 \times 298} = -9.6599$$

$K = e^{-9.6599} = 6.37 \times 10^{-5} = 6 \times 10^{-5}$

b. The change in entropy is negative, greater order, so this causes H_3PO_4 to be a weak acid. The enthalpy change reduces the acid strength of H_3PO_4, and the entropy is a very important term.

18.104.

a. $\Delta H^\circ = [-626.2 - (-608.8)] \text{ kJ} = -17.4 \text{ kJ} = -17.4 \times 10^3 \text{ J}$

$\Delta S^\circ = [139.8 - 232.2] \text{ J/K} = -92.4 \text{ J/K}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = -17.4 \times 10^3 \text{ J} - (298 \text{ K})(-92.4 \text{ J/K}) = 10.135 \times 10^3 \text{ J}$

Now, substitute numerical values into the equation relating ln K and ΔG°.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{10.135 \times 10^3}{-8.31 \times 298} = -4.092$$

$K = e^{-4.092} = 0.01669 = 0.017$

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b. The change in entropy is negative, greater order, so this causes H_2SO_3 to be a weak acid. The enthalpy change favors the acid strength of H_2SO_3, and the entropy is a very important term.

18.105. You must find a way to couple this nonspontaneous reaction to one that is sufficiently spontaneous; that is, you must couple this reaction to one having a more negative $\Delta G°$. Consider the spontaneous reaction of carbon monoxide with oxygen (the burning of CO):

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g); \quad \Delta G° = -514.4 \text{ kJ}$$

For 3 mol O_2, $\Delta G°$ is −1543 kJ, which is more negative than for the direct decomposition of 2 mol Fe_2O_3 to its elements (1487 kJ). The net result is to reduce iron(III) oxide to the metal by reacting the oxide with carbon monoxide

$$Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g); \quad \Delta G° = -56 \text{ kJ}$$

This is the reaction that occurs in a blast furnace, where iron ore is commercially reduced to iron.

18.106. ATP is first synthesized in a living organism; the energy for this synthesis is obtained from food. The spontaneous reaction of ATP to give ADP is then coupled to various nonspontaneous reactions in the organism to accomplish necessary life processes. The mitochondria are parts of a cell that obtain energy in the form of ATP from glucose (from food), $C_6H_{12}O_6$. ATP molecules are used in various cell processes, such as protein synthesis from amino acids, which occur in the ribosomes.

■ SOLUTIONS TO STRATEGY PROBLEMS

18.107. The standard enthalpies of formation and the standard entropies of formation are

	$N_2H_4(g)$	$\rightarrow$	$N_2(g)$	+	$2H_2(g)$
$\Delta H_f°$:	95.35		0		0 kJ
S°:	238.6		191.6		2 x (130.6) J/K

a. The change in standard enthalpy is

$$\Delta H° = 0 - \Delta H_f°[N_2H_4(g)] = -95.35 \text{ kJ}$$

b. The change in standard entropy is

$$\Delta S° = [(191.6) + 2(130.6) - (238.6)] \text{ J/K} = 214.2 \text{ J/K}$$

The sign of the entropy change is positive, which is what you would expect since there is an increase in the number of moles of gas.

c. Since the enthalpy change is negative and the entropy change is positive, this reaction is spontaneous at all temperatures.

d. ΔG is less negative at lower temperatures, so this reaction will give greater product at higher temperatures.

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18.108.

a. The standard enthalpy of formation of $H_2O(g)$ is −241.8 kJ/mol.

b. The standard entropy of formation of $H_2O(g)$ is 188.7 J/mol•K.

c. The reaction and standard thermodynamic values for the formation of $H_2O(g)$ are

	$H_2(g)$	→	$1/2O_2(g)$	+	$H_2O(g)$
$\Delta H_f°$:	0		0		-241.8 kJ
S°:	130.6		1/2(205.0)		188.7 J/K

The change in enthalpy and the change in entropy for the reaction are

$\Delta H° = \Delta H_f°[H_2O(g)] = -241.8$ kJ

$\Delta S° = [(188.7) - (130.6) - 1/2(205.0)]$ J/K $= -44.\underline{4}$ J/K $= -0.0444$ kJ/K

The free-energy change for the reaction, and the free energy of formation of $H_2O(g)$, are

$\Delta G° = \Delta H° - T\Delta S° = (-241.8$ kJ$) - (298.15$ K$)(-0.0444$ kJ/K$) = -228.\underline{5}6$ kJ

$\Delta G° = \Delta G_f°[H_2O(g)]$ $-228.\underline{5}6 = -228.6$ kJ/mol

This is the same as the value given in Appendix C.

d. This is not correct because ΔS for the reaction is not equal to $S°$ for $H_2O(g)$.

18.109. Write out the expression for $\Delta G°$ for the reaction and solve for the free energy of formation of acetone. The reaction and standard thermodynamic values are

	$CH_3COCH_3(l)$	+	$4O_2(g)$	→	$3CO_2(g)$	+	$3H_2O(l)$
$\Delta G_f°$:	x		0		3 x (-394.4)		3 x (-237.1) kJ

$\Delta G° = -1739$ kJ $= 3(-394.4$ kJ$) + 3(-237.1$ kJ$) - (1$ mol$)(x)$

$x = \Delta G_f°[CH_3COCH_3(l)] = -155.5$ kJ/mol

18.110. First calculate the free-energy change for the reaction.

	$CoCl_2•6H_2O(s)$	→	$CoCl_2(s)$	+	$6H_2O(g)$
$\Delta G_f°$:	-1725		-270.		6 x (-228.6) kJ

$\Delta G° = [(-270.) + 6(-228.6) - (-1725)]$ kJ $= 8\underline{3}.4$ kJ

Now calculate the equilibrium constant for the reaction.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-83.40 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})(298.15 \text{ K})} = -3\underline{3}.645$$

$K = P_{H_2O}{}^6 = e^{-33.645} = 2.\underline{4}4 \times 10^{-15}$

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The partial pressure of water vapor is

$$P = \sqrt[6]{2.44 \times 10^{-15}} \times 760 \text{ mmHg/atm} = 2.\underline{7}8 = 2.8 \text{ mmHg}$$

The vapor pressure of water at 25°C is 23.8 mmHg, so the relative humidity is

$$\text{Humidity} = \frac{2.78 \text{ mmHg}}{23.8 \text{ mmHg}} \times 100\% = 1\underline{1}.7 = 12\%$$

Next, calculate the change in enthalpy for the reaction.

$$\Delta H° = [(-313) + 6(-241.8) - (-2115)] \text{ kJ} = 351.2 \text{ kJ}$$

The reaction is endothermic, so as the temperature is increased, the reaction will shift to the right, and the equilibrium partial pressure of water will increase.

18.111.

a. First, calculate the value of the equilibrium constant at 458°C.

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.550)^2}{(0.225)(0.225)} = 47.\underline{4}56$$

The free-energy change can now be calculated.

$$\Delta G = -RT \ln K = (8.31 \times 10^{-3} \text{ kJ/mol•K})(731 \text{ K}) \ln(47.456) = -23.\underline{4}4 = -23.4 \text{ kJ/mol}$$

b. The enthalpy change for the reaction at 458°C is

	$H_2(g)$	+	$I_2(g)$	→	$2HI(g)$
$\Delta H_f°$:	0		62.42		2 x (26.36) kJ

$$\Delta H = \Delta H° = [2(26.36) - (62.42)] \text{ kJ} = -9.70 \text{ kJ}$$

Now rearrange the equation $\Delta G = \Delta H - T\Delta S$ and solve for ΔS.

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{(-9.70 \text{ kJ}) - (-23.44 \text{ kJ})}{731 \text{ K}} = 0.018\underline{8}0 \text{ kJ/K} = 18.8 \text{ J/K}$$

18.112.

a. The standard free-energy change for the reaction at 25°C is

	$H_2(g)$	+	$I_2(g)$	→	$2HI(g)$
$\Delta G_f°$:	0		19.36		2 x (1.576) kJ

$$\Delta G° = [2(1.576) - (19.36)] \text{ kJ} = -16.2\underline{0}8 \text{ kJ}$$

Next, calculate the value of the reaction quotient Q and the free-energy change.

$$Q = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = \frac{(1/3)^2}{(1/3)(1/3)} = 1.0$$

$$\Delta G = \Delta G° + RT \ln Q = \Delta G° = -16.2\underline{0}8 = -16.21 \text{ kJ}$$

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b. Calculate the value of the reaction quotient Q and the free-energy change.

$$Q = \frac{P_{HI}^{\ 2}}{P_{H_2} P_{I_2}} = \frac{(1/90)^2}{(1/3)(1/3)} = 0.001111$$

$$\Delta G = \Delta G° + RT \ln Q$$

$$= -16.208 + (8.31 \times 10^{-3} \text{ kJ/mol•K})(298 \text{ K}) \ln(0.001111) = -33.053 = -33.1 \text{ kJ}$$

The system in part a is closer to equilibrium since the free-energy change for part a is closer to zero.

18.113. First, calculate the value of the equilibrium constant and the free energy at 220°C.

$$K = P_{CO_2} = 1.37$$

$$\Delta G = -RT \ln K = -(8.31 \times 10^{-3} \text{ kJ/mol•K})(493 \text{ K}) \ln(1.37) = -1.289 \text{ kJ}$$

Next, calculate the change in standard enthalpy for the reaction.

	$Ag_2CO_3(s)$	$\rightarrow$	$Ag_2O(s)$	+	$CO_2(g)$
$\Delta H_f°$:	-505.9		-31.05		(-393.5) kJ

$$\Delta H° = [(-31.05) + (-393.5) - (-505.9)] \text{ kJ} = 81.35 \text{ kJ}$$

A reasonable assumption is that ΔH at 220°C is approximately equal to $\Delta H°$.This is a valid assumption because ΔH does not vary much with temperature. Now calculate ΔS at 220°C.

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{(81.35 \text{ kJ}) - (-1.289 \text{ kJ})}{493 \text{ K}} = 0.1676 \text{ kJ/K}$$

Next, assume that $\Delta S°$ is approximately equal to ΔS at 220°C. This is a valid assumption because ΔS does not vary much with temperature. Now calculate $\Delta G°$.

$$\Delta G° = \Delta H° - T\Delta S° = 81.35 \text{ kJ} - (298 \text{ K})(0.1676 \text{ kJ/K}) = 31.39 \text{ kJ}$$

Finally, calculate the equilibrium constant and pressure of CO_2 at 25°C.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-31.397 \times 10^3 \text{ J/mol}}{(8.31 \text{ J/mol•K}) \times (298 \text{ K})} = -12.678$$

$$K = P_{CO_2} = e^{-12.678} = = 3.11 \times 10^{-6} = 3 \times 10^{-6} \text{ atm}$$

18.114. Calculate $\Delta H°$ and $\Delta S°$ for the reaction using the values from Appendix C.

	$2H_2S(g)$	+	$SO_2(g)$	$\rightarrow$	3S(s, rhombic)	+	$2H_2O(g)$
$\Delta H_f°$:	2 x (-20.50)		-296.8		0		2 x (-241.8) kJ
S°:	2 x (205.6)		248.1		3 x (32.06)		2 x (188.7) J/K

$$\Delta H° = [2(-241.8) - 2(-20.50) - (296.8)] \text{ kJ} = -145.8 \text{ kJ}$$

$$\Delta S° = [3(32.06) + 2(188.7) - 2(205.6) + (241.8)] \text{ J/K} = -185.72 \text{ J/K}$$
$$= -0.18572 \text{ kJ/K}$$

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A reasonable assumption is that ΔS and ΔH do not vary much with temperature, and they are equal to their values at 25°C. Now calculate the free-energy change and the equilibrium constant at 1170°C.

$$\Delta G = \Delta H - T\Delta S = (-145.8 \text{ kJ}) - (1443 \text{ K})(0.18572 \text{ kJ/K}) = 122.\underline{2}2 \text{ kJ}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-122.22 \times 10^3 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) \times (1443 \text{ K})} = -10.1\underline{8}6$$

$$K = e^{-10.186} = 3.\underline{7}67 \times 10^{-5}$$

Now, write out the equilibrium-constant expression for the reaction.

$$K = \frac{P_{H_2O}{}^2}{P_{H_2S}{}^2 P_{SO_2}}$$

This can be rearranged and solved for the ratio of the partial pressure of water vapor to the partial pressure of sulfur dioxide.

$$\frac{P_{H_2O}}{P_{H_2S}} = \sqrt{K \times P_{SO_2}} = \sqrt{(3.767 \times 10^{-5}) \times \left(\frac{89 \text{ mmHg}}{760 \text{ mmHg/atm}}\right)}$$

$$= 2.\underline{1}0 \times 10^{-3} = 2.1 \times 10^{-3}$$

18.115.

a. The ratio of [B] to [A] is

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-15.0 \times 10^3 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) \times (298 \text{ K})} = -6.0\underline{5}13$$

$$K = \frac{[B]}{[A]} = e^{-6.0513} = 2.\underline{3}54 \times 10^{-3}$$

b. Combine the two equations and add the ΔG° values to get the overall reaction.

$$A(aq) + ATP(aq) + H_2O(l) \rightarrow B(aq) + ADP(aq) + H_2PO_4^-(aq)$$

$$\Delta G^\circ = (-30.5 \text{ kJ/mol}) + (15.0 \text{ kJ/mol}) = -15.5 \text{ kJ/mol}$$

Now calculate the equilibrium constant.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-15.5 \times 10^3 \text{ J/mol})}{(8.31 \text{ J/mol} \cdot \text{K}) \times (298 \text{ K})} = 6.2\underline{5}3$$

$$K = e^{6.253} = 5\underline{1}9.56$$

Write out the equilibrium constant for the reaction.

$$K = \frac{[B][ADP][H_2PO_4^-]}{[A][ATP]}$$

Rearrange this expression to get the ratio of [B] over [A].

$$\frac{[B]}{[A]} = \frac{K[ATP]}{[ADP][H_2PO_4^-]} = (519.56)(500) = 2.\underline{5}9 \times 10^5$$

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Finally, the ratio of coupled to uncoupled is

$$\frac{\text{Ratio(coupled)}}{\text{Ratio(uncoupled)}} = \frac{2.597 \times 10^{5}}{2.354 \times 10^{-3}} = 1.\underline{1}0 \times 10^{8} = 1.1 \times 10^{8}$$

18.116. Calculate $\Delta G°$ for the reaction.

	$C_3H_8(g)$	+	$5O_2(g)$	→	$3CO_2(g)$	+	$4H_2O(g)$
$\Delta G_f°$:	-23.6		0		3 x (-394.4)		4 x (-228.6) kJ

$\Delta G° = [3(-394.4) + 4(-228.6) - (-23.6)]$ kJ $= -2074.0$ kJ

The maximum work that you can obtain from 1.00 kg of propane is

$$w_{max} = \frac{2074.0 \text{ kJ}}{1 \text{ mol } C_3H_8} \times \frac{1 \text{ mol } C_3H_8}{44.094 \text{ g}} \times 1.00 \times 10^{3} \text{ g} = 4.7\underline{0}3 \times 10^{4} = 4.70 \times 10^{4} \text{ kJ}$$

The maximum height a car can go up a hill is

$$h = \frac{w_{max}}{mg} = \frac{(4.703 \times 10^{4} \text{ kJ})(1000 \text{ J/kJ})}{(4000. \text{ lb})(9.81 \text{ m/s}^2)} \times \frac{1 \text{ lb}}{0.4536 \text{ kg}} \times \frac{1 \text{ mi}}{1609 \text{ m}}$$

$= 1.6\underline{4}2 = 1.64$ mi

■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

18.117. For the dissociation of HBr, assume ΔH and ΔS are constant over the temperature range from 25°C to 375°C, and calculate the value of each to use to calculate K at 375°C. Start by calculating $\Delta H°$ and $\Delta S°$ at 25°C, using $\Delta H_f°$ and $S°$ values.

	2HBr(g)	→	$H_2(g)$	+	$Br_2(g)$
$\Delta H_f°$:	2 x (-36.44)		0		30.91 kJ
S°:	2 x 198.6		130.6		245.3 J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$\Delta H° = [30.91 - 2(-36.44)]$ kJ $= 103.79$ kJ

$\Delta S° = [245.3 + 130.6 - 2(198.6)]$ J/K $= -21.3$ J/K

Substitute $\Delta H°$, $\Delta S°$ ($= -0.02130$ kJ/K), and T (648 K) into the equation for $\Delta G_T°$.

$\Delta G_T° = \Delta H° - T\Delta S° = 103.79$ kJ $- (648 \text{ K})(-0.02130 \text{ kJ/K}) = 117.\underline{5}9$ kJ

$= 117.\underline{5}9 \times 10^{3}$ J

Now, substitute numerical values into the equation relating ln K and $\Delta G°$ ($= \Delta G_T°$).

$$\ln K = \frac{-\Delta G°}{RT} = \frac{117.59 \times 10^{3}}{-8.31 \times 648} = -21.\underline{8}37$$

$K = e^{-21.837} = \underline{3}.28 \times 10^{-10}$

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Assuming x equals $[H_2]$ equals $[Br_2]$, and assuming $[HBr] = (1.00 - 2x) \cong 1.00$ atm, substitute into the equilibrium expression:

$$K = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{(x)(x)}{(1.00)^2} = \underline{3}.28 \times 10^{-10}$$

Solve for the approximate pressure of x:

$$x = \sqrt{(3.28 \times 10^{-10})(1.00)^2} = \underline{1}.81 \times 10^{-5} \text{ atm}$$

The percent dissociation at 1.00 atm is

$$\text{Percent dissociation} = \frac{2(1.81 \times 10^{-5} \text{ atm})}{1.00 \text{ atm}} \times 100\% = 0.00\underline{3}6\%$$

Based on Le Châtelier's principle, pressure has no effect on equilibrium. Therefore, the percent dissociation is 0.004% at 1.00 atm and at 10.0 atm.

18.118. For the formation of HI, assume ΔH and ΔS are constant over the temperature range from 25°C to 205°C, and calculate the value of each to use to calculate K at 205°C. Start by calculating $\Delta H°$ and $\Delta S°$ at 25°C using $\Delta H_f°$ and $S°$ values. From Appendix C, we have

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
$\Delta H_f°$:	0		62.42		2 x 26.36 kJ
S°:	130.6		260.6		2 x 206.5 J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$$\Delta H° = [2(26.36) - 62.42] \text{ kJ} = -9.70 \text{ kJ}$$

$$\Delta S° = [2(206.5) - 130.6 - 260.6)] \text{ J/K} = 21.\underline{8}0 \text{ J/K} = 0.02180 \text{ kJ/K}$$

Substitute $\Delta H°$, $\Delta S°$ ($= -0.02180$ kJ/K), and T (478 K) into the equation for $\Delta G_T°$.

$$\Delta G_T° = \Delta H° - T\Delta S° = -9.70 \text{ kJ} - (478 \text{ K})(0.02180 \text{ kJ/K}) = -20.\underline{1}20 \text{ kJ}$$

$$= -20.\underline{1}20 \times 10^3 \text{ J}$$

Now, substitute numerical values into the equation relating $\ln K$ and $\Delta G°$ ($= \Delta G_T°$).

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-20.120 \times 10^3}{-8.31 \times 478} = 5.0\underline{6}53$$

$$K = e^{5.0653} = 1\underline{5}8.43$$

Letting $[HI] = 2x$, $[H_2] = 0.500 \text{ mol} - x$, and $[I_2] = 1.00 \text{ mol} - x$, substitute into the equilibrium expression:

$$K = \frac{[HI]}{[H_2][I_2]} = \frac{(2x)^2}{(0.500 - x)(1.00 - x)} = 1\underline{5}8.43$$

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Rearranging gives a quadratic equation: $(154.43)x^2 + (-237.64)x + (79.216) = 0$. Using the quadratic formula, solve for x:

$$x = \frac{-(-237.64) \pm \sqrt{(-237.64)^2 - 4(154.43)(79.216)}}{2 \times 154.43} = \frac{237.648 \pm 86.850}{308.86}$$

$$= 0.4\underline{8}82 \text{ mol (negative root)}$$

$$[HI] = 2x = 0.9\underline{7}64 \text{ mol}$$

The mole fraction of HI is

$$\frac{0.9764 \text{ mol HI}}{(0.500 - 0.4882) \text{ mol } H_2 + (1.00 - 0.4882) \text{ mol } I_2 + 0.9764 \text{ mol HI}} = 0.6\underline{5}09 = 0.65$$

18.119. For the dissociation of NH_3, assume ΔH and ΔS are constant over the temperature range from 25°C to 345°C, and calculate values of each to calculate K at 345°C.

	$2NH_3(g)$	$\rightarrow$	$3H_2(g)$	+	$N_2(g)$
$\Delta H_f°$:	2 x (-45.90)		0		0 kJ
S°:	2 x 192.7		3 x 130.6		191.6 J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$$\Delta H° = [0 - 2(-45.90)] \text{ kJ} = 91.80 \text{ kJ}$$

$$\Delta S° = [3(130.6) + 191.6 - 2(192.7)] \text{ J/K} = 198.0 \text{ J/K}$$

Substitute $\Delta H°$, $\Delta S°$ (= 0.1980 kJ/K), and T (618 K) into the equation for $\Delta G_T°$.

$$\Delta G_T° = \Delta H° - T\Delta S° = 91.8 \text{ kJ} - (618 \text{ K})(0.1980 \text{ kJ/K}) = -30.\underline{5}64 \text{ kJ}$$
$$= -30.564 \times 10^3 \text{ J}$$

Now, substitute numerical values into the equation relating ln K and $\Delta G°$ (= $\Delta G_T°$).

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-30.564 \times 10^3}{-8.31 \times 618} = 5.9\underline{5}1$$

$$K = K_p = e^{5.951} = 3\underline{8}4.2$$

Now obtain K_c.

$$K_c = K_p(RT)^{-2} = (384.2)(0.0821 \times 618)^{-2} = 0.1\underline{4}92$$

The starting concentration of NH_3 is 1.00 mol/20.0L = 0.0500 M. You obtain the following table:

	$2NH_3(g)$	$\rightarrow$	$3H_2(g)$	+	$N_2(g)$
Starting	0.0500		0		0
Change	-2x		+3x		+x
Equilibrium	0.0500 - 2x		3x		x

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The equilibrium equation is

$$K_c = \frac{[H_2]^3[N_2]}{[NH_3]^2}$$

or

$$\frac{(3x)^3 x}{(0.0500 - 2x)^2} = 0.1492$$

$$\frac{x^4}{(0.0500 - 2x)^2} = \frac{0.1492}{27} = 5.528 \times 10^{-3}$$

Taking the square root of both sides of this equation gives

$$\frac{x^2}{(0.0500 - 2x)} = 0.07\underline{4}35$$

This can be rearranged into the following quadratic equation.

$$x^2 + (0.1487)x - (3.717 \times 10^{-3}) = 0$$

From the quadratic formula, you obtain

$$x = \frac{-0.1487 \pm \sqrt{(0.1487)^2 + 4(3.717 \times 10^{-3})}}{2}$$

The positive root is

$$x = 0.02\underline{1}80\ M$$

Hence,

$$[NH_3] = 0.0500 - 2(0.02180) = 0.006\underline{4}\ M$$

$$\text{Percent } NH_3 \text{ dissociated} = \left(1 - \frac{0.0064\ M}{0.0500\ M}\right) \times 100\% = 8\underline{7}.2 = 87\%$$

18.120. The reaction, with $\Delta H_f°$ and $S°$ values underneath the equation, is

	$CO(g)$	+	$3H_2(g)$	$\rightarrow$	$CH_4(g)$	+	$H_2O(g)$
$\Delta H_f°$:	-110.5		0		-74.87		-241.8 kJ
S°:	197.5		3 x 130.6		186.1		188.7 J/K

Calculate $\Delta H°$ and $\Delta S°$ from these values.

$$\Delta H° = [(-74.87) + (-241.8) - (-110.5)]\ \text{kJ} = -206.\underline{1}7\ \text{kJ}$$

$$\Delta S° = [186.1 + 188.7 - (197.5) - 3(130.6)]\ \text{J/K} = -214.5\ \text{J/K}$$

Substitute $\Delta H°$, $\Delta S°$ (= 0.−0.21450 kJ/K), and T (1058 K) into the equation for $\Delta G_T°$.

$$\Delta G_T° = \Delta H° - T\Delta S° = -206.17\ \text{kJ} - (1058\text{K})(-0.21450\ \text{kJ/K}) = 20.\underline{7}71\ \text{kJ}$$

$$= 20.\underline{7}71 \times 10^3\ \text{J}$$

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Now, substitute numerical values into the equation relating ln K and $\Delta G°$ (= $\Delta G_T°$).

$$\ln K = \frac{-\Delta G°}{RT} = \frac{20.771 \times 10^3}{-8.31 \times 1058} = -2.362$$

$$K = K_p = e^{-2.362} = 0.09\underline{4}18$$

$$K_c = K_p(RT)^2 = 0.09418(0.0821 \times 1058)^2 = 7\underline{1}0.6$$

The starting concentrations of CO and H_2 are

$$[CO] = \frac{0.0100 \text{ mol}}{25.0 \text{ L}} = 4.00 \times 10^{-4}\ M$$

$$[H_2] = \frac{0.0300 \text{ mol}}{25.0 \text{ L}} = 1.20 \times 10^{-3}\ M$$

You obtain the following table:

	$CO(g)$ +	$3H_2(g)$ →	$CH_4(g)$ +	$H_2O(g)$
Starting	4.00×10^{-4}	1.20×10^{-3}	0	0
Change	-x	-3x	+x	+x
Equilibrium	$(4.00 \times 10^{-4}) - x$	$(1.20 \times 10^{-3}) - 3x$	x	x

The equilibrium equation is

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

or

$$\frac{x^2}{[(4.00 \times 10^{-4}) - x][(1.20 \times 10^{-3}) - 3x]^3} = 7\underline{1}0.6$$

The denominator can be written as $3^3\,[(4.00 \times 10^{-4}) - x]^4$, so this equation can be reduced to a quadratic equation and solved exactly.

Multiply both sides of the equation by 27, and then take the square root. This gives

$$\frac{x}{(4.00 \times 10^{-4} - x)^2} = 1\underline{3}8.51$$

This can be rearranged into the following quadratic equation:

$$x^2 + (-8.019 \times 10^{-3})x + (1.60 \times 10^{-7}) = 0$$

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From the quadratic formula, you obtain

$$x = \frac{-(-8.019 \times 10^{-3}) \pm \sqrt{(-8.019 \times 10^{-3})^2 - 4(1.60 \times 10^{-7})}}{2}$$

$$= \frac{8.019 \times 10^{-3} \pm 7.979 \times 10^{-3}}{2} = 2.00 \times 10^{-5} \text{ (negative root)}$$

$x = [CH_4] = [H_2O] = 2.\underline{0}0 \times 10^{-5}\ M$

mol CH_4 = mol H_2O = 25.0 L x $(2.00 \times 10^{-5}$ mol/L) = $5.\underline{0}0 \times 10^{-4} = 5.0 \times 10^{-4}$ mol

18.121. First, calculate $\Delta G°$ at each temperature, using $\Delta G° = -RT \ln K$:

25.0°C: $\Delta G° = -(0.008314 \text{ kJ/K})(298.2 \text{ K})(\ln 1.754 \times 10^{-5}) = 27.15\underline{0}1$ kJ

50.0°C: $\Delta G_T° = -(0.008314 \text{ kJ/K})(323.2 \text{ K})(\ln 1.633 \times 10^{-5}) = 29.6\underline{1}84$ kJ

Next, solve two equations in two unknowns assuming $\Delta H°$ and $\Delta S°$ are constant over the range of 25.0°C to 50.0°C. Use 0.2982 K(kJ/J) and 0.3232 K(kJ/J) to convert $\Delta S°$ in J to $T\Delta S°$ in kJ.

(1) 27.1501 kJ = $\Delta H°$ − [0.2982 K(kJ/J) $\Delta S°$]

(2) 29.6184 kJ = $\Delta H°$ − [0.3232 K(kJ/J) $\Delta S°$]

Then, rearrange Equation 2, and substitute for $\Delta H°$ into Equation 2:

(3)a. $\Delta H° = 0.3232$ K(kJ/J) $\Delta S° + 29.6184$ kJ

(3)b. 27.1501 kJ = [0.3232 K(kJ/J) $\Delta S° + 29.6184$ kJ] − [0.2982 K(kJ/J) $\Delta S°$]

Solve for $\Delta S°$:

$$\Delta S° = \frac{(29.6184 - 27.1501) \text{ kJ}}{(0.2982 - 0.3232) \text{ K/(kJ/J)}} = -98.\underline{7}3 = -98.7 \text{ J/K}$$

Substitute this value into Equation 3a and solve for $\Delta H°$:

$\Delta H° = [(0.3232\ )$ K(kJ/J) x (−98.73 J/K)] + 29.6184 kJ = $-2.2\underline{9}1 = -2.29$ kJ

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18.122. First, calculate $\Delta G°$ at each temperature using $\Delta G° = -RT \ln K$:

25.0°C: $\Delta G° = -(0.008314 \text{ kJ/K})(298.2 \text{ K})(\ln 1.782 \times 10^{-10}) = 55.6\underline{5}41 \text{ kJ}$

35.0°C: $\Delta G_T° = -(0.008314 \text{ kJ/K})(308.2 \text{ K})(\ln 4.159 \times 10^{-10}) = 55.34\underline{8}7 \text{ kJ}$

Next, solve two equations in two unknowns assuming $\Delta H°$ and $\Delta S°$ are constant over the range of 25.0°C to 35.0°C. Use 0.2982 K(kJ/J) and 0.3082 K(kJ/J) to convert $\Delta S°$ in J to $T\Delta S°$ in kJ.

(3) $55.6541 \text{ kJ} = \Delta H° - [0.2982 \text{ K(kJ/J)} \, \Delta S°]$

(4) $55.3487 \text{ kJ} = \Delta H° - [0.3082 \text{ K(kJ/J)} \, \Delta S°]$

Then, rearrange Equation 2, and substitute for $\Delta H°$ into Equation 2:

(3)a. $\Delta H° = 0.3082 \text{ K(kJ/J)} \, \Delta S° + 55.3487 \text{ kJ}$

(3)b. $55.6541 \text{ kJ} = [0.3082 \text{ K(kJ/J)} \, \Delta S° + 55.3487 \text{ kJ}] - [(0.2982 \text{ K(kJ/J)} \, \Delta S°]$

Solve for $\Delta S°$:

$$\Delta S° = \frac{(55.6541 - 55.3487) \text{ kJ}}{(0.3082 - 0.2982) \text{ K/(kJ/J)}} = 3\underline{0}.54 = 31 \text{ J/K}$$

Substitute this value into Equation 3a and solve for $\Delta H°$:

$\Delta H° = [(0.3082 \text{) K(kJ/J)} \times (30.54 \text{ J/K})] + 55.3487 \text{ kJ} = 64.\underline{7}6 = 65 \text{ kJ}$

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CHAPTER 19

Electrochemistry

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

19.1. Assign oxidation numbers to the skeleton equation (Step 1).

$$\overset{0}{I_2} + \overset{+5}{NO_3^-} \rightarrow \overset{+5}{IO_3^-} + \overset{+4}{NO_2}$$

Separate into two incomplete half-reactions (Step 2). Note that iodine is oxidized (increases in oxidation number), and nitrogen is reduced (decreases in oxidation number).

$$I_2 \rightarrow IO_3^-$$

$$NO_3^- \rightarrow NO_2$$

Balance each half-reaction separately. The oxidation half-reaction is not balanced in I, so place a two in front of IO_3^- (Step 3a). Then add six H_2O's to the left side to balance O atoms (Step 3b), and add twelve H^+ ions to the right side to balance H atoms (Step 3c). Finally, add ten electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$$

The reduction half-reaction is balanced in N (Step 3a). Add one H_2O to the right side to balance O atoms (Step 3b), and add two H^+ ion to the left side to balance H atoms. Finally, add one electron to the left side to balance the charge (Step 3d).

The balanced reduction half-reaction is

$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$$

Multiply the reduction half-reaction by 5 so that, when added, the electrons cancel (Step 4a).

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$$

$$10NO_3^- + 20H^+ + 10e^- \rightarrow 10NO_2 + 10H_2O$$

$$I_2 + 10NO_3^- + 20H^+ + 6H_2O + \cancel{10e^-} \rightarrow 2IO_3^- + 10NO_2 + 12H^+ + 10H_2\cancel{O} + 10e^-$$

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Simplify the equation by canceling the twelve H^+ and six H_2O that appear on both sides. The coefficients do not need to be reduced (Step 4b). The net ionic equation is

$$I_2(s) + 10NO_3^-(aq) + 8H^+(aq) \rightarrow 2IO_3^-(aq) + 10NO_2(g) + 4H_2O(l)$$

19.2. After balancing the equation as though it were in acid solution, you obtain

$$H_2O_2 + 2ClO_2 \rightarrow 2ClO_2^- + O_2 + 2H^+$$

Add two OH^- to both sides of the equation (Step 5), and replace the two H^+ and two OH^- on the right side with two H_2O. No further cancellation is required. The balanced equation for the reaction in basic solution is

$$H_2O_2 + 2ClO_2 + 2OH^- \rightarrow 2ClO_2^- + O_2 + 2H_2O$$

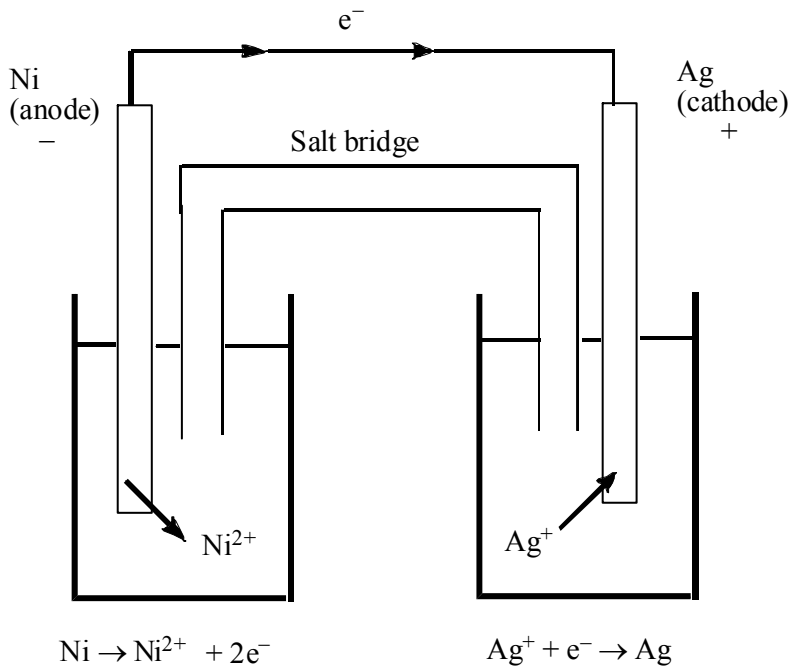
19.3. Silver ion is reduced at the silver electrode (cathode). The half-reaction is

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

The nickel electrode (anode) is where oxidation occurs. The half-reaction is

$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$$

Electron flow in the external circuit is from the nickel electrode (anode) to the silver electrode (cathode). Positive ions will flow in the solution portion of the circuit opposite to the direction of the electrons. A sketch of the cell is given below:



19.4. The notation for the cell is $Zn(s)|Zn^{2+}(aq)||H^+(aq)|H_2(g)|Pt(s)$.

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19.5. The half-cell reactions are

$$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Summing the half-cell reactions gives the overall cell reaction.

$$Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$$

19.6. The half-reactions are

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

n equals 2, and the maximum work for the reaction as written is

$$w_{max} = -nFE_{cell} = -2 \text{ x } 9.6485 \text{ x } 10^4 \text{ C x } 1.10 \text{ V} = -2.122 \text{ x } 10^5 \text{ V•C} = -2.12 \text{ x } 10^5 \text{ J}$$

For 6.54 g of zinc metal, the maximum work is

$$6.54 \text{ g Zn x } \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \text{ x } \frac{-2.123 \text{ x } 10^5 \text{ J}}{1 \text{ mol Zn}} = -2.123 \text{ x } 10^4 = -2.12 \text{ x } 10^4 \text{ J}$$

19.7. The half-reactions and corresponding electrode potentials are

$$Ag^-(aq) + e^- \rightarrow Ag(s) \qquad 0.80 \text{ V}$$

$$NO_3^-(aq) + 4H^-(aq) + 4e^- \rightarrow NO(g) + 2H_2O(l) \qquad 0.96 \text{ V}$$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so NO_3^- is the stronger oxidizing agent.

19.8. In this reaction, Cu^{2+} is the oxidizing agent on the left side; I_2 is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s); \quad E° = 0.34 \text{ V}$$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq); \quad E° = 0.54 \text{ V}$$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so I_2 is the stronger oxidizing agent. The reaction is nonspontaneous as written.

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19.9. The reduction half-reactions and standard electrode potentials are

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s);\ E°_{Zn} = -0.76\ V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s);\ E°_{Cu} = 0.34\ V$$

Reverse the first half-reaction and its half-cell potential to obtain

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-;\ -E°_{Zn} = 0.76\ V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s);\ E°_{Cu} = 0.34\ V$$

Obtain the cell potential by adding the half-cell potentials.

$$E°_{cell} = E°_{Cu} - E°_{Zn} = 0.34\ V + 0.76\ V = 1.10\ V$$

19.10. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^- \quad -E° = -0.15\ V$$

$$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq) \quad E° = 0.90\ V$$

$$Sn^{2+}(aq) + 2Hg^{2+}(aq) \rightarrow Sn^{4+}(aq) + Hg_2^{2+}(aq) \quad E°_{cell} = 0.75\ V$$

Note that each half-reaction involves two electrons; hence n equals 2. Also, $E°_{cell}$ equals 0.75 V, and the faraday constant, F, is 9.6485 x 10^4 C. Therefore,

$$\Delta G° = -nFE°_{cell} = -2 \times 9.6485 \times 10^4\ C \times 0.75\ V = -1.4472 \times 10^5\ J = -1.4 \times 10^5\ J$$

Thus, the standard free-energy change is −1.4 x 10^2 kJ.

19.11. Write the equation with ΔG_o°'s beneath each substance.

	$Mg(s)$	+	$Cu^{2-}(aq)$	→	$Mg^{2-}(aq)$	+	$Cu(s)$
ΔG_f°:	0		65.52		-454.80		0KJ

Hence,

$$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants})$$

$$= [(-454.8) - 65.52]\ kJ = -520.32\ kJ = -5.2032 \times 10^5\ J$$

Obtain n by splitting the reaction into half-reactions.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Each half-reaction involves two electrons, so n equals 2. Therefore,

$$\Delta G° = -nFE°_{cell}$$

$$-5.2032 \times 10^5\ J = -2 \times 9.6485 \times 10^4\ C \times E°_{cell}$$

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Rearrange and solve for $E°_{cell}$. Recall that J = C•V.

$$E°_{cell} = \frac{-5.2032 \times 10^5 \text{ J}}{-2 \times 9.6485 \times 10^4 \text{ C}} = 2.69\underline{6}3 = 2.696 \text{ V}$$

19.12. The half-reactions and standard electrode potentials are

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-; \quad -E°_{Fe} = 0.41 \text{ V}$$

$$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(s); \quad E°_{Sn^{2+}} = 0.15 \text{ V}$$

The standard cell potential for the cell is

$$E°_{cell} = E°_{Fe} - E°_{Sn^{2+}} = 0.41 \text{ V} + 0.15 \text{ V} = 0.56 \text{ V}$$

Note that n equals 2. Substitute into the equation relating $E°$ and K. Also, $K = K_c$.

$$0.56 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K_c, yields

$$\log K_c = 1\underline{8}.91$$

Take the antilog of both sides, you get

$$K_c = \text{antilog}\,(18.91) = 8.1 \times 10^{1\underline{8}} = 10^{19}$$

19.13. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad -E° = 0.76 \text{ V}$$

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s) \qquad E° = 0.80 \text{ V}$$

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s) \qquad E°_{cell} = 1.56 \text{ V}$$

Note that n equals 2. The reaction quotient is

$$Q = \frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{0.200}{(0.00200)^2} = 5.0\underline{0} \times 10^4$$

The standard cell potential is 1.56 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

$$= 1.56 - \frac{0.0592}{2} \log (5.00 \times 10^4)$$

$$= 1.56 - 0.13\underline{9}09 = 1.4\underline{2}09 = 1.42 \text{ V}$$

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19.14. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{e}^- \qquad -E^\circ = 0.76\ \text{V}$$

$$\text{Ni}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Ni}(s) \qquad E^\circ = -0.23\ \text{V}$$

$$\text{Zn}(s) + \text{Ni}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Ni}(s) \qquad E^\circ_{\text{cell}} = 0.53\ \text{V}$$

Note that n equals 2. The standard cell potential is 0.53 V, and the cell potential is 0.34 V, so the Nernst equation becomes

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{\text{n}} \log Q$$

$$0.34\ \text{V} = 0.53\ \text{V} - \frac{0.0592}{2} \log Q$$

Rearrange and solve for log Q.

$$\log Q = \frac{2}{0.0592} \times (0.53 - 0.34) = 6.\underline{4}18$$

Take the antilog of both sides.

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = \text{antilog}\,(6.418) = \underline{2}.623 \times 10^6$$

Substitute in $[\text{Zn}^{2+}] = 1.00\ M$ and solve for $[\text{Ni}^{2+}]$.

$$\frac{1.00\ \text{M}}{[\text{Ni}^{2+}]} = 2.624 \times 10^6$$

$$[\text{Ni}^{2+}] = \underline{3}.81 \times 10^{-7} = 4 \times 10^{-7}\ M$$

19.15.

a. The cathode reaction is $\text{K}^+(l) + \text{e}^- \rightarrow \text{K}(l)$.

The anode reaction is $2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2\text{e}^-$.

b. The cathode reaction is $\text{K}^+(l) + \text{e}^- \rightarrow \text{K}(l)$.

The anode reaction is $4\text{OH}^-(aq) \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O}(g) + 4\text{e}^-$.

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19.16. The species you should consider for half-reactions are Ag^+ and H_2O. Two possible cathode reactions are

$$Ag^+(aq) + e^- \rightarrow Ag(s);\ E° = 0.80\ V$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq);\ E° = -0.83\ V$$

Because the silver electrode potential is larger than the reduction potential of water, Ag^+ is reduced. The only possible anode reaction is the oxidation of water. The expected half-reactions are

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

19.17. The conversion of grams of silver to coulombs required to deposit this amount of silver is

$$0.365\ g\ Ag \times \frac{1\ mol\ Ag}{107.9\ g} \times \frac{1\ mol\ e^-}{1\ mol\ Ag} \times \frac{96{,}485\ C}{1\ mol\ e^-} = 32\underline{6}.3\ C$$

The time lapse, 216 min, equals $1.2\underline{9}6 \times 10^3$ s. Thus,

$$\text{Current} = \frac{\text{charge}}{\text{time}} = \frac{326.4\ C}{1.296 \times 10^4\ s} = 2.5\underline{1}88 \times 10^{-2} = 2.52 \times 10^{-2}\ A$$

19.18. When the current flows for 1.85×10^4 s, the amount of charge is

$$0.0565\ A \times 1.85 \times 10^4\ s = 1.0\underline{4}5 \times 10^3\ C$$

Note that 4 mol of electrons are equivalent to 1 mol of O_2. Hence,

$$1.045 \times 10^3\ C \times \frac{1\ mol\ e^-}{96{,}485\ C} \times \frac{1\ mol\ O_2}{4\ mol\ e^-} \times \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 0.086\underline{6}6 = 0.0867\ g\ O_2$$

■ ANSWERS TO CONCEPT CHECKS

19.1. No sustainable current would flow. The wire does not contain mobile positively and negatively charged species necessary to balance the accumulation of charges in each of the half cells.

19.2.

a. Standard reduction potentials are measured against some arbitrarily chosen standard reference half-reaction. Only differences in potentials can be measured. A voltaic cell made from H_2 and I_2 and corresponding solutions will have the same voltage regardless of the choice of the reference cell. If the I_2/I^- half-reaction is assigned a value of $E° = 0.00$ V, the H_2/H^+ half-reaction must have a voltage of $E° = -0.54$ V to keep the overall voltage the same.

b. The voltage of a voltaic cell made from Cu and Zn and corresponding solutions will have the same measured voltage regardless of the choice of the reference half-reaction.

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c. The calculated voltage is 1.10 V and is the same either way.

19.3.

a. Using the standard reduction potentials in Table 19.1, you see the voltage for this cell is positive, which suggests $\Delta G°$ is negative.

b. In order to reduce E_{cell}, change the concentrations in a way that increases the value of Q, where

$$Q = \frac{[Fe^{2+}]}{[Cu^{2+}]}$$

For example: $Fe(s)|Fe^{2+}(1.10\ M)||Cu^{2+}(0.50\ M)|Cu(s)$

19.4. The dissolved ions make seawater a better conductor than fresh water, thus the seawater plays a role similar to a salt bridge.

ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

19.1. A voltaic cell is an electrochemical cell in which a spontaneous reaction generates an electric current (energy). An electrolytic cell is an electrochemical cell that requires electric current (energy) to drive a nonspontaneous reaction to the right.

19.2. In both the voltaic and electrolytic cells, the cathode is the electrode at which reduction occurs, and the anode is the electrode at which oxidation occurs.

19.3. The SI unit of electrical potential is the volt (V).

19.4. The faraday (F) is the magnitude of charge on 1 mol of electrons; it equals 96,485 C, or 96,485 J/V.

19.5. It is necessary to measure the voltage of a voltaic cell when no current is flowing because the cell voltage exhibits its maximum value only when no current flows. Even if the current flows just for the time of measurement, the voltage drops enough so that what is measured is significantly less than the maximum.

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19.6. Standard electrode potentials are defined relative to a standard electrode potential of zero volts (0.00, 0.000 V, etc.) for the $H^+/H_2(g)$ electrode. Because the cell potential is measured using the hydrogen electrode at standard conditions and a second electrode at standard conditions, the cell potential equals the $E°$ of the half-reaction at the second electrode.

19.7. The SI unit of energy equals joules equals coulombs times volts.

19.8. The mathematical relationships are as follows:

$$\Delta G° = -nFE°_{\text{cell}}$$

$$\Delta G° = -RT \ln K$$

Combining these two equations gives

$$\ln K = \frac{nFE°_{\text{cell}}}{RT}$$

19.9. The first step in the corrosion of iron is

$$2\text{Fe}(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{OH}^- + 2\text{Fe}^{2+}$$

The Nernst equation for this reaction is

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592}{4} \log \frac{[\text{OH}^-]^4[\text{Fe}^{2+}]^2}{P_{\text{O}_2}}$$

If the pH increases, the $[OH^-]$ increases, and thus E_{cell} becomes more negative (this predicts that the reaction becomes less spontaneous). If the pH decreases, the $[OH^-]$ decreases, and thus E_{cell} becomes more positive (this predicts that the reaction becomes more spontaneous).

19.10. The zinc-carbon cell has a zinc can as the anode; the cathode is a graphite rod surrounded by a paste of manganese dioxide and carbon black. Around this is a second paste of ammonium and zinc chlorides. The electrode reactions involve oxidation of zinc metal to zinc(II) ion and reduction of $MnO_2(s)$ to $Mn_2O_3(s)$ at the cathode. The lead storage battery consists of a spongy lead anode and a lead dioxide cathode, both immersed in aqueous sulfuric acid. At the anode, the lead is oxidized to lead sulfate; at the cathode, lead dioxide is reduced to lead sulfate.

19.11. A fuel cell is essentially a battery that does not use up its electrodes. Instead, it operates with a continuous supply of reactants (fuel). An example is the hydrogen-oxygen fuel cell in which oxygen is reduced at one electrode to the hydroxide ion, and hydrogen is oxidized at the other electrode to water (H in the +1 oxidation state). Such a cell produces electrical energy in a spacecraft for long periods of time.

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19.12. During the rusting of iron, one end of a drop of water exposed to air acts as one electrode of a voltaic cell; at this electrode, an oxygen molecule is reduced by four electrons to four hydroxide ions. Oxidation of metallic iron to iron(II) ion at the center of the drop of water supplies the electrons, and the center serves as the other electrode of the voltaic cell. Thus, electrons flow from the center of the drop through the iron to the end of the drop.

19.13. When iron or steel is connected to an active metal such as zinc, a voltaic cell is formed with zinc as the anode and iron as the cathode. Any type of moisture forms the electrolyte solution, and the zinc metal is then oxidized to zinc(II) ion in preference to the oxidation of iron metal. Oxygen is reduced at the cathode to hydroxide ions. If iron or steel is exposed to oxygen while connected to a less active metal such as tin, a voltaic cell is formed with iron as the anode and tin as the cathode, and iron is oxidized to iron(II) ion rather than tin being oxidized to tin(II) ion. Thus, exposed iron corrodes rapidly in a tin can. Fortunately, as long as the iron is covered by the tin, it cannot corrode.

19.14. The addition of an ionic species such as strongly ionized sulfuric acid facilitates the passage of current through the solution.

19.15. Sodium metal can be prepared by electrolysis of molten sodium chloride.

19.16. The anode reaction in the electrolysis of molten potassium hydroxide is

$$4OH^- \rightarrow O_2(g) + 2H_2O(g) + 4e^-$$

19.17. The reason why different products are obtained is that water instead of Na^+ is reduced at the cathode during the electrolysis of aqueous NaCl. This is because water has a more positive $E°$ (smaller decomposition voltage). At the anode, water instead of chloride ion is oxidized because water has a less positive $E°$ (smaller decomposition voltage).

19.18. The Nernst equation for the electrode reaction of $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ is

$$E = -1.36\ \text{V} - \frac{0.0592}{2}\log\frac{1\ \text{atm}}{[Cl^-]^2} = -1.36\ \text{V} + 0.0592\log[Cl^-]$$

This equation implies that E increases as $[Cl^-]$ increases. For a sufficiently large $[Cl^-]$, Cl^- will be more readily oxidized than the water solvent.

19.19. The answer is c, 11.

19.20. The answer is c, $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$.

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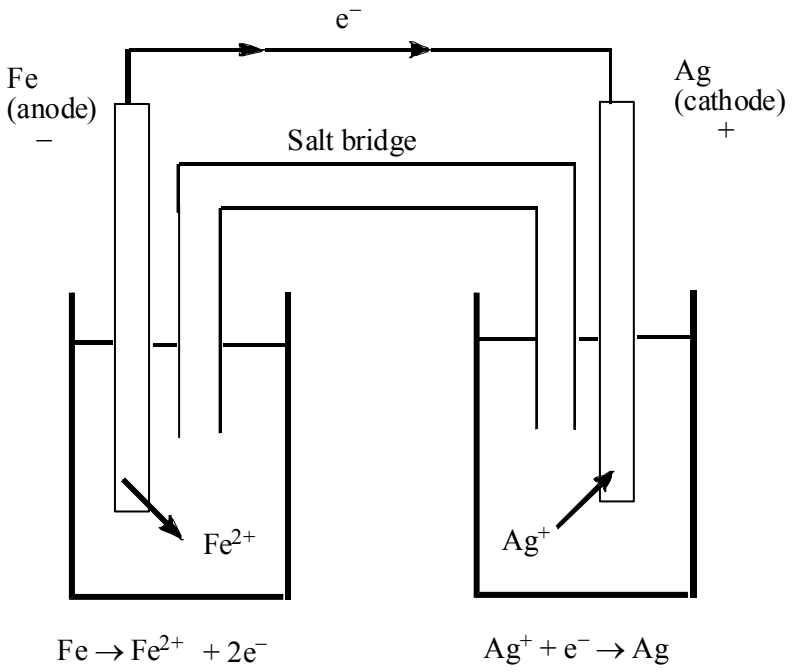
19.21. The answer is a, 123 A.

19.22. The answer is b, the copper electrode is the anode.

■ ANSWERS TO CONCEPT EXPLORATIONS

19.23.

a. The completed cell is



$Fe \rightarrow Fe^{2+} + 2e^-$ $\qquad$ $Ag^+ + e^- \rightarrow Ag$

b. The cell potential is

$$\begin{array}{rcll} Fe(s) & \rightarrow & Fe^{2+}(aq) + 2e^- & -E^\circ = 0.41\ V \\ Ag^+(aq) + 2e^- & \rightarrow & 2Ag(s) & E^\circ = 0.80\ V \\ \hline Fe(s) + 2Ag^+(aq) & \rightarrow & Fe^{2+}(aq) + 2Ag(s) & E^\circ_{cell} = 1.21\ V \end{array}$$

Since the cell voltage is positive, the reaction is spontaneous.

c. Look for 1.0 *M* solutions of $Fe(NO_3)_2$ and $AgNO_3$. Other Fe^{2+} solutions can be used, but Ag^+ precipitates with many anions.

d. The volume of solution in the cells does not affect the cell potential as long as the concentration does not change.

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e. If deionized water were added to the solution that contains the $Ag^+(aq)$, the cell voltage would change. The effect of the change can be seen by looking at the Nernst equation.

$$E = E° - \frac{0.0592}{n} \log Q = E° - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

Adding deionized water decreases $[Ag^+]$, which then causes E to decrease. Therefore, adding deionized water to the $Ag^+(aq)$ will cause the voltage to drop.

f. Swapping a copper rod for the silver rod would not affect the cell potential. The reaction at the cathode is $Ag^+(aq) + e^- \rightarrow Ag(s)$, and the Ag will deposit on the copper electrode as it forms.

g. If the iron rod is replaced with a copper rod, the cell no longer has the same cell potential. The reaction at the anode is now $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ ($E°_{ox} = -0.34$ V). The cell potential would be 0.46 V.

19.24.

a. The reactions and cell potential are

$$\begin{array}{rll} Ni(s) \rightarrow Ni^{2+}(aq) + 2e^- & -E° = 0.23 \text{ V} \\ 2Cu(aq) + 2e^- \rightarrow 2Cu(s) & E° = 0.52 \text{ V} \\ \hline Ni(s) + 2Cu^+(aq) \rightarrow Ni^{2+}(aq) + 2Cu(s) & E°_{cell} = 0.75 \text{ V} \end{array}$$

Since the cell potential is positive, the reaction is spontaneous, and the cell is a voltaic cell.

b. The current in this cell flows spontaneously.

c. The maximum cell potential is $E°$, which is 0.75 V.

d. The initial voltage would be 0.75 V. As time went by, the voltage would gradually decrease, until equilibrium was reached, at which time, the voltage would be zero.

e. The free energy is

$$\Delta G° = -nFE°_{cell} = -(2 \text{ mol})(96{,}485 \text{ C/mol})(0.75 \text{ V}) = -144727.5 \text{ J}$$
$$= -1.4 \times 10^3 \text{ kJ}$$

f. Over time, ΔG changes, getting larger (less negative) as the cell runs. When equilibrium is reached, ΔG will be zero.

■ ANSWERS TO CONCEPTUAL PROBLEMS

19.25.

a. Since there is no species present to donate or accept electrons other than zinc, you would expect no change.

b. Since there is no species present to donate or accept electrons other than copper, you would expect no change.

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c. According to the table of standard reduction potentials, the Cu^{2+} would undergo reduction, and the Zn would undergo oxidation. You would expect the Zn strip to dissolve as it becomes Zn^{2+}, the blue color of the solution to fade as the Cu^{2+} becomes Cu, and solid copper precipitate to form.

d. According to the table of standard reduction potentials, since Zn^{2+} cannot oxidize Cu, you would expect no change.

19.26. You could construct the battery by hooking together, in series, five individual cells, each with $E° = 1.20$ V.

19.27. The Zn is a sacrificial electrode that keeps the hull from undergoing oxidation by the dissolved ions in seawater. Zn works because it is more easily oxidized than Fe.

19.28. When an electrochemical reaction reaches equilibrium, E_{cell} equals 0, which means no current will flow, and nothing will happen when you turn on the flashlight. This is typically what has occurred when you have a dead battery.

19.29. Since there is more zinc present, the oxidation-reduction reactions in the battery will run for a longer period of time. This assumes zinc is the limiting reactant.

19.30. Any metal that has a more negative standard reduction potential (Mg, Al, etc.) could be used, keeping in mind that Group IA metals that fall into this category are too reactive to be of practical use.

19.31. Pick elements or compounds to be reduced and one to be oxidized so that when the half-reactions are added together, the $E°_{cell}$ is about 0.90 V. For example

$$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^- \quad E°_{ox} = 0.40 \text{ V}$$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \quad E°_{red} = 0.54 \text{ V}$$

The overall balanced reaction and cell potential are

$$I_2(s) + Cd(s) \rightarrow 2I^-(aq) + Cd^{2+}(aq) \quad E°_{cell} = 0.94 \text{ V}$$

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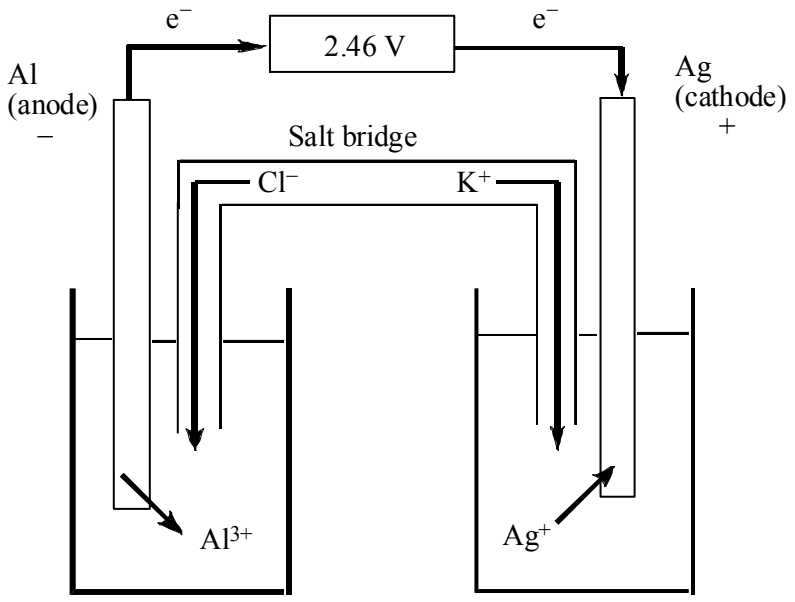
19.32. (parts a to f) The completed diagram with all parts labeled is shown below.



$Al \rightarrow Al^{3+} + 3e^-$ Oxidation

$Ag^+ + e^- \rightarrow Ag$ Reduction

d. The cell potential is determined as follows:

$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$ $\quad E°_{red} = -1.66$ V

$g^+(aq)\ e^- \rightarrow Ag(s)$ $\quad E°_{red} = 0.80$ V

$E°_{cell} = E°_{cathode} - E°_{anode} = 0.80\text{ V} - (-1.66\text{ V}) = 2.46$ V

g. The species undergoing oxidation is Al(*s*), and the species undergoing reduction is $Ag^+(aq)$.

h. The balanced overall reaction is

$$Al(s) + 3\ Ag^+(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$$

19.33. The effect of the various changes on the intensity of the light can be determined using the Nernst equation,

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

For this reaction, $E° = 1.10$ V, $n = 2$, and Q is the reaction quotient.

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

If $Q > 1$, log Q is positive, and the net result will be a decrease in cell potential and a decrease in the intensity of light. If $Q < 1$, log Q is negative, and the net result will be an increase in cell potential and an increase in the intensity of light. At the start, both $[Zn^{2+}]$ and $[Cu^{2+}]$ are 1.0 *M*, so $Q = 1$, and log $Q = 0$, so $E_{cell} = E°_{cell}$.

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a. If more $CuSO_4(s)$ is dissolved in the $CuSO_4$ solution, $[Cu^{2+}]$ would be greater than 1, so $Q < 1$. The effect is to increase the intensity of light.

b. If more $Zn(NO_3)_2(s)$ is dissolved in the $Zn(NO_3)_2$ solution, $[Zn^{2+}]$ would be greater than 1, so $Q > 1$. The effect is to decrease the intensity of light.

c. If H_2O is added to the $CuSO_4$ solution, $[Cu^{2+}]$ would be less than 1, so $Q > 1$. The effect is to decrease the intensity of light.

d. If the salt bridge is removed, the circuit would not be complete, and the cell potential would be zero. No current would flow.

19.34. The most important consideration in battery design is the spontaneity of the cell reaction since this determines the cell voltage. The half-reactions for the reduction of oxygen gas given in Appendix I are

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E° = +0.40 \text{ V}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E° = +1.23 \text{ V}$$

These represent the reduction of oxygen under basic and under acidic conditions. Thus, in basic solution, we would require an oxidation half-reaction (anode half-reaction) with a potential greater than −0.40 V to obtain a spontaneous reaction.

The density of the reducing agent is the next-most-important consideration. Hydrogen, the element with the lowest density, should certainly be considered. It does have some drawbacks, however. Because it is a gas, some method of storage needs to be developed. Liquid storage and metal hydride storage have been investigated. Storage of liquid hydrogen presents problems of safety and weight. Storage of hydrogen as a hydride is used in nickel-hydride cells presently available for portable computers, cellular phones, etc. (These batteries are rechargeable but do not use oxygen.) The metal hydride obviously adds weight to the battery. Other elements you might consider are Na, Li, Al, K, Ca, and Zn, which have favorable power-to-mass ratios. Lithium and sodium might present some disposal problems since they are very reactive metals. Batteries using aluminum with atmospheric oxygen are available.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

19.35. In balancing oxidation-reduction reactions in acid, the four steps in the text will be followed. For part a, each step is shown. For the other parts, only a summary is shown.

a. Assign oxidation numbers to the skeleton equation (Step 1).

$$\overset{+6}{Cr_2O_7^{2-}} + \overset{+3}{C_2O_4^{2-}} \rightarrow \overset{+3}{Cr^{3+}} + \overset{+4}{CO_2}$$

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Separate into two incomplete half-reactions (Step 2). Note that carbon is oxidized (increases in oxidation number), and chromium is reduced (decreases in oxidation number).

$$C_2O_4^{2-} \rightarrow CO_2$$

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Balance each half-reaction separately. The oxidation half-reaction is not balanced in C, so place a 2 in front of CO_2 (Step 3a). Finally, add two electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

The reduction half-reaction is not balanced in Cr, so place a 2 in front of Cr^{3+} (Step 3a). Add seven H_2O to the right side to balance O atoms (Step 3b), and add fourteen H^+ ions to the left side to balance H atoms (step 3c). Finally, add six electrons to the left side to balance the charge (Step 3d). The balanced reduction half-reaction is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Multiply the oxidation half-reaction by 3 so that, when added, the electrons cancel (Step 4a).

$$3C_2O_4^{2-} \rightarrow 6CO_2 + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ + \cancel{6e^-} \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O + \cancel{6e^-}$$

The equation does not need to be simplified any further (Step 4b). The net ionic equation is

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$$

b. The two balanced half-reactions are

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad \text{(oxidation)}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \qquad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 4, and then add together. Cancel the six electrons from each side. No further simplification is needed. The balanced equation is

$$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$$

c. The two balanced half-reactions are

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^- \qquad \text{(oxidation)}$$

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad \text{(reduction)}$$

Add the two half-reactions together and cancel the two electrons from each side. Also, cancel three H^+ ions and one H_2O from each side. The balanced equation is

$$MnO_2 + HNO_2 + H^+ \rightarrow Mn^{2+} + NO_3^- + H_2O$$

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d. The two balanced half-reactions are

$$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^- \quad \text{(oxidation)}$$

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 5, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen H^+ and eight H_2O from each side. The balanced equation is

$$5PbO_2 + 2Mn^{2+} + 5SO_4^{2-} + 4H^+ \rightarrow 5PbSO_4 + 2MnO_4^- + 2H_2O$$

e. The two balanced half-reactions are

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^- \quad \text{(oxidation)}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3, and then add together. Cancel the six electrons from each side. Also, cancel nine H^+ and three H_2O from each side. The balanced equation is

$$3HNO_2 + Cr_2O_7^{2-} + 5H^+ \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

19.36. In balancing oxidation-reduction reactions in acid, the four steps in the text will be followed. For part a, each step is shown. For the other parts, only a summary is shown.

a. Assign oxidation numbers to the skeleton equation (Step 1).

$$\overset{+2}{Mn^{2+}} + \overset{+5}{BiO_3^-} \rightarrow \overset{+7}{MnO_4^-} + \overset{+3}{Bi^{3+}}$$

Separate into two incomplete half-reactions (Step 2). Note that manganese is oxidized (increases in oxidation number), and bismuth is reduced (decreases in oxidation number).

$$Mn^{2+} \rightarrow MnO_4^-$$

$$BiO_3^- \rightarrow Bi^{3+}$$

Balance each half-reaction separately. For the oxidation half-reaction, add four H_2O to the left side to balance O atoms (Step 3b), and add eight H^+ ion to the right side to balance H atoms (step 3c). Finally, add five electrons to the right side to balance the charge (Step 3d). The balanced oxidation half-reaction is

$$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$$

For the reduction half-reaction, add three H_2O to the right side to balance O atoms (Step 3b), and add six H^+ ion to the left side to balance H atoms (step 3c). Finally, add two electrons to the left side to balance the charge (Step 3d). The balanced reduction half-reaction is

$$BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{3+} + 3H_2O$$

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Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 5, so that, when added, the electrons cancel (Step 4a).

$$2Mn^{2+} + 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10e^-$$

$$5BiO_3^- + 30H^+ + 10e^- \rightarrow 5Bi^{3+} + 15H_2O$$

$$2Mn^{2+} + 5BiO_3^- + 30H^+ + 8H_2O + \cancel{10}e^- \rightarrow$$

$$2MnO_4^- + 5Bi^{3+} + 16H^+ + 15H_2O + \cancel{10e^-}$$

The equation can be further simplified by canceling sixteen H^+ and eight H_2O from each side (Step 4b). The net ionic equation is

$$2Mn^{2+} + 5BiO_3^- + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

b. The two balanced half-reactions are

$$I^- + 3H_2O \rightarrow IO_3^- + 6H^+ + 6e^- \quad \text{(oxidation)}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad \text{(reduction)}$$

Add the two half-reactions together, and cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation is

$$Cr_2O_7^{2-} + I^- + 8H^+ \rightarrow 2Cr^{3+} + IO_3^- + 4H_2O$$

c. The two balanced half-reactions are

$$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 5 and the reduction half-reaction by 2, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen H^+ and five H_2O from each side. The balanced equation is

$$2MnO_4^- + 5H_2SO_3 \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+ + 3H_2O$$

d. The two balanced half-reactions are

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad \text{(oxidation)}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by six, and then add together. Cancel the six electrons from each side. The balanced equation is

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

e. The two balanced half-reactions are

$$As + 3H_2O \rightarrow H_3AsO_3 + 3H^+ + 3e^- \quad \text{(oxidation)}$$

$$ClO_3^- + 5H^+ + 4e^- \rightarrow HClO + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 4 and the reduction half-reaction by 3, and then add together. Cancel the twelve electrons from each side. Also, cancel twelve H^+ and six H_2O from each side. The balanced equation is

$$4As + 3ClO_3^- + 3H^+ + 6H_2O \rightarrow 4H_3AsO_3 + 3HClO$$

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19.37. In balancing oxidation-reduction reactions in basic solution, the equation will first be balanced as if the equation were in acidic solution; then the extra two steps in the text will be followed.

a. The two balanced half-reactions are

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

Add the two half-reactions together, and cancel the two electrons from each side. Also, cancel two H^+ and two H_2O from each side. The balanced equation in acidic solution is

$$Mn^{2+} + H_2O_2 \rightarrow MnO_2 + 2H^+$$

Now add two OH^- to each side (Step 5). Simplify by combining the H^+ and OH^- to give H_2O. No further simplification is required (Step 6). The balanced equation in basic solution is

$$Mn^{2+} + H_2O_2 + 2OH^- \rightarrow MnO_2 + 2H_2O$$

b. The two balanced half-reactions are

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation in acidic solution is

$$2MnO_4^- + 3NO_2^- + 2H^+ \rightarrow 2MnO_2 + 3NO_3^- + H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel one H_2O from each side. The balanced equation in basic solution is

$$2MnO_4^- + 3NO_2^- + H_2O \rightarrow 2MnO_2 + 3NO_3^- + 2OH^-$$

c. The two balanced half-reactions are

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 2 and then add together. Cancel the two electrons from each side. Also, cancel four H^+ and two H_2O from each side. The balanced equation in acidic solution is

$$Mn^{2+} + 2ClO_3^- \rightarrow MnO_2 + 2ClO_2$$

Since there are no H^+ ions on either side, no further simplification is needed. The balanced equation in basic solution is identical to the balanced equation in acidic solution.

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d. The two balanced half-reactions are

$$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and then add together. Cancel the three electrons from each side. Also, cancel four H^+ and two H_2O from each side. The balanced equation in acidic solution is

$$MnO_4^- + 3NO_2 + H_2O \rightarrow MnO_2 + 3NO_3^- + 2H^+$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel one H_2O from each side. The balanced equation in basic solution is

$$MnO_4^- + 3NO_2 + 2OH^- \rightarrow MnO_2 + 3NO_3^- + H_2O$$

e. The two balanced half-reactions are

$$Cl^2 + 6H_2O \rightarrow 2ClO_3^- + 12H^+ + 10e^- \quad \text{(oxidation)}$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 5 and then add together. Cancel the ten electrons from each side. Also, divide all the coefficients by 2. The balanced equation in acidic solution is

$$3Cl_2 + 3H_2O \rightarrow 5Cl^- + ClO_3^- + 6H^+$$

Now add six OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel three H_2O from each side. The balanced equation in basic solution is

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

19.38. In balancing oxidation-reduction reactions in basic solution, the equation will first be balanced as if the equation were in acidic solution, then the extra two steps in the text will be followed.

a. The two balanced half-reactions are

$$Cr(OH)_4^- \rightarrow CrO_4^{2-} + 4H^+ + 3e^- \quad \text{(oxidation)}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation in acidic solution is

$$2Cr(OH)_4^- + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 2H^+ + 6H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then combine the H_2O on the right side into one term. The balanced equation in basic solution is

$$2Cr(OH)_4^- + 3H_2O_2 + 2OH^- \rightarrow 2CrO_4^{2-} + 8H_2O$$

b. The two balanced half-reactions are

$$Br^- + 3H_2O \rightarrow BrO_3^- + 6H^+ + 6e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

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Multiply the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side.

The balanced equation in acidic solution is

$$2MnO_4^- + Br^- + 2H^+ \rightarrow 2MnO_2 + BrO_3^- + H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel one H_2O on each side. The balanced equation in basic solution is

$$2MnO_4^- + Br^- + H_2O \rightarrow 2MnO_2 + BrO_3^- + 2OH^-$$

c. The two balanced half-reactions are

$$Co^{2+} + 3H_2O \rightarrow Co(OH)_3 + 3H^+ + e^- \quad \text{(oxidation)}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 2, and then add together. Cancel the two electrons from each side. Also, cancel two H^+ and two H_2O from each side.

The balanced equation in acidic solution is

$$2Co^{2+} + H_2O_2 + 4H_2O \rightarrow 2Co(OH)_3 + 4H^+$$

Now add four OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel four H_2O on each side. The balanced equation in basic solution is

$$2Co^{2+} + H_2O_2 + 4OH^- \rightarrow 2Co(OH)_3$$

d. The two balanced half-reactions are

$$Pb(OH)_4^{2-} \rightarrow PbO_2 + 2H_2O + 2e^- \quad \text{(oxidation)}$$

$$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \quad \text{(reduction)}$$

Add the two half-reactions together, and cancel the two electrons from each side. The balanced equation in acidic solution is

$$Pb(OH)_4^{2-} + ClO^- + 2H^+ \rightarrow PbO_2 + Cl^- + 3H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel two H_2O on each side. The balanced equation in basic solution is

$$Pb(OH)_4^{2-} + ClO^- \rightarrow PbO_2 + Cl^- + 2OH^- + H_2O$$

e. The two balanced half-reactions are

$$Zn + 4H_2O \rightarrow Zn(OH)_4^{2-} + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 4, and then add together. Cancel the eight electrons from each side. Also, cancel nine H^+ and three H_2O from each side. The balanced equation in acidic solution is

$$4Zn + NO_3^- + 13H_2O \rightarrow 4Zn(OH)_4^{2-} + NH_3 + 7H^+$$

Now add seven OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel seven H_2O on each side. The balanced equation in basic solution is

$$4Zn + NO_3^- + 7OH^- + 6H_2O \rightarrow NH_3 + 4Zn(OH)_4^{2-}$$

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19.39.

a. The two balanced half-reactions are

$$8H_2S \rightarrow S_8 + 16H^+ + 16e^- \quad \text{(oxidation)}$$

$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 16, and then add together. Cancel the sixteen electrons and sixteen H^+ from each side. The balanced equation is

$$8H_2S + 16NO_3^- + 16H^+ \rightarrow S_8 + 16NO_2 + 16H_2O$$

b. The two balanced half-reactions are

$$Cu + Cu^{2+} \rightarrow Cu^{2+} + 2e^- \quad \text{(oxidation)}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. The balanced equation is

$$2NO_3^- + 3Cu + 8H^+ \rightarrow 2NO + 3Cu^{2+} + 4H_2O$$

c. The two balanced half-reactions are

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 5 and the reduction half-reaction by 2, and then add together. Cancel the ten electrons from each side. Also, cancel sixteen H^+ and eight H_2O from each side. The balanced equation is

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$$

d. The two balanced half-reactions are

$$Sn(OH)_3^- + 3H_2O \rightarrow Sn(OH)_6^{2-} + 3H^+ + 2e^- \quad \text{(oxidation)}$$

$$Bi(OH)_3 + 3H^+ + 3e^- \rightarrow Bi + 3H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and six H_2O from each side. The balanced equation in acidic solution is

$$2Bi(OH)_3 + 3Sn(OH)_3^- + 3H_2O \rightarrow 3Sn(OH)_6^{2-} + 2Bi + 3H^+$$

Now add three OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel three H_2O on each side. The balanced equation in basic solution is

$$2Bi(OH)_3 + 3Sn(OH)_3^- + 3OH^- \rightarrow 3Sn(OH)_6^{2-} + 2Bi$$

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19.40.

a. The two balanced half-reactions are

$$8H_2S \rightarrow S_8 + 16H^+ + 16e^- \quad \text{(oxidation)}$$

$$Hg_2^{2+} + 2e^- \rightarrow 2Hg \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 8, and then add together. Cancel the sixteen electrons from each side. The balanced equation in acidic solution is

$$8Hg_2^{2+} + 8H_2S \rightarrow 16Hg + S_8 + 16H^+$$

b. The two balanced half-reactions are

$$S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 8e^- \quad \text{(oxidation)}$$

$$I_2 + 2e^- \rightarrow 2I^- \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 4, and then add together. Cancel the eight electrons from each side. The balanced equation in acidic solution is

$$S^{2-} + 4I_2 + 4H_2O \rightarrow 8I^- + SO_4^{2-} + 8H^+$$

Now add eight OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel four H_2O on each side. The balanced equation in basic solution is

$$S^{2-} + 4I_2 + 8OH^- \rightarrow 8I^- + SO_4^{2-} + 4H_2O$$

c. The two balanced half-reactions are

$$Al + 4H_2O \rightarrow Al(OH)_4^- + 4H^+ + 3e^- \quad \text{(oxidation)}$$

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 8 and the reduction half-reaction by 3, and then add together. Cancel the twenty-four electrons from each side. Also, cancel twenty-seven H^+ and nine H_2O from each side. The balanced equation in acidic solution is

$$8Al + 3NO_3^- + 23H_2O \rightarrow 8Al(OH)_4^- + 3NH_3 + 5H^+$$

Now add five OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel five H_2O on each side. The balanced equation in basic solution is

$$8Al + 3NO_3^- + 5OH^- + 18H_2O \rightarrow 8Al(OH)_4^- + 3NH_3$$

d. The two balanced half-reactions are

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. The balanced equation in acidic solution is

$$2MnO_4^- + 3C_2O_4^{2-} + 8H^+ \rightarrow 2MnO_2 + 6CO_2 + 4H_2O$$

Now add eight OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel four H_2O on each side. The balanced equation in basic solution is

$$2MnO_4^- + 3\,C_2O_4^{2-} + 4H_2O \rightarrow 2MnO_2 + 6CO_2 + 8OH^-$$

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19.41.

a. The two balanced half-reactions are

$$I^- + 3H_2O \rightarrow IO_3^- + 6H^+ + 6e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation in acidic solution is

$$2MnO_4^- + I^- + 2H^+ \rightarrow 2MnO_2 + IO_3^- + H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel one H_2O on each side. The balanced equation in basic solution is

$$2MnO_4^- + I^- + H_2O \rightarrow 2MnO_2 + IO_3^- + 2OH^-$$

b. The two balanced half-reactions are

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \text{(oxidation)}$$

$$Cr_2O_4^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3, and then add together. Cancel the six electrons from each side. The balanced equation is

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$$

c. The two balanced half-reactions are

$$S_8 + 16H_2O \rightarrow 8SO_2 + 32H^+ + 32e^- \quad \text{(oxidation)}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 32, and then add together. Cancel the ninety-six electrons from each side. Also, cancel ninety-six H^+ and forty-eight H_2O from each side. The balanced equation is

$$3S_8 + 32NO_3^- + 32H^+ \rightarrow 32NO + 24SO_2 + 16H_2O$$

d. The two balanced half-reactions are

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation in acidic solution is

$$3H_2O_2 + 2MnO_4^- + 2H^+ \rightarrow 3O_2 + 2MnO_2 + 4H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel two H_2O on each side. The balanced equation in basic solution is

$$3H_2O_2 + 2MnO_4^- \rightarrow 3O_2 + 2MnO_2 + 2H_2O + 2OH^-$$

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e. The two balanced half-reactions are

$$Zn \rightarrow Zn^{2+} + 2e^- \quad \text{(oxidation)}$$

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 5, and then add together. Cancel the ten electrons from each side. The balanced equation is

$$5Zn + 2NO_3^- + 12H^+ \rightarrow N_2 + 5Zn^{2+} + 6H_2O$$

19.42.

a. The two balanced half-reactions are

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad \text{(oxidation)}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation is

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 7H_2O$$

b. The two balanced half-reactions are

$$CN^- + H_2O \rightarrow CNO^- + 2H^+ + 2e^- \quad \text{(oxidation)}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation in acidic solution is

$$3CN^- + 2MnO_4^- + 2H^+ \rightarrow 3CNO^- + 2MnO_2 + H_2O$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel one H_2O on each side. The balanced equation in basic solution is

$$3CN^- + 2MnO_4^- + H_2O \rightarrow 3CNO^- + 2MnO_2 + 2OH^-$$

c. The two balanced half-reactions are

$$Cr(OH)_4^- \rightarrow CrO_4^{2-} + 4H^+ + 3e^- \quad \text{(oxidation)}$$

$$OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ from each side. The balanced equation in acidic solution is

$$2Cr(OH)_4^- + 3OCl^- \rightarrow 2CrO_4^{2-} + 3Cl^- + 3H_2O + 2H^+$$

Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then combine the H_2O on the right side into a single term. The balanced equation in basic solution is

$$2Cr(OH)_4^- + 3OCl^- + 2OH^- \rightarrow 2CrO_4^{2-} + 3Cl^- + 5H_2O$$

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d. The two balanced half-reactions are

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$Br_2 + 2e^- \rightarrow 2Br^- \quad \text{(reduction)}$$

Add the two half-reactions together. Cancel the two electrons from each side. The balanced equation is

$$Br_2 + SO_2 + 2H_2O \rightarrow 2Br^- + SO_4^{2-} + 4H^+$$

e. The two balanced half-reactions are

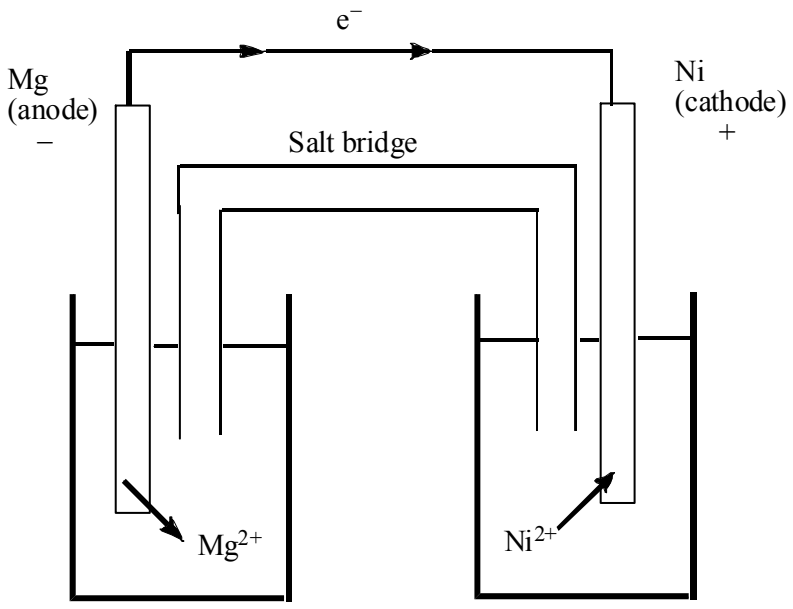
$$8CuS \rightarrow S_8 + 8Cu^{2+} + 16e^- \quad \text{(oxidation)}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 16, and then add together. Cancel the forty-eight electrons from each side. The balanced equation is

$$24CuS + 16NO_3^- + 64H^+ \rightarrow 24Cu^{2+} + 16NO + 3S_8 + 32H_2O$$

19.43. Sketch of the cell:



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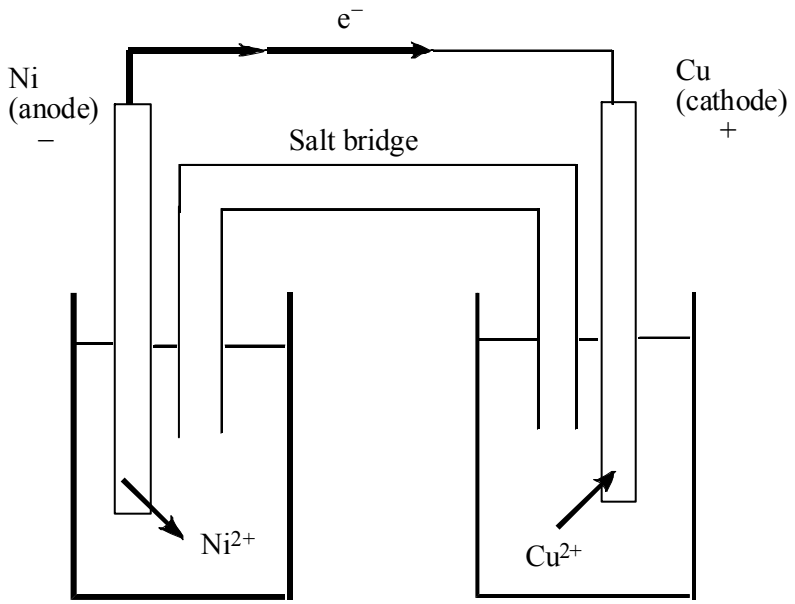
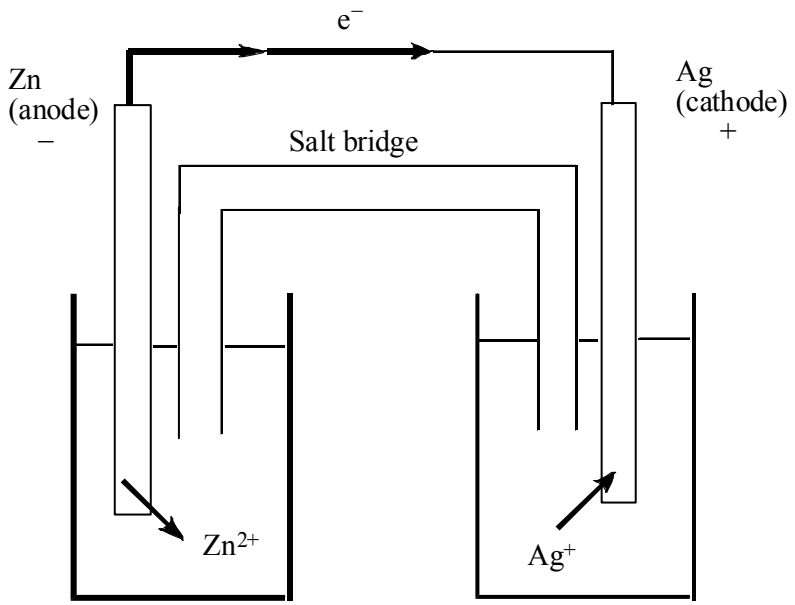
19.44. Sketch of the cell:



$Ni \rightarrow Ni^{2+} + 2e^-$ $\quad\quad$ $Cu^{2+} + 2e^- \rightarrow Cu$

19.45. Sketch of the cell:



$Zn \rightarrow Zn^{2+} + 2e^-$ $\quad\quad$ $Ag^+ + e^- \rightarrow Ag$

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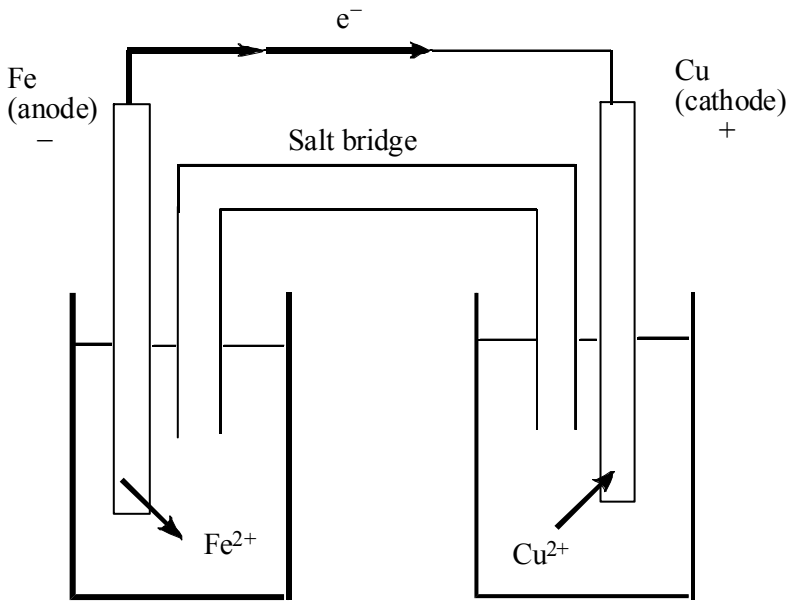
19.46. Sketch of the cell:



$Fe \rightarrow Fe^{2+} + 2e^-$ $\quad$ $Cu^{2+} + 2e^- \rightarrow Cu$

19.47. The electrode half-reactions and the overall cell reaction are

Anode: $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

Cathode: $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Overall: $Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + 2Ag(s)$

19.48. The electrode half-reactions and the overall cell reaction are

Anode: $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

Cathode: $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$

Overall: $Zn(s) + HgO(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Hg(l)$

19.49. Because of its less negative $E°$, Pb^{2+} is reduced at the cathode and is written on the right; $Ni(s)$ is oxidized at the anode and is written first, at the left, in the cell notation. The notation is $Ni(s)|Ni^{2+}(aq)||Pb^{2+}(aq)|Pb(s)$.

19.50. Because of its less negative $E°$, H^+ is reduced at the cathode and is written on the right; $Al(s)$ is oxidized at the anode and is written first, at the left, in the cell notation. The notation is $Al(s)|Al^{3+}(aq)||H^+(aq)|H_2(g)|Pt$.

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19.51. Because of its less negative $E°$, H^+ is reduced at the cathode and is written on the right; Ni(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is $Ni(s)|Ni^{2+}(1\ M)||H^+(1\ M)|H_2(g)|Pt$.

19.52. Because of its less negative $E°$, Fe^{3+} is reduced at the cathode and is written on the right; Zn(s) is oxidized at the anode and is written first, at the left, in the cell notation. The notation is $Zn(s)|Zn^{2+}(0.20\ M)||Fe^{3+}(0.30\ M)|Fe(s)$.

19.53. The Fe(s), on the left, is the reducing agent. The Ag^+, on the right, is the oxidizing agent, gaining just one electron. Multiplying its half-reaction by 2 to equalize the numbers of electrons and writing both half-reactions give the overall cell reaction:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$
$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

$$Fe(s) + 2Ag^+(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)$$

19.54. The $H_2(g)$, on the left, is the reducing agent. The $Br_2(l)$, on the right, is the oxidizing agent. The half-reactions and the overall cell reaction are

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$
$$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$$

$$H_2(g) + Br_2(l) \rightarrow 2H^+(aq) + 2Br^-(aq)$$

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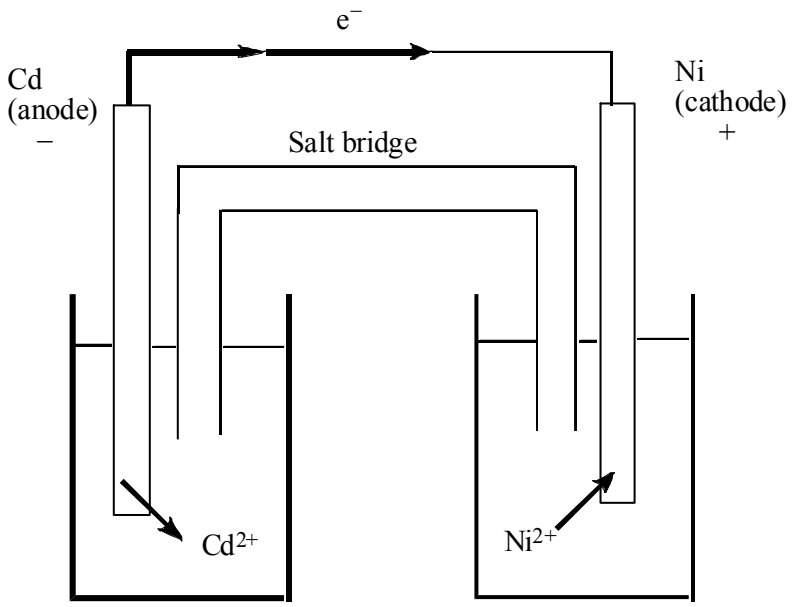
19.55. The half-cell reactions, the overall cell reaction, and the sketch are

$$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$$

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+}(aq) + Ni(s)$$



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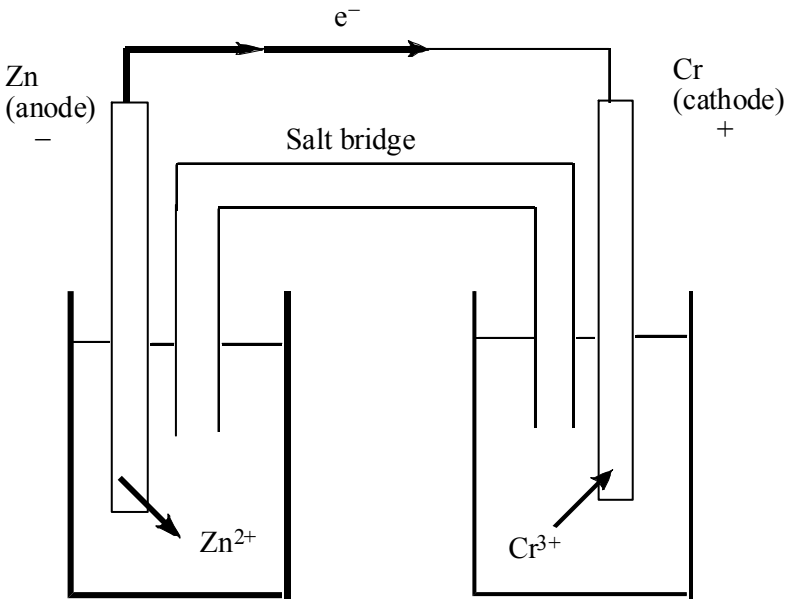
19.56. The half-cell reactions, the overall cell reaction, and the sketch are

$3\ Zn(s) \rightarrow 3Zn^{2+}(aq) + 6e^-$

$2Cr^{3+}(aq) + 6e^- \rightarrow 2Cr(s)$

$3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$



19.57. The half-cell reactions are

$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

n equals 2, and the maximum work for the reaction as written is

$w_{max} = -nFE_{cell} = -2 \times 9.6485 \times 10^4\ C \times 0.72\ V = -1.\underline{3}89 \times 10^5\ C \bullet V = -1.\underline{3}89 \times 10^5\ J$

Because this is the work obtained by reduction of 2 mol of Fe^{3+}, the work for 1 mol is

$w_{max} = (-1.389 \times 10^5\ J)/2\ mol = -6.\underline{9}45 \times 10^4 = -6.9 \times 10^4\ J = -69\ kJ$

19.58. The half-cell reactions are

$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

n equals 2, and the maximum work for the reaction as written is

$w_{max} = -nFE_{cell} = -2 \times 9.6485 \times 10^{-4}\ C \times 0.853\ V = -1.6\underline{4}6 \times 10^5\ C \bullet V$
$= -1.6\underline{4}6 \times 10^5\ J$

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For 20.0 g of zinc, the maximum work is

$$20.0 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{-1.646 \times 10^5 \text{ J}}{1 \text{ mol Zn}} = -5.0\underline{3}44 \times 10^4 = -5.03 \times 10^4 \text{ J}$$

19.59. The half-cell reactions are

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$$

n equals 2, and the maximum work for the reaction as written is

$$w_{max} = -nFE_{cell} = -2 \times 9.6485 \times 10^4 \text{ C} \times 0.97 \text{ V} = -1.\underline{8}7 \times 10^5 \text{ C}\bullet\text{V} = -1.\underline{8}7 \times 10^5 \text{ J}$$

For 30.0 g of nickel, the maximum work is

$$30.0 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \times \frac{-1.87 \times 10^5 \text{ J}}{1 \text{ mol Ni}} = -9.\underline{5}6 \times 10^4 \text{ J} = -96 \text{ kJ}$$

19.60. The half-cell reactions are

$$3O_2(g) + 12H^+ + 12e^- \rightarrow 6H_2O(l)$$

$$4Al(s) \rightarrow 4Al^{3+}(aq) + 12e^-$$

n equals 12, and the maximum work for the reaction as written is

$$w_{max} = -nFE_{cell} = -(12)(9.6485 \times 10^4 \text{ C})(1.15 \text{ V}) = -1.3\underline{3}1 \times 10^6 \text{ C}\bullet\text{V} = -1.3\underline{3}1 \times 10^6 \text{ J}$$

For 50.0 g of aluminum, the maximum work is

$$50.0 \text{ g} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{-1.331 \times 10^6 \text{ J}}{4 \text{ mol Al}} = -6.1\underline{6}9 \times 10^5 = -6.17 \times 10^5 \text{ J}$$

19.61. The half-reactions and corresponding electrode potentials are

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l) \qquad 0.96 \text{ V}$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad 1.23 \text{ V}$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad 1.49 \text{ V}$$

The order by increasing oxidizing strength is $NO_3^-(aq)$, $O_2(g)$, $MnO_4^-(aq)$.

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19.62. The half-reactions and corresponding electrode potentials are

$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \qquad 0.54\ V$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad 0.80\ V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad 1.49\ V$$

The order by increasing oxidizing strength is $I_2(s)$, $Ag^+(aq)$, $MnO_4^-(aq)$.

19.63. The half-reactions and corresponding electrode potentials are

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \quad -0.76\ V$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \quad -0.41\ V$$

$$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq) \quad 0.16\ V$$

$Zn(s)$ is the strongest, and $Cu^+(aq)$ is the weakest.

19.64. The half-reactions and corresponding electrode potentials are

$$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq) \qquad 0.15\ V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad 0.34\ V$$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \qquad 0.54\ V$$

$Sn^{2+}(aq)$ is the strongest and $I^-(aq)$ is the weakest reducing agent.

19.65.

a. In this reaction, Sn^{4+} is the oxidizing agent on the left side; Fe^{3+} is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq) \quad E^\circ = 0.15\ V$$

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad E^\circ = 0.77\ V$$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe^{3+} is the stronger oxidizing agent. The reaction is nonspontaneous as written.

b. In this reaction, MnO_4^- is the oxidizing agent on the left side; O_2 is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E^\circ = 1.23\ V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E^\circ = 1.49\ V$$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so MnO_4^- is the stronger oxidizing agent. The reaction is spontaneous as written.

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19.66.

a. The reduction half-reactions and standard potentials are

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E° = 0.77\ V$$

$$Cr_2O_7^{2-}(aq) + 14H^+ + 6e^- \rightarrow 2Cr^{2+}(aq) + 7H_2O(l) \qquad E° = 1.33\ V$$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so $Cr_2O_7^{2-}$ is the stronger oxidizing agent. Thus, $Cr_2O_7^{2-}$ will oxidize iron(II) ion in acidic solution under standard conditions.

b. The reduction half-reactions and standard electrode potentials are

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E° = -0.23\ V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = 0.34\ V$$

The stronger reducing agent is the one involved in the half-reaction with the smaller standard electrode potential, so Ni(*s*) is the stronger reducing agent. Thus, copper metal will not reduce Ni(II) ion spontaneously.

19.67. The reduction half-reactions and standard electrode potentials are

$$Br_2(l) + 2e^- \rightarrow 2Br^-(aq) \quad E° = 1.07\ V$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \quad E° = 1.36\ V$$

$$F_2(g) + 2e^- \rightarrow 2F^-(aq) \quad E° = 2.87\ V$$

From these, you see that the order of increasing oxidizing strength is Br_2, Cl_2, F_2. Therefore, chlorine gas will oxidize Br^- but will not oxidize F^-. The balanced equation for the reaction is

$$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$$

19.68. The reduction half-reactions and standard electrode potentials are

$$Br_2(l) + 2e^- \rightarrow 2Br^-(aq) \qquad E° = 1.07\ V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E° = 1.33\ V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E° = 1.49\ V$$

From these, you see that the order of increasing oxidizing strength is Br_2, $Cr_2O_7^{2-}$, MnO_4^-. Thus, $Cr_2O_7^{2-}$ will oxidize Br^- but will not oxidize Mn^{2+}. The balanced equation for the reaction is

$$Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(l) + 7H_2O(l)$$

19.69. The half-reactions and standard electrode potentials are

$$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^- \quad -E°_{Cr} = 0.74\ V$$

$$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l) \quad E°_{Hg} = 0.80\ V$$

Obtain the cell potential by adding the half-cell potentials.

$$E°_{cell} = E°_{Hg} - E°_{Cr} = 0.80\ V + 0.74\ V = 1.54\ V$$

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19.70. The half-reactions and standard electrode potentials are

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \quad -E°_{Sn} = 0.14 \text{ V}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E°_{Cu} = 0.34 \text{ V}$$

Obtain the cell potential by adding the half-cell potentials.

$$E°_{cell} = E°_{Cu} - E°_{Sn} = 0.34 \text{ V} + 0.14 \text{ V} = 0.48 \text{ V}$$

19.71. The half-reactions and standard electrode potentials are

$$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^- \quad -E°_{Cr} = 0.74 \text{ V}$$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \quad E°_{I_2} = 0.54 \text{ V}$$

Obtain the cell potential by adding the half-cell potentials.

$$E°_{cell} = E°_{Cr} - E°_{I_2} = 0.54 \text{ V} + 0.74 \text{ V} = 1.28 \text{ V}$$

19.72. The half-reactions and standard electrode potentials are

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \quad -E°_{Al} = 1.66 \text{ V}$$

$$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l) \quad E°_{Hg} = 0.80 \text{ V}$$

Obtain the cell potential by adding the half-cell potentials.

$$E°_{cell} = E°_{Hg} - E°_{Al} = 0.80 \text{ V} + 1.66 \text{ V} = 2.46 \text{ V}$$

19.73. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$3Cu(s) \rightarrow 3Cu^{2+}(aq) + 6e^- \qquad E° = -0.34 \text{ V}$$

$$2NO_3^-(aq) + 8H^+(aq) + 6e^- \rightarrow 2NO(g) + 4H_2O(l) \qquad E° = 0.96 \text{ V}$$

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l) \qquad E° = 0.62 \text{ V}$$

Note that each half-reaction involves six electrons, hence $n = 6$. Therefore,

$$\Delta G° = -nFE°_{cell} = -6 \times 9.6485 \times 10^4 \text{ C} \times 0.62 \text{ V} = -3.58 \times 10^5 \text{ J} = -3.6 \times 10^5 \text{ J}$$

Thus, the standard free-energy change is -3.6×10^2 kJ.

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19.74. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$4Al(s) \rightarrow 4Al^{3+}(aq) + 12e^-$	$-E° = 1.66$ V
$3O_2(g) + 12H^+(aq) + 12e^- \rightarrow 6H_2O(l)$	$E° = 1.23$ V
$4Al(s) + 3O_2(g) + 12H^+(aq) \rightarrow 4Al^{3+}(aq) + 6H_2O(l)$	$E°_{cell} = 2.89$ V

Note that each half-reaction involves twelve electrons, hence $n = 12$. Therefore,

$$\Delta G° = -nFE°_{cell} = -12 \text{ x } 9.6485 \text{ x } 10^4 \text{ C x } 2.89 \text{ V} = -3.346 \text{ x } 10^6 \text{ J} = -3.35 \text{ x } 10^6 \text{ J}$$

Thus, the standard free-energy change is $-3.35 \text{ x } 10^3$ kJ.

19.75. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$2I(aq) \rightarrow I_2(s) + 2e$	$E° = 0.54$ V
$Cl_2(g) + 2e \rightarrow 2Cl(aq)$	$E° = 1.36$ V
$2I(aq) + Cl_2(g) \rightarrow I_2(s) + 2Cl(aq)$	$E°_{cell} = 0.82$ V

Note that each half-reaction involves two electrons, hence $n = 2$. Therefore,

$$\Delta G° = -nFE°_{cell} = -2 \text{ x } 9.6485 \text{ x } 10^4 \text{ C x } 0.82 \text{ V} = -1.58 \text{ x } 10^5 \text{ J} = -1.6 \text{ x } 10^5 \text{ J}$$

Thus, the standard free-energy change is $-1.6 \text{ x } 10^2$ kJ.

19.76. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$Na(s) \rightarrow Na^+(aq) + e$	$E° = 2.71$ V
$1/2Br_2(g) + e \rightarrow Br(aq)$	$E° = 1.07$ V
$Na(s) + 1/2Br_2(g) \rightarrow Na^+(aq) + Br(aq)$	$E°_{cell} = 3.78$ V

Note that each half-reaction involves one electron, hence $n = 1$. Therefore,

$$\Delta G° = -nFE°_{cell} = -1 \text{ x } 9.6485 \text{ x } 10^4 \text{ C x } 3.78 \text{ V} = -3.647 \text{ x } 10^5 \text{ J} = -3.65 \text{ x } 10^5 \text{ J}$$

Thus, the standard free-energy change is −365 kJ.

19.77. Write the equation with the appropriate $\Delta G_f°$ beneath each substance.

	$Mg(s)$	$+ 2Ag^+(aq) \rightarrow$	$Mg^{2+}(aq)$	$+ 2Ag(s)$
$\Delta Gf°$:	0	2 x 77.12	-454.8	0KJ

Hence,

$$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants})$$
$$= [-454.8 - 2 \text{ x } 77.12] \text{ kJ} = -609.04 \text{ kJ} = -6.0904 \text{ x } 10^5 \text{ J}$$

Obtain n by splitting the reaction into half-reactions.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

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Each half-reaction involves two electrons, so $n = 2$. Therefore,

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$-6.0904 \times 10^5 \text{ J} = -2 \times 9.6485 \times 10^4 \text{ C} \times E^\circ_{cell}$$

Rearrange and solve for E°_{cell}. Recall that J = C•V.

$$E^\circ_{cell} = \frac{-6.0904 \times 10^5 \text{ J}}{-2 \times 9.6485 \times 10^4 \text{ C}} = 3.15\underline{6}1 = 3.156 \text{ V}$$

19.78. Write the equation with the appropriate ΔG_f° beneath each substance.

$$\begin{array}{lccccc} & 2Al(s) & + & 3Cu^{2+}(aq) & \rightarrow & 2Al^{3+}(aq) + 3Cu(s) \\ \Delta G_f^\circ: & 0 & & 3 \times 65.52 & & 2 \times (-485) \end{array}$$

Hence,

$$\Delta G^\circ = \Sigma n\Delta G_f^\circ(\text{products}) - \Sigma m\Delta G_f^\circ(\text{reactants})$$

$$= [2 \times -485 - 3 \times 65.52] \text{ kJ} = -116\underline{6}.56 \text{ kJ} = -1.16\underline{6}56 \times 10^6 \text{ J}$$

Obtain n by splitting the reaction into half-reactions.

$$2Al(s) \rightarrow 2Al^{3+}(aq) + 3e^-$$

$$3Cu^{2+}(aq) + 3e^- \rightarrow 3Cu(s)$$

Each half-reaction involves three electrons, so $n = 3$. Therefore,

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$-1.16656 \times 10^6 \text{ J} = -3 \times 9.6485 \times 10^4 \text{ C} \times E^\circ_{cell}$$

Rearrange and solve for E°_{cell}. Recall that J = C•V.

$$E^\circ_{cell} = \frac{-1.16656 \times 10^6 \text{ J}}{-3 \times 9.6485 \times 10^4 \text{ C}} = 4.03\underline{0}1 = 4.030 \text{ V}$$

19.79. Write the equation with the appropriate ΔG_f° beneath each substance:

$$\begin{array}{lccccccc} & PbO_2(s) & + & 2HSO_4^+(aq) & + & 2H^+(aq) + Pb(s) & \rightarrow & 2PbSO_4(s) + 2H_2O(l) \\ \Delta G_f^\circ: & -189.3 & & 2(-756) & & 0 \quad 0 & & 2(-813.2) \quad 2(-237.1)\text{KJ} \end{array}$$

Hence,

$$\Delta G^\circ = [2 \times (-813.2) + 2 \times (-237.1) - (-189.3) - 2 \times (-756)] \text{ kJ}$$

$$= -39\underline{9}.30 \text{ kJ} = -3.9\underline{9}30 \times 10^5 \text{ J}$$

Obtain n by splitting the reaction into half-reactions.

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

$$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

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Each half-reaction involves two electrons, so $n = 2$. Therefore,

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$-3.9930 \times 10^5 \text{ J} = -2 \times 9.6485 \times 10^4 \text{ C} \times E^\circ_{cell}$$

Rearrange and solve for E°_{cell}. Recall that J = C•V.

$$E^\circ_{cell} = \frac{-3.9930 \times 10^5 \text{ J}}{-2 \times 9.6485 \times 10^4 \text{ C}} = 2.0\underline{6}92 = 2.07 \text{ V}$$

19.80. Write the equation with the appropriate ΔG_f° beneath each substance:

$$5H_2C_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 8H_2O(l) + 2Mn^{2-}(aq)$$

ΔG_f°: 5(-698) 2(-447.3) 0 10(-394.4) 8(-237.1) 2(-223)KJ

Hence,

$$\Delta G^\circ = [10(-394.4) + 8(-237.1) + 2(-223) - 5(-698) - 2(-447.3)] \text{ kJ}$$

$$= -190\underline{2}.2 \text{ kJ} = -1.90\underline{2}2 \times 10^6 \text{ J}$$

Obtain n by splitting the reaction into half-reactions.

$$5H_2C_2O_4(aq) \rightarrow 10CO_2(g) + 10H^+(aq) + 10e^-$$

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

Each half-reaction involves ten electrons, so $n = 10$. Therefore,

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$-1.9022 \times 10^6 \text{ J} = -10 \times 9.6485 \times 10^4 \text{ C} \times E^\circ_{cell}$$

Rearrange and solve for E°_{cell}. Recall that J = C•V.

$$E^\circ_{cell} = \frac{-1.9022 \times 10^6 \text{ J}}{-10 \times 9.6485 \times 10^4 \text{ C}} = 1.97\underline{1}5 = 1.972 \text{ V}$$

19.81. The half-reactions and standard electrode potentials are

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \qquad -E^\circ_{Cu} = -0.34 \text{ V}$$

$$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq) \qquad E^\circ_{Fe^{3+}} = 0.77 \text{ V}$$

The standard cell potential for the cell is

$$E^\circ_{cell} = E^\circ_{Fe^{3+}} - E^\circ_{Cu} = 0.77 \text{ V} - 0.34 \text{ V} = 0.43 \text{ V}$$

Note that $n = 2$. Substitute into the equation relating E° and K. Note that $K = K_c$.

$$0.43 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K_c yields

$$\log K_c = 1\underline{4}.52$$

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Take the antilog of both sides:

$$K_c = \text{antilog}\,(14.52) = 3.4 \times 10^{\underline{14}} = 10^{14}$$

19.82. The half-reactions and standard electrode potentials are

$$2\text{Hg}(l) \rightarrow \text{Hg}_2^{2+}(aq) + 2\text{e}^- \qquad -E°_{\text{Hg}} = -0.80\ \text{V}$$

$$\text{Sn}^{4+}(aq) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(aq) \qquad E°_{\text{Sn}^{2+}} = 0.15\ \text{V}$$

The standard cell potential for the cell is

$$E°_{\text{cell}} = E°_{\text{Sn}^{2+}} - E°_{\text{Hg}} = 0.15\ \text{V} - 0.80\ \text{V} = -0.65\ \text{V}$$

Note that $n = 2$. Substitute into the equation relating $E°$ and K. Note that $K = K_c$.

$$-0.65\ \text{V} = \frac{0.0592}{2} \log K_c$$

Solving for K_c yields

$$\log K_c = -2\underline{1}.959$$

Take the antilog of both sides:

$$K_c = \text{antilog}\,(-2\underline{1}.959) = 1.09 \times 10^{-\underline{22}} = 10^{-22}$$

19.83. The half-reactions and standard electrode potentials are

$$\text{Cu}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{e}^- \quad -E° = -0.16\ \text{V}$$

$$\text{Cu}^+(aq) + \text{e}^- \rightarrow \text{Cu}(s) \qquad E° = 0.52\ \text{V}$$

The standard cell potential for the cell is

$$E°_{\text{cell}} = 0.52\ \text{V} - 0.16\ \text{V} = 0.36\ \text{V}$$

Note that n equals 1. Substitute into the equation relating $E°$ and K. Note that K equals K_c.

$$0.36\ \text{V} = \frac{0.0592}{1} \log K_c$$

Solving for K_c, you get

$$\log K_c = 6.\underline{0}81$$

Take the antilog of both sides:

$$K_c = \text{antilog}\,(6.081) = \underline{1}.2 \times 10^6 = 1 \times 10^6$$

19.84. The half-reactions and standard electrode potentials are

$$\text{ClO}_2^-(aq) + 2\text{OH}^-(aq) \rightarrow \text{ClO}_3^-(aq) + \text{H}_2\text{O}(l) + 2\text{e}^- \qquad -E° = -0.35\ \text{V}$$

$$\text{ClO}_4^-(aq) + \text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{ClO}_3^-(aq) + 2\text{OH}^-(aq) \qquad E° = 0.17\ \text{V}$$

The standard cell potential for the cell is

$$E°_{\text{cell}} = 0.17\ \text{V} - 0.35\ \text{V} = -0.18\ \text{V}$$

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Note that n equals 2. Substitute into the equation relating $E°$ and K. Note that K equals K_c.

$$-0.18 \text{ V} = \frac{0.0592}{2} \log K_c$$

Solving for K_c yields

$$\log K_c = -6.\underline{0}81$$

Take the antilog of both sides:

$$K_c = \text{antilog}(-6.081) = \underline{8}.29 \times 10^{-7} = 8 \times 10^{-7}$$

19.85. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$2\text{Cr}(s) \rightarrow 2\text{Cr}^{3+}(aq) + 6\text{e}^-$	$-E° = 0.74$ V
$3\text{Ni}^{2+}(aq) + 6\text{e}^- \rightarrow 3\text{Ni}(s)$	$E° = -0.23$ V
$2\text{Cr}(s) + 3\text{Ni}^{2+}(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 3\text{Ni}(s)$	$E°_{\text{cell}} = 0.51$ V

Note that n equals 6. The reaction quotient is

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(1.0 \times 10^{-3})^2}{(1.5)^3} = 2.\underline{9}62 \times 10^{-7}$$

The standard cell potential is 0.51 V, so the Nernst equation becomes

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592}{\text{n}} \log Q$$

$$= 0.51 - \frac{0.0592}{6} \log (2.962 \times 10^{-7})$$

$$= 0.51 - (-0.06\underline{4}41) = 0.5\underline{7}4 = 0.57 \text{ V}$$

19.86. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2\text{e}^-$	$-E° = 0.23$ V
$\text{Sn}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Sn}(s)$	$E° = -0.14$ V
$\text{Ni}(s) + \text{Sn}^{2+}(aq) \rightarrow \text{Ni}^{2+}(aq) + \text{Sn}(s)$	$E°_{\text{cell}} = 0.09$ V

Note that n equals 2. The reaction quotient is

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Sn}^{2+}]} = \frac{1.0}{1.0 \times 10^{-4}} = 1.\underline{0}0 \times 10^4$$

The standard cell potential is 0.09 V, so the Nernst equation becomes

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592}{\text{n}} \log Q$$

$$= 0.09 - \frac{0.0592}{2} \log (1.00 \times 10^4)$$

$$= 0.09 \text{ V} - (0.1\underline{1}84 \text{ V}) = -0.0\underline{2}84 = -0.03 \text{ V}$$

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19.87. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$10Br^-(aq) \rightarrow 5Br_2(l) + 10e^- \qquad -E° = -1.07\ V$$
$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) \qquad E° = 1.49\ V$$
$$2MnO_4^-(aq) + 10Br^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Br_2(l) + 8H_2O(l) \qquad E°_{cell} = 0.42\ V$$

Note that n equals 10. The reaction quotient is

$$Q = \frac{[Mn^{2+}]^2}{[MnO_4^{2-}]^2[Br^-]^{10}[H^+]^{16}} = \frac{(0.15)^2}{(0.010)^2(0.010)^{10}(1.0)^{16}} = 2.\underline{2}5 \times 10^{22}$$

The standard cell potential is 0.42 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n}\log Q = 0.42 - \frac{0.0592}{10}\log(2.25 \times 10^{22})$$
$$= 0.42 - (0.1\underline{3}23) = 0.2\underline{8}76 = 0.29\ V$$

19.88. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$$6I^-(aq) \rightarrow 3I_2(s) + 6e^- \qquad -E° = -0.54\ V$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E° = 1.33\ V$$
$$Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3I_2(s) + 7H_2O(l) \qquad E°_{cell} = 0.79\ V$$

Note that n equals 6. The reaction quotient is

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][I^-]^6[H^+]^{14}} = \frac{(0.40)^2}{(0.020)(0.015)^6(0.50)^{14}} = 1.\underline{1}507 \times 10^{16}$$

The standard cell potential is 0.79 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n}\log Q = 0.79 - \frac{0.0592}{6}\log(1.1507 \times 10^{16})$$
$$= 0.79 - (0.1\underline{5}84) = 0.6\underline{3}15 = 0.63\ V$$

19.89. The overall reaction is

$$Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+}(aq) + Ni(s)$$

Note that n equals 2. The reaction quotient is

$$Q = \frac{[Cd^{2+}]}{[Ni^{2+}]} = \frac{[Cd^{2+}]}{1.0} = [Cd^+]$$

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The standard cell potential is 0.170 V, and the cell potential is 0.240 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

$$0.240 = 0.170 - \frac{0.0592}{2} \log Q$$

Rearrange and solve for log Q.

$$\log Q = \frac{-2}{0.0592} \times (0.240 - 0.170) = -2.\underline{3}648$$

Take the antilog of both sides.

$$Q = [Cd^{2+}] = \text{antilog}(-2.3648) = \underline{4}.31 \times 10^{-3} = 0.004\ M$$

The Cd^{2+} concentration is 0.004 M.

19.90. The overall reaction is

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Note that n equals 2. The reaction quotient is

$$Q = \frac{[Zn^{2+}] \times P_{H_2}}{[H^+]^2} = \frac{(1.0)(1.0)}{[H^+]^2} = \frac{1}{[H^+]^2}$$

The standard cell potential is equal to the standard oxidation potential for Zn, which is 0.76 V. The cell potential is 0.475 V, so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

$$0.475 = 0.76 - \frac{0.0592}{2} \log Q$$

Rearrange and solve for log Q.

$$\log Q = \frac{-2}{0.0592} \times (0.475 - 0.76) = 9.\underline{6}28$$

Use the properties of logs to simplify log Q as follows:

$$\log Q = \log \frac{1}{[H^+]^2} = \log [H^+]^{-2} = -2 \log [H^+] = 2(-\log [H^+]) = 2 \times \text{pH}$$

Therefore,

$$\log Q = 2 \times \text{pH} = 9.628$$

$$\text{pH} = 9.628 \div 2 = 4.\underline{8}14 = 4.8$$

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19.91.

a. The cathode reaction is $Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$.

The anode reaction is $S^{2-}(l) \rightarrow S(l) + 2e^-$.

b. The cathode reaction is $Cs^+(l) + e^- \rightarrow Cs(l)$.

The anode reaction is $4OH^-(l) \rightarrow O_2(g) + 2H_2O(g) + 4e^-$.

19.92.

a. The cathode reaction is $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$.

The anode reaction is $2Br^-(l) \rightarrow Br_2(l) + 2e^-$.

b. The cathode reaction is $Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$.

The anode reaction is $4OH^-(l) \rightarrow O_2(g) + 2H_2O(g) + 4e^-$.

19.93.

a. The species you should consider for half-reactions are Na^+, SO_4^{2-}, and H_2O. The possible cathode reactions are

$Na^+(aq) + e^- \rightarrow Na(s)$ $\quad E° = -2.71$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E° = -0.83$ V

Because the electrode potential for H_2O is larger (less negative), it is easier to reduce.

The possible anode reactions are

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -1.23$ V

$2SO_4^{2-}(aq) \rightarrow S_2O_4^{2-}(aq) + 2e^-$ $\quad E° = -2.01$ V

Because the electrode potential for H_2O is less negative, it is easier to oxidize.

The expected half-reactions are

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -1.23$ V

$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$ $\quad E° = -0.83$ V

The overall reaction is

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

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b. The species you should consider for half-reactions are K^+, Br^-, and H_2O. The possible cathode reactions are

$$K^+(aq) + e^- \rightarrow K(s) \qquad E° = -2.92\ V$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\ V$$

Because the electrode potential for H_2O is larger (less negative), it is easier to reduce. The possible anode reactions are

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23\ V$$
$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \qquad E° = -1.07\ V$$

Because the electrode potential for Br^- is less negative, it is easier to oxidize.

The expected half-reactions are

$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \qquad E° = -1.07\ V$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\ V$$

The overall reaction is

$$2Br^-(aq) + 2H_2O(l) \rightarrow Br_2(l) + H_2(g) + 2OH^-$$

19.94.

a. The species you should consider for half-reactions are Cu^{2+}, Cl^-, and H_2O. The possible cathode reactions are

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = 0.34\ V$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\ V$$

Because the electrode potential for Cu^{2+} is larger (positive), it is easier to reduce. The possible anode reactions are

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23\ V$$
$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad E° = -1.36\ V$$

Because the electrode potential for H_2O is less negative, it is easier to oxidize.

The expected half-reactions are

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23\ V$$
$$2Cu^{2+}(aq) + 4e^- \rightarrow 2Cu(s) \qquad E° = 0.34\ V$$

The overall reaction is

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + 4H^+(aq) + O_2(g)$$

b. The species you should consider for half-reactions are Cu^{2+} and H_2O. The possible cathode reactions are

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = 0.34\ V$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\ V$$

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Because the electrode potential for Cu^{2+} is larger (less negative), it is easier to reduce. The anode reaction is

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23 \text{ V}$$

The expected half-reactions are

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23 \text{ V}$$

$$2Cu^{2+}(aq) + 4e^- \rightarrow 2Cu(s) \qquad E° = 0.34 \text{ V}$$

The overall reaction is

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + 4H^+(aq) + O_2(g)$$

19.95. The conversion of grams of aluminum (3.61 kg = 3.61 x 10^3 g) to coulombs required to give this amount of aluminum is

$$3.61 \times 10^3 \text{ g} \times \frac{1 \text{ mol Al}}{26.98 \text{ g}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \times \frac{9.6485 \times 10^4 \text{ C}}{1 \text{ mol e}^-} = 3.872 \times 10^7 = 3.87 \times 10^7 \text{ C}$$

19.96. The conversion of grams of chlorine (1.18 kg = 1.18 x 10^3 g) to coulombs required to produce this amount of chlorine is

$$1.18 \times 10^3 \text{ g} \times \frac{1 \text{ mol } Cl_2}{70.91 \text{ g}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol } Cl_2} \times \frac{9.6485 \times 10^4 \text{ C}}{1 \text{ mol e}^-}$$

$$= 3.211 \times 10^6 = 3.21 \times 10^6 \text{ C}$$

Using the current of 5.00 x 10^2 A, calculate the time in seconds:

$$\text{Time} = \frac{1 \text{ mol } Cl_2}{70.91 \text{ g}} = \frac{1 \text{ mol } Cl_2}{70.91 \text{ g}} = 6.423 \times 10^3 = 6.42 \times 10^3 \text{ s}$$

19.97. The conversion of coulombs to grams of lithium is

$$5.00 \times 10^3 \text{ C} \times \frac{1 \text{ mol e}^-}{9.6485 \times 10^4 \text{ C}} \times \frac{1 \text{ mol Li}}{1 \text{ mol e}^-} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} = 0.3596 = 0.360 \text{ g Li}$$

19.98. The conversion of current and time (221 min = 1.326 x 10^4 s) to coulombs is

$$C = \text{amp} \times \text{sec} = 1.51 \text{ A} \times 1.326 \times 10^4 \text{ s} = 2.002 \times 10^4 \text{ C}$$

The conversion of coulombs to grams of cadmium is

$$2.002 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^-}{9.6485 \times 10^4 \text{ C}} \times \frac{1 \text{ mol Cd}}{2 \text{ mol e}^-} \times \frac{112.4 \text{ g Cd}}{1 \text{ mol Cd}} = 11.66 = 11.7 \text{ g Cd}$$

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■ SOLUTIONS TO GENERAL PROBLEMS

19.99.

a. The half-reactions and net ionic equation are

$$\begin{array}{lcl} 3Fe(s) & \rightarrow & 3Fe^{2+}(aq) + 6e \\ 2NO_3(aq) + 8H^+(aq) + 6e & \rightarrow & 2NO(g) + 4H_2O(l) \\ \hline 3Fe(s) + 2NO_3(aq) + 8H^+(aq) & \rightarrow & 3Fe^{2+}(aq) + 2NO(g) + 4H_2O(l) \end{array}$$

b. The half-reactions and net ionic equation are

$$\begin{array}{lcl} 3Fe^{2+}(aq) & \rightarrow & 3Fe^{3+}(aq) + 3e^- \\ NO_3^-(aq) + 4H^+(aq) + 3e^- & \rightarrow & NO(g) + 2H_2O(l) \\ \hline 3Fe^{2+}(aq) + NO_3^-(aq) + 4H^+(aq) & \rightarrow & 3Fe^{3+}(aq) + NO(g) + 2H_2O(l) \end{array}$$

c. Add the results from parts a and b, and divide all coefficients by a factor of 3.

$$\begin{array}{lcl} 3Fe(s) + 2NO_3^-(aq) + 8H^+(aq) & \rightarrow & 3Fe^{2+}(aq) + 2NO(g) + 4H_2O(l) \\ 3Fe^{2+}(aq) + NO_3^-(aq) + 4H^+(aq) & \rightarrow & 3Fe^{3+}(aq) + NO(g) + 2H_2O(l) \\ \hline Fe(s) + NO_3^-(aq) + 4H^+(aq) & \rightarrow & Fe^{3+}(aq) + NO(g) + 2H_2O(l) \end{array}$$

19.100.

a. The half-reactions and net ionic equation are

$$\begin{array}{lcl} 3Tl(s) & \rightarrow & 3Tl^+(aq) + 3e^- \\ NO_3^-(aq) + 4H^+(aq) + 3e^- & \rightarrow & NO(g) + 2H_2O(l) \\ \hline 3Tl(s) + NO_3^-(aq) + 4H^+(aq) & \rightarrow & 3Tl^+(aq) + NO(g) + 2H_2O(l) \end{array}$$

b. The half-reactions and net ionic equation are

$$\begin{array}{lcl} 3Tl^+(aq) & \rightarrow & 3Tl^{3+}(aq) + 6e^- \\ 2NO_3^-(aq) + 8H^+(aq) + 6e^- & \rightarrow & 2NO(g) + 4H_2O(l) \\ \hline 3Tl^+(aq) + 2NO_3^-(aq) + 8H^+(aq) & \rightarrow & 3Tl^+(aq) + 2NO(g) + 4H_2O(l) \end{array}$$

c. Add the results from parts a and b, and divide all coefficients by a factor of 3.

$$\begin{array}{lcl} 3Tl(s) + NO_3^-(aq) + 4H^+(aq) & \rightarrow & 3Tl^+(aq) + NO(g) + 2H_2O(l) \\ 3Tl^+(aq) + 2NO_3^-(aq) + 8H^+(aq) & \rightarrow & 3Tl^+(aq) + 2NO(g) + 4H_2O(l) \\ \hline Tl(s) + NO_3^-(aq) + 4H^+(aq) & \rightarrow & Tl^{3+}(aq) + NO(g) + 2H_2O(l) \end{array}$$

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19.101.

a. The two balanced half-reactions are

$$8S^{2-} \rightarrow S_8 + 16e^- \quad \text{(oxidation)}$$

$$MnO_4(l) + 4H^+ + 3e^- \rightarrow MnO_2 + H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction half-reaction by 16, and then add together. Cancel the forty-eight electrons from each side. The balanced equation in acidic solution is

$$16MnO_4^- + 24S^{2-} + 64H^+ \rightarrow 16MnO_2 + 3S_8 + 32H_2O$$

Now add sixty-four OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel thirty-two H_2O on each side. The balanced equation in basic solution is

$$16MnO_4^-(aq) + 24S^{2-}(aq) + 32H_2O(l) \rightarrow 16MnO_2(aq) + 3S_8(aq) + 64OH^-(l)$$

b. The two balanced half-reactions are

$$HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^- \quad \text{(oxidation)}$$

$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3, and then add together. Cancel the six electrons from each side. Also, cancel six H^+ and three H_2O from each side. The balanced equation is

$$IO_3^-(aq) + 3HSO_3^-(aq) \rightarrow I^- + 3SO_4^{2-}(aq) + 3H^+(aq)$$

c. The two balanced half-reactions are

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^- \quad \text{(oxidation)}$$

$$CrO_4^{2-} + 4H^+ + 3e^- \rightarrow Cr(OH)_4^- \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3, and then add together. Cancel the three electrons and cancel three H^+ from each side. The balanced equation in acidic solution is

$$CrO_4^{2-}(aq) + 3Fe(OH)_2(s) + H^+(aq) + 3H_2O(l) \rightarrow Cr(OH)_4^-(aq) + 3Fe(OH)_3(s)$$

Now add one OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then, combine the H_2O's on the left side into a single term. The balanced equation in basic solution is

$$CrO_4^{2-}(aq) + 3Fe(OH)_2(aq) + 4H_2O(l) \rightarrow Cr(OH)_4^-(aq) + 3Fe(OH)_3(s) + OH^-(aq)$$

d. The two balanced half-reactions are

$$Cl_2 + 2H_2O \rightarrow 2ClO^- + 4H^+ + 2e^- \quad \text{(oxidation)}$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \quad \text{(reduction)}$$

Add the two half-reactions together. Cancel the two electrons from each side. Divide all the coefficients by a factor of 2. The balanced equation in acidic solution is

$$Cl_2 + H_2O \rightarrow Cl^- + ClO^- + 2H^+$$

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Now add two OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel one H_2O on each side. The balanced equation in basic solution is

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

19.102.

a. The two balanced half-reactions are

$$8H_2S \rightarrow S_8 + 16H^+ + 2e^- \quad \text{(oxidation)}$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 5 and the reduction half-reaction by 16 and then add together. Cancel the eighty electrons from each side. Also, cancel eighty H^+ from each side.

The balanced equation is

$$16MnO_4^-(aq) + 40H_2S(aq) + 48H^+(aq) \rightarrow 16Mn^{2+}(aq) + 5S_8(aq) + 64H_2O(l)$$

b. The two balanced half-reactions are

$$Zn \rightarrow Zn^{2+} + 2e^- \quad \text{(oxidation)}$$
$$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 4, and then add together. The balanced equation is

$$2NO_3^-(aq) + 4Zn(s) + 10H^+(aq) \rightarrow N_2O(g) + 4Zn^{2+}(aq) + 5H_2O(l)$$

c. The two balanced half-reactions are

$$MnO_4^{2-} \rightarrow MnO_4^- + e^- \quad \text{(oxidation)}$$
$$MnO_4^{2-} + 4H^+ + 2e^- \rightarrow MnO_2 + 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 2, and then add together. Cancel the two electrons from each side. Also, combine the MnO_4^{2-} on the left into a single term. The balanced equation in acidic solution is

$$3MnO_4^{2-} + 4H^+ \rightarrow MnO_2 + 2MnO_4^- + 2H_2O$$

Now add four OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel two H_2O on each side. The balanced equation in basic solution is

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 2MnO_4^-(aq) + 4OH^-(aq)$$

d. The two balanced half-reactions are

$$Br_2 + 6H_2O \rightarrow 2BrO_3^- + 12H^+ + 10e^- \quad \text{(oxidation)}$$
$$Br_2 + 2e^- \rightarrow 2Br^- \quad \text{(reduction)}$$

Multiply the reduction half-reaction by 5, and then add together. Cancel the ten electrons from each side. Also, combine the Br_2 on the left into a single term. Divide all the coefficients by a factor of two. The balanced equation in acidic solution is

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

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Now add six OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel three H_2O on each side. The balanced equation in basic solution is

$$3Br_2(aq) + 6OH^-(aq) \rightarrow 5Br^-(aq) + BrO_3^-(aq) + 3H_2O(l)$$

19.103. This reaction takes place in basic solution. The skeleton equation is

$$Fe(OH)_2(s) + O_2(g) \rightarrow Fe(OH)_3(s)$$

The two balanced half-reactions are

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^- \quad \text{(oxidation)}$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 4, and then add together. Cancel the four electrons from each side. Also, cancel four H^+ and two H_2O from each side. The balanced equation in acidic or in basic solution is

$$4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$$

19.104. This reaction takes place in basic solution. The skeleton equation is

$$SnO_2^{2-}(aq) + Bi^{3+}(aq) \rightarrow SnO_3^{2-}(aq) + Bi(s)$$

The two balanced half-reactions are

$$SnO_2^{2-} + H_2O \rightarrow SnO_3^{2-} + 2H^+ + 2e^- \quad \text{(oxidation)}$$
$$Bi^{3+} + 3e^- \rightarrow Bi \quad \text{(reduction)}$$

Multiply the oxidation half-reaction by 3 and the reduction reaction by 2, and then add together. Cancel the six electrons from each side. The balanced equation in acidic solution is

$$2Bi^{3+} + 3SnO_2^{2-} + 3H_2O \rightarrow 2Bi + 3SnO_3^{2-} + 6H^+$$

Now add six OH^- to each side. Simplify by combining the H^+ and OH^- to give H_2O. Then cancel three H_2O on each side. The balanced equation in basic solution is

$$2Bi^{3+}(aq) + 3SnO_2^{2-}(aq) + 6OH^-(aq) \rightarrow 2Bi(s) + 3SnO_3^{2-}(aq) + 3H_2O(l)$$

19.105. The cell notation is $Ca(s)|Ca^{2+}(aq)||Cl_2(g)|Cl^-(aq)|Pt(s)$. The reactions are

Anode: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$ $\quad -E° = 2.76$ V

Cathode: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $\quad E° = 1.36$ V

$E°_{cell} = 1.36 \text{ V} + 2.76 \text{ V} = 4.12 \text{ V}$

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19.106. The cell notation is $Mg(s)|Mg^{2+}(aq)||Ag^{+}(aq)|Ag(s)$. The reactions are

Anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$ $\quad -E° = 2.38\ V$

Cathode: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $\quad E° = 0.80\ V$

$E°_{cell} = 0.80\ V + 2.38\ V = 3.18\ V$

19.107.

a. In this reaction, Fe^{3+} is the oxidizing agent on the left side; Ni^{2+} is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$ $\quad E° = -0.23\ V$

$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ $\quad E° = 0.77\ V$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe^{3+} is the stronger oxidizing agent. The oxidation of nickel by iron(III) is a spontaneous reaction.

b. In this reaction, Fe^{3+} is the oxidizing agent on the left side; Sn^{4+} is the oxidizing reagent on the right side. The corresponding standard electrode potentials are

$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$ $\quad E° = 0.15\ V$

$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ $\quad E° = 0.77\ V$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe^{3+} is the stronger oxidizing agent. The oxidation of tin(II) by iron(III) is a spontaneous reaction.

19.108.

a. The half-reactions and the corresponding standard electrode potential values are

$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ $\quad E° = 1.36\ V$

$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $\quad E° = 1.49\ V$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so MnO_4^{-} is the stronger oxidizing agent. The oxidation of chloride ion by permanganate ion is a spontaneous reaction.

b. The half-reactions and the corresponding standard electrode potential values are

$Cr_2O_2^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E° = 1.33\ V$

$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ $\quad E° = 1.36\ V$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Cl_2 is the stronger oxidizing agent. The oxidation of chloride ion by dichromate ion is not a spontaneous reaction.

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19.109. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$Pb(s)$	$\rightarrow$	$Pb^{2+}(aq) + 2e^-$	$-E° = 0.13$ V
$2H^+(aq) + 2e^-$	$\rightarrow$	$H_2(g)$	$E° = 0.00$ V
$Pb(s) + 2H^+(aq)$	$\rightarrow$	$Pb^{2+}(aq) + H_2(g)$	$E°_{cell} = 0.13$ V

Note that n equals 2. Next, use K_{sp} to calculate $[Pb^{2+}]$.

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{1.7 \times 10^{-8}}{1.0} = 1.7 \times 10^{-8}\ M$$

The reaction quotient for the cell reaction is

$$Q = \frac{[Pb^{2+}] \times P_{H_2}}{[H^+]^2} = \frac{(1.7 \times 10^{-8})(1.0)}{(1.0)^2} = 1.7 \times 10^{-8}$$

The standard cell potential is 0.13 V , so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

$$E_{cell} = 0.13\ \text{V} - \frac{0.0592}{2} \log (1.7 \times 10^{-8})$$

$$= 0.13\ \text{V} - (-0.2\underline{2}99\ \text{V}) = 0.3\underline{5}99 = 0.36\ \text{V}$$

19.110. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$H_2(g)$	$\rightarrow$	$2H^+(aq) + 2e^-$	$-E° = 0.00$ V
$2Ag^+(aq) + 2e^-$	$\rightarrow$	$2Ag(s)$	$E° = 0.80$ V
$H_2(g) + 2Ag^+(aq)$	$\rightarrow$	$2H^+(aq) + 2Ag(s)$	$E°_{cell} = 0.80$ V

Note that n equals 2. Next, use K_{sp} to calculate $[Ag^+]$.

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{1.0} = 1.8 \times 10^{-10}\ M$$

The reaction quotient for the cell reaction is

$$Q = \frac{[H^+]^2}{[Ag^+]^2 P_{H_2}} = \frac{(1.0)^2}{(1.8 \times 10^{-10})^2 (1.0)} = 3.\underline{0}86 \times 10^{19}$$

The standard cell potential is 0.80 V , so the Nernst equation becomes

$$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$$

$$E_{cell} = 0.80\ \text{V} - \frac{0.0592}{2} \log (3.086 \times 10^{19})$$

$$= 0.80\ \text{V} - (0.5\underline{7}68\ \text{V}) = 0.2\underline{2}31 = 0.22\ \text{V}$$

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19.111.

a. Note that $E° = 0.010$ V and n equals 2. Substitute into the equation relating $E°$ and K.

$$E° = \frac{0.0592}{n} \log K$$

$$0.010 \text{ V} = \frac{0.0592}{2} \log K$$

Solving for K, you get

$$\log K = 0.3\underline{3}78$$

Take the antilog of both sides:

$$K = K_c = \text{antilog}\,(0.3378) = 2.\underline{1}76 = 2.2$$

b. Substitute into the equilibrium expression using $[Sn^{2+}] = x$, and $[Pb^{2+}] = 1.0\ M - x$.

$$K_c = \frac{[Sn^{2+}]}{[Pb^{2+}]} = \frac{x}{1.0 - x} = 2.176$$

$$x = 0.6\underline{8}51\ M$$

$$[Pb^{2+}] = 1.0\ M - x = 0.\underline{3}149 = 0.3\ M$$

19.112.

a. Note that $E° = 0.030$ V and n equals 1. Substitute into the equation relating $E°$ and K.

$$E° = \frac{0.0592}{n} \log K$$

$$0.030 \text{ V} = \frac{0.0592}{1} \log K$$

Solving for K, you get

$$\log K = 0.5\underline{0}67$$

Take the antilog of both sides:

$$K = K_c = \text{antilog}\,(0.5067) = 3.\underline{2}11 = 3.2$$

b. After mixing equal volumes, the initial concentrations of Ag^+ and Fe^{2+} are 0.50 M. Substitute into the equilibrium expression using $[Fe^{3+}] = x$, and $[Ag^+] = [Fe^{2+}] = 0.50\ M - x$.

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{x}{(0.50 - x)^2} = 3.211$$

This equation can be rearranged to give the following quadratic equation:

$$3.211x^2 - 4.211x + 0.8029 = 0$$

$$x = \frac{-(-4.211) \pm \sqrt{(-4.211)^2 - 4(3.211)(0.8029)}}{2(3.211)} = 0.2\underline{3}14\ M$$

$$[Fe^{2+}] = 0.50 - x = 0.50\ M - 0.2314\ M = 0.2\underline{6}86 = 0.27\ M$$

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19.113.

a. The number of faradays is

$$1.0 \text{ mol } Na^+ \times \frac{1 \text{ mol } e^-}{1 \text{ mol } Na^+} \times \frac{1\ F}{1 \text{ mol } e^-} = 1.0\ F$$

The number of coulombs is

$$1.0\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 9.\underline{6}4 \times 10^4 = 9.6 \times 10^4 \text{ C}$$

b. The number of faradays is

$$1.0 \text{ mol } Cu^{2+} \times \frac{2 \text{ mol } e^-}{1 \text{ mol } Cu^{2+}} \times \frac{1\ F}{1 \text{ mol } e^-} = 2.0\ F$$

The number of coulombs is

$$2.0\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 1.\underline{9}2 \times 10^5 = 1.9 \times 10^5 \text{ C}$$

c. The number of faradays is

$$1.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.01 \text{ g } H_2O} \times \frac{2 \text{ mol } e^-}{1 \text{ mol } H_2O} \times \frac{1\ F}{1 \text{ mol } e^-} = 0.1\underline{1}10 = 0.11\ F$$

The number of coulombs is

$$0.1110\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 1.\underline{0}7 \times 10^4 = 1.1 \times 10^4 \text{ C}$$

d. The number of faradays is

$$1.0 \text{ g } Cl^- \times \frac{1 \text{ mol } Cl^-}{35.45 \text{ g } Cl^-} \times \frac{2 \text{ mol } e^-}{2 \text{ mol } Cl^-} \times \frac{1\ F}{1 \text{ mol } e^-} = 0.02\underline{8}20 = 0.028\ F$$

The number of coulombs is

$$0.02820\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 2.\underline{7}21 \times 10^3 = 2.7 \times 10^3 \text{ C}$$

19.114.

a. The number of faradays is

$$1.0 \text{ mol } Fe^{3+} \times \frac{1 \text{ mol } e^-}{1 \text{ mol } Fe^{3+}} \times \frac{1\ F}{1 \text{ mol } e^-} = 1.0\ F$$

The number of coulombs is

$$1.0\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 9.\underline{6}4 \times 10^4 = 9.6 \times 10^4 \text{ C}$$

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b. The number of faradays is

$$1.0 \text{ mol } Fe^{3+} \times \frac{3 \text{ mol } e^-}{1 \text{ mol } Fe^{3+}} \times \frac{1\ F}{1 \text{ mol } e^-} = 3.0\ F$$

The number of coulombs is

$$3.0\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 2.\underline{8}94 \times 10^5 = 2.9 \times 10^5 \text{ C}$$

c. The number of faradays is

$$1.0 \text{ g } Sn^{2+} \times \frac{1 \text{ mol } Sn^{2+}}{118.7 \text{ g } Sn^{2+}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol } Sn^{2+}} \times \frac{1\ F}{1 \text{ mol } e^-} = 0.01\underline{6}84 = 0.017\ F$$

The number of coulombs is

$$0.01684\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 1.\underline{6}2 \times 10^3 = 1.6 \times 10^3 \text{ C}$$

d. The number of faradays is

$$1.0 \text{ g } Au^{3+} \times \frac{1 \text{ mol } Au^{3+}}{197.0 \text{ g } Au^{3+}} \times \frac{3 \text{ mol } e^-}{1 \text{ mol } Au^{3+}} \times \frac{1\ F}{1 \text{ mol } e^-} = 0.01\underline{5}22 = 0.015\ F$$

The number of coulombs is

$$0.01522\ F \times \frac{96{,}485 \text{ C}}{1\ F} = 1.\underline{4}69 \times 10^3 = 1.5 \times 10^3 \text{ C}$$

19.115. From the electrolysis information, calculate the total moles of I_2 formed

$$65.4 \text{ s} \times (10.5 \times 10^{-3} \text{ A}) \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol } I_2}{2 \text{ mol } e^-} = 3.5\underline{5}8 \times 10^{-6} \text{ mol } I_2$$

From the balanced equation,

$$3.558 \times 10^{-6} \text{ mol } I_2 \times \frac{1 \text{ mol } H_3AsO_3}{1 \text{ mol } I_2} \times \frac{1 \text{ mol As}}{1 \text{ mol } H_3AsO_3} \times \frac{79.42 \text{ g As}}{1 \text{ mol As}}$$

$$= 2.8\underline{2}57 \times 10^{-4} = 2.83 \times 10^{-4} \text{ g As}$$

19.116. From the electrolysis information, calculate the total moles of OH^- formed.

$$115 \text{ s} \times (15.6 \times 10^{-3} \text{ A}) \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} \times \frac{2 \text{ mol } OH^-}{2 \text{ mol } e^-}$$

$$= 1.8\underline{5}9 \times 10^{-5} \text{ mol } OH^-$$

From the balanced equation

$$1.859 \times 10^{-5} \text{ mol } OH^- \times \frac{1 \text{ mol } HC_3H_5O_3}{1 \text{ mol } OH^-} \times \frac{90.08 \text{ g } HC_3H_5O_3}{1 \text{ mol } HC_3H_5O_3}$$

$$= 1.6\underline{7}45 \times 10^{-3} = 1.67 \times 10^{-3} \text{ g } HC_3H_5O_3$$

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19.117.

a. The spontaneous chemical reaction and maximum cell potential are

$Cd(s)$	$\rightarrow$	$Cd^{2+}(aq) + 2e^-$	$-E° = 0.40$ V
$2Ag^+(aq) + 2e^-$	$\rightarrow$	$2Ag(s)$	$E° = 0.80$ V
$Cd(s) + 2Ag^+(aq)$	$\rightarrow$	$2Ag(s) + Cd^{2+}(aq)$	$E°_{cell} = 1.20$ V

b. Addition of S^{2-} would greatly decrease the $Cd^{2+}(aq)$ concentration and help shift the equilibrium to the right, thus forming more Ag. The cell potential would increase.

c. No effect. The size of the electrode makes no difference in the potential.

19.118.

a. The spontaneous chemical reaction and maximum cell potential are

$Fe(s)$	$\rightarrow$	$Fe^{2+}(aq) + 2e^-$	$-E° = 0.41$ V
$Cu^{2+}(aq) + 2e^-$	$\rightarrow$	$Cu(s)$	$E° = 0.34$ V
$Fe(s) + Cu^{2+}(aq)$	$\rightarrow$	$Cu(s) + Fe^{2+}(aq)$	$E°_{cell} = 0.75$ V

b. The $Cu^{2+}(aq)$ concentration is greatly decreased, shifting the equilibrium to the left and thus forming less Cu. The cell potential would increase.

c. No effect. The size of the electrode makes no difference in the potential.

19.119. Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

19.120. Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(aq) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

19.121.

a. First, find the moles of silver.

$$2.48 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} = 0.02298 \text{ mol Ag}$$

The number of coulombs is

$$0.02298 \text{ mol Ag} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \times \frac{9.6485 \times 10^4 \text{ C}}{1 \text{ mol e}^-} = 2218 \text{ C}$$

Since amp x sec = coul, the number of seconds is

$$\text{Time} = \frac{2218 \text{ C}}{1.50 \text{ amp}} = 1.478 \times 10^3 = 1.48 \times 10^3 \text{ s}$$

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b. For the same amount of current, the grams of Cr would be

$$2218\ \text{C} \times \frac{1\ \text{mol e}^-}{96{,}485\ \text{C}} \times \frac{1\ \text{mol Cr}}{3\ \text{mol e}^-} \times \frac{52.00\ \text{g Cr}}{1\ \text{mol Cr}} = 0.398\underline{3} = 0.398\ \text{g}$$

19.122.

a. First, find the moles of copper.

$$2.20\ \text{g Cu} \times \frac{1\ \text{mol Cu}}{63.55\ \text{g Cu}} = 0.034\underline{6}18\ \text{mol Cu}$$

The number of coulombs is

$$0.034618\ \text{mol Cu} \times \frac{2\ \text{mol e}^-}{1\ \text{mol Cu}} \times \frac{9.6485 \times 10^4\ \text{C}}{1\ \text{mol e}^-} = 668\underline{1}\ \text{C}$$

Since amp x sec = coul, the number of seconds is

$$\text{Time} = \frac{6681\ \text{C}}{1.25\ \text{amp}} = 5.3\underline{4}5 \times 10^3 = 5.35 \times 10^3\ \text{s}$$

b. For the same amount of current, the grams of Ag would be

$$6681\ \text{C} \times \frac{1\ \text{mol e}^-}{96{,}485\ \text{C}} \times \frac{1\ \text{mol Ag}}{1\ \text{mol e}^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 7.4\underline{7}0 = 7.47\ \text{g}$$

19.123.

a. Note that 3.50 hours = 12600 s, and the efficiency is 90.0%.

$$2.75\ \text{amp} \times 12600\ \text{s} \times \frac{1\ F}{96{,}485\ \text{C}} \times 0.900 = 0.323\underline{2} = 0.323\ F$$

b. The moles of Au that were deposited is

$$\text{mol Au} = 21.221\ \text{g Au} \times \frac{1\ \text{mol Au}}{197.0\ \text{g}} = 0.107720\ \text{mol}$$

Since 1 F = 1 mol e^-, the ratio of moles of e^- to moles of Au is

$$\frac{\text{mol e}^-}{\text{mol Au}} = \frac{0.3232}{0.10772} = \frac{3.00}{1}$$

Thus, the ion must be Au^{3+}. The reaction is

$$Au^{3+} + 3e^- \rightarrow Au$$

19.124.

a. Note that 1.90 hours = 6840 s, and the efficiency is 95.0%.

$$2.50\ \text{amp} \times 6840\ \text{s} \times \frac{1\ F}{96{,}485\ \text{C}} \times 0.950 = 0.168\underline{3} = 0.168\ F$$

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b. The moles of V that were deposited is

$$\text{mol V} = 2.850 \text{ g V} \times \frac{1 \text{ mol V}}{50.94 \text{ g V}} = 0.055948 \text{ mol V}$$

Since 1 F = 1 mol e^-, the ratio of moles of e^- to moles of V is

$$\frac{\text{mol e}^-}{\text{mol V}} = \frac{0.1683}{0.055948} = \frac{3.00}{1}$$

Thus, the ion must be V^{3+}. The reaction is

$$V^{3+} + 3e^- \rightarrow V$$

19.125.

a. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$Zn(s)$	$\rightarrow$	$Zn^{2+}(aq) + 2e^-$	$-E° = 0.76$ V
$Cu^{2+}(aq) + 2e^-$	$\rightarrow$	$Cu(s)$	$E° = 0.34$ V
$Cu^{2+}(aq) + Zn(s)$	$\rightarrow$	$Zn^{2+}(aq) + Cu(s)$	$E° = 1.10$ V

Use the Nernst equation to calculate the voltage of the cell.

$$E = E° - \frac{0.0592}{n} \log Q = E° - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Note that n equals 2, $[Zn^{2+}] = 0.200$ M, and $[Cu^{2+}] = 0.0100$ M.

$$E° = 1.10 \text{ V} - \frac{0.0592}{2} \log \frac{[0.200]}{[0.0100]} = 1.10 \text{ V} - 0.038\underline{5}1 \text{ V} = 1.0\underline{6}1 = 1.06 \text{ V}$$

b. First, calculate the moles of electrons passing through the cell.

$$1.00 \text{ amp} \times 225 \text{ s} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} = 0.002\underline{3}32 \text{ mol e}^-$$

The moles of Cu deposited are

$$0.002332 \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} = 0.001\underline{6}6 \text{ mol Cu}$$

The moles of Cu remaining in the 1.00 L of solution are

$$0.0100 - 0.001166 = 0.008\underline{8}34 = 0.0088 \text{ mol}$$

Since the volume of the solution is 1.00 L, the molarity of Cu^{2+} is 0.0088 M.

19.126.

a. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$Fe(s)$	$\rightarrow$	$Fe^{2+}(aq) + 2e^-$	$-E° = 0.41$ V
$Cu^{2+}(aq) + 2e^-$	$\rightarrow$	$Cu(s)$	$E° = 0.34$ V
$Fe(s) + Cu^{2+}(aq)$	$\rightarrow$	$Fe^{2+}(aq) + Cu(s)$	$E° = 0.75$ V

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Use the Nernst equation to calculate the voltage of the cell.

$$E = E° - \frac{0.0592}{n}\log Q = E° - \frac{0.0592}{n}\log\frac{[Fe^{2+}]}{[Cu^{2+}]}$$

Note that n equals 2, $[Fe^{2+}] = 0.15\ M$, and $[Cu^{2+}] = 0.036\ M$.

$$E° = 0.75\text{ V} - \frac{0.0592}{2}\log\frac{[0.15]}{[0.036]}$$

$$= 0.7\underline{3}16 = 0.73\text{ V}$$

b. First, calculate the moles of electrons passing through the cell.

$$1.25\text{ amp} \times 335\text{ s} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} = 0.004\underline{3}39\text{ mol e}^-$$

The moles of Cu deposited are

$$0.004339\text{ mol e}^- \times \frac{1\text{ mol Cu}}{2\text{ mol e}^-} = 0.002\underline{1}70\text{ mol}$$

The moles of Cu remaining in the 1.00 L of solution are

$$0.036 - 0.002170 = 0.0\underline{3}38 = 0.034\text{ mol}$$

Since the volume of the solution is 1.00 L, the molarity of Cu^{2+} is 0.034 M.

19.127.

a. Write the cell reaction with the $\Delta G_f°$'s beneath.

	$Cd(s)$	+ $Co^{2+}(aq)$	→ $Cd^{2+}(aq)$	+ $Co(s)$
$\Delta G_f°$:	0	-54.4	-77.6	0 KJ

Hence,

$$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants})$$

$$= [-77.6 + 54.4]\text{ kJ} = -23.\underline{2}\text{ kJ} = -2.32 \times 10^4\text{ J}$$

b. Next, determine the standard cell potential for the cell. Note that n equals 2.

$$\Delta G° = -nFE°$$

$$-2.32 \times 10^4\text{ J} = -2(9.6485 \times 10^4\text{ C}) \times E°$$

Solve for $E°$ to get

$$E° = \frac{-2.32 \times 10^4\text{ J}}{-2(9.6485 \times 10^4\text{ C})} = 0.12\underline{0}2 = 0.120\text{ V}$$

The half-reactions and voltages are

$Cd(s)$	→ $Cd^{2+}(aq) + 2e^-$		$-E°_{ox} = 0.40$ V
$Co^{2+}(aq) + 2e^-$	→ $Co(s)$		$E°_{red}$ = ?
$Cd(s) + Co^{2+}(aq)$	→ $Cd^{2+}(aq) + Co(s)$		$E° = 0.1202$ V

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The cell potential is

$$E^\circ = E^\circ_{red} + (-E^\circ_{ox})$$

$$0.1202\ V = E^\circ_{red} + 0.40\ V$$

$$E^\circ_{red} = 0.1202\ V - 0.40\ V = -0.2797 = -0.28\ V$$

19.128.

a. Write the cell reaction with the ΔG_f°'s beneath.

$$\begin{array}{lccccc} & 2Tl(s) & + & Pb^{2+}(aq) & \rightarrow & 2Tl^+(aq) + Pb(s) \\ \Delta G_f^\circ: & 0 & & -24.39 & & 2(-32.4) \quad 0\ KJ \end{array}$$

Hence,

$$\Delta G^\circ = [2(-32.4) - (-24.39)]\ kJ = -40.41\ kJ = -4.041 \times 10^4\ J$$

b. Next, determine the standard cell potential for the cell. Note that n equals 2.

$$\Delta G^\circ = -nFE^\circ$$

$$-4.041 \times 10^4\ J = -2(9.6485 \times 10^4\ C) \times E^\circ$$

Solve for E° to get

$$E^\circ = \frac{-4.041 \times 10^4\ J}{-2(9.6485 \times 10^4\ C)} = 0.2094 = 0.209\ V$$

The half-reactions and voltages are

$2Tl(s)$	$\rightarrow$	$2Tl^+(aq) + 2e^-$	$-E^\circ_{ox} = E^\circ_{red}$
$Pb^{2+}(aq) + 2e^-$	$\rightarrow$	$Pb(s)$	$E^\circ_{red} = -0.13\ V$
$Cd(s) + Co^{2+}(aq)$	$\rightarrow$	$Cd^{2+}(aq) + Co(s)$	$E^\circ = 0.2094\ V$

The cell potential is

$$E^\circ = E^\circ_{red} + (-E^\circ_{ox})$$

$$0.2094\ V = -13\ V + E^\circ_{red}$$

$$E^\circ_{red} = 0.2094\ V + 0.13\ V = 0.3394 = 0.34\ V$$

■ SOLUTIONS TO STRATEGY PROBLEMS

19.129. Since chromium metal is oxidized, and since reduction occurs at the cathode, the reaction at the cathode is

$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$$

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19.130. The half-reactions and voltages are

$3Mg(s)$	$\rightarrow$	$3Mg^{2+}(aq) + 6e^-$	$E°_{ox} = 2.38$ V
$2Fe^{3+}(aq) + 6e^-$	$\rightarrow$	$2Fe(s)$	$E°_{red} = -0.04$ V
$3Mg(s) + 2Fe^{3+}(aq)$	$\rightarrow$	$3Mg^{2+}(aq) + 2Fe(s)$	$E° = 2.34$ V

19.131. The maximum work that can be obtained is

$$w_{max} = \Delta G° = -nFE°_{cell} = -(6 \text{ mol})(96{,}485 \text{ C/mol})(1.14 \text{ V}) = -65\underline{9}957 \text{ J} = -65\underline{9}.9 \text{ kJ}$$

This is the maximum amount of work for 2 moles of chromium. For 6.61 g Cr, the maximum work is

$$6.61 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g}} \times \frac{-659.9 \text{ kJ}}{2 \text{ mol Cr}} = -41.\underline{9}48 = -41.9 \text{ kJ}$$

19.132. The half-reactions are

$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s) \quad E° = -2.38 \text{ V}$$

$$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l) \quad E° = 0.85 \text{ V}$$

$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \quad E° = -0.13 \text{ V}$$

The strength of oxidizing agent increases as the reduction potential increases (gets less negative). Thus, $Mg^{2+} < Pb^{2+} < Hg^{2+}$.

19.133. The half-reactions and voltages are

$Cr(s)$	$\rightarrow$	$Cr^{3+}(aq) + 3e^-$	$E°_{ox} = 0.74$ V
$3Ag^+(aq) + 3e^-$	$\rightarrow$	$3Ag(s)$	$E°_{red} = 0.80$ V
$Cr(s) + 3Ag^+(aq)$	$\rightarrow$	$Cr^{3+}(aq) + 3Ag(s)$	$E° = 1.54$ V

Now use the Nernst equation to calculate the cell potential.

$$E = E° - \frac{0.0592}{\text{n}} \log Q = E° - \frac{0.0592}{n} \log \frac{[Cr^{3+}]}{[Ag^+]^3}$$

Note that n equals 3, $[Cr^{3+}] = 0.10$ M, and $[Ag^+] = 1.0 \times 10^{-4}$ M.

$$E° = 1.54 \text{ V} - \frac{0.0592}{3} \log \frac{[0.10]}{[1.0 \times 10^{-4}]^3} = 1.3\underline{2}2 = 1.32 \text{ V}$$

19.134. The half-reactions and voltages are

$2Al(s)$	$\rightarrow$	$2Al^{3+}(aq) + 6e^-$	$E°_{ox} = 1.66$ V
$3Cu^{2+}(aq) + 6e^-$	$\rightarrow$	$3Cu(s)$	$E°_{red} = 0.34$ V
$2Al(s) + 3Cu^{2+}(aq)$	$\rightarrow$	$2Al^{3+}(aq) + 3Cu(s)$	$E° = 2.00$ V

A spontaneous reaction would occur. You would observe the aluminum electrode slowly dissolving while the copper would plate out on the electrode.

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19.135. The answer is b, $Li + NaCl \rightarrow LiCl + Na$.

19.136. The half-reaction that occurs is

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The amount of hydrogen that can be produced is

$$0.325\ A \times 300.00\ s \times \frac{1\ mol\ e^-}{96{,}485\ C} \times \frac{1\ mol\ H_2}{2\ mol\ e^-} \times \frac{2.016\ g}{1\ mol\ H_2}$$

$$= 1.01\underline{8} \times 10^{-3} = 1.02 \times 10^{-3}\ g = 1.02\ mg$$

19.137. For a spontaneous reaction, the following reactions would occur.

Anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ $\quad E°_{ox} = 0.25\ V$

Cathode: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ $\quad E°_{red} = 0.80\ V$

As the reaction proceeds, $Ag(s)$ is produced at the cathode, and $Ni^{2+}(aq)$ is produced at the anode.

19.138.

a. Write the equation with the appropriate $\Delta G_f°$ beneath each substance.

	$2Al(s)$	$+\ 3Fe^{2+}(aq)$	$\rightarrow\ 2Al^{3+}(aq)$	$+\ 3Fe(s)$
$\Delta G_f°$:	0	3 x (-78.87)	2 x (-485)	0 KJ

Hence,

$$\Delta G° = \Sigma n\Delta G_f°(\text{products}) - \Sigma m\Delta G_f°(\text{reactants})$$

$$= [3(-78.87) - 2(-485)]\ kJ = -73\underline{3}.39\ kJ = -7.3\underline{3}39 \times 10^5\ J$$

Each half-reaction involves six electrons, so n equals 6. Therefore,

$$\Delta G° = -nFE°_{cell}$$

$$-7.3339 \times 10^5\ J = -6 \times 9.6485 \times 10^4\ C \times E°_{cell}$$

Rearrange and solve for $E°_{cell}$. Recall that J = C•V.

$$E°_{cell} = \frac{-7.3339 \times 10^5\ J}{-6 \times 9.6485 \times 10^4\ C} = 1.2\underline{6}68 = 1.27\ V$$

b. The equilibrium constant is

$$E°_{cell} = \frac{0.0592}{n} \log K$$

$$\log K = \frac{n \times E°}{0.0592} = \frac{6 \times 1.2668}{0.0592} = 12\underline{8}.39$$

$$K = 10^{128.39} = \underline{2}.49 \times 10^{128} = 2 \times 10^{128}$$

c. The value of the equilibrium constant is not affected by the concentration of the ions.

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SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

19.139. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$3Zn(s)$	$\rightarrow$	$3Zn^{2+}(aq) + 6e^-$	$-E° = 0.76$ V
$2Cr^{3+}(aq) + 6e^-$	$\rightarrow$	$2Cr(s)$	$E° = -0.74$ V
$2Cr^{3+}(aq) + 3Zn(s)$	$\rightarrow$	$3Zn^{2+}(aq) + 2Cr(s)$	$E° = 0.02$ V

Note that n equals 6. Therefore,

$$\Delta G° = -nFE° = -6(9.6485 \times 10^4 \text{ C})(0.02 \text{ V}) = -1.158 \times 10^4 \text{ J} = -11.58 \text{ kJ}$$

Write the cell reaction with the $\Delta H_f°$'s beneath.

	$2Cr^{3+}(aq)$	$+ 3Zn(s) \rightarrow$	$3Zn^{2+}(aq) +$	$2Cr(s)$
$\Delta H_f°$:	2(-143.5)	0	3(-153.9)	0 KJ

Hence,

$$\Delta H° = \Sigma n\Delta H_f°(\text{products}) - \Sigma m\Delta H_f°(\text{reactants})$$
$$= [3(-153.9) - 2(-143.5)] \text{ kJ} = -174.7 \text{ kJ}$$

Now calculate $\Delta S°$.

$$\Delta G° = \Delta H° - T\Delta S°$$

$$-11.58 \text{ kJ} = -174.7 \text{ kJ} - 298 \text{ K} \times \Delta S°$$

Solving for $\Delta S°$ gives

$$\Delta S° = \frac{-174.7 \text{ kJ} + 11.58 \text{ kJ}}{298 \text{ K}} = -0.5473 \text{ kJ/K} = -547 \text{ J/K}$$

19.140. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$2Cr(s)$	$\rightarrow$	$2Cr^{3+}(aq) + 6e^-$	$-E° = 0.74$ V
$3Fe^{2+}(aq) + 6e^-$	$\rightarrow$	$3Fe(s)$	$E° = -0.41$ V
$2Cr(s) + 3Fe^{2+}(aq)$	$\rightarrow$	$2Cr^{3+}(aq) + 3Fe(s)$	$E° = 0.33$ V

Note that n equals 6. Therefore,

$$\Delta G° = -nFE° = -6(9.6485 \times 10^4 \text{ C})(0.33 \text{ V}) = -1.9107 \times 10^5 \text{ J} = -191.07 \text{ kJ}$$

Write the cell reaction with the $\Delta H_f°$'s beneath.

	$2Cr(s)$	$+ 3Fe^{2+}(aq) \rightarrow$	$2Cr^{3+}(aq) +$	$3Fe(s)$
$\Delta H_f°$:	0	2(-87.9)	2(-143.5)	0 KJ

Hence,

$$\Delta H° = \Sigma n\Delta H_f°(\text{products}) - \Sigma m\Delta H_f°(\text{reactants})$$
$$= [2(-143.5) - 3(-87.9] \text{ kJ} = -23.3 \text{ kJ}$$

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Now calculate ΔS°.

$$\Delta G° = \Delta H° - T\Delta S°$$

$$-191.07 \text{ kJ} = -23.3 \text{ kJ} - 298 \text{ K} \times \Delta S°$$

Solving for $\Delta S°$ gives

$$\Delta S° = \frac{-23.3 \text{ kJ} + 191.07 \text{ kJ}}{298 \text{ K}} = 0.56299 \text{ kJ/K} = 563 \text{ J/K}$$

19.141. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$4Br^-(aq)$	$\rightarrow$	$2Br_2(l) + 4e^-$	$-E° = -1.07$ V
$O_2(g) + 4H^+(aq) + 4e^-$	$\rightarrow$	$2H_2O(l)$	$E° = 1.23$ V
$O_2(g) + 4H^+(aq) + 4Br^-(aq)$	$\rightarrow$	$2H_2O(l) + 2Br_2(l)$	$E° = 0.16$ V

Now, convert the pH to $[H^+]$.

$$[H^+] = \text{antilog}(-3.60) = 2.51 \times 10^{-4}\ M$$

Under standard conditions, $[Br^-] = 1\ M$, and the pressure of O_2 is 1 atm. Thus, substitute into the Nernst equation, where n equals 4.

$$E = E° - \frac{0.0592}{n}\log Q = E° - \frac{0.0592}{n}\log \frac{1}{[H^+]^4[Br^-]^4 \times P_{O_2}}$$

$$= 0.16 \text{ V} - \frac{0.0592}{4}\log\frac{1}{(2.51 \times 10^{-4})^4}$$

$$= 0.16 \text{ V} - 0.2131 \text{ V} = -0.0531 = -0.05 \text{ V}$$

Thus, the reaction is nonspontaneous at this $[H^+]$.

19.142. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$2Co^{2+}(aq)$	$\rightarrow$	$2Co^{3+}(aq) + 2e^-$	$-E° = -1.82$ V
$O_3(g) + 2H^+(aq) + 2e^-$	$\rightarrow$	$O_2(g) + H_2O(l)$	$E° = 2.07$ V

$$O_3(g) + 2H^+(aq) + 2Co^{2+}(aq) \rightarrow O_2(g) + H_2O(l) + 2Co^{3+}(aq) \qquad E° = 0.25 \text{ V}$$

Now, convert the pH to $[H^+]$.

$$[H^+] = \text{antilog}(-9.10) = 7.943 \times 10^{-10}\ M$$

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Under standard conditions, $[Co^{2+}]$ and $[Co^{3+}] = 1\ M$, and the partial pressures of O_2 and O_3 equal 1 atm. Thus, substitute into the Nernst equation, where n equals 2.

$$E = E° - \frac{0.0592}{n}\log Q = E° - \frac{0.0592}{n}\log \frac{[Co^{3+}]^2 \times P_{O_2}}{[H^+]^2[Co^{2+}]^4 \times P_{O_3}}$$

$$= 0.25\ V - \frac{0.0592}{2}\log\frac{1}{(7.94 \times 10^{-10})^2}$$

$$= 0.25\ V - 0.5\underline{3}87\ V = -0.2\underline{8}87 = -0.29\ V$$

Thus, the reaction is nonspontaneous at this $[H^+]$.

19.143. Use the K_a to calculate [H+] for the buffer.

$$K_a = \frac{[H^+][OCN^-]}{[HOCN]} = 3.5 \times 10^{-4}$$

Rearrange, and solve for $[H^+]$, assuming [HOCN] and $[OCN^-]$ remain constant in the buffer. Thus, $[H^+] = K_a = 3.5 \times 10^{-4}\ M$.

In Problem 19.141, $E°$ for this cell reaction was found to be 0.16 V. Under standard conditions, $[Br^-] = 1\ M$, and the pressure of O_2 is 1 atm. Thus, substitute into the Nernst equation, where n equals 4.

$$E = E° - \frac{0.0592}{n}\log Q = E° - \frac{0.0592}{n}\log \frac{1}{[H^+]^4[Br^-]^4 \times P_{O_2}}$$

$$= 0.16\ V - \frac{0.0592}{4}\log\frac{1}{(3.5 \times 10^{-4})^4}$$

$$= 0.16\ V - 0.20\underline{4}59\ V = -0.0\underline{4}455 = -0.04\ V$$

Thus, the reaction is nonspontaneous at this $[H^+]$.

19.144. Use the K_a to calculate $[H^+]$ for the buffer.

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = 3.5 \times 10^{-8}$$

Rearrange, and solve for $[H^+]$, assuming [HOCl] and $[OCl^-]$ remain constant in the buffer. Thus, $[H^+] = K_a = 3.5 \times 10^{-8}\ M$.

In Problem 19.142, $E°$ for this cell reaction was found to be 0.25 V. Under standard conditions, $[Co^{2+}]$ and $[Co^{3+}] = 1\ M$, and the partial pressures of O_2 and O_3 equal 1 atm. Thus, substitute into the Nernst equation, where n equals 2.

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$$E = E° - \frac{0.0592}{n}\log Q = E° - \frac{0.0592}{n}\log \frac{[Co^{3+}]^2 \times P_{O_2}}{[H^+]^2[Co^{2+}]^4 \times P_{O_3}}$$

$$= 0.25\text{ V} - \frac{0.0592}{2}\log\frac{1}{(3.5 \times 10^{-8})^2}$$

$$= 0.25\text{ V} - 0.44139\text{ V} = -0.19139 = -0.19\text{ V}$$

Thus, the reaction is nonspontaneous at this $[H^+]$.

19.145. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$H_2(g)$	$\rightarrow$	$2H^+(aq) + 2e^-$	$-E° = -0.00$ V
$2Ag^+(aq) + 2e^-$	$\rightarrow$	$2Ag(s)$	$E° = 0.80$ V
$H_2(g) + 2Ag^+(aq)$	$\rightarrow$	$2H^+(aq) + 2Ag(s)$	$E° = 0.80$ V

The standard hydrogen electrode has $[H^+] = 1.0\ M$ and the pressure of H_2 equals 1 atm. Substitute into the Nernst equation, where $E = 0.45$ V and n equals 2.

$$E = E° - \frac{0.0592}{n}\log Q = E° - \frac{0.0592}{n}\log \frac{[H^+]^2}{[Ag^+]^2 \times P_{H_2}}$$

$$0.45\text{ V} = 0.80\text{ V} - \frac{0.0592}{2}\log\frac{1}{[Ag^+]^2}$$

Using the properties of logs, rearrange to get

$$0.45\text{ V} = 0.80\text{ V} + 0.0592\log[Ag^+]$$

Solve for $[Ag^+]$.

$$\log[Ag^+] = \frac{0.45 - 0.80}{0.0592} = -5.912$$

$$[Ag^+] = 10^{-5.912} = 1.224 \times 10^{-6}\ M$$

Finally, determine the solubility product, using $[SCN^-] = 0.10\ M$.

$$K_{sp} = [Ag^+][SCN^-] = (1.224 \times 10^{-6})(0.10) = 1.224 \times 10^{-7} = 1 \times 10^{-7}$$

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19.146. The half-cell reactions, the corresponding half-cell potentials, and their sums are displayed below:

$H_2(g)$	$\rightarrow$	$2H^+(aq) + 2e^-$	$-E° = -0.00$ V
$Hg_2^{2+}(aq) + 2e^-$	$\rightarrow$	$2Hg(l)$	$E° = 0.80$ V
$Hg_2^{2+}(aq) + H_2(g)$	$\rightarrow$	$2Hg(l) + 2H^+(aq)$	$E° = 0.80$ V

The standard hydrogen electrode has $[H^+] = 1.0\ M$ and the pressure of H_2 equals 1 atm. Substitute into the Nernst equation, where $E = 0.268$ V and n equals 2.

$$E = E° - \frac{0.0592}{n} \log Q = E° - \frac{0.0592}{n} \log \frac{[H^+]^2}{[Hg_2^{2+}] \times P_{H_2}}$$

$$0.268 \text{ V} = 0.80 \text{ V} - \frac{0.0592}{2} \log \frac{1}{[Hg_2^{2+}]}$$

Using the properties of logs, rearrange to get

$$0.268 \text{ V} = 0.80 \text{ V} + \frac{0.0592}{2} \log[Hg_2^{2+}]$$

Solve for $[Hg_2^{2+}]$.

$$\log[Hg_2^{2+}] = \frac{2(0.268 - 0.80)}{0.0592} = -17.972$$

$$[Hg_2^{2+}] = 10^{-17.972} = 1.06 \times 10^{-18}\ M$$

Finally, determine the solubility product, using $[Cl^-] = 1.00\ M$.

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (1.06 \times 10^{-18})(1.00)^2 = 1.06 \times 10^{-18} = 10^{-18}$$

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CHAPTER 20

Nuclear Chemistry

■ SOLUTIONS TO EXERCISES

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

20.1. The nuclide symbol for potassium-40 is $^{40}_{19}\mathrm{K}$. Similarly, the nuclide symbol for calcium-40 is $^{40}_{20}\mathrm{Ca}$. The equation for beta emission is

$$^{40}_{19}\mathrm{K} \rightarrow {}^{40}_{20}\mathrm{Ca} + {}^{0}_{-1}\mathrm{e}$$

20.2. Plutonium-239 has the nuclide symbol is $^{239}_{94}\mathrm{Pu}$. An alpha particle has the symbol $^{4}_{2}\mathrm{He}$. The nuclear equation is

$$^{239}_{94}\mathrm{Pu} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{4}_{2}\mathrm{He}$$

From the superscripts you can write

$$239 = A + 4, \text{ or } A = 235$$

Similarly, from the subscripts you can write

$$94 = Z + 2, \text{ or } Z = 92$$

Hence, $A = 235$ and $Z = 92$, so the product is $^{235}_{92}\mathrm{X}$. Because element 92 is uranium, symbol U, you write the product nucleus as $^{235}_{92}\mathrm{U}$.

20.3.

a. $^{118}_{50}\mathrm{Sn}$ has atomic number 50. It has 50 protons and 68 neutrons. Because its atomic number is less than 83 and it has an even number of protons and neutrons, it is expected to be stable.

b. $^{76}_{33}\mathrm{As}$ has atomic number 33. It has 33 protons and 43 neutrons. Because stable odd-odd nuclei are rare, you would expect $^{76}_{33}\mathrm{As}$ to be one of the radioactive isotopes.

c. $^{227}_{89}\mathrm{Ac}$ has atomic number 89. Because its atomic number is greater than 83, $^{227}_{89}\mathrm{Ac}$ is radioactive.

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20.4.

a. $^{13}_{7}\text{N}$ has seven protons and six neutrons (fewer neutrons than protons). Its mass number is less than that of N, which is 14, so it is expected to decay by electron capture or positron emission (more likely, because this is a light isotope).

b. $^{26}_{11}\text{Na}$ has 11 protons and 15 neutrons. It is expected to decay by beta emission.

20.5.

a. The abbreviated notation is $^{40}_{20}\text{Ca}\,(\text{d,p})\,^{41}_{20}\text{Ca}$.

b. The nuclear equation is $^{12}_{6}\text{C} + {}^{2}_{1}\text{H} \rightarrow {}^{13}_{6}\text{C} + {}^{1}_{1}\text{H}$.

20.6. You can write the nuclear equation as follows:

$$^{A}_{Z}\text{X} + {}^{1}_{0}\text{n} \rightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$$

To balance this equation in charge (subscripts) and mass number (superscripts), write the equations

$A + 1 = 14 + 1$ (from superscripts)

$Z + 0 = 6 + 1$ (from subscripts)

Hence, $A = 14$ and $Z = 7$. Therefore, the nucleus that produces carbon-14 by this reaction is $^{14}_{7}\text{N}$.

20.7. Because an activity of 1.0 Ci is 3.7×10^{10} nuclei/s, the rate of decay in this sample is

$$\text{Rate} = 13\ \text{Ci} \times \frac{3.7 \times 10^{10}\ \text{nuclei/s}}{1.0\ \text{Ci}} = 4.\underline{8}1 \times 10^{11}\ \text{nuclei/s}$$

The number of nuclei in this 2.5-μg (2.5×10^{-6}-g) sample of $^{99m}_{43}\text{Tc}$ is

$$2.5 \times 10^{-6}\ \text{g Tc-99m} \times \frac{1\ \text{mol Tc-99m}}{99\ \text{g Tc-99m}} \times \frac{6.02 \times 10^{23}\ \text{Tc-99m nuclei}}{1\ \text{mol Tc-99m}}$$

$$= 1.\underline{5}2 \times 10^{16}\ \text{Tc-99m nuclei}$$

The decay constant is

$$k = \frac{\text{rate}}{N_t} = \frac{4.81 \times 10^{11}\ \text{nuclei/s}}{1.52 \times 10^{16}\ \text{nuclei}} = 3.\underline{1}6 \times 10^{-5} = 3.2 \times 10^{-5}/\text{s}$$

20.8. First, substitute the value of k into the equation relating half-life to the decay constant:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.18 \times 10^{-9}\ /\text{s}} = 1.6\underline{5}8 \times 10^{8}\ \text{s}$$

Convert the half-life from seconds to years:

$$1.6\underline{5}8 \times 10^{8}\ \text{s} \times \frac{1\ \text{min}}{60\ \text{s}} \times \frac{1\ \text{h}}{60\ \text{min}} \times \frac{1\ \text{d}}{24\ \text{h}} \times \frac{1\ \text{y}}{365\ \text{d}} = 5.2\underline{5}7 = 5.26\ \text{y}$$

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20.9. The conversion of the half-life to seconds gives

$$28.1 \text{ y} \times \frac{365 \text{ d}}{1 \text{ y}} \times \frac{24 \text{ h}}{1 \text{ d}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} = 8.861 \times 10^{8} \text{ s}$$

Because $t_{1/2} = 0.693/k$, solve this for k, and substitute the half-life in seconds.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{8.861 \times 10^{8} \text{ s}} = 7.8208 \times 10^{-10} \text{ /s}$$

Before substituting into the rate equation, you need to know the number of nuclei in a sample containing 5.2×10^{-9} g of strontium-90.

$$5.2 \times 10^{-9} \text{ g Sr-90} \times \frac{1 \text{ mol Sr-90}}{90 \text{ g Sr-90}} \times \frac{6.02 \times 10^{23} \text{ Sr-90 nuclei}}{1 \text{ mol Sr-90}}$$

$$= 3.478 \times 10^{13} \text{ Sr-90 nuclei}$$

Now, substitute into the rate equation:

$$\text{Rate} = kN_t = (7.8208 \times 10^{-10}/\text{s}) \times (3.478 \times 10^{13} \text{ nuclei}) = 2.72 \times 10^{4} \text{ nuclei/s}$$

Calculate the activity by dividing the rate (disintegrations of nuclei per second) by 3.70×10^{10} disintegrations of nuclei per second per curie.

$$\text{Activity} = 2.72 \times 10^{4} \text{ nuclei/s} \times \frac{1.0 \text{ Ci}}{3.7 \times 10^{10} \text{ nuclei/s}} = 7.351 \times 10^{-7} = 7.4 \times 10^{-7} \text{ Ci}$$

20.10. The decay constant, k, is $0.693/t_{1/2}$. If you substitute this into the equation

$$\ln \frac{N_t}{N_o} = -kt = -\frac{0.693\, t}{t_{1/2}}$$

Substitute the values $t = 25.0$ y and $t_{1/2} = 10.76$ y to get

$$\ln \frac{N_t}{N_o} = \frac{-0.693 \times 25.0 \text{ y}}{10.76 \text{ y}} = -1.6101$$

The fraction of krypton-85 remaining after 25.0 y is N_t/N_o.

$$\frac{N_t}{N_o} = e^{-1.6101} = 0.1999 = 0.20$$

20.11. The ratio of rates of disintegration is

$$\frac{N_o}{N_t} = \frac{15.3}{4.5} = 3.400$$

Therefore, substituting this value of N_o/N_t and $t_{1/2} = 5730$ y into the previous equation gives

$$t = \frac{t_{1/2}}{0.693} \ln \frac{N_o}{N_t} = \frac{5730 \text{ y}}{0.693} \ln (3.400) = 1.01 \times 10^{4} = 1.0 \times 10^{4} \text{ y}$$

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20.12.

a. First, determine the nuclear masses.

Nuclear mass of $^{234}_{90}$Th = 234.03660 amu − (90 x 0.000549 amu) = 233.987190 amu

Nuclear mass of $^{234}_{91}$Pa = 234.04330 amu − (91 x 0.000549 amu) = 233.993341 amu

Write the appropriate nuclear mass below each nuclide symbol. Then calculate Δm.

$$^{234}_{90}\text{Th} \rightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$$

233.987190 233.993341 0.000549 amu

Hence,

Δm = (233.993341 + 0.000549 − 233.987190) amu = 0.006700 amu

The mass change for molar amounts in this reaction is 0.006700 g, or 6.700 x 10^{-6} kg. The energy change is

$\Delta E = (\Delta m)c^2$ = (6.700 x 10^{-6} kg)(3.00 x 10^8 m/s)^2 = 6.030 x 10^{11} J/mol

For 1.00 g Th-234, the energy change is

$$1.00 \text{ g Th-234} \times \frac{1 \text{ mol Th-234}}{234 \text{ g Th-234}} \times \frac{6.030 \times 10^{11} \text{ J}}{1 \text{ mol Th-234}} = 2.576 \times 10^9 = 2.58 \times 10^9 \text{ J}$$

b. Convert the mass change for the reaction from amu to grams.

$$\Delta m = 0.006700 \text{ amu} \times \frac{1 \text{ g}}{1 \text{ amu} \times 6.02 \times 10^{23}} = 1.112 \times 10^{-26} \text{ g} = 1.112 \times 10^{-29} \text{ kg}$$

$\Delta E = (\Delta m)c^2$ = (1.112 x 10^{-29} kg)(3.00 x 10^8 m/s)^2 = 1.001 x 10^{-12} J

Convert this to MeV:

$$\Delta E = 1.001 \times 10^{-12} \text{ J} \times \frac{1 \text{ MeV}}{1.602 \times 10^{-13} \text{ J}} = 6.252 = 6.25 \text{ MeV}$$

■ ANSWERS TO CONCEPT CHECKS

20.1.

a. Yes. Isotopes have similar chemical properties.

b. No, since the $^{3}_{1}H_2O$ molecule is more massive than $^{1}_{1}H_2O$.

c. $^{3}_{1}H_2O$ should be radioactive.

20.2. For the same radiation dosage (10 rads), the form of radiation with the highest RBE will cause the greatest biological damage. Therefore, the α particle will cause the most damage since it has the highest RBE (10).

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20.3. After 50,000 years, enough half-lives have passed (about 10) so there would be almost no carbon-14 present to detect and measure (about 0.1% would be left).

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

20.1. The two types of nuclear reactions and their equations are

Radioactive decay: $^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$

Nuclear bombardment reactions: $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}$

20.2. Magic numbers are the numbers of nuclear particles in completed shells of protons or neutrons. Examples of nuclei with magic numbers of protons are $^{4}_{2}\text{He}$, $^{16}_{8}\text{O}$, and $^{40}_{20}\text{Ca}$.

20.3. To predict whether a nucleus will be stable, look for nuclei that have one of the magic numbers of protons and neutrons. Also look for nuclei that have an even number of protons and an even number of neutrons. Nuclei that fall in the band of stability are also very stable. There are no stable nuclei above atomic number 83.

20.4. The six common types of radioactive decay and the usual condition that leads to each type are listed below (see Table 20.2).

Alpha emission:	$Z > 83$.
Beta emission:	N/Z is too large.
Positron emission:	N/Z is too small.
Electron capture:	N/Z is too small.
Gamma emission:	The nucleus is in an excited state.
Spontaneous fission:	Mass number > 89.

20.5. The isotopes that begin each of the natural radioactive decay series are uranium-238, uranium-235, and thorium-232.

20.6. The equations are as follows:

a. $^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$

b. $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}$

20.7. Particle accelerators are devices used to accelerate electrons, protons, alpha particles, and ions to very high speeds. They operate by accelerating the charged particle toward a plate with a charge opposite to that of the particle. Particle accelerators are required to accelerate alpha particles to speeds high enough to penetrate nuclei of large positive charge that normally scatter alpha particles.

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20.8. Before the discovery of transuranium elements, it was thought that americium ($Z = 95$) and curium ($Z = 96$) should be placed after actinium ($Z = 89$) in the periodic table as *d*-block transition elements. However, Seaborg and others discovered these elements had properties similar to the lanthanides and placed them in a second series under the lanthanides.

20.9. The Geiger counter measures alpha particles by means of a tube filled with gas. When particles pass through the tube, they ionize the gas, freeing electrons, which creates a pulse of current that is detected by electronic equipment and is counted. A scintillation counter consists of phosphor, a substance that emits photons when struck by radiation; zinc sulfide is used for the detection of alpha particles; and sodium iodide containing thallium(I) iodide is used for gamma rays. The photons travel from the phosphor to a photoelectric detector, such as a photomultiplier, which magnifies the effect and gives a pulse of electric current that is measured.

20.10. A curie (Ci) equals 3.700×10^{10} nuclear disintegrations per second. A rad is the dosage of radiation that deposits 1×10^{-2} J of energy per kilogram of tissue. A rem is a unit of radiation dosage for biological destruction; it equals the rad multiplied by the relative biological effectiveness (RBE).

20.11. It will take cesium-137 three times its half-life of 30.2 y, or 90.6 y, to decay to 1/8 its original mass: 1 to 1/2 to 1/4 to 1/8 = 3 half-lives.

20.12. Because the $^{40}_{18}\mathrm{Ar}$ was produced by radioactive decay of $^{40}_{19}\mathrm{K}$, half the initial amount of $^{40}_{19}\mathrm{K}$ has decomposed. The age equals the half-life of 1.28×10^{9} y.

20.13. A radioactive tracer is a radioactive isotope added to a chemical, biological, or physical system to study it. For instance, $^{131}\mathrm{I}^-$ is used as a tracer in the study of the dissolving of lead(II) iodide and its equilibrium in a saturated solution.

20.14. Isotope dilution is a technique designed to determine the quantity of a substance in a mixture or to determine the total volume of a solution by adding a known amount of an isotope to it. After removing a portion of the mixture, the fraction by which the isotope has been diluted provides a way of determining the quantity of substance or the total volume of solution.

20.15. Neutron activation analysis is an analysis based on the conversion of stable isotopes to radioactive isotopes by bombarding a sample with neutrons. An unstable nucleus results that then emits gamma rays or radioactive particles (such as beta particles). The amount of stable isotope is proportional to the measured emission.

20.16. The reason why the deuteron, $^{2}_{1}\mathrm{H}$, has a mass smaller than the sum of the masses of its constituents is that when nucleons come together to form a nucleus, energy is released. There must be an equivalent decrease in mass, because mass and energy are equivalent.

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20.17. Iron-56 has a binding energy per nucleon near the maximum value. Two light nuclei, such as two C-12 nuclei, will undergo fusion (with the release of energy) as long as the product nuclei are lighter than iron-56 (which is the case with Na-23 and H-1).

20.18. The nuclear fission reactor operates by means of a chain reaction of nuclear fissions controlled to produce energy without explosion.

20.19. The answer is b, $^{216}_{84}\text{Po} \rightarrow {}^{212}_{82}\text{Pb} + {}^{4}_{2}\text{He}$.

20.20. The answer is e, 8.6×10^{3} y.

20.21. The answer is d, 4.1×10^{-3}.

20.22. The answer is c, 19.7 min.

■ ANSWERS TO CONCEPTUAL PROBLEMS

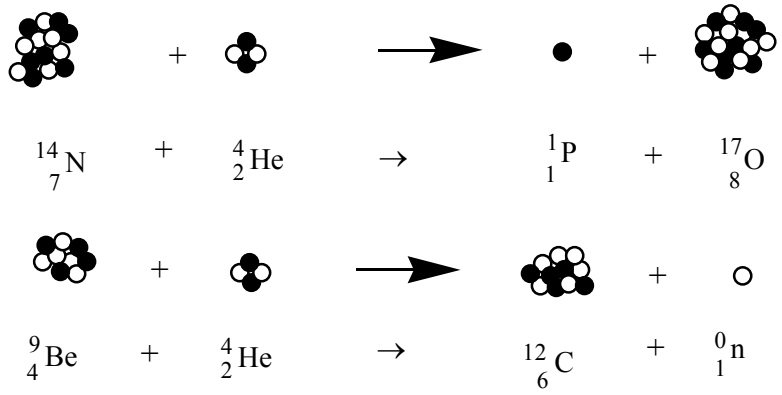
20.23.

a. After 10 half-lives have passed, the percentage of the original material that is left is

$$\left(\frac{1}{2}\right)^{10} \times 100\% = 0.0976 \cong 0.1\%$$

b. If you had a large quantity of material, 0.1% still would be a significant quantity. Also, if the material were particularly toxic in addition to being radioactive, the amount would be a significant quantity.

20.24. In the following drawings, a white ball represents a neutron, and a black ball represents a proton.



$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow {}^{1}_{1}\text{P} + {}^{17}_{8}\text{O}$$

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{1}\text{n}$$

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20.25. An atom of sodium-23 has 11 protons, 12 neutrons, and 11 electrons. Using the values in Table 20.3, the atomic mass of sodium-23 would be

(11)(1.00728 amu) + (12)(1.008665 amu) + (11)(0.000549 amu) = 23.190099 amu

Since the observed atomic weight is 22.98976 amu, it is not the same as the sum of the masses of the protons, neutrons, and electrons. Some of the expected mass is in the form of energy, the mass defect.

20.26.

a. fusion

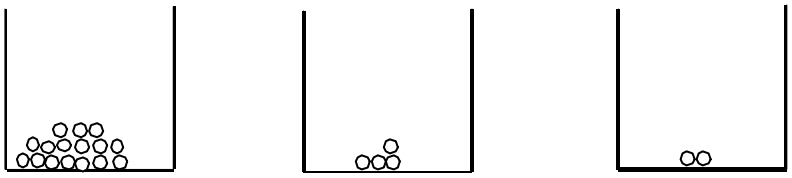
b. radioactive decay

c. fission

d. transmutation

20.27.

a. The container in the middle is depicted after 20 minutes have passed. This is equivalent to two half-lives ($t_{1/2}$ = 10 min). At this time, one-quarter of the original material remains present. Since there are four nuclides after 20 minutes, the original sample (t = 0) must have consisted of 16 nuclides. After 30 minutes have passed (three half-lives), one-eighth of the original material, or 2 nuclides, would be present. The pictures are



t = 0 min t = 20 min t = 30 min

b. The middle picture is not correct. The pile on the right (t = 10 min) containing 500 nuclides is one-half the original 1000 nuclides, so the half-life of the material is 10 minutes. The pile in the middle (t = 5 min) contains 750 nuclides, which represents one-quarter of the original material reacted. This is 1/2 x 1/2, which is not the correct way to determine the number of remaining nuclides. Instead, it is $(1/2)^{1/2}$, or 0.707. Thus, there should be 707 nuclides remaining after 5 min.

20.28. The total amount of radioactive material at the start is 10 g Pu-239 + 10 g Np-239 = 20 g total. In order to reduce this by 50%, the total mass must be reduced to 10 g. Since the half-life of Pu-239 (2.4×10^4 years) is long compared to the half-life of Np-239 (2.4 days), all of the Np-239 will have decomposed before any measurable amount of Pu-239 decays. This would require approximately 10 half-lives, or about 24 days.

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20.29. The large, positively charged He nucleus that makes up alpha (α) radiation is unable to pass through the atoms that make up solid materials such as wood without coming into contact or being deflected by the nuclei. Gamma (γ) radiation, however, with its small wavelength and high energy, can pass through large amounts of material without interaction, just as x rays can pass through skin and other soft tissue.

20.30. Examples of elements and compounds that would be impossible to avoid include radioactive ^{40}K that is in bananas and any food that contains potassium, H_2O that contains $^{3}_{1}H$, CO_2 that contains carbon-14, and radon gas that comes from soil and rocks.

20.31. Irradiation of food atoms with gamma radiation does not result in the creation of radioactive elements; therefore, the food cannot become radioactive. The addition of a radioactive element directly to the meat would make the meat radioactive. Under the right conditions, nuclear bombardment could also lead to the production of radioactive elements.

20.32. No, half-life can tell you only the quantity of material that will undergo decay, not the identity of the individual atoms.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

20.33. $^{87}_{37}Rb \rightarrow {}^{87}_{38}Sr + {}^{0}_{-1}e$

20.34. $^{32}_{15}P \rightarrow {}^{32}_{16}S + {}^{0}_{-1}e$

20.35. $^{232}_{90}Th \rightarrow {}^{228}_{88}Ra + {}^{4}_{2}He$

20.36. $^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$

20.37. Let X be the product nucleus. The nuclear equation is

$$^{18}_{9}F \rightarrow {}^{A}_{Z}X + {}^{0}_{1}e$$

From the superscripts: $18 = A + 0$, or $A = 18$; from the subscripts: $9 = Z + 1$, or $Z = 8$. Thus, the product of the reaction is $^{18}_{8}X$, and because element 8 is oxygen, symbol O, the nuclear equation is

$$^{18}_{9}F \rightarrow {}^{18}_{8}O + {}^{0}_{1}e$$

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20.38. Let X be the product nucleus. The nuclear equation is

$$^{41}_{21}\text{Sc} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{1}\text{e}$$

From the superscripts: 41 = A + 0, or A = 41; from the subscripts: 21 = Z + 1, or Z = 20. Thus, the product nucleus is $^{41}_{20}\text{X}$, and because element 20 is calcium, symbol Ca, the nuclear equation is

$$^{41}_{21}\text{Sc} \rightarrow {}^{41}_{20}\text{Ca} + {}^{0}_{1}\text{e}$$

20.39. Let X be the product nucleus. The nuclear equation is

$$^{210}_{84}\text{Po} \rightarrow {}^{A}_{Z}\text{X} + {}^{4}_{2}\text{He}$$

From the superscripts: 210 = A + 4, or A = 206; from the subscripts: 84 = Z + 2, or Z = 82. Thus, the product nucleus is $^{206}_{82}\text{X}$, and because element 82 is lead, symbol Pb, the nuclear equation is

$$^{210}_{84}\text{Po} \rightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

20.40. Let X be the product nucleus. The nuclear equation is

$$^{227}_{89}\text{Ac} \rightarrow {}^{A}_{Z}\text{X} + {}^{4}_{2}\text{He}$$

From the superscripts: 227 = A + 4, or A = 223; from the subscripts: 89 = Z + 2, or Z = 87. Thus, the product nucleus is $^{223}_{87}\text{X}$, and because element 87 is francium, symbol Fr, the nuclear equation is

$$^{227}_{89}\text{Ac} \rightarrow {}^{223}_{87}\text{Fr} + {}^{4}_{2}\text{He}$$

20.41.

a. Neither nucleus has an atomic number that is a magic number of protons. Find how many neutrons are in each nucleus.

Sb: No. of neutrons = $A - Z$ = 122 − 51 = 71

Xe: No. of neutrons = $A - Z$ = 136 − 54 = 82

Because 82 is a magic number for neutrons (implying stability of nucleus), you predict that $^{136}_{54}\text{Xe}$ is stable and $^{122}_{51}\text{Sb}$ is radioactive.

b. $^{204}_{82}\text{Pb}$ has a magic number of protons (82), so it is expected to be the stable nucleus, and $^{204}_{85}\text{At}$ is expected to be radioactive (atomic number greater than 83).

c. Rb does not have an atomic number that is a magic number of protons. Find the numbers of neutrons in the two isotopes.

$^{87}_{37}\text{Rb}$: No. of neutrons = 87 − 37 = 50

$^{80}_{37}\text{Rb}$: No. of neutrons = 80 − 37 = 43

Because 50 is a magic number for neutrons, you predict that $^{87}_{37}\text{Rb}$ is stable and $^{80}_{37}\text{Rb}$ is radioactive.

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20.42.

a. Ag does not have an atomic number that is a magic number of protons. Find the numbers of neutrons in the two isotopes.

$^{102}_{47}\text{Ag}$: No. of neutrons = 102 − 47 = 55

$^{109}_{47}\text{Ag}$: No. of neutrons = 109 − 47 = 62

Neither isotope has a magic number of neutrons, but $^{109}_{47}\text{Ag}$ has an even number of neutrons, whereas $^{102}_{47}\text{Ag}$ has an odd number of neutrons. Because stable odd-odd nuclei are rare, $^{109}_{47}\text{Ag}$ is expected to be stable and $^{102}_{47}\text{Ag}$ radioactive.

b. Neither nucleus has a magic number of protons or neutrons. Of the two isotopes $^{25}_{12}\text{Mg}$ has an even number of protons and is close to the true atomic mass of magnesium, 24.3050 amu. $^{24}_{10}\text{Ne}$ is not close to the true atomic mass of neon, 20.179 amu. Therefore, $^{25}_{12}\text{Mg}$ is expected to be stable and $^{24}_{10}\text{Ne}$ radioactive.

c. No element with atomic number greater than 83 has a stable isotope. Thus, $^{223}_{90}\text{Th}$ is radioactive, and $^{203}_{81}\text{Tl}$ is stable.

20.43.

a. α-emission is most likely for nuclei with $Z > 83$.

b. positron emission (more likely; $Z < 20$) or electron capture because the mass number is less than that of Cu = 63.5

c. β-emission (mass no. > He = 4)

20.44.

a. positron emission or electron capture ($N/Z = 30/30 = 1$)

b. positron emission ($N/Z = 4/6 < 1$,and $Z < 20$)

c. α-emission ($Z > 83$)

20.45. α-emission decreases the mass number by 4; β-emission does not affect the mass number. $^{219}_{86}\text{Rn}$ belongs to the $^{235}_{92}\text{U}$ decay series because the difference in mass numbers is 16, which is divisible by 4. $^{220}_{86}\text{Rn}$ belongs to the $^{232}_{90}\text{Th}$ decay series because the difference in mass numbers is 12, which is divisible by 4.

20.46. α-emission decreases the mass number by 4; β-emission does not affect the mass number. $^{227}_{89}\text{Ac}$ belongs to the $^{235}_{92}\text{U}$ decay series because the difference in mass numbers is 8, which is divisible by 4. $^{225}_{89}\text{Ac}$ belongs to the $^{241}_{94}\text{Pu}$ decay series because the difference in mass numbers is 16, which is divisible by 4.

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20.47.

a. $^{26}_{12}\text{Mg}\,(\text{d},\alpha)\,^{24}_{11}\text{Na}$

b. $^{16}_{8}\text{O}\,(\text{n},\text{p})\,^{16}_{7}\text{N}$

20.48.

a. $^{14}_{7}\text{N}\,(\text{n},\text{p})\,^{14}_{6}\text{C}$

b. $^{63}_{29}\text{Cu}\,(\alpha,\text{n})\,^{66}_{31}\text{Ga}$

20.49.

a. $^{27}_{13}\text{Al} + {}^{2}_{1}\text{H} \rightarrow {}^{25}_{12}\text{Mg} + {}^{4}_{2}\text{He}$

b. $^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \rightarrow {}^{13}_{6}\text{C} + {}^{1}_{1}\text{H}$

20.50.

a. $^{45}_{21}\text{Sc} + {}^{1}_{0}\text{n} \rightarrow {}^{42}_{19}\text{K} + {}^{4}_{2}\text{He}$

b. $^{63}_{29}\text{Cu} + {}^{1}_{1}\text{H} \rightarrow {}^{63}_{30}\text{Zn} + {}^{1}_{0}\text{n}$

20.51. $$\frac{12.6\text{ MeV}}{1\text{ proton}} = \frac{12.6 \times 10^{6}\text{ eV}}{1\text{ proton}} \times \frac{1.602 \times 10^{-19}\text{ J}}{1\text{ eV}} \times \frac{1\text{ kJ}}{10^{3}\text{ J}} \times \frac{6.02 \times 10^{23}\text{ protons}}{1\text{ mol}}$$

$$= 1.21\underline{5} \times 10^{9} = 1.22 \times 10^{9}\text{ kJ/mol}$$

20.52. $$\frac{23.1\text{ MeV}}{1\ \alpha} = \frac{23.1 \times 10^{6}\text{ eV}}{1\ \alpha} \times \frac{1.602 \times 10^{-19}\text{ J}}{1\text{ eV}} \times \frac{1\text{ kJ}}{10^{3}\text{ J}} \times \frac{6.02 \times 10^{23}\ \alpha\text{'s}}{1\text{ mol}}$$

$$= 2.22\underline{7}8 \times 10^{9} = 2.23 \times 10^{9}\text{ kJ/mol}$$

20.53.

a. $^{6}_{3}\text{Li} + {}^{1}_{0}\text{n} \rightarrow {}^{A}_{Z}\text{X} + {}^{3}_{1}\text{H}$

From the superscripts: $6 + 1 = A + 3$, or $A = 6 + 1 - 3 = 4$; from the subscripts: $3 + 0 = Z + 1$, or $Z = 3 - 1 = 2$. The product nucleus is $^{4}_{2}\text{X}$. The element with $Z = 2$ is helium (He), so the missing nuclide is $^{4}_{2}\text{He}$.

b. The reaction may be written

$$^{232}_{90}\text{Th} + {}^{A}_{Z}\text{X} \rightarrow {}^{235}_{92}\text{U} + {}^{1}_{0}\text{n}$$

From the superscripts: $232 + A = 235 + 1$, or $A = 235 + 1 - 232 = 4$; from the subscripts: $90 + Z = 92 + 0$, or $Z = 92 - 90 = 2$. The projectile nucleus is $^{4}_{2}\text{X}$. The element with $Z = 2$ is helium, so the missing nuclide is $^{4}_{2}\text{He}$, or α. The reaction is then written

$$^{232}_{90}\text{Th}\,(\alpha,\text{n})\,^{235}_{92}\text{U}$$

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20.54.

a. $^{27}_{13}\text{Al} + {}^{3}_{1}\text{H} \rightarrow {}^{27}_{12}\text{Mg} + {}^{A}_{Z}\text{X}$

From the superscripts: 27 + 3 = 27 + *A*, or *A* = 27 + 3 − 27 = 3; from the subscripts: 13 + 1 = 12 + *Z*, or *Z* = 13 + 1 − 12 = 2. The ejected particle is $^{3}_{2}\text{X}$. The element with *Z* = 2 is helium, so the missing nuclide is $^{3}_{2}\text{He}$.

b. The reaction may be written

$$^{12}_{6}\text{C} + {}^{3}_{1}\text{H} \rightarrow {}^{14}_{6}\text{C} + {}^{A}_{Z}\text{X}$$

From the superscripts: 12 + 3 = 14 + *A*, or *A* = 12 + 3 − 14 = 1; from the subscripts: 6 + 1 = 6 + *Z*, or *Z* = 6 + 1 − 6 = 1. The ejected particle is $^{1}_{1}\text{X}$. The element with *Z* = 1 is hydrogen, so the missing nuclide is $^{1}_{1}\text{H}$, or p. The reaction is then written

$$^{12}_{6}\text{C}\,(^{3}_{1}\text{H},\text{p})\,^{14}_{6}\text{C}$$

20.55. The reaction may be written

$$^{A}_{Z}\text{X} + {}^{4}_{2}\text{He} \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$$

From the superscripts: *A* + 4 = 242 + 1, or *A* = 242 + 1 − 4 = 239; from the subscripts: *Z* + 2 = 96 + 0, or *Z* = 96 − 2 = 94. The element with *Z* = 94 is plutonium (the target nucleus was $^{239}_{94}\text{Pu}$).

20.56. The reaction may be written

$$^{A}_{Z}\text{X} + {}^{4}_{2}\text{He} \rightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$$

From the superscripts: *A* + 4 = 245 + 1, or *A* = 245 + 1 − 4 = 242; from the subscripts: *Z* + 2 = 98 + 0, or *Z* = 98 − 2 = 96. The element with *Z* = 96 is curium (the target nucleus was $^{242}_{96}\text{Cm}$).

20.57. The rate of decay is 8.94×10^{10} nuclei/s. The number of nuclei in the sample is

$$0.250 \times 10^{-3}\ \text{g H–3} \times \frac{1\ \text{mol H-3}}{3.02\ \text{g H-3}} \times \frac{6.02 \times 10^{23}\ \text{nuclei}}{1\ \text{mol H-3}} = 4.98\underline{3} \times 10^{19}\ \text{nuclei}$$

The rate equation is rate = kN_t. Solve for *k*.

$$k = \frac{\text{rate}}{N_t} = \frac{8.94 \times 10^{10}\ \text{nuclei/s}}{4.98 \times 10^{19}\ \text{nuclei}} = 1.79\underline{4} \times 10^{-9} = 1.79 \times 10^{-9}\ \text{s}^{-1}$$

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20.58. Convert the mass of Pu-238 to the number of nuclei. The molar mass in grams is approximately equal to the mass number.

$$2.8 \times 10^{-6} \text{ g Pu-238} \times \frac{1 \text{ mol Pu-238}}{238 \text{ g Pu-238}} \times \frac{6.02 \times 10^{23} \text{ nuclei}}{1 \text{ mol Pu-238}} = 7.\underline{0}8 \times 10^{15} \text{ nuclei}$$

Solve the rate equation for k and substitute.

$$k = \frac{\text{rate}}{N_t} = \frac{1.8 \times 10^{6} \text{ nuclei/s}}{7.08 \times 10^{15} \text{ nuclei}} = 2.\underline{5}42 \times 10^{-10} = 2.5 \times 10^{-10}/\text{s}$$

20.59. Find the rate of decay from the activity.

$$\text{Rate} = 20.4 \text{ Ci} \times \frac{3.700 \times 10^{10} \text{ nuclei/s}}{1 \text{ Ci}} = 7.5\underline{4}8 \times 10^{11} \text{ nuclei/s}$$

Convert the mass of S-35 to the number of nuclei. The molar mass in grams is approximately equal to the mass number.

$$0.48 \times 10^{-3} \text{ g S-35} \times \frac{1 \text{ mol S-35}}{35 \text{ g S-35}} \times \frac{6.02 \times 10^{23} \text{ nuclei}}{1 \text{ mol S-35}} = 8.\underline{2}56 \times 10^{18} \text{ nuclei}$$

Solve the rate equation for k and substitute.

$$k = \frac{\text{rate}}{N_t} = \frac{7.548 \times 10^{11} \text{ nuclei/s}}{8.256 \times 10^{18} \text{ nuclei}} = 9.\underline{1}4 \times 10^{-8} = 9.1 \times 10^{-8} \text{ s}^{-1}$$

20.60. Find the rate of decay from the activity.

$$\text{Rate} = 45.3 \text{ Ci} \times \frac{3.700 \times 10^{10} \text{ nuclei/s}}{1 \text{ Ci}} = 1.6\underline{7}61 \times 10^{12} \text{ nuclei/s}$$

Convert the mass of the Na-24 to the number of nuclei. The molar mass in grams is approximately equal to the mass number.

$$5.2 \times 10^{-6} \text{ g Na-24} \times \frac{1 \text{ mol Na-24}}{24 \text{ g Na-24}} \times \frac{6.02 \times 10^{23} \text{ nuclei}}{1 \text{ mol Na-24}} = 1.\underline{3}04 \times 10^{17} \text{ nuclei}$$

Solve the rate equation for k and substitute.

$$k = \frac{\text{rate}}{N_t} = \frac{1.6761 \times 10^{12} \text{ nuclei/s}}{1.304 \times 10^{17} \text{ nuclei}} = 1.\underline{2}85 \times 10^{-5} = 1.3 \times 10^{-5}/\text{s}$$

20.61. $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.7 \times 10^{-21} \text{ /s}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ y}}{365 \text{ d}} = 1.\underline{2}92 \times 10^{13}$$

$$= 1.3 \times 10^{13} \text{ y}$$

20.62. $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.03 \times 10^{-14} \text{ /s}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ y}}{365 \text{ d}} = 2.1\underline{3}3 \times 10^{6}$$

$$= 2.13 \times 10^{6} \text{ y}$$

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20.63. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{5.73 \times 10^3 \text{ y}} \times \dfrac{1 \text{ y}}{365 \text{ d}} \times \dfrac{1 \text{ d}}{24 \text{ h}} \times \dfrac{1 \text{ h}}{3600 \text{ s}}$

$= 3.8\underline{3}505 \times 10^{-12} = 3.84 \times 10^{-12}/\text{s}$

20.64. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{2.5 \text{ y}} \times \dfrac{1 \text{ y}}{365 \text{ d}} \times \dfrac{1 \text{ d}}{24 \text{ h}} \times \dfrac{1 \text{ h}}{3600 \text{ s}} = 8.\underline{7}89 \times 10^{-9} = 8.8 \times 10^{-9}/\text{s}$

20.65. Find k from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.69 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 2.9\underline{8}2 \times 10^{-6}/\text{s}$$

Before substituting into the rate equation, find the number of gold nuclei from the mass.

$$0.86 \times 10^{-3} \text{ g Au-198} \times \frac{1 \text{ mol Au-198}}{198 \text{ g Au-198}} \times \frac{6.02 \times 10^{23} \text{ Au-198 nuclei}}{1 \text{ mol Au-198}}$$

$$= 2.\underline{6}1 \times 10^{18} \text{ Au-198 nuclei}$$

Now find the rate.

$$\text{Rate} = kN_t = (2.982 \times 10^{-6}/\text{s})(2.61 \times 10^{18} \text{ nuclei}) = 7.\underline{7}9 \times 10^{12} \text{ nuclei/s}$$

$$\text{Activity} = 7.79 \times 10^{12} \text{ nuclei/s} \times \frac{1 \text{ Ci}}{3.700 \times 10^{10} \text{ nuclei/s}} = 2\underline{1}0.7 = 2.1 \times 10^2 \text{ Ci}$$

20.66. Find k from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.05 \text{ y}} \times \frac{1 \text{ y}}{365 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 1.0\underline{7}19 \times 10^{-8}/\text{s}$$

Find the number of cesium nuclei from the mass.

$$0.50 \times 10^{-3} \text{ g Cs-134} \times \frac{1 \text{ mol Cs-134}}{134 \text{ g Cs-134}} \times \frac{6.02 \times 10^{23} \text{ Cs-134 nuclei}}{1 \text{ mol Cs-134}}$$

$$= 2.\underline{2}46 \times 10^{18} \text{ nuclei}$$

Now find the rate.

$$\text{Rate} = kN_t = (1.0719 \times 10^{-8}/\text{s})(2.246 \times 10^{18} \text{ nuclei}) = 2.\underline{4}07 \times 10^{10} \text{ nuclei/s}$$

$$\text{Activity} = 2.407 \times 10^{10} \text{ nuclei/s} \times \frac{1 \text{ Ci}}{3.700 \times 10^{10} \text{ nuclei/s}} = 0.6\underline{5}07 = 0.65 \text{ Ci}$$

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20.67. Find k from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3\text{ d}} \times \frac{1\text{ d}}{24\text{ h}} \times \frac{1\text{ h}}{3600\text{ s}} = 5.6\underline{0}9 \times 10^{-7}/\text{s}$$

Solve the rate equation for N_t.

$$N_t = \frac{\text{rate}}{k} = \frac{6.0 \times 10^{12}\text{ nuclei/s}}{5.609 \times 10^{-7}\text{ /s}} = 1.\underline{0}7 \times 10^{19}\text{ nuclei}$$

Convert N_t to the mass of P-32.

$$1.07 \times 10^{19}\text{ P-32 nuclei} \times \frac{1\text{ mol P-32}}{6.02 \times 10^{23}\text{ P-32 nuclei}} \times \frac{32\text{ g P-32}}{1\text{ mol P-32}}$$

$$= 5.\underline{6}8 \times 10^{-4} = 5.7 \times 10^{-4}\text{ g P-32}$$

20.68. Find k from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{88\text{ d}} \times \frac{1\text{ d}}{24\text{ h}} \times \frac{1\text{ h}}{3600\text{ s}} = 9.\underline{1}1 \times 10^{-8}/\text{s}$$

Solve the rate equation for N_t.

$$N_t = \frac{\text{rate}}{k} = \frac{7.7 \times 10^{11}\text{ nuclei/s}}{9.11 \times 10^{-8}/\text{s}} = 8.\underline{4}5 \times 10^{18}\text{ nuclei}$$

Convert N_t to the mass of S-35.

$$8.45 \times 10^{18}\text{ S-35 nuclei} \times \frac{1\text{ mol S-35}}{6.02 \times 10^{23}\text{ S-35 nuclei}} \times \frac{35\text{ g S-35}}{1\text{ mol S-35}}$$

$$= 4.\underline{9}1 \times 10^{-4} = 4.9 \times 10^{-4}\text{ g S-35}$$

20.69. Substituting for $k = 0.693/t_{1/2}$ gives

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (12.0\text{ h})}{15.0\text{ h}} = -0.55\underline{4}4$$

Taking the antilog of both sides of this equation gives

$$\frac{N_t}{N_o} = e^{-0.5544} = 0.57\underline{4}41$$

After 12.0 h, 57.4% of the Na-24 remains.

$$6.0\ \mu\text{g} \times 0.57441 = 3.\underline{4}46\ \mu\text{g} = 3.4\ \mu\text{g}$$

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20.70. Substituting for $k = 0.693/t_{1/2}$ gives

$$\ln \frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (7.0\ \text{d})}{8.07\ \text{d}} = -0.6011$$

Taking the antilog of both sides of this equation gives

$$\frac{N_t}{N_o} = e^{-0.6011} = 0.5481$$

After 7.0 days, 54.8% of the I-131 remains; therefore, the mass of I-131 remaining is

$$2.5\ \mu\text{g I-131} \times 0.5481 = 1.37 = 1.4\ \mu\text{g I-131}$$

20.71. After 1.97 s, the amount of nitrogen-17 remaining is 100% − 28.0% = 72.0%, so $N_t/N_o = 0.720$.

$$\ln \frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}}$$

$$\ln (0.720) = \frac{-0.693(1.97\ \text{s})}{t_{1/2}}$$

Solve for $t_{1/2}$.

$$t_{1/2} = \frac{-0.693(1.97\ \text{s})}{\ln(0.720)} = 4.1558 = 4.16\ \text{s}$$

20.72. After 69.9 d, the amount of zinc-65 remaining is 100% − 20.0% = 80.0%, so $N_t/N_o = 0.800$.

$$\ln \frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}}$$

$$\ln (0.800) = \frac{-0.693(69.9\ \text{d})}{t_{1/2}}$$

Solve for $t_{1/2}$.

$$t_{1/2} = \frac{-0.693(69.9\ \text{d})}{\ln(0.800)} = 217.1 = 217\ \text{d}$$

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20.73. At $t = 0$, the rate is 125 nuclei/s, and at time $t = 10.0$ d, the rate is 107 nuclei/s. Thus,

$$\ln \frac{N_t}{N_o} = -kt = = \frac{-0.693\ t}{t_{1/2}}$$

Substituting yields

$$\ln\left(\frac{107 \text{ nuclei/s}}{125 \text{ nuclei/s}}\right) = \frac{-0.693\ (10.0 \text{ d})}{t_{1/2}}$$

Solve for the half-life.

$$t_{1/2} = \frac{-0.693\ (10.0 \text{ d})}{\ln\left(\frac{107}{125}\right)} = 44.\underline{5}7 = 44.6 \text{ d}$$

20.74. At $t = 0$, the rate is 88 nuclei/s, and at time $t = 9.5$ h, the rate is 53 nuclei/s. Thus,

$$\ln \frac{N_t}{N_o} = -kt = = \frac{-0.693\ \text{t}}{t_{1/2}}$$

Substituting yields

$$\ln\left(\frac{53 \text{ nuclei/s}}{88 \text{ nuclei/s}}\right) = \frac{-0.693\ (9.5 \text{ h})}{t_{1/2}}$$

Solve for the half-life.

$$t_{1/2} = \frac{-0.693\ (9.5 \text{ h})}{\ln\left(\frac{53}{88}\right)} = 1\underline{2}.98 = 13 \text{ h}$$

20.75. Use the equation for the number of nuclei in a sample after a time, t.

$$\ln \frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}}$$

Rearrange this to give an expression for t.

$$t = \frac{t_{1/2}}{0.693} \ln \frac{N_o}{N_t}$$

At $t = 0$, the rate is 15.3 nuclei/s, and at a later time t, the rate is 8.1 nuclei/s. Since the half-life for carbon-14 is 5730 y,

$$t = \frac{5730 \text{ y}}{0.693} \ln\left(\frac{15.3}{8.1}\right) = 5.\underline{2}58 \times 10^3 = 5.3 \times 10^3 \text{ y}$$

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20.76. Use the equation for the number of nuclei in a sample after a time, *t*.

$$\ln \frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}}$$

Rearrange this to give an expression for *t*.

$$t = \frac{t_{1/2}}{0.693} \ln \frac{N_o}{N_t}$$

At $t = 0$, the rate is 15.3 nuclei/s, and at a later time *t*, the rate is 12.1 nuclei/s. Since the half-life for carbon-14 is 5730 y,

$$t = \frac{5730\text{ y}}{0.693} \ln\left(\frac{15.3}{12.1}\right) = 1.9\underline{4}0 \times 10^3 = 1.94 \times 10^3\text{ y}$$

20.77. The half-life of carbon-14 is 5730 y, and the age of the sandals is 9.0×10^3 y. Substitute into the equation

$$\ln \frac{N_t}{N_o} = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (9.0 \times 10^3\text{ y})}{5730\text{ y}} = -1.\underline{0}88$$

Taking the antilog of both sides, you obtain

$$\frac{N_t}{N_o} = \frac{(\text{activity})_t}{(\text{activity})_o} = e^{-1.088} = 0.\underline{3}367$$

Therefore, the activity for a gram sample is

$$(\text{activity})_t = 15.3\text{ disintegrations/(min•g)} \times 0.\underline{3}367$$
$$= \underline{5}.15\text{ disintegrations/(min•g)}$$
$$= 5\text{ disintegrations/(min•g)}$$

20.78. The half-life of carbon-14 is 5730 y, and the age of the bones is 1.13×10^4 y. Substitute into the equation

$$\ln \frac{N_t}{N_o} = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (1.13 \times 10^4\text{ y})}{5730\text{ y}} = -1.3\underline{6}66$$

Taking the antilog of both sides, you obtain

$$\frac{N_t}{N_o} = \frac{(\text{activity})_t}{(\text{activity})_o} = e^{-1.3666} = 0.2\underline{5}49$$

Therefore, the activity for a gram sample is

$$(\text{activity})_t = 15.3\text{ disintegrations/(min • g)} \times 0.2549$$
$$= 3.\underline{9}00\text{ disintegrations/(min • g)}$$
$$= 3.9\text{ disintegrations/(min • g)}$$

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20.79. $\Delta m = \dfrac{\Delta E}{c^2} = \dfrac{-393.5 \times 10^3 \text{ J}}{(3.00 \times 10^8 \text{ m/s})^2} = \dfrac{-3.935 \times 10^5 \text{ kg} \bullet \text{m}^2/\text{s}^2}{(3.00 \times 10^8 \text{ m/s})^2}$

$= -4.372 \times 10^{-12} = -4.37 \times 10^{-12} \text{ kg} = -4.37 \times 10^{-9} \text{ g}$

20.80. $\Delta m = \dfrac{\Delta E}{c^2} = \dfrac{-297 \times 10^3 \text{ J}}{(3.00 \times 10^8 \text{ m/s})^2} = \dfrac{-2.97 \times 10^5 \text{ kg} \bullet \text{m}^2/\text{s}^2}{(3.00 \times 10^8 \text{ m/s})^2}$

$= -3.300 \times 10^{-12} = -3.30 \times 10^{-12} \text{ kg} = -3.30 \times 10^{-9} \text{ g}$

20.81. First, determine the nuclear masses.

Nuclear mass of ^2_1H = 2.01400 amu − 0.000549 amu = 2.013451 amu

Nuclear mass of ^3_1H = 3.01605 amu − 0.000549 amu = 3.015501 amu

Nuclear mass of ^4_2He = 4.00260 amu − (2 x 0.000549 amu) = 4.001502 amu

Write the appropriate nuclear mass below each nuclide symbol, and calculate Δm.

$$^2_1\text{H} + {}^3_1\text{H} \rightarrow {}^4_2\text{He} + {}^1_0\text{n}$$

Masses: 2.013451 3.015501 4.001502 1.008665 amu

Δm = (4.001502 + 1.008665 − 2.013451 − 3.015501) amu = −0.018785 amu

The energy change for 1 mol is

$\Delta E = (\Delta m)c^2 = (-0.018785 \times 10^{-3} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2$

$= -1.68839 \times 10^{12} \text{ kg} \bullet \text{m}^2/\text{s}^2 = -1.688 \times 10^{12} \text{ J}$

Finally, calculate the energy change in MeV for one ^2_1H nucleus.

$$\frac{-1.68839 \times 10^{12} \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ nuclei}} \times \frac{1 \text{ MeV}}{1.602 \times 10^{-13} \text{ J}} = -17.501 = -17.50 \text{ MeV}$$

20.82. First, determine the nuclear mass of ^2_1H.

Nuclear mass of ^2_1H = 2.01400 amu − 0.000549 amu = 2.013451 amu

Write the appropriate nuclear mass below each nuclide symbol, and calculate Δm.

$$^1_1\text{H} + {}^1_1\text{H} \rightarrow {}^2_1\text{H} + {}^0_1\text{e}$$

Masses: 1.00728 1.00728 2.013451 0.000549 amu

Δm = [2.013451 + 0.000549 − (2 x 1.00728)] amu = −0.000560 amu

The energy change for 1 mol is

$\Delta E = (\Delta m)c^2 = (-5.6 \times 10^{-7} \text{ kg})(3.00 \times 10^8 \text{ m/s})^2 = -5.04 \times 10^{10} \text{ kg} \bullet \text{m}^2/\text{s}^2 = -5.0 \times 10^{10} \text{ J}$

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Finally, calculate the energy change for one $^{1}_{1}H$ nucleus.

$$\frac{-5.04 \times 10^{10}\ \text{J}}{1\ \text{mol}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{nuclei}} \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = -0.522 = -0.52\ \text{MeV}$$

20.83. Mass of three protons = 3 x 1.00728 amu = 3.02184 amu

Mass of three neutrons = 3 x 1.008665 amu = 3.025995 amu

Total mass of nucleons = (3.02184 + 3.025995) amu = 6.047835 amu

Nuclear mass of $^{6}_{3}Li$ = 6.01512 amu − (3 x 0.000549 amu) = 6.013473 amu

Mass defect = total nucleon mass − nuclear mass = (6.047835 − 6.013473) amu

= 0.034362 = 0.03436 amu

$$\Delta E = (\Delta m)c^2 = 0.034362\ \text{amu} \times \frac{1\ \text{g}}{6.022 \times 10^{23} \times 1\ \text{amu}} \times \frac{1\ \text{kg}}{10^{3}\ \text{g}}$$

$$\times (2.998 \times 10^{8}\ \text{m/s})^2 \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = 32.013\ \text{MeV}$$

$$\text{Binding energy per nucleon} = \frac{32.013\ \text{MeV}}{6\ \text{nucleons}} = 5.3356 = 5.336\ \text{MeV/nucleon}$$

20.84. Mass of twenty-eight protons = 28 x 1.00728 amu = 28.20384 amu

Mass of thirty neutrons = 30 x 1.008665 amu = 30.25995 amu

Total mass of nucleons = (28.20384 + 30.25995) amu = 58.46379 amu

Nuclear mass of $^{58}_{28}Ni$ = 57.93534 amu − (28 x 0.000549 amu) = 57.919968 amu

Mass defect = total nucleon mass − nuclear mass = (58.46379 − 57.919968) amu

= 0.54382 amu

$$\Delta E = (\Delta m)c^2 = 0.54382\ \text{amu} \times \frac{1\ \text{g}}{6.022 \times 10^{23} \times 1\ \text{amu}} \times \frac{1\ \text{kg}}{10^{3}\ \text{g}}$$

$$\times (2.998 \times 10^{8}\ \text{m/s})^2 \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = 506.66\ \text{MeV}$$

$$\text{Binding energy per nucleon} = \frac{506.66\ \text{MeV}}{58\ \text{nucleons}} = 8.7355 = 8.736\ \text{MeV/nucleon}$$

■ SOLUTIONS TO GENERAL PROBLEMS

20.85. Na-20, having fewer neutrons than the stable Na-23, is expected to decay to a nucleus with a lower atomic number (and hence a higher *N*/*Z* ratio) by electron capture or positron emission. Na-26, having more neutrons than the stable isotope, is expected to decay by beta emission to give a nucleus with a higher atomic number (and hence a lower *N*/*Z* ratio).

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20.86. Al-24 has fewer neutrons than the stable Al-27, so it is expected to decay to a nucleus with a lower atomic number and higher *N*/*Z* value. Al-24 is expected to decay by positron emission or electron capture. Al-30 has more neutrons than the stable Al-27, so it is expected to decay to a nucleus with a higher atomic number and lower *N*/*Z* value. Al-30 is expected to decay by beta emission.

20.87. The overall reaction may be written

$$^{235}_{92}\text{U} \rightarrow {}^{207}_{82}\text{Pb} + n\ {}^{4}_{2}\text{He} + m\ {}^{0}_{-1}\text{e}$$

From the superscripts:

$$235 = 207 + (n \times 4) + (m \times 0)$$

$$n = \frac{235 - 207}{4} = 7$$

From the subscripts, and with n equal to 7, you get

$$92 = 82 + (n \times 2) + m \times (-1)$$

$$m = 82 - 92 + (7 \times 2) = 4$$

Therefore, there are seven α emissions and four β emissions.

20.88. The overall reaction is

$$^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Pb} + n\ {}^{4}_{2}\text{He} + m\ {}^{0}_{-1}\text{e}$$

From the superscripts:

$$232 = 208 + (n \times 4) + (m \times 0)$$

$$n = \frac{232 - 208}{4} = 6$$

From the subscripts, and with n equal to 6, you get

$$90 = 82 + (n \times 2) + [m \times (-1)]$$

$$m = 82 - 90 + (6 \times 2) = 4$$

Therefore, there are six α emissions and four β emissions.

20.89. $^{209}_{83}\text{Bi} + {}^{4}_{2}\text{He} \rightarrow {}^{A}_{85}\text{At} + 2\ {}^{1}_{0}\text{n}$

From the superscripts: $209 + 4 = A + (2 \times 1)$, or $A = 213 - 2 = 211$.

The reaction is

$$^{209}_{83}\text{Bi} + {}^{4}_{2}\text{He} \rightarrow {}^{211}_{85}\text{At} + 2\ {}^{1}_{0}\text{n}$$

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20.90. $^{209}_{83}\text{Bi} + {}^{2}_{1}\text{H} \rightarrow {}^{A}_{84}\text{Po} + {}^{1}_{0}\text{n}$

From the superscripts: 209 + 2 = A + 1, or A = 211 − 1 = 210.

The reaction is

$$^{209}_{83}\text{Bi} + {}^{2}_{1}\text{H} \rightarrow {}^{210}_{84}\text{Po} + {}^{1}_{0}\text{n}$$

20.91. $^{238}_{92}\text{Bi} + {}^{12}_{6}\text{C} \rightarrow {}^{A}_{Z}\text{X} + 4\ {}^{1}_{0}\text{n}$

From the superscripts: 238 + 12 = A + (4 x 1), or A = 250 − 4 = 246; from the subscripts: 92 + 6 = Z + (4 x 0), or Z = 98.

The element with Z = 98 is californium (Cf), so the equation is

$$^{238}_{92}\text{Bi} + {}^{12}_{6}\text{C} \rightarrow {}^{246}_{98}\text{Cf} + 4\ {}^{1}_{0}\text{n}$$

20.92. $^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \rightarrow {}^{A}_{Z}\text{X} + 4\ {}^{1}_{0}\text{n}$

From the superscripts: 246 + 12 = A + 4 x 1, or A = 258 − 4 = 254; from the subscripts: 96 + 6 = Z + (4 x 0), or Z = 102.

The element with Z = 102 is nobelium (No), so the equation is

$$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \rightarrow {}^{254}_{102}\text{No} + 4\ {}^{1}_{0}\text{n}$$

20.93. Use the equation for the number of nuclei in a sample after a time, t.

$$\ln\frac{N_t}{N_o} = \frac{-0.693\ t}{t_{1/2}}$$

Rearrange this to give an expression for t.

$$t = \frac{t_{1/2}}{0.693}\ln\frac{N_o}{N_t}$$

Substituting yields

$$t = \frac{(12.3\text{ y})}{0.693}\ln\frac{N_o}{0.70\ N_o} = 6.\underline{3}2 = 6.3\text{ y}$$

20.94. Use the equation for the number of nuclei in a sample after a time, t.

$$\ln\frac{N_t}{N_o} = \frac{-0.693\ t}{t_{1/2}}$$

Rearrange this to give an expression for t.

$$t = \frac{t_{1/2}}{0.693}\ln\frac{N_o}{N_t}$$

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The amount of Rb-87 initially present is the amount remaining plus the amount converted to Sr-87. Therefore,

$$\frac{N_o}{N_t} = \frac{102.1\ \mu g + 5.3\mu g}{102.1\ \mu g} = 1.\underline{0}52$$

The age of the rock is

$$t = \frac{4.8 \times 10^{10}\ y}{0.693} \ln (1.052) = 3.\underline{5}1 \times 10^{9} = 3.5 \times 10^{9}\ y$$

20.95. In the annihilation, the final mass is zero; that is, all mass is converted to energy. Therefore,

$$\Delta m = 0 - \text{mass of positron} - \text{mass of electron}$$

$$= -2(0.000549\ \text{amu}) \times \frac{1\ g}{6.022 \times 10^{23}\ \text{amu}} \times \frac{1\ kg}{10^{3}\ g} = -1.8\underline{2}33 \times 10^{-30}\ kg$$

The energy of each photon is $-\Delta E/2$.

$$E_{\text{photon}} = \frac{-\Delta E}{2} = \frac{-(\Delta m)c^2}{2} = \frac{-(-1.8233 \times 10^{-30}\ kg)(2.998 \times 10^{8}\ m/s)^2}{2}$$

$$= 8.1\underline{9}39 \times 10^{-14}\ J$$

The energy of a photon is related to its wavelength by the equation

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant. Therefore,

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ J \bullet s)(2.998 \times 10^{8}\ m/s)}{(8.1939 \times 10^{-14}\ J)} = 2.4\underline{2}43 \times 10^{-12} = 2.42 \times 10^{-12}\ m$$

The wavelength of the photons is 2.42 pm.

20.96. The energy of a photon is

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant. Therefore,

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ J \bullet s)(2.998 \times 10^{8}\ m/s)}{0.143\ \text{MeV}} \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ J}$$

$$= 8.6\underline{7}13 \times 10^{-12} = 8.67 \times 10^{-12}\ m\ (8.67\ pm)$$

To obtain the difference in mass, note that

$$\Delta E = -E = (\Delta m)c^2$$

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Therefore,

$$\Delta m = \frac{-E}{c^2} = \frac{-0.143 \text{ MeV}}{(2.998 \times 10^8 \text{ m/s})^2} \times \frac{1.602 \times 10^{-13} \text{ J}}{1 \text{ MeV}}$$

$$= -2.5\underline{4}87 \times 10^{-31} = -2.55 \times 10^{-31} \text{ kg} \ (-2.55 \times 10^{-28} \text{ g})$$

The difference in mass between a Tc-99m nucleus and a Tc-99 nucleus is 2.55×10^{-28} g.

20.97. First, determine the nuclear mass of uranium.

Nuclear mass of $^{235}_{92}\text{U}$ = 235.04392 amu − (92 x 0.000549 amu) = 234.993412 amu

Write the appropriate nuclear mass below each nuclide symbol, and calculate Δm.

$$^{1}_{0}\text{n} + {}^{235}_{92}\text{U} \rightarrow {}^{136}_{53}\text{I} + {}^{96}_{39}\text{Y} + 4\,{}^{1}_{0}\text{n}$$

Masses: 1.008665 234.993412 135.811003 95.841489 1.008665 amu

$$\Delta m = [135.8401 + 95.8629 + 4 \times 1.008665 - (1.008665 + 234.993412)] \text{ amu}$$

$$= -0.264\underline{4}17 \text{ amu}$$

When 1 mol of U-235 decays, the change in mass is −0.264417 g. Therefore, for 5.00 kg of U-235, the change in mass is

$$5.00 \times 10^3 \text{ g U-235} \times \frac{1 \text{ mol U-235}}{235.04392 \text{ g U-235}} \times \frac{-0.264417 \text{ g}}{1 \text{ mol U-235}} = -5.6\underline{2}48 \text{ g}$$

Converting mass to energy gives

$$E = (\Delta m)c^2 = (-5.6248 \times 10^{-3} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 = -5.0\underline{5}56 \times 10^{14} \text{ J}$$

For the combustion of carbon:

	C(graphite)	+	$O_2(g)$	→	$CO_2(g)$
ΔH_f°	0		0		-394 kJ/mol

For the reaction, $\Delta H = \Delta E = -394$ kJ/mol.

$$5.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{-394 \text{ kJ}}{1 \text{ mol C}} = -1.6\underline{4}029 \times 10^5 = -1.64 \times 10^5 \text{ kJ}$$

The energy released in the fission of 5.00 kg of U-235 (5.06×10^{11} kJ) is larger by several orders of magnitude than the energy released by burning 5.00 kg of C (1.64×10^5 kJ).

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20.98. First, determine the nuclear mass of $^{4}_{2}\text{He}$.

Nuclear mass of $^{4}_{2}\text{He}$ = 4.00260 amu − (2 x 0.000549 amu) = 4.001502 amu

Write the appropriate nuclear mass below each nuclide symbol, and calculate Δm.

$$4\,^{1}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + 2\,^{0}_{1}\text{e}$$

Masses: 1.00728 4.001502 0.000549 amu

Δm = [4.001502 + (2 x 0.000549) − (4 x 1.00728)] amu = −0.026520 amu

When 4 mol $^{1}_{1}\text{H}$ are fused, the change in mass is −0.026520 g. Therefore, for 1.00 kg $^{1}_{1}\text{H}$, the mass change is

$$1.00 \times 10^{3}\text{ g} \times \frac{1\text{ mol }^{1}_{1}\text{H}}{1.00728\text{ g }^{1}_{1}\text{H}} \times \frac{-0.026520\text{ g}}{4\text{ mol }^{1}_{1}\text{H}} = -6.5820\text{ g}$$

Converting mass to energy gives

$$\Delta E = (\Delta m)c^2 = (-6.5820 \times 10^{-3}\text{ kg})(2.998 \times 10^{8}\text{ m/s})^2$$
$$= -5.9159 \times 10^{14} = -5.92 \times 10^{14}\text{ J } (-5.92 \times 10^{11}\text{ kJ})$$

For the combustion of carbon:

	C(graphite)	+	$O_2(g)$	→	$CO_2(g)$
ΔH_f°	0		0		-394 kJ/mol

For the reaction, $\Delta H = \Delta E = -394$ kJ/mol.

$$1.00 \times 10^{3}\text{ g} \times \frac{1\text{ mol C}}{12.01\text{ g C}} \times \frac{-394\text{ kJ}}{1\text{ mol C}} = -3.280 \times 10^{4} = -3.28 \times 10^{4}\text{ kJ}$$

The energy released in the fusion of 1.00 kg of $^{1}_{1}\text{H}$ is 5.92×10^{11} kJ, which is several orders of magnitude larger than the energy released in the combustion of 1.00 kg of C (3.28×10^{4} kJ).

20.99.

a. The balanced equation is

$$^{47}_{20}\text{Ca} \rightarrow {}^{47}_{21}\text{Sc} + {}^{0}_{-1}\beta$$

b. Use the rate law to find the initial amount. The time is 48 h (2.0 d), and the half-life is 4.536 d. Substituting

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\,t}{t_{1/2}} = \frac{-0.693\text{ (2.0 d)}}{4.536\text{ d}} = -0.3055$$

Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-0.3055} = 0.7367$$

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Since A_t is 10.0 μg, you can solve for A_o.

$$A_o = \frac{10.0\ \mu g}{0.7367} = 1\underline{3}.57 = 14\ \mu g\ Ca\text{-}47$$

Convert this to mass of $^{47}CaSO_4$.

$$13.57\ \mu g\ Ca\text{-}47 \times \frac{143.07\ g\ CaSO_4}{47\ g\ Ca} = 4\underline{1}.31 = 41\ \mu g\ (4.1 \times 10^{-5}\ g)$$

20.100.

a. The balanced equation is

$$^{32}_{15}P \rightarrow {}^{32}_{16}S + {}^{0}_{-1}\beta$$

b. Use the rate law to find the fraction remaining after 35.0 d. Since the half-life is 14.28 d, you get

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (35.0\ d)}{14.28\ d} = -1.6\underline{9}85$$

Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-1.6985} = 0.1\underline{8}295$$

The amount of P-32 in 275 mg of $K_3{}^{32}PO_4$ is

$$275\ mg \times \frac{32\ g\ P}{213.3\ g\ K_3PO_4} = 4\underline{1}.256\ mg\ P\text{-}32$$

Therefore, the amount of P-32 remaining after 35.0 d is

$$A_t = 41.256\ mg \times 0.18295 = 7.\underline{5}47 = 7.5\ mg\ P\text{-}32$$

The percent p-32 decayed is

$$(1 - 0.18295) \times 100\% = 8\underline{1}.70 = 82\%$$

20.101.

a. The balanced equations are

$$^{82}_{35}Br \rightarrow {}^{82}_{36}Kr + {}^{0}_{-1}\beta$$

$$2H\,{}^{82}_{35}Br\,(g) \rightarrow H_2 + 2\,{}^{82}_{36}Kr$$

b. Use the rate law to find the fraction remaining. The time is 12.0 h (0.500 d), and the half-life is 1.471 d. Substituting yields

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (0.500\ d)}{1.471\ d} = -0.23\underline{5}55$$

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Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-0.23555} = 0.79013$$

Therefore, the number of moles remaining after 12.0 h is

$$A_t = 0.0150 \text{ mol} \times 0.79013 = 0.011851 = 0.0119 \text{ mol}$$

The reaction can be summarized as follows:

$2HBr$	$\rightarrow$	H_2	+	$2Kr$
$0.0150 - 2y$		y		$2y$

From this, you can determine y.

$$0.0150 \text{ mol} - 2y = 0.011851 \text{ mol, or } y = 0.001574 \text{ mol}$$

To calculate the pressure in the flask, you need the total moles of gas. This is

$$\text{Total moles} = \text{mol HBr} + \text{mol } H_2 + \text{mol Kr} = (0.0150 - 2y) + y + 2y$$
$$= 0.0150 + y = 0.0150 + 0.001574 = 0.016574 \text{ mol}$$

Therefore, the pressure in the flask is

$$P = \frac{nRT}{V} = \frac{0.016574 \text{ mol} \times 0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol} \times 295 \text{ K}}{1.00 \text{ L}}$$

$$= 0.401416 = 0.401 \text{ atm}$$

20.102.

a. $^{132}_{52}\text{Te} \rightarrow {}^{132}_{54}\text{Xe} + 2\,{}^{0}_{-1}\beta$

b. $H_2{}^{132}_{52}\text{Te}\,(g) \rightarrow H_2 + {}^{132}_{54}\text{Xe}$

c. Use the rate law to find the fraction remaining. The time is 99.0 h, and the half-life is 3.26 d. Substituting yields

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\,t}{t_{1/2}} = \frac{-0.693\,(99.0 \text{ h})}{3.26 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ h}} = -0.87687$$

Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-0.87687} = 0.41607$$

Therefore, the number of moles remaining after 99.0 h is

$$A_t = 0.0125 \text{ mol} \times 0.41607 = 0.005209 \text{ mol}$$

The reaction can be summarized as follows:

H_2Te	$\rightarrow$	H_2	+	Xe
$0.0125 - y$		y		y

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From this, you can determine y.

$$0.0125 - y = 0.0052009, \text{ or } y = 0.007\underline{2}99 \text{ mol } H_2Te \text{ reacted}$$

To calculate the pressure in the flask, you need the total moles of gas. This is

$$\text{Total moles} = \text{mol } H_2Te + \text{mol } H_2 + \text{mol Xe} = (0.0125 - y) + y + y$$

$$= 0.0125 + y = 0.0125 + 0.007299 = 0.019\underline{7}99 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{0.019799 \text{ mol x } 0.0821 \text{ L} \bullet \text{atm/K} \bullet \text{mol x } 298 \text{ K}}{1.50 \text{ L}} = 0.32\underline{2}9 = 0.323 \text{ atm}$$

20.103. An alpha particle is a helium-4 nuclide, with two protons and two neutrons. In terms of the shell model, helium has two protons in a 1*s* level and two neutrons in a 1*s* level, both of which are equal to the magic number 2. Thus, it is especially stable.

20.104. The next three energy levels following the 1*f* level are 1*g*, 1*h*, and 1*i*. As in the case of the 1*d* and 2*s* levels, each of these levels may have other levels with about the same energy.

20.105. Positron emission tomography (PET) is a technique for following biochemical processes within the organs of the human body. Like magnetic resonance imaging, a PET scan produces an image of a two-dimensional slice through a body organ of a patient. The image shows the distribution of some positron-emitting isotope present in a compound that was administered earlier by injection. By comparing the PET scan of the patient with that of a healthy subject, a physician can diagnose the presence or absence of disease. Some isotopes used in PET scans are carbon-11, nitrogen-13, oxygen-15, and flurine-18. All have short half-lives, so the radiation dosage to the patient is minimal.

20.106. When a nucleus emits a positron within the body, the positron travels only a few millimeters before it reacts with an electron. This reaction is an example of the annihilation of matter (an electron) by antimatter (a positron). Both the electron and the positron disappear and produce two gamma photons. The gamma photons easily pass through human tissue, so they can be recorded by scintillation detectors placed around the body. The detectors record the distribution of gamma radiation, and from this information a computer constructs images that can be used by the physician.

■ SOLUTIONS TO STRATEGY PROBLEMS

20.107.

a. $^{31}_{14}\text{Si} \rightarrow {}^{31}_{15}\text{P} + {}^{A}_{Z}\text{X}$

From the superscripts: $31 = 31 + A$, or $A = 0$; from the subscripts: $14 = 15 + Z$, or $Z = -1$. The missing particle is $^{0}_{-1}\text{X}$, which represents an electron. The reaction is then written

$$^{31}_{14}\text{Si} \rightarrow {}^{31}_{15}\text{P} + {}^{0}_{-1}\text{e}$$

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b. $^{44}_{22}\text{Ti} + {}^{A}_{Z}\text{X} \rightarrow {}^{44}_{21}\text{Sc}$

From the superscripts: $44 + A = 44$, or $A = 0$; from the subscripts: $22 + Z = 21$, or $Z = -1$. The missing particle is $^{0}_{-1}\text{X}$, which represents an electron. The reaction is then written

$$^{44}_{22}\text{Ti} + {}^{0}_{-1}\text{e} \rightarrow {}^{44}_{21}\text{Sc}$$

c. $^{252}_{98}\text{Cf} \rightarrow {}^{142}_{56}\text{Ba} + {}^{A}_{Z}\text{X} + 4\ {}^{1}_{0}\text{n}$

From the superscripts: $252 = 142 + A + 4(1)$, or $A = 106$; from the subscripts: $98 = 56 + Z$, or $Z = 42$. The missing particle is $^{106}_{42}\text{X}$. The element with atomic number 42 is molybdenum. The reaction is then written

$$^{252}_{98}\text{Cf} \rightarrow {}^{142}_{56}\text{Ba} + {}^{106}_{42}\text{Mo} + 4\ {}^{1}_{0}\text{n}$$

20.108. The balanced nuclear equation is

$$^{241}_{95}\text{Am} \rightarrow {}^{237}_{93}\text{Np} + {}^{4}_{2}\text{He}$$

20.109.

a. $^{238}_{94}\text{Pu} \rightarrow {}^{234}_{92}\text{U} + {}^{4}_{2}\text{He}$

b. Use the first-order rate equation to determine the fraction remaining after 50 y.

$$\ln \frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (50\ \text{y})}{87.7\ \text{y}} = -0.3\underline{9}50$$

Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-0.3950} = 0.6\underline{7}36$$

Therefore, the mass remaining after 50 y is

$$A_t = 250.0\ \text{g} \times 0.6736 = 1\underline{6}8.4 = 1.7 \times 10^2\ \text{g}$$

20.110. First, determine the nuclear masses.

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

Nuclear mass of $^{238}_{92}\text{U}$ = 238.05078 amu − (92 x 0.000549 amu) = 238.000272 amu

Nuclear mass of $^{234}_{90}\text{Th}$ = 234.03660 amu − (90 x 0.000549 amu) = 233.987190 amu

Nuclear mass of $^{4}_{2}\text{He}$ = 4.00260 amu − (2 x 0.000549 amu) = 4.001502 amu

On a mole basis, the mass difference, Δm, is

$$\Delta m = [233.987190 + 4.001502 - 238.000272]\ \text{g/mol} = -0.011580\ \text{g/mol}$$
$$= -1.1580 \times 10^{-5}\ \text{kg/mol}$$

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Now calculate the energy released during the decay.

$$\Delta E = (\Delta m)c^2 = (1.1580 \times 10^{-5} \text{ kg/mol})(2.998 \times 10^8 \text{ m/s})^2$$
$$= 1.04\underline{0}8 \times 10^{12} = 1.041 \times 10^{12} \text{ J/mol}$$

20.111.

a. Rn-222 has an atomic number of 86. Nuclides with atomic numbers above 83 decay by alpha emission.

b. The equation for the decay is

$$^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$$

c. Use the first-order rate equation to determine the fraction remaining after 15.0 d.

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (15.0 \text{ d})}{3.82 \text{ d}} = -2.7\underline{2}12$$

Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-2.7212} = 0.065\underline{7}95$$

Therefore, the mass remaining after 15.0 d is

$$A_t = 150.0 \text{ g} \times 0.065795 = 9.8\underline{6}3 = 9.86 \text{ g}$$

20.112. First, calculate the fraction of gold-198 remaining after 72 h (3 d).

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (3.0 \text{ d})}{2.69 \text{ d}} = -0.7\underline{7}28$$

Taking the antilog of each side gives

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-0.7728} = 0.4\underline{6}16$$

Now rearrange and solve for N_o, the amount needed to be ordered.

$$N_o = \frac{N_t}{0.4616} = \frac{15 \text{ mg}}{0.4616} = 3\underline{2}.4 = 32 \text{ mg}$$

20.113. Use the equation for the number of nuclei in a sample after a time, t.

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}}$$

Rearrange this to give an expression for t.

$$t = \frac{t_{1/2}}{0.693}\ln\frac{N_o}{N_t} = \frac{57 \text{ h}}{0.693}\ln\frac{N_o}{0.25N_o} \times \frac{1 \text{ d}}{24 \text{ h}} = 4.\underline{7}5 = 4.8 \text{ d}$$

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20.114.

a. The equation for the decay is

$$^{87}_{37}\text{Rb} \rightarrow {}^{87}_{38}\text{Sr} + {}^{0}_{-1}\text{e}$$

b. Use the equation for the number of nuclei in a sample after a time, t

$$\ln\frac{N_t}{N_o} = \frac{-0.693\ t}{t_{1/2}}$$

Rearrange this to give an expression for t.

$$t = \frac{t_{1/2}}{0.693}\ln\frac{N_o}{N_t}$$

The amount of Rb-87 initially present is the amount remaining plus the amount converted to Sr-87. Therefore,

$$\frac{N_o}{N_t} = \frac{0.100 + 0.00250}{0.100} = 1.02\underline{5}0$$

The age of the rock is

$$t = \frac{4.8 \times 10^{10}\ \text{y}}{0.693}\ln(1.0250) = 1.\underline{7}1 \times 10^{9} = 1.7 \times 10^{9}\ \text{y}$$

20.115. The rate of a radioactive decay process is given by

$$\text{Rate} = kN_t = \frac{0.693\ N_t}{t_{1/2}} = \frac{0.693\ m_t}{M_m t_{1/2}}$$

Because the isotopes are different and have different molar masses (M_m), the appropriate ratio for the comparison of the different masses is $m_t/M_m t_{1/2}$.Since pile A has twice the mass of pile B, if the half-life multiplied by the atomic mass of radioactive substance A is twice the half-life multiplied by the atomic mass of radioactive substance B, the rates of decay will be the same for both piles.

20.116. For a 500-Ci gamma-ray source, the rate of the nuclear decay is

$$\text{Rate} = 500\ \text{Ci} \times \frac{3.7 \times 10^{10}\ \text{nuclei/s}}{1\ \text{Ci}} = 1.\underline{8}50 \times 10^{13}\ \text{nuclei/s}$$

The rate of a radioactive decay process is given by

$$\text{Rate} = kN_t = \frac{0.693\ N_t}{t_{1/2}}$$

Rearrange this equation and solve for the number of nuclei N_t.

$$N_t = \frac{(1.850 \times 10^{13}\ \text{nuclei/s})(5.26\ \text{y})}{0.693} \times \frac{365\ \text{d}}{1\ \text{y}} \times \frac{24\ \text{h}}{1\ \text{d}} \times \frac{3600\ \text{s}}{1\ \text{h}} = 4.\underline{4}28 \times 10^{21}\ \text{nuclei}$$

Finally, convert the number of nuclei to mass.

$$4.428 \times 10^{21}\ \text{nuclei} \times \frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{nuclei}} \times \frac{60\ \text{g}}{1\ \text{mol}} = 0.4\underline{4}1 = 0.44\ \text{g}$$

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■ SOLUTIONS TO CUMULATIVE-SKILLS PROBLEMS

20.117. Calculate the number of P-32 nuclei in the sample (N_t). For this, you need the formula mass of N_3PO_4 containing 15.6% of P-32 and (100.0 – 15.6)% = 84.4% naturally occurring P. The formula mass of Na_3PO_4 containing naturally occurring P is 163.9 amu; the formula mass of Na_3PO_4 with 100% P-32 is 165.0. The formula mass of Na_3PO_4 containing 15.6% P-32 is obtained from the weighted average of the formula masses:

$$(163.9 \text{ amu} \times 0.844) + (165.0 \text{ amu} \times 0.156) = 16\underline{4}.1 \text{ amu}$$

The moles of P in the sample equal

$$0.0545 \text{ g } Na_3PO_4 \times \frac{1 \text{ mol } Na_3PO_4}{164.1 \text{ g } Na_3PO_4} \times \frac{1 \text{ mol P}}{1 \text{ mol } Na_3PO_4} = 3.3\underline{2}1 \times 10^{-4} \text{ mol P}$$

and the moles of P-32 equal

$$(3.321 \times 10^{-4} \text{ mol P}) \times 0.156 = 5.1\underline{8}1 \times 10^{-5} \text{ mol P-32}$$

Then, the number of P-32 nuclei is

$$(5.181 \times 10^{-5} \text{ mol P-32}) \times \frac{6.022 \times 10^{23} \text{ P-32 nuclei}}{1 \text{ mol P-32}} = 3.1\underline{2}0 \times 10^{19} \text{ P-32 nuclei}$$

Now, calculate the rate of disintegrations. Because the rate = kN_t, first find the value of k in reciprocal seconds:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3 \text{ d}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 5.6\underline{0}9 \times 10^{-7} \text{ /s}$$

Therefore, the rate of disintegrations is

$$\text{Rate} = kN_t = (5.609 \times 10^{-7}/\text{s}) \times (3.120 \times 10^{19} \text{ P-32 nuclei}) = 1.7\underline{5}0 \times 10^{13}$$
$$= 1.75 \times 10^{13} \text{ P-32 nuclei/s}$$

20.118. The formula mass of $Na_2S_2O_3$ containing 22.3% S-35 is the weighted average of the formula mass containing naturally occurring sulfur (158.1 amu) and the formula mass containing S-35 (164.0 amu):

$$(158.1 \text{ amu} \times 0.777) + (164.0 \times 0.223) = 15\underline{9}.4 \text{ amu}$$

The moles of S in the sample equal

$$0.0381 \text{ g } Na_2S_2O_3 \times \frac{1 \text{ mol } Na_2S_2O_3}{159.4 \text{ g } Na_2S_2O_3} \times \frac{2 \text{ mol S}}{1 \text{ mol } Na_2S_2O_3} = 4.7\underline{8}0 \times 10^{-4} \text{ mol S}$$

and the moles of S-35 equal

$$(4.780 \times 10^{-4} \text{ mol S}) \times 0.223 = 1.0\underline{6}6 \times 10^{-4} \text{ mol S-35}$$

The number of S-35 nuclei is

$$(1.066 \times 10^{-4} \text{ mol S-35}) \times \frac{6.022 \times 10^{23} \text{ S-35 nuclei}}{1 \text{ mol S-35}} = 6.4\underline{2}0 \times 10^{19} \text{ S-35 nuclei}$$

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Now, calculate the rate of disintegrations. Because the rate = kN_t, first find the value of k in reciprocal seconds:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{87.9\text{ d}} \times \frac{1\text{ d}}{24\text{ h}} \times \frac{1\text{ h}}{3600\text{ s}} = 9.125 \times 10^{-8}\text{ /s}$$

Therefore, the rate of disintegrations is

$$\text{Rate} = kN_t = (9.125 \times 10^{-8}\text{/s}) \times (6.420 \times 10^{19}\text{ S-35 nuclei})$$
$$= 5.858 \times 10^{12} = 5.86 \times 10^{12}\text{ S-35 nuclei/s}$$

20.119. First, determine the mass of polonium-210 nuclei in 1.0000 g of PoO_2.

$$1.0000\text{ g } PoO_2 \times \frac{210\text{ g Po}}{242\text{ g } PoO_2} = 0.867768\text{ g Po-210}$$

Use the rate law to find the fraction of polonium-210 that decayed. The time is 48.0 h (2.00 d), and the half-life is 138.4 d. Substituting

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (2.00\text{ d})}{138.4\text{ d}} = -0.010014$$

Take the antilog of each side to get the fraction of polonium-210 remaining.

$$\frac{N_t}{N_o} = e^{-0.010014} = 0.990035$$

Thus, the fraction of polonium-210 that decayed is $1 - 0.990035 = 0.009964$. This can now be converted to moles of helium formed.

$$0.867768\text{ g Po} \times 0.009964 \times \frac{1\text{ mol Po}}{210\text{ g Po}} \times \frac{1\text{ mol He}}{1\text{ mol Po}} = 4.117 \times 10^{-5}\text{ mol He}$$

Now, calculate the volume of He at 25°C and 735 mmHg.

$$V = \frac{nRT}{P} = \frac{(4.117 \times 10^{-5}\text{ mol})(0.0821\text{ L} \bullet \text{atm/(K} \bullet \text{ mol)}(298\text{ K})}{(735/760)\text{ atm}}$$

$$= 0.00104 = 0.0010\text{ L} = 1.0\text{ mL}$$

20.120. First, determine the mass of radium-226 nuclei in 543.0 mg of $RaBr_2$.

$$0.5430\text{ g } RaBr_2 \times \frac{226\text{ g Ra}}{385.8\text{ g } RaBr_2} = 0.31808\text{ g Ra-226}$$

Use the rate law to find the fraction of radium-226 that decayed. The time is 37.5 y, and the half-life is 1602 y. Substituting yields

$$\ln\frac{N_t}{N_o} = -kt = \frac{-0.693\ t}{t_{1/2}} = \frac{-0.693\ (37.5\text{ y})}{1602\text{ y}} = -0.016221$$

Take the antilog of each side to get the fraction of radium-226 remaining.

$$\frac{N_t}{N_o} = \frac{A_t}{A_o} = e^{-0.016221} = 0.983908$$

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Thus, the fraction of radium-226 that decayed is 1 − 0.983908 = 0.016091. This can now be converted to moles of radon-222 formed.

$$0.31808 \text{ g Ra} \times 0.016091 \times \frac{1 \text{ mol Ra}}{226 \text{ g Ra}} \times \frac{1 \text{ mol Rn}}{1 \text{ mol Ra}} = 2.264 \times 10^{-5} \text{ mol Rn}$$

Now calculate the volume of Rn at 23°C and 785 mmHg.

$$V = \frac{nRT}{P} = \frac{(2.264 \times 10^{-5} \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol})(296 \text{ K})}{(785/760) \text{ atm}}$$

$$= 5.328 \times 10^{-4} \text{ L} = = 5.33 \times 10^{-4} \text{ L} = 0.533 \text{ mL}$$

20.121. $2p + 2n \rightarrow {}^{4}_{2}He$

Nuclear mass of ${}^{4}_{2}He = 4.00260 \text{ amu} - (2 \times 0.000549 \text{ amu}) = 4.001502 \text{ amu}$

On a mole basis, the mass difference, Δm, is

$$\Delta m = [4.001502 - 2(1.00728) - 2(1.00867)] \text{ g/mol} = -0.030398 \text{ g/mol}$$
$$= -3.0398 \times 10^{-5} \text{ kg/mol}$$

The energy evolved per mole is

$$\Delta E = (\Delta m)c^2 = -3.0398 \times 10^{-5} \text{ kg/mol} \times (2.998 \times 10^{8} \text{ m/s})^2$$
$$= -2.7321 \times 10^{12} \text{ kg} \cdot \text{m}^2/\text{s}^2 = -2.7321 \times 10^{12} \text{ J} = -2.7321 \times 10^{9}$$
$$= 2.732 \times 10^{9} \text{ kJ/mol}$$

Next calculate $\Delta H°$ for burning of ethane:

	$C_2H_6(g)$	+	$7/2O_2(g)$	→	$2CO_2(g)$	+	$3H_2O(g)$
ΔH_f° =	-84.667		0		2(-393.5)		3(-241.826) kJ

$$\Delta H^\circ = [2(-393.5) + 3(-241.826) - (-84.667)] \text{ kJ} = (-1427.81) \text{ kJ/mol ethane}$$

Now calculate the moles of ethane needed to obtain 2.7321×10^{9} kJ heat:

$$-2.7321 \times 10^{9} \text{ kJ} \times \frac{1 \text{ mol ethane}}{-1427.81 \text{ kJ}} = 1.91354 \times 10^{6} \text{ mol ethane}$$

Finally, convert moles to liters at 25°C and 725 mmHg.

$$V = \frac{nRT}{P} = \frac{(1.91354 \times 10^{6} \text{ mol})\,[0.0821 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol})]\,(298 \text{ K})}{(725/760) \text{ atm}}$$

$$= 4.907 \times 10^{7} = 4.91 \times 10^{7} \text{ L}$$

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20.122. $^{239}_{94}\text{Pu} \rightarrow {}^{235}_{92}\text{U} + {}^{4}_{2}\text{He}$

First, calculate the nuclear masses.

Nuclear mass of $^{239}_{94}\text{Pu}$ = 239.05216 amu − (94 x 0.000549 amu) = 239.000554 amu

Nuclear mass of $^{235}_{92}\text{U}$ = 235.04392 amu − (92 x 0.000549 amu) = 234.993412 amu

Nuclear mass of $^{4}_{2}\text{He}$ = 4.00260 amu − (2 x 0.000549 amu) = 4.001502 amu

On a mole basis, the mass difference, Δm, is

$$\Delta m = [234.993412 + 4.001502 - 239.000554]\ \text{g/mol} = -0.005640\ \text{g/mol}$$
$$= -5.640 \times 10^{-6}\ \text{kg/mol}$$

The energy evolved is

$$\Delta E = (\Delta m)c^2 = -5.640 \times 10^{-6}\ \text{kg/mol Pu} \times (2.998 \times 10^{8}\ \text{m/s})^2$$
$$= -5.069 \times 10^{11}\ \text{kg}\bullet\text{m}^2/\text{s}^2 = -5.069 \times 10^{11}\ \text{J/mol Pu}$$

For 215 mg of plutonium-239, the energy released is

$$\Delta E = 215 \times 10^{-3}\ \text{g Pu} \times \frac{1\ \text{mol Pu}}{239.0006\ \text{g Pu}} \times \frac{-5.069 \times 10^{11}\ \text{J}}{1\ \text{mol Pu}} = -4.560 \times 10^{8}\ \text{J}$$

Now calculate 25.0% of this energy.

$$-4.560 \times 10^{8}\ \text{J} \times 0.250 = -1.1400 \times 10^{8}\ \text{J}$$

Next, calculate $E°$ for the standard voltaic Zn/Cu^{2+} cell.

$$E°_{\text{cell}} = 0.34\ \text{V} - (-0.76\ \text{V}) = 1.10\ \text{V} = 1.10\ \text{V/mol Zn}$$

Now calculate $\Delta G°$.

$$\Delta G° = -nFE°_{\text{cell}} = -\frac{2\ \text{mol e}}{1\ \text{mol Zn}} \times \frac{9.65 \times 10^{4}\ \text{C}}{1\ \text{mol e}} \times 1.10\ \text{V} = -2.123 \times 10^{5}\ \text{J/mol Zn}$$

The mass of Zn needed to release -1.1400×10^{8} J is

$$-1.1400 \times 10^{8}\ \text{J} \times \frac{1\ \text{mol Zn}}{-2.123 \times 10^{5}\ \text{J}} \times \frac{65.39\ \text{g Zn}}{1\ \text{mol Zn}} = 3.511 \times 10^{4} = 3.5 \times 10^{4}\ \text{g Zn}$$

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CHAPTER 21

Chemistry of the Main-Group Elements

■ ANSWERS TO CONCEPT CHECKS

21.1. Given the high energy needs of animals to move and maintain body temperature, breaking the very strong triple bond of N_2 requires too much energy compared to the lower-energy double bond of O_2.

21.2. The only intermolecular forces in these materials are very weak van der Waals forces.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

21.1. An alloy is a material with metallic properties that is either a compound or a mixture. If the alloy is a mixture, it may be homogeneous (a solution) or heterogeneous. Gold jewelry is made from an alloy that is a solid solution of gold containing some silver.

21.2. A metal is a material that is lustrous (shiny), has high electrical and heat conductivities, and is malleable and ductile.

21.3. A rock is a naturally occurring solid material composed of one or more minerals. A mineral is a naturally occurring inorganic solid substance or solid solution with a definite crystalline structure. An ore is a rock or mineral from which a metal or nonmetal can be economically produced. Bauxite, the principal ore of aluminum, is a rock.

21.4. The basic steps in the production of a pure metal from a natural source follow. (1) Preliminary treatment: separating the metal-containing mineral from the less desirable parts of the ore. The mineral may also be transformed by chemical reaction to a metal compound that is more easily reduced to the free metal. (2) Reduction: The metal compound is reduced to the free metal by electrolysis or chemical reduction. (3) Refining: The free metal is purified.

(1) Preliminary treatment: Aluminum oxide is obtained from bauxite by the Bayer process. Bauxite contains aluminum hydroxide, aluminum oxide hydroxide, and other worthless constituents. It is mixed with hot, aqueous sodium hydroxide solution, which dissolves the amphoteric aluminum minerals along with some silicates. When the solution is cooled, $Al(OH)_3$ precipitates, leaving the silicates behind. The aluminum hydroxide is finally calcined (heated strongly in a furnace) to produce purified aluminum oxide, Al_2O_3. (2) Reduction: Aluminum is then obtained by reduction using the Hall-Héroult process, which is the electrolysis of a molten mixture of aluminum oxide in cryolyte (Na_3AlF_6). (3) Refining: The aluminum can be further refined and purified.

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21.5. Lead is obtained from its sulfide ore by roasting, which forms lead(II) oxide. It is then heated with coke in a blast furnace, where it is reduced to lead metal.

21.6. (1) Iron oxide is reduced to iron using coke and limestone. The molten iron flows to the bottom of the blast furnace while carbon dioxide gas escapes. Impurities in the iron react with the calcium oxide from the limestone and produce slag, which floats to the top. (2) The Mond process is a chemical procedure that depends on the formation, and later decomposition, of a volatile compound of the metal (nickel tetracarbonyl). The compound decomposes over pellets of pure nickel heated to 230°C. (3) Copper is purified by electrolysis using a pure copper negative electrode. Electrons from the impure copper positive electrode flow to the positive pole of the battery, leaving copper(II) ions behind in the solution. These electrons replace the ones that plate out on the pure copper electrode, enlarging it.

21.7. The Dow process use seashells ($CaCO_3$) as a source of the base. When heated, calcium carbonate decomposes to calcium oxide (CaO) and carbon dioxide (CO_2).

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

The calcium oxide reacts with water to produce calcium hydroxide, the base.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

The calcium hydroxide reacts with the magnesium ion in seawater to form a magnesium hydroxide precipitate.

$$Ca(OH)_2(aq) + Mg^{2+}(aq) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

The magnesium hydroxide is then treated with hydrochloric acid (HCl) to yield magnesium chloride.

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$

The dry magnesium chloride is melted and electrolyzed at 700°C to yield the metal.

$$MgCl_2(l) \rightarrow Mg(l) + Cl_2(g)$$

21.8. The flowchart for the preparation of aluminum from its ore (bauxite) follows.

(1) Preliminary treatment (the Bayer process): Mix the ore with hot NaOH(*aq*). Cool and filter the $Al(OH)_3$ precipitate. Heat the precipitate in a furnace to convert to Al_2O_3.

(2) Reduction (the Hall-Héroult process): Melt a mixture of Al_2O_3 with cryolyte produced from $Al(OH)_3$ by the reaction

$$Al(OH)_3(s) + 3NaOH(aq) + 6HF(aq) \longrightarrow Na_3AlF_6(aq) + 6H_2O(l)$$

The electrolytic cell has carbon electrodes and a molten cryolyte electrolyte, at about 1000°C, into which some aluminum oxide is dissolved. The reaction is

$$2Al_2O_3(s) + 3C(sq) \xrightarrow{\text{electrolysis}} 4Al(l) + 3CO_2(g)$$

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21.9. In a metal, the outer orbits of an enormous number of metal atoms overlap to form an enormous number of molecular orbitals that are delocalized over the metal. As a result, a large number of energy levels are crowded together into bands. These bands are half-filled with electrons. When a voltage is applied to the metal crystal, electrons are excited to the unoccupied orbitals and move toward the positive pole of the voltage source. This is electrical conductivity.

21.10. The mineral source is given after the name of the metal: lithium–lithium aluminum silicate; sodium–sodium chloride; magnesium–seawater (Dow process) and dolomite or magnesite; calcium–calcium oxide; aluminum–bauxite; tin–cassiterite; and lead–galena.

21.11. The reactions are

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

$$4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$$

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

$$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

21.12. The reaction is similar to that of lithium carbonate with calcium hydroxide:

$$Li_2CO_3(aq) + Ba(OH)_2(aq) \rightarrow 2LiOH(aq) + BaCO_3(s)$$

21.13. Potassium is expected to be more reactive than lithium because metals become more reactive going down Group IA. This is partly because potassium is much larger, so its 4*s* electron is lost more readily than the 2*s* electron of lithium.

21.14. The reaction is $2Na(s) + 2C_2H_5OH(l) \rightarrow H_2(g) + 2NaOC_2H_5(aq)$.

21.15.

a. Cathode reaction: $Na^+(l) + e^- \rightarrow Na(l)$

Anode reaction: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

b. Cathode reaction: $Na^+(l) + e^- \rightarrow Na(l)$

Anode reaction: $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(g) + 4e^-$

21.16. Sodium hydroxide is manufactured by the electrolysis of aqueous sodium chloride, which also produces chlorine gas as a major product.

21.17. The uses are given after each compound: sodium chloride–used for making sodium hydroxide and in seasoning; sodium hydroxide–used in aluminum production and in producing sodium compounds such as soap; and sodium carbonate–used to make glass and as washing soda with many detergent preparations.

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21.18. The main step in the Solvay process involves the reaction of carbon dioxide with ammonia and sodium chloride to form sodium bicarbonate:

$$NH_3(g) + H_2O(l) + CO_2(g) + NaCl(aq) \rightarrow NaHCO_3(s) + NH_4Cl(aq)$$

21.19. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$

$2Mg(s) + CO_2(g) \rightarrow 2MgO(s) + C(s)$

21.20.

a. Calcium oxide is prepared industrially from calcium carbonate:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

b. Calcium hydroxide is prepared from the reaction of calcium oxide and water:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

21.21. $CaCO_3(s) + 2HCl(aq) \rightarrow CO_2(g) + CaCl_2(aq) + H_2O(l)$

21.22. $Ca(OH)_2 + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

$Ca(OH)_2 + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaOH(aq)$

21.23. $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$

21.24. Some major uses of aluminum oxide: making abrasives for grinding tools, fusing with small amounts of other metal oxides to make synthetic sapphires and rubies, and making industrial ceramics.

21.25. To purify municipal water, aluminum sulfate and calcium hydroxide are added to waste water, forming a gelatinous precipitate of aluminum hydroxide. Colloidal particles of clay (usually present in the waste water) and other substances adhere to the aluminum hydroxide, whose particles are large enough to be filtered from the water to purify it.

21.26. Lead(IV) oxide, PbO_2, is formed by first packing a paste of PbO into the lead metal grids of the storage battery. When the battery is charged at the factory, the PbO is oxidized by electrolysis to PbO_2. This gives the proper cathode for a new battery.

21.27. Lead pigments are no longer used for house paints because of the possibility of lead poisoning. If chips of lead paint are eaten by children, or if the dust from lead paint that has been removed is breathed by adults or children, lead(II) ion can enter the bloodstream. The lead(II) ion can ultimately inhibit the production of red blood cells, causing anemia. (The Pb^{2+} ion can also be absorbed in the brains of children and cause irreversible brain damage.)

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21.28. $Pb(NO_3)_2(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s) + 2NO_3^-(aq)$

21.29. In the steam-reforming process, steam and hydrocarbons from natural gas or petroleum react at high temperature and pressure in the presence of a catalyst to form carbon monoxide and hydrogen. A typical reaction involving propane (C_3H_8) is

$$C_3H_8(g) + 3H_2O(g) \xrightarrow[\Delta]{Ni} 3CO(g) + 7H_2(g)$$

The carbon monoxide is removed from the mixture by reacting with steam in the presence of a catalyst to give carbon dioxide and more hydrogen.

$$CO(g) + H_2O(g) \xrightarrow[\Delta]{\text{catalyst}} CO_2(g) + H_2(g)$$

Finally, the carbon dioxide is removed by dissolving it in a basic aqueous solution.

21.30. The three isotopes of hydrogen and their symbols are as follows: protium, ${}_1^1H$, or H, which is most abundant; deuterium, ${}_1^2H$, or D; and tritium, ${}_1^3H$, or T. Tritium is radioactive, with a half-life of 12.3 years.

21.31. The combustion of hydrogen produces more heat per gram than that of any other fuel (120 kJ/g). Unlike hydrocarbons, it is a clean fuel since the product is environmentally benign water. These features, in the face of a dwindling supply of hydrocarbons, indicate that hydrogen gas may become the favorite fuel of the twenty-first century.

21.32. A binary hydride is a compound that contains hydrogen and one other element. There are three categories of binary hydrides. The first type is an ionic hydride, which contains the hydride ion, H^-, and is formed via reaction with an alkali metal or larger Group IIA metal. An example is LiH. A second type is a covalent hydride, which is a molecular compound in which hydrogen is covalently bonded to another element. An example is NH_3. The third type is a metallic hydride formed from a transition metal and hydrogen. These compounds contain hydrogen spread throughout a metal crystal and occupying the holes in the crystal lattice, sometimes in nonstoichiometric amounts. Thus, the composition is variable. An example is $TiH_{1.7}$.

21.33. Catenation is the ability of an atom to bond covalently to like atoms, as in ethylene, $H_2C{=}CH_2$.

21.34. Carbon monoxide attaches to the iron in the hemoglobin of red blood cells and blocks the combination of hemoglobin with oxygen molecules normally carried by the hemoglobin.

21.35. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

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21.36. Elementary silicon is obtained by reducing quartz sand (SiO_2) with coke (C) in an electric furnace at 3000°C. The reaction is

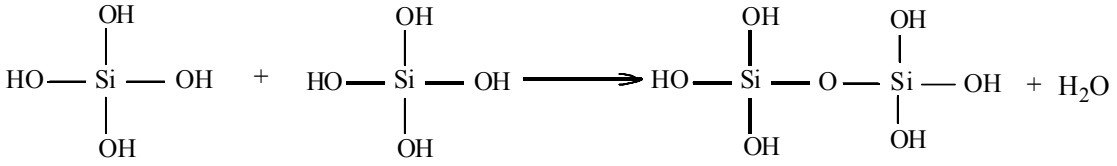
$$SiO_2(l) + 2C(s) \longrightarrow Si(l) + 2CO(g)$$

The impure silicon is converted into silicon tetrachloride ($SiCl_4$), which is purified by distillation (b.p. 58°C).

$$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g)$$

The purified $SiCl_4$ is reduced by passing the vapor with hydrogen through a hot tube, where pure silicon crystallizes on the tube. In the final step, this polycrystalline silicon is fashioned into a rod that consists of a single crystal from which wafers are cut.

21.37. The condensation reaction between two silicic acid molecules is represented by



21.38. Certain bacteria in the soil and in the roots of plants convert N_2 to ammonium and nitrate compounds. The plants then use these nitrogen compounds to make proteins and other complex nitrogen compounds. Animals eat the plants. Ultimately, the animals die, and bacteria in the decaying organic matter convert the nitrogen compounds back to N_2.

21.39. Rutherford removed oxygen from the air by burning a substance that would combine with the oxygen. He also removed any carbon dioxide formed by the burning by reacting it with KOH. The gas left contained primarily nitrogen, as well as small amounts (< 1%) of noble gases.

21.40. These oxides are nitrous oxide, N_2O; nitrogen monoxide, NO; N_2O_3; nitrogen dioxide, NO_2; dinitrogen tetroxide, N_2O_4; and N_2O_5. The oxidation numbers in each are +1, +2, +3, +4, +4, and +5, respectively.

21.41. Natural gas, or CH_4, and steam react to form CO and H_2. The CO is reacted with steam to form CO_2 plus additional H_2. The CO_2 is removed from the H_2 by dissolving it in basic aqueous solution; the H_2 is then reacted with N_2 in the Haber process to form NH_3.

21.42. Ammonia is burned in the presence of a platinum catalyst to form NO, which is then reacted with O_2 to form NO_2. The NO_2 is dissolved in water to form HNO_3 and NO. The NO is recycled back to the second step to react with more O_2 to form more NO_2.

21.43. White phosphorus is a molecular solid with the formula P_4. The phosphorus atoms are arranged at the corners of a regular tetrahedron with a 60° P–P–P bond angle, an angle considerably smaller than the normal tetrahedral bond angle. This accounts for the weakness of the P–P bonds and their high reactivity, as stronger bonds such as P–O can replace them.

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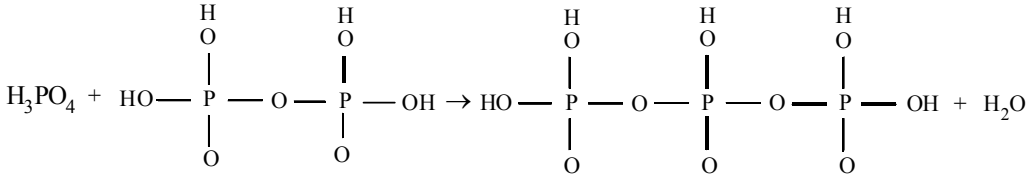
21.44. $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

21.45. The first method is the treatment of $Ca_3(PO_4)_2$ with sulfuric acid, giving phosphoric acid and insoluble calcium sulfate. The second method is the treatment of $Ca_3(PO_4)_2$ with HF, giving phosphoric acid and insoluble calcium fluoride.

21.46.



21.47. Polyphosphates are added to detergents to form complexes with metal ions and thus prevent their precipitation onto clothes.

21.48. Priestley prepared oxygen by heating mercury(II) oxide:

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

21.49. The most important commercial means of producing oxygen is by distillation of liquid air. Air is filtered to remove dust particles, cooled to freeze out water and carbon dioxide, liquefied, and finally warmed until nitrogen and argon distill, leaving liquid oxygen behind.

21.50. Oxides are binary oxygen compounds in which oxygen is in the −2 oxidation state, whereas in peroxides, the oxidation number of oxygen is −1 and the anion is O_2^{2-}. In the superoxides, the oxidation number of oxygen is −1/2 and the anion is O_2^-. Examples: H_2O (oxide), H_2O_2 (peroxide), and KO_2 (superoxide).

21.51. CrO_3 is an example of an acidic oxide; Cr_2O_3, MgO, and Fe_3O_4 are basic oxides.

21.52. Three natural sources of sulfur or sulfur compounds are sulfate minerals, sulfide minerals, and coal or petroleum products.

21.53. Rhombic sulfur is a yellow crystalline solid with a lattice consisting of crown-shaped S_8 molecules; that is, eight sulfur atoms are arranged in a crown-shaped ring.

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21.54. The monoclinic sulfur allotrope can be prepared from rhombic sulfur by first melting the rhombic sulfur and then cooling it to crystals of monoclinic sulfur. A liquid sulfur allotrope of long spiral chains of sulfur atoms can be prepared by heating rhombic sulfur above 160°C but keeping it below 200°C. Plastic sulfur allotrope can be prepared by pouring this liquid sulfur allotrope into water. Finally, gaseous allotropes of S_8, S_6, S_4, and S_2 molecules can be formed by boiling sulfur at 445°C.

21.55. The Frasch process involves melting sulfur deposits with superheated water, using air to force the melted sulfur upward to the surface, and cooling it to form solid sulfur.

21.56. The initial burning of hydrogen sulfide produces some sulfur as well as sulfur dioxide:

$$8H_2S(g) + 4O_2(g) \rightarrow S_8(s) + 8H_2O(g)$$

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$$

The sulfur dioxide reacts with hydrogen sulfide to form more sulfur:

$$16H_2S(g) + 8SO_2(g) \rightarrow 3S_8(s) + 16H_2O(g)$$

21.57.

a. $2HCl(aq) + ZnS(s) \rightarrow ZnCl_2(aq) + H_2S(g)$

b. $S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$

21.58. First step: $S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$

Second step: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Third step: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

21.59.

a. $16H_2S(g) + 8SO_2(g) \rightarrow 3S_8(s) + 16H_2O(g)$

b. $Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$

c. $Cu(s) + 2H_2SO_4(l) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$

d. $8Na_2SO_3(aq) + S_8(s) \rightarrow 8Na_2S_2O_3(aq)$

21.60. $4HCl + MnO_2(s) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$

21.61.

a. $I_2(aq) + Cl^-(aq) \rightarrow NR$

b. $Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

c. $Br_2(aq) + 2I^-(aq) \rightarrow I_2(s) + 2Br^-(aq)$

d. $Br_2(aq) + Cl^-(aq) \rightarrow NR$

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21.62. Add chlorine water and methylene chloride. For NaCl, there will be no reaction; for NaBr, the lower organic layer will turn orange; and for NaI, the lower organic layer will turn violet.

21.63. Chlorine is used in preparing chlorinated hydrocarbons, as a bleaching agent, and as a disinfectant.

21.64. Sodium hypochlorite is prepared by reacting chlorine with NaOH:

$$Cl_2(g) + 2NaOH(aq) \rightarrow NaClO(aq) + NaCl(aq) + H_2O(l)$$

21.65. Industrially, sodium chloride is electrolyzed to form chlorine gas. The chlorine gas is then heated with sodium hydroxide solution, forming $NaClO_3$ (and NaCl). The ClO_3^- is electrolyzed at the anode to form the ClO_4^- anion. This is mixed with sulfuric acid, and the $HClO_4$ is distilled at reduced pressure (below 92°C) to isolate $HClO_4$.

21.66. Bartlett found that PtF_6 reacted with molecular oxygen. Because the first ionization energy of xenon was slightly less than that of molecular oxygen, he reasoned that PtF_6 ought to react with xenon also.

21.67. The answer is d, I and II only.

21.68. The answer is e, jet fuel.

21.69. The answer is d, phosphoric acid.

21.70. the answer is b, NaClO.

■ ANSWERS TO CONCEPTUAL PROBLEMS

21.71. If air were present, the oxygen in the air would react with the coal (undergo oxidation) by the following equation:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

21.72. It has one valence electron like the other elements in Group IA.

21.73. The metallic character decreases from left to right and increases going down a column.

21.74. Lithium hydroxide is contaminated by reaction with carbon dioxide absorbed from the air:

$$2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(s) + H_2O(l)$$

$$Li_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2LiHCO_3(s)$$

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21.75. This means aluminum hydroxide reacts with both acids and bases. For example,

$$Al(OH)_3(s) + 3HCl(aq) \rightarrow 3H_2O(l) + AlCl_3(aq)$$

and

$$Al(OH)_3(s) + NaOH(aq) \rightarrow Na^+(aq) + Al(OH)_4^-(aq)$$

21.76. Below 13°C, the stable white metallic allotrope of tin undergoes a transition to the brittle powder allotrope called gray tin.

21.77. Oxygen is a very electronegative element, and its bonding involves only the *s* and *p* orbitals, in contrast to bonding using the *d* orbitals in sulfur, etc. Molecular oxygen is a reactive gas, but it forms mainly compounds in which its oxidation state is −2, compared with compounds of sulfur, etc., which exhibit positive oxidation states as well as the −2 state.

21.78. Applying your chemical knowledge and consulting the table of standard reduction potentials (Appendix I), you would not expect I_2 to be a better oxidizing agent than Cl_2.

21.79. Consulting the table of standard reduction potentials (Appendix I), you find that HBr cannot be prepared by adding sulfuric acid to NaBr because the hot, concentrated acid will oxidize the bromide ion to bromine.

21.80. An aqueous solution of sodium hypochlorite should be basic because HClO is a eak acid. A solution of sodium perchlorate should be neutral because $HClO_4$ is a strong acid, and NaOH is a strong base.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

21.81. $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

21.82. $3MnO_2(s) + 4Al(s) \rightarrow 3Mn(s) + 2Al_2O_3(s)$

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21.83. In the reaction (Problem 21.81), 3 mol of H_2 are used to form 2 mol of iron. Using the respective atomic masses of 55.85 g/mol for Fe and 2.016 g/mol for H_2, you can calculate the mass of Fe as follows:

$$2.00 \times 10^3 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{2 \text{ mol Fe}}{3 \text{ mol } H_2} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}}$$

$$= 3.693 \times 10^4 = 3.69 \times 10^4 \text{ g} = 36.9 \text{ kg Fe}$$

21.84. In the reaction (Problem 21.82), 4 mol of Al are used to form 3 mol of manganese. Using the respective atomic masses of 54.94 g/mol for Mn and 26.98 g/mol for Al, you can calculate the mass of Mn as follows:

$$1.00 \times 10^3 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol Mn}}{4 \text{ mol Al}} \times \frac{54.94 \text{ g Mn}}{1 \text{ mol Mn}}$$

$$= 1.527 \times 10^3 \text{ g} = 1.53 \text{ kg Mn}$$

21.85. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

$$\underset{-98.3}{PbS(s)} + \underset{0}{3/2O_2(g)} \rightarrow \underset{-219.4}{PbO(s)} + \underset{-296.8\ (kJ)}{SO_2(g)}$$

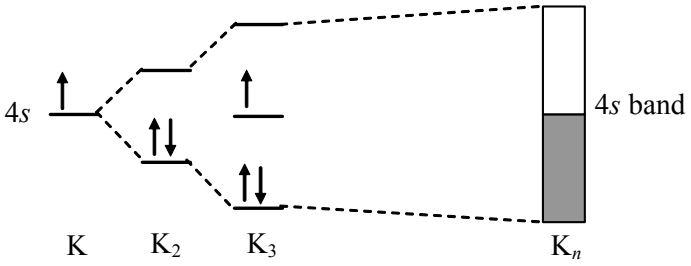
$$\Delta H^\circ = [(-219.4 + (-296.8) - (-98.3)] \text{ kJ} = -417.9 \text{ kJ (exothermic)}$$

21.86. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

$$\underset{3(-520.0)}{3MnO_2(s)} + \underset{0}{4Al(s)} \rightarrow \underset{0}{3Mn(s)} + \underset{2(-1675.7)\ (kJ)}{2Al_2O_3(s)}$$

$$\Delta H^\circ = [2(-1675.7 - 3(-520.0)] \text{ kJ} = -1791.4 \text{ kJ (exothermic)}$$

21.87. The energy levels in potassium metal are



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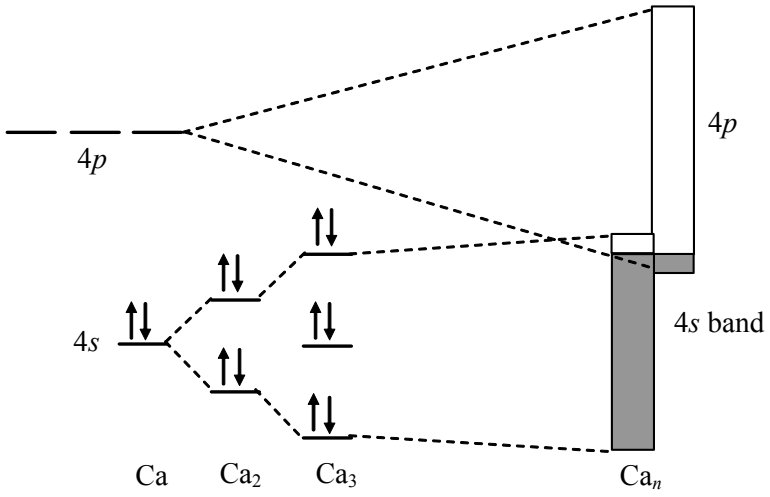
21.88. The energy levels in calcium metal are shown below. The other 4*p* orbitals from the additional calcium atoms have been omitted for clarity.



21.89. The number of sodium atoms in a 1.00-mg crystal of sodium is

$$1.00 \times 10^{-3} \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{6.02 \times 10^{23} \text{ Na atoms}}{1 \text{ mol Na}} = 2.6\underline{1}8 \times 10^{19} \text{ Na atoms}$$

Each sodium atom contributes an energy level for the 3*s* orbital to the valence band, so the number of energy levels in the valence band is 2.62×10^{19}.

21.90. The number of magnesium atoms in a 1.00-mg crystal of sodium is

$$1.00 \times 10^{-3} \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{6.02 \times 10^{23} \text{ Mg atoms}}{1 \text{ mol Mg}} = 2.4\underline{7}6 \times 10^{19} \text{ Mg atoms}$$

Each magnesium atom contributes an energy level for the three 3*p* orbitals to the valence band, so the number of energy levels in the valence band is 2.48×10^{19}.

21.91. $CO_2(g) + NH_3(g) + NaCl(aq) + H_2O(l) \xrightarrow{\Delta} NaHCO_3(s) + NH_4Cl(aq)$

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

$Na_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow 2NaOH(aq) + CaCO_3(s)$

21.92. $P_4 + 5O_2(g) \rightarrow P_4O_{10}(s)$

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

$2NaCl(aq) + 2H_2O(l)$ (electrolysis) $\rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$

$H_3PO_4 + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$

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21.93.

a. $2K(s) + Br_2(l) \rightarrow 2KBr(s)$

b. $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$

c. $2NaOH(s) + CO_2(g) \rightarrow Na_2CO_3(s) + H_2O(l)$

d. $Li_2CO_3(aq) + 2HNO_3(aq) \rightarrow H_2O(l) + 2LiNO_3(aq) + CO_2(g)$

e. $K_2SO_4(aq) + Pb(NO_3)_2(aq) \rightarrow PbSO_4(s) + 2KNO_3(aq)$

21.94.

a. $2LiHCO_3(s)\ (\text{heat}) \rightarrow Li_2CO_3(s) + CO_2(g) + H_2O(g)$

b. $Na_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

c. $K_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + 2KOH(aq)$

d. $2Li(s) + 2HCl(aq) \rightarrow 2LiCl(aq) + H_2(g)$

e. $4Na(s) + ZrCl_4(g) \rightarrow 4NaCl(s) + Zr(s)$

21.95. $^{227}_{89}Ac \rightarrow {}^{223}_{87}Fr + {}^{4}_{2}He$

21.96. $^{223}_{87}Fr \rightarrow {}^{223}_{88}Ra + {}^{0}_{-1}e$

21.97. $Ca(OH)_2$ can be identified directly by adding an anion that will precipitate the Ca^{2+} (and not the Na^+). For example, adding CO_3^{2-} will precipitate $CaCO_3$ but will not precipitate Na^+ ion.

21.98. $Ba(OH)_2$ can be identified directly by adding SO_4^{2-} ion, precipitating $BaSO_4$ but not K_2SO_4, which is soluble (see Table 4.1). Thus, the presence of a solid will indicate $Ba(OH)_2$.

21.99. $BaCl_2$ can be separated by adding SO_4^{2-} ion, precipitating $BaSO_4$ and leaving $MgCl_2$ in solution because it is soluble (see Table 4.1). Filtering the solution will separate the $BaSO_4$. The filtrate contains soluble $MgCl_2$.

21.100. $MgCl_2$ can be separated by adding OH^- ion, precipitating $Mg(OH)_2$ and leaving NaCl in solution because it is soluble (see Table 4.1). Filtering the solution will separate the $Mg(OH)_2$. The filtrate contains aqueous NaCl.

21.101. $^{230}_{90}Th \rightarrow {}^{226}_{88}Ra + {}^{4}_{2}He$

21.102. $^{223}_{88}Ra \rightarrow {}^{219}_{86}Rn + {}^{4}_{2}He$

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21.103.

a. $BaCO_3(s) \xrightarrow{\Delta} BaO(s) + CO_2(g)$

b. $Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$

c. $Mg(OH)_2(s) + 2HNO_3(aq) \rightarrow 2H_2O(l) + Mg(NO_3)_2(aq)$

d. $Mg(s) + NiCl_2(aq) \rightarrow Ni(s) + MgCl_2(aq)$

e. $2NaOH(aq) + MgSO_4(aq) \rightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$

21.104.

a. $2KOH(aq) + MgCl_2(aq) \rightarrow Mg(OH)_2(s) + 2KCl(aq)$

b. $Mg(s) + CuSO_4(aq) \rightarrow Cu(s) + MgSO_4(aq)$

c. $Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)$

d. $SrCO_3(s) + 2HCl(aq) \rightarrow CO_2(g) + H_2O(l) + SrCl_2(aq)$

e. $Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$

21.105. The equation is $Ca(HCO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow 2CaCO_3(s) + 2H_2O(l)$. Using a 1:1 ratio of $Ca(OH)_2$ to Ca^{2+} ion in the reaction, calculate the mass of $Ca(OH)_2$:

$$0.0250 \text{ L } Ca^{2+} \times \frac{0.12 \text{ mol } Ca^{2+}}{\text{L } Ca^{2+}} \times \frac{1 \text{ mol } Ca(OH)_2}{1 \text{ mol } Ca^{2+}} \times \frac{74.09 \text{ g } Ca(OH)_2}{1 \text{ mol } Ca(OH)_2}$$

$$= 0.222 = 0.22 \text{ g } Ca(OH)_2$$

21.106. The equation is $Ca(OH)_2(aq) + Mg^{2+}(aq) \rightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$. Using a 1:1 ratio of $Ca(OH)_2$ to Mg^{2+} ion in the reaction, calculate the mass of $Ca(OH)_2$:

$$0.050 \text{ L } Mg^{2+} \times \frac{0.21 \text{ mol } Mg^{2+}}{1 \text{ L } Mg^{2+}} \times \frac{1 \text{ mol } Ca(OH)_2}{1 \text{ mol } Mg^{2+}} \times \frac{74.09 \text{ g } Ca(OH)_2}{1 \text{ mol } Ca(OH)_2}$$

$$= 0.777 \text{ g } Ca(OH)_2 = 0.78 \text{ g } Ca(OH)_2$$

21.107. $Al(H_2O)_6^{3+}(aq) + HCO_3^-(aq) \rightarrow Al(H_2O)_5OH^{2+}(aq) + H_2O(l) + CO_2(g)$

21.108.

a. As the pH begins to rise, a precipitate of $Al(OH)_3$ forms. As the pH gets even higher, the precipitate redissolves.

b. $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$

$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

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21.109. Test portions of solutions of each compound with each other; the results can differentiate the compounds. For example, if one solution is poured into one of the other solutions and gives no precipitate, then that means $BaCl_2$ was mixed with KOH, and the third solution is $Al_2(SO_4)_3$. Adding the third solution of $Al_2(SO_4)_3$ to both of the first two solutions will form a precipitate with only $BaCl_2$. [$Al_2(SO_4)_3$ and excess KOH form soluble $Al(OH)_4^-$.] If, instead, one solution is poured into one of the other solutions and a precipitate forms, that means $BaCl_2$ was mixed with $Al_2(SO_4)_3 \rightarrow BaSO_4$, and the third solution is KOH, etc. Thus, all three are identified.

21.110. Test portions of solutions of each compound with each other; the results can differentiate the compounds. For example, if one solution is poured into both of the other solutions, and both give a precipitate [$\rightarrow Al(OH)_3$] and $\rightarrow [Mg(OH)_2 + BaSO_4]$, that solution must be $Ba(OH)_2$. Continuing the addition of the $Ba(OH)_2$ will dissolve the $Al(OH)_3$ as $Al(OH)_4^-$ but will not dissolve the $Mg(OH)_2 + BaSO_4$. Thus, all three will be identified. If, instead, $MgSO_4$ is poured into $AlCl_3$, no reaction will occur, and that will mean the third solution is $Ba(OH)_2$.

21.111. $Sn(H_2O)_6^{2+}(aq) + H_2O(l) \rightarrow Sn(H_2O)_5(OH)^+(aq) + H_3O^+(aq)$

21.112. $Pb(H_2O)_6^{2+}(aq) + H_2O(l) \rightarrow Pb(H_2O)_5(OH)^+(aq) + H_3O^+(aq)$

21.113. The half-reactions and their sum are as follows:

$$\begin{array}{lcl} PbO_2 + 4H^+ + 2e^- & \rightarrow & Pb^{2+} + 2H_2O \\ 2Cl^- & \rightarrow & Cl_2 + 2e^- \\ \hline PbO_2 + 4H^+ + 2Cl^- & \rightarrow & Pb^{2+} + Cl_2 + 2H_2O \end{array}$$

Adding $2Cl^-$ to both sides gives

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$

21.114.

$$\begin{array}{lcl} ClO^- + H_2O + 2e & \rightarrow & Cl^- + 2OH \\ Pb(OH)_3^- + OH^- & \rightarrow & PbO_2(s) + 2H_2O + 2e^- \\ \hline Pb(OH)_3^- + ClO^- + H_2O + OH^- & \rightarrow & PbO_2(s) + Cl^- + 2H_2O + 2OH^- \end{array}$$

Eliminating one H_2O and one OH^- from each side simplifies the equation to

$$Pb(OH)_3^- + ClO^- \rightarrow PbO_2(s) + Cl^- + H_2O + OH^-$$

21.115.

a. $Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$

b. $Al(s) + 3AgNO_3(aq) \rightarrow 3Ag(s) + Al(NO_3)_3(aq)$

c. $Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$

d. $8Al(s) + 3Mn_3O_4(s) \rightarrow 9Mn(s) + 4Al_2O_3(s)$

e. $2Ga(OH)_3(s) \rightarrow Ga_2O_3(s) + 3H_2O(g)$

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21.116.

a. $3Pb(NO_3)_2(aq) + 2Al(s) \rightarrow 3Pb(s) + 2Al(NO_3)_3(aq)$

b. $Pb(NO_3)_2(aq) + Na_2CrO_4(aq) \rightarrow PbCrO_4(s) + 2NaNO_3(aq)$

c. $Al_2(SO_4)_3(aq) + 6LiOH(aq) \rightarrow 2Al(OH)_3(s) + 3Li_2SO_4(aq)$

d. $2Al(s) + 6HCl(aq) \rightarrow 3H_2(g) + 2AlCl_3(aq)$

e. $Sn(s) + 2HBr(aq) \rightarrow H_2(g) + SnBr_2(aq)$

21.117. For 3.5×10^4 kg (3.5×10^7 g) of hydrogen, you get

$$3.5 \times 10^7 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} \times \frac{-484 \text{ kJ}}{2 \text{ mol } H_2} = -4.\underline{2}01 \times 10^9 = -4.2 \times 10^9 \text{ kJ}$$

Thus, 4.2×10^9 kJ of heat is evolved in the process.

21.118. For 20.0 g of HF (molar mass 20.01 g/mol), you get

$$20.0 \text{ g} \times \frac{1 \text{ mol HF}}{20.01 \text{ g HF}} \times \frac{-545 \text{ kJ}}{2 \text{ mol HF}} = -27\underline{2}.36 = -272 \text{ kJ}$$

Thus, 272 kJ of heat is evolved in the process.

21.119.

a. The oxidation state of H in CaH_2 is −1.

b. The oxidation state of H in H_2O is +1.

c. The oxidation state of C in CH_4 is −4.

d. The oxidation state of *S* in H_2SO_4 is +6.

21.120.

a. The oxidation state of H in H_2 is 0.

b. The oxidation state of H in C_2H_4 is +1.

c. The oxidation state of Si in SiH_4 is −4.

d. The oxidation state of N in HNO_3 is +5.

21.121.

a. Carbon has four valence electrons. These are directed tetrahedrally, and the orbitals should be sp^3 hybrid orbitals. Each C–H bond is formed by the overlap of a 1*s* orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the carbon atom.

b. Silicon has four valence electrons. (Two more electrons are added for the −2 charge.) These are directed octahedrally, and the orbitals should be sp^3d^2 hybrid orbitals. Each Si–F bond is formed by the overlap of a 2*p* orbital of a fluorine atom with one of the singly occupied sp^3d^2 hybrid orbitals of the silicon atom.

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c. Carbon has four valence electrons. The single C–C bond is a sigma bond formed by the overlap of the sp^2 orbital of the middle carbon and the sp^3 orbital of the CH_3 carbon. The other three orbitals of the CH_3 carbon are used to form the C–H bonds by overlapping with the orbital of the hydrogen atom. The C=C double bond is a sigma bond formed by the overlap of the sp^2 hybrid orbitals of those carbon atoms, and a pi bond formed by the overlap of the unhybridized *p* orbitals. The C–H bonds on the middle carbon and the CH_2 carbon are formed by the overlap of the sp^2 orbital of carbon and the *s* orbital of hydrogen.

d. Silicon has four valence electrons. These are directed tetrahedrally, and the orbitals should be sp^3 hybrid orbitals. Each Si–H bond is formed by the overlap of a 1*s* orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the silicon atom.

21.122.

a. Carbon has four valence electrons. These are directed tetrahedrally, and the orbitals should be sp^3 hybrid orbitals. Each C–Cl bond is formed by the overlap of a 3*p* orbital of a chlorine atom with one of the singly occupied sp^3 hybrid orbitals of the carbon atom.

b. Carbon has four valence electrons, and nitrogen has five valence electrons. The carbon-nitrogen triple bond is a sigma bond formed by the overlap of *sp* hybrid orbitals and two pi bonds formed by the overlap of the unhybridized *p* orbitals of the C and N atoms. The C–H bond is formed by the overlap of a 1*s* orbital of a hydrogen atom with one of the singly occupied *sp* hybrid orbitals of the carbon atom.

c. Silicon has four valence electrons. These are directed tetrahedrally, and the orbitals should be sp^3 hybrid orbitals. Each Si–F bond is formed by the overlap of a 2*p* orbital of a fluorine atom with one of the singly occupied sp^3 hybrid orbitals of the silicon atom.

d. Carbon has four valence electrons. In the CH_3 group, these are directed tetrahedrally, and the orbitals should be sp^3 hybrid orbitals. Each C–H bond is formed by the overlap of a 1*s* orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the carbon atom. The C–C bond between the CH_3 and the COOH groups is formed by the overlap of the sp^2 orbital of the middle carbon and the sp^3 orbital of the CH_3 carbon. In the COOH group, there is a C=O double bond and a C–O single bond. The C=O double bond is a sigma bond formed by the overlap of the sp^2 hybrid orbitals, and a pi bond formed by the overlap of the unhybridized *p* orbitals of the C and O atoms. The C–O bond is a sigma bond formed by the overlap of the C sp^2 hybrid orbital and the O sp^3 hybrid orbital. The O–H bond is similar to the C–H bond.

21.123.

a. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

$$\begin{array}{lccccc} & CH_4(g) & \rightarrow & C(\text{graphite}) & + & 2H_2(g) \\ \Delta H_f°: & -74.87 & & 0 & & 0\ \text{kJ} \end{array}$$

$\Delta H° = [0 - (-74.87)]\ \text{kJ} = 74.87\ \text{kJ}$

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b. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

$\Delta H_f°$: -84.68 52.47 0 kJ

$\Delta H° = [52.47 - (-84.68)]\ \text{kJ} = 137.15\ \text{kJ}$

21.124.

a. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

$\Delta H_f°$: -110.5 0 -200.7 kJ

$\Delta H° = [-200.7 - (-110.5)]\ \text{kJ} = -90.2\ \text{kJ}$

b. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$

$\Delta H_f°$: -110.5 0 -74.87 -241.8 kJ

$\Delta H° = [(-74.87) + (-241.8) - (-110.5)]\ \text{kJ} = -206.\underline{1}7 = -206.2\ \text{kJ}$

21.125.

a. $CO_2(g) + Ba(OH)_2(aq) \rightarrow BaCO_3(s) + H_2O(l)$

b. $MgCO_3(s) + 2HBr(aq) \rightarrow CO_2(g) + H_2O(l) + MgBr_2(aq)$

21.126.

a. $NaHCO_3(aq) + HC_2H_3O_2(aq) \rightarrow CO_2(g) + H_2O(l) + NaC_2H_3O_2(aq)$

b. $Ca(HCO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow 2CaCO_3(s) + 2H_2O(l)$

21.127. $C(s) + O_2(\text{air}) \rightarrow CO_2(g)$

$CO_2(g) + NaOH(aq) \rightarrow NaHCO_3(aq)$

$2NaHCO_3(aq) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(l) + CO_2(g)$

21.128. $C_2H_6(g) + 2H_2O(g) \xrightarrow{\text{Ni}} 2CO(g) + 5H_2(g)$

$CO(g) + 2H_2(g) \xrightarrow{\text{catalyst}} CH_3OH(g)$

21.129. The diamond-like structure of silicon implies that each silicon atom is tetrahedrally bonded to four other silicon atoms. The hybridization is sp^3. Each bond is formed by the overlap of an sp^3 hybrid orbital on each silicon atom to make a sigma bond.

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21.130. Each of the silicon atoms and each of the carbon atoms is bonded to four other identical atoms in a tetrahedral arrangement. All of the atoms are sp^3 hybridized. A bond is formed by the overlap of an sp^3 hybrid orbital on a silicon atom overlapping with an sp^3 hybrid orbital of a neighboring carbon atom.

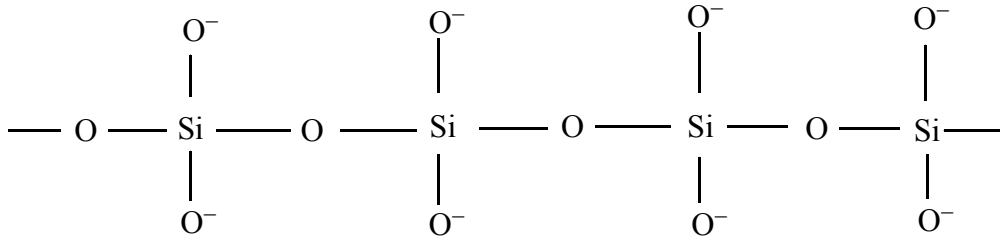
21.131. The molar mass of silicon dioxide (SiO_2) is 60.09 g/mol. Thus,

$$5.00 \text{ kg Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} \times \frac{1 \text{ mol } SiO_2}{1 \text{ mol Si}} \times \frac{60.09 \text{ g } SiO_2}{1 \text{ mol } SiO_2} = 10.\underline{6}959 = 10.7 \text{ kg } SiO_2$$

21.132. The molar mass of silicon tetrachloride ($SiCl_4$) is 169.89 g/mol. Thus,

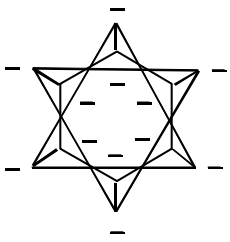
$$5.00 \text{ kg } SiCl_4 \times \frac{1 \text{ mol } SiCl_4}{169.89 \text{ g } SiCl_4} \times \frac{1 \text{ mol Si}}{1 \text{ mol } SiCl_4} \times \frac{28.09 \text{ g Si}}{1 \text{ mol Si}} = 0.82\underline{6}7 = 0.827 \text{ kg Si}$$

21.133. Spodumene, $LiAl(SiO_3)_2$ has the following structure:



The drawing represents two of the sets of tetrahedra forming a portion of a long chain. There is a net −8 charge on the fragment, which includes two sets of two SiO_3 units. Thus, the $(SiO_3)_2$ unit has a −4 charge. This would have to be balanced by one Li^+ and one Al^{3+} for every two SiO_3. Thus, the empirical formula is $LiAl(SiO_3)_2$.

21.134. Beryl, $Be_3Al_2(SiO_3)_6$, has the following structure.



There is a net −12 charge, so the empirical formula is $Be_3Al_2(SiO_3)_6$.

21.135. The equation is $Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(aq) + 2NH_3(g)$. Using a 1:2 ratio of Mg_3N_2 to NH_3, calculate the mass of NH_3 formed as follows:

$$7.50 \text{ g } Mg_3N_2 \times \frac{1 \text{ mol } Mg_3N_2}{100.915 \text{ g } Mg_3N_2} \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } Mg_3N_2} \times \frac{17.03 \text{ g } NH_3}{1 \text{ mol } NH_3}$$

$$= 2.5\underline{3}1 = 2.53 \text{ g}$$

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21.136. The equation is $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$. Using a 5:4 ratio of O_2 to NO, calculate the mass of O_2 required as follows:

$$3.00 \text{ g NO} \times \frac{1 \text{ mol NO}}{30.0 \text{ g NO}} \times \frac{5 \text{ mol } O_2}{4 \text{ mol NO}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 4.0\underline{0}0 = 4.00 \text{ g } O_2$$

21.137. Prepare HNO_3 from NH_3:

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt} 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

To prepare N_2O, use the HNO_3 just prepared:

$$NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$$

$$NH_4NO_3(aq) \rightarrow NH_4NO_3(s)$$

$$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$$

21.138. Prepare NH_3 and HNO_3 separately:

$$2NaOH(aq) + (NH_4)_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2NH_3(g) + H_2O(l)$$

$$H_2SO_4(l) + NaNO_3(s) \rightarrow NaHSO_4(s) + HNO_3(g)$$

React NH_3 and HNO_3 to give NH_4NO_3, which can be decomposed to N_2O:

$$NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$$

$$NH_4NO_3(aq) \rightarrow NH_4NO_3(s)$$

$$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$$

21.139. The reduction of NO_3^- ion to NH_4^+ ion is an eight-electron reduction, and the oxidation of zinc to zinc(II) ion is a two-electron oxidation. Balancing the equation involves multiplying the zinc half-reaction by 4 to achieve an eight-electron oxidation. The final equation is

$$4Zn(s) + NO_3^-(aq) + 10H^+(aq) \rightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$$

21.140. The reduction of NO_3^- ion to NO is a three-electron reduction, and the oxidation of silver to silver(I) ion is a one-electron oxidation. Balancing the equation involves multiplying the silver half-reaction by 3 to achieve a three-electron oxidation. The final equation is

$$3Ag(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow 3Ag^+(aq) + NO(g) + 2H_2O(l)$$

21.141. PBr_4^+ has four pairs of electrons around the P atom, arranged in a tetrahedral fashion. The hybridization of P is sp^3. Each bond is formed by the overlap of a 4*p* orbital from Br with an sp^3 hybrid orbital from P.

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21.142. The PCl_6^- ion should have an octahedral geometry. Phosphorus has five valence electrons, which, together with the electron added for the charge, account for the sp^3d^2 hybridization of P. Each sp^3d^2 hybrid orbital is used in the formation of a P–Cl bond.

21.143. The balanced half-reactions are

Oxidation: $H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^+ + 2e^-$

Reduction: $H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

The overall balanced equation is

$$H_3PO_3 + H_2SO_4 \rightarrow H_3PO_4 + SO_2 + H_2O$$

21.144. The balanced half-reactions are

Oxidation: $H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H^+ + 2e^-$

Reduction: $HNO_3 + 3H^+ + 3e^- \rightarrow NO + 2H_2O$

Multiply the oxidation half-reaction by 3, and the reduction half-reaction by 2. After adding and cancellation of the water, hydrogen ions, and electrons, the resulting overall balanced equation is

$$3H_3PO_3 + 2HNO_3 \rightarrow 3H_3PO_4 + 2NO + H_2O$$

21.145. In the equation, there is a 2:1 ratio of H_3PO_4 to $Ca_3(PO_4)_2$ that can be used to calculate the mass of H_3PO_4 from the mass of $Ca_3(PO_4)_2$. The mass of $Ca_3(PO_4)_2$ in the 30.0 g of rock is

$$0.746 \times 30.0 \text{ g rock} = 22.\underline{3}8 \text{ g } Ca_3(PO_4)_2 \text{ (= CaP)}$$

The mass of H_3PO_4 can be calculated from this mass as follows:

$$22.38 \text{ g CaP} \times \frac{1 \text{ mol CaP}}{310.2 \text{ g CaP}} \times \frac{2 \text{ mol } H_3PO_4}{1 \text{ mol CaP}} \times \frac{98.0 \text{ g } H_3PO_4}{1 \text{ mol } H_3PO_4}$$

$$= 14.\underline{1}4 = 14.1 \text{ g } H_3PO_4$$

21.146. In the equation, there is a 3:1 ratio of $Ca(H_2PO_4)_2$ to $Ca_3(PO_4)_2$ that can be used to calculate the mass of $Ca(H_2PO_4)_2$ from the mass of $Ca_3(PO_4)_2$. The mass of $Ca_3(PO_4)_2$ in the 10.0 g of rock is

$$0.712 \times 10.0 \text{ g rock} = 7.12 \text{ g } Ca_3(PO_4)_2 \text{ (= CaP)}$$

The mass of $Ca(H_2PO_4)_2$ can be calculated from this mass as follows:

$$7.12 \text{ g CaP} \times \frac{1 \text{ mol } Ca_3(PO_4)_2}{310.2 \text{ g } Ca_3(PO_4)_2} \times \frac{3 \text{ mol } Ca(H_2PO_4)_2}{1 \text{ mol } Ca_3(PO_4)_2} \times \frac{234.0 \text{ g } Ca(H_2PO_4)_2}{1 \text{ mol } Ca(H_2PO_4)_2}$$

$$= 16.\underline{1}1 = 16.1 \text{ g } Ca(H_2PO_4)_2$$

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21.147.

a. $4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$

b. Organic materials burn in excess O_2 to give CO_2 and H_2O. The nitrogen becomes N_2:

$$4CH_3NH_2(g) + 9O_2(g) \rightarrow 4CO_2(g) + 2N_2(g) + 10H_2O(g)$$

c. $2(C_2H_5)_2S + 15O_2 \rightarrow 8CO_2(g) + 10H_2O(g) + 2SO_2(g)$

21.148.

a. $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$

b. $4PH_3(g) + 8O_2(g) \rightarrow P_4O_{10}(s) + 6H_2O(g)$

c. $4HOCH_2CH_2NH_2(l) + 13O_2(g) \rightarrow 8CO_2(g) + 14H_2O(g) + 2N_2(g)$

21.149.

a. $x_S + 6x_F = 0$

The oxidation number of F in compounds is always −1.

$$x_S = -6x_F = -6(-1) = +6$$

b. $x_S + 3x_O = 0$

The oxidation number of O in most compounds is −2.

$$x_S = -3x_O = -3(-2) = +6$$

c. $x_S + 2x_H = 0$

The oxidation number of H in most compounds is +1.

$$x_S = -2x_H = -2(+1) = -2$$

d. $x_{Ca} + x_S + 3x_O = 0$

The oxidation number of Ca in compounds is +2; the oxidation number of O in most compounds is −2.

$$x_S = -x_{Ca} - 3x_O = -(+2) - 3(-2) = +4$$

21.150.

a. $x_S = 0$

The oxidation number in any element is 0.

b. $x_{Ca} + x_S = 0$

The oxidation number of Ca in compounds is +2.

$$x_S = -x_{Ca} = -(+2) = -2$$

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c. $x_{Ca} + x_S + 4x_O = 0$

The oxidation number of Ca in compounds is +2; the oxidation number of O in most compounds is −2.

$$x_S = -x_{Ca} - 4x_O = -(+2) - 4(-2) = +6$$

d. $x_S + 4x_{Cl} = 0$

The oxidation number of Cl in a binary compound with a less electronegative element is −1.

$$x_S = -4x_{Cl} = -4(-1) = +4$$

21.151. The reduction of $8H_2SeO_3$ to Se_8 is a 32-electron reduction, and the oxidation of $8H_2S$ to S_8 is a 16-electron oxidation. Balancing the equation requires multiplying the H_2S half-reaction by 2 to achieve a 32-electron oxidation. The final equation is

$$8H_2SeO_3(aq) + 16H_2S(g) \rightarrow Se_8(s) + 2S_8(s) + 24H_2O(l)$$

21.152. $H_2SO_4(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow SO_2(g) + I_2(s) + 2H_2O(l)$

21.153. In the equation, there is a 2:1 ratio of $NaHSO_3$ to Na_2CO_3 that can be used to calculate the mass of $NaHSO_3$ from 25.0 g of Na_2CO_3. The mass of $NaHSO_3$ is calculated as follows:

$$25.0 \text{ g } Na_2CO_3 \times \frac{1 \text{ mol } Na_2CO_3}{106.0 \text{ g } Na_2CO_3} \times \frac{2 \text{ mol } NaHSO_3}{1 \text{ mol } Na_2CO_3} \times \frac{104.0 \text{ g } NaHSO_3}{1 \text{ mol } NaHSO_3}$$

$$= 49.\underline{0}56 = 49.1 \text{ g } NaHSO_3$$

21.154. In the equation, there is an 8:1 ratio of $Na_2S_2O_3$ to S_8 that can be used to calculate the mass of $Na_2S_2O_3$ from 50.0 g of S_8. The mass of $Na_2S_2O_3$ is calculated as follows:

$$50.0 \text{ g } S_8 \times \frac{1 \text{ mol } S_8}{256.5 \text{ g } S_8} \times \frac{8 \text{ mol } Na_2S_2O_3}{1 \text{ mol } S_8} \times \frac{158.1 \text{ g } Na_2S_2O_3}{1 \text{ mol } Na_2S_2O_3}$$

$$= 24\underline{6}.54 = 247 \text{ g } Na_2S_2O_3$$

21.155. $Ba(ClO_3)_2(aq) + H_2SO_4(aq) \rightarrow 2HClO_3(aq) + BaSO_4(s)$

21.156. $Ba(ClO_2)_2(aq) + H_2SO_4(aq) \rightarrow 2HClO_2(aq) + BaSO_4(s)$

21.157. The balanced half-reactions are

Oxidation: $2HCl \rightarrow Cl_2 + 2H^+ + 2e^-$

Reduction: $K_2Cr_2O_7 + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 2K^+ + 7H_2O$

Multiply the oxidation half-reaction by 3. After adding and cancellation of the hydrogen ions and electrons, the resulting overall balanced equation is

$$K_2Cr_2O_7 + 6HCl + 8H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 2K^+ + 7H_2O$$

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If eight Cl^- are added to each side, the equation can also be written as a molecular equation.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2CrCl_3 + 3Cl_2 + 2KCl + 7H_2O$$

21.158. The balanced half-reactions are

Oxidation: $I_2 + 6H_2O \rightarrow 2HIO_3 + 10H^+ + 10e^-$

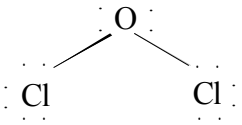
Reduction: $HNO_3 + H^+ + e^- \rightarrow NO_2 + H_2O$

Multiply the reduction half-reaction by 10. After adding and cancellation of the water, hydrogen ions, and electrons, the resulting overall balanced equation is

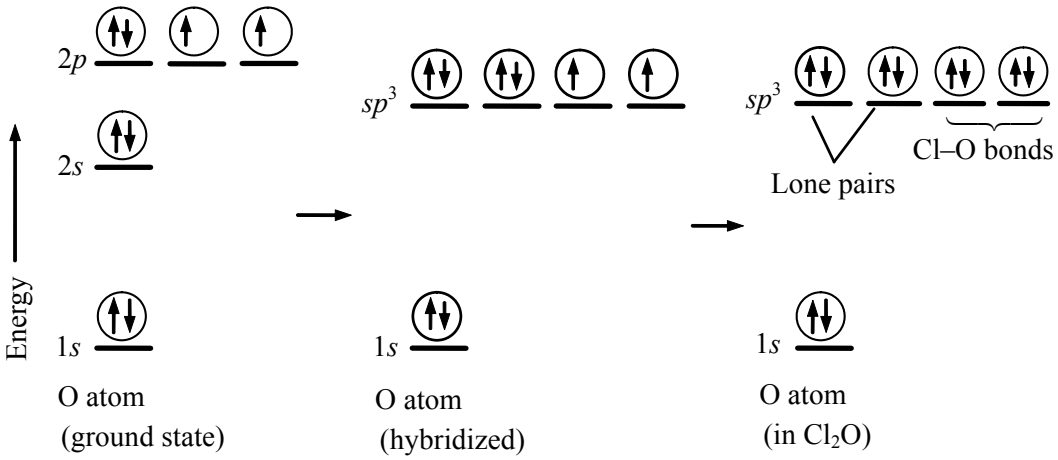
$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

21.159.

a. The electron-dot formula of Cl_2O is



The VSEPR model predicts a bent (angular) molecular geometry. You can describe the four electron pairs on O using sp^3 hybrid orbitals. The diagramming for the bond formation follows:



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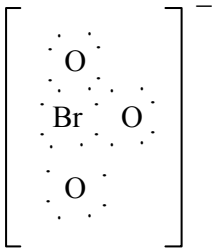
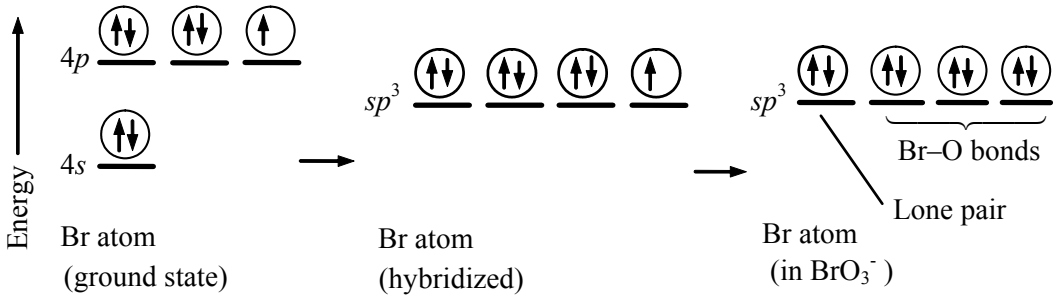
b. An electron-dot formula of BrO_3^- is

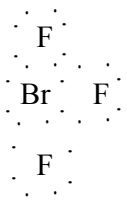


The VSEPR model predicts a trigonal pyramidal geometry. You can describe the four electron pairs on Br using sp^3 hybrid orbitals. The diagramming for the bond formation follows:

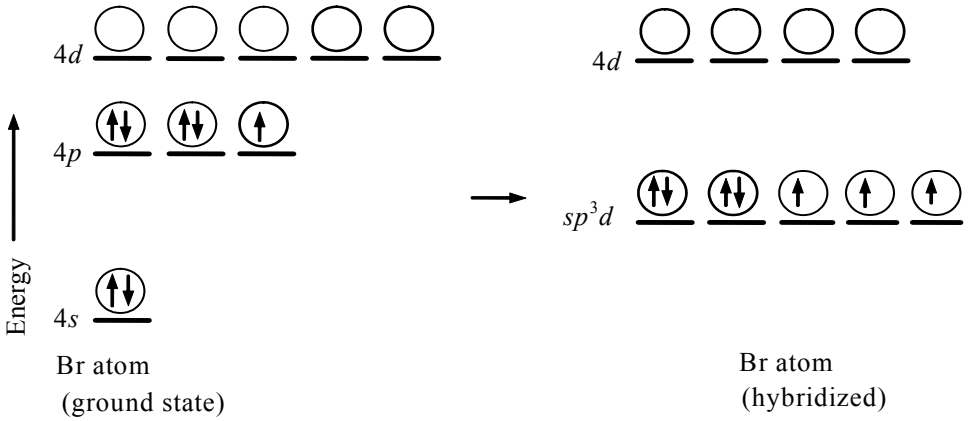


(Note: The additional electron accounts for the −1 charge of the ion; the bonds to O atoms are coordinate covalent.)

c. The electron-dot formula of BrF_3 is



The five electron pairs on Br have a trigonal bipyramidal arrangement. Putting the lone pairs in equatorial positions to reduce repulsions gives a T-shaped molecular geometry for BrF_3. You can describe the five electron pairs on Br in terms of sp^3d hybrid orbitals. The diagramming for the bond formation follows:



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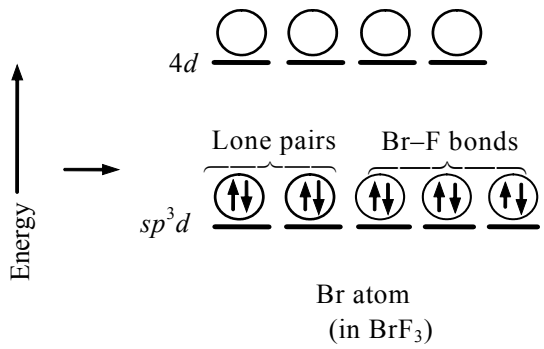

21.160.

a. The electron-dot formula of HClO involves a pair of bonding electrons between H and O and a pair of bonding electrons between Cl and O. Chlorine has 3 lone pairs of electrons. The VSEPR model predicts a bent (angular) molecular geometry like the geometry of H_2O discussed in Section 10.1 and shown in Figure 10.6. There is a total of four electron pairs around oxygen; two are bonding and two are lone pairs. Figure 10.4 predicts a tetrahedral arrangement of the four electron pairs with sp^3 hybridization of the O atom and a Cl–O–H structure.

b. The electron-dot formula of ClO_4^- involves a pair of bonding electrons between each oxygen and chlorine. Thus, chlorine has four pairs of electrons. The VSEPR model predicts a tetrahedral molecular geometry like the geometry of $SiCl_4$ discussed in Example 10.1 and shown for CH_4 in Figure 10.6. Figure 10.4 predicts a tetrahedral arrangement of the four electron pairs with sp^3 hybridization of the Cl atom.

c. The electron-dot formula of ClF_5 involves a pair of bonding electrons between each fluorine and chlorine. In addition, chlorine has a lone pair of electrons. The VSEPR model predicts a square pyramidal geometry like the geometry of IF_5, which is shown at the end of Section 10.1. The lone-pair electrons of Cl occupy one of the six equivalent positions in the octahedral arrangement. Figure 10.8 predicts an octahedral arrangement of the five electron pairs with sp^3d^2 hybridization of the Cl atom.

21.161.

a. $Br_2(aq) + 2NaOH(aq) \rightarrow H_2O(l) + NaOBr(aq) + NaBr(aq)$

b. Assume, by analogy with H_2SO_4 and NaCl, that the usual heating causes a loss of one H^+ per molecule of acid. Stronger heating would result in a loss of additional H^+ from $H_2PO_4^-$.

$$NaBr(s) + H_3PO_4(aq) \xrightarrow{\Delta} HBr(g) + NaH_2PO_4(aq)$$

21.162.

a. Assume, by analogy with H_2SO_4 and NaCl, that the usual heas remaining H^+ of HSO_4^-.

$$CaF_2(s) + 2H_2SO_4(l) \rightarrow 2HF(g) + Ca(HSO_4)_2(s)$$

b. The oxidation of ClO_3^- to ClO_4^- involves two electrons; the reduction of ClO_3^- to Cl^- involves a gain of six electrons. Thus, three ClO_4^- must be formed in the final equation:

$$4KClO_3(s) \rightarrow KCl(s) + 3KClO_4(s)$$

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21.163. Reverse the iron half-reaction and the sign of its $E°$, and double the half-reaction to obtain the same number of electrons as the OCl^- half-reaction:

$2Fe^{2+}(aq)$	$\rightarrow 2Fe^{3+}(aq) + 2e^-$	$-E° = -0.77$ V
$OCl^-(aq) + H_2O(l) + 2e^-$	$\rightarrow Cl^-(aq) + 2OH^-(aq)$	$E° = 0.90$ V
$OCl^-(aq) + H_2O(l) + 2Fe^{2+}(aq)$	$\rightarrow 2Fe^{3+}(aq) + Cl^-(aq) + 2OH^-(aq)$	$E°_{cell} = 0.13$ V

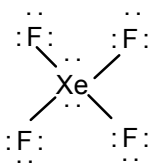
Because $E°_{cell}$ is positive, the reaction is spontaneous at standard conditions.

21.164. Reverse the Br^- half-reaction and the sign of its $E°$. Both half-reaction have the same number of electrons, so the half-reactions are simply added:

$2Br^-(aq)$	$\rightarrow Br_2(l) + 2e^-$	$-E° = 1.07$ V
$Ocl^-(aq) + H_2O(l) + 2e^-$	$\rightarrow Cl^-(aq) + 2OH^-(aq)$	$E° = 0.90$ V
$Ocl^-(aq) + H_2O(l) + 2Br^-(aq)$	$\rightarrow Br_2(l) + Cl^-(aq) + 2OH^-(aq)$	$E°_{cell} = 0.17$ V

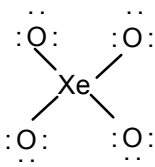
Because $E°_{cell}$ is negative, the reaction is nonspontaneous at standard conditions.

21.165. The total number of valence electrons is 8 + (4 x 7) = 36. These are distributed to give the following Lewis formula:



The six electron pairs on Xe would have an octahedral arrangement, suggesting sp^3d^2 hybridization. The lone pairs on Xe would be directed above and below the molecule, which has a square planar geometry.

21.166. The total number of valence electrons is 8 + (4 x 6) = 32. This gives the following Lewis formula:



Because there are four electron pairs on Xe, the arrangement of pairs is tetrahedral, suggesting sp^3 hybridization. The molecular geometry would be predicted to be tetrahedral.

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21.167. From the information given,

$XeF_2 \rightarrow Xe + O_2 + F^-$ (basic solution; not balanced)

The oxygen (and hydrogen) will be balanced by OH^- and H_2O from the basic solution. Balance the half-reactions.

Reduction: $XeF_2 \rightarrow Xe + F^-$

Balance F atoms: $XeF_2 \rightarrow Xe + 2F^-$

Balance charge: $2e^- + XeF_2 \rightarrow Xe + 2F^-$

Oxidation: $H_2O \rightarrow O_2$

Balance O atoms: $2H_2O \rightarrow O_2$

Balance H atoms: $2H_2O \rightarrow 4H^+ + O_2$

Balance charge: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Convert to base: $2H_2O + 4OH^- \rightarrow 4H_2O + O_2 + 4e^-$

Double the Xe half-reaction, and add half-reactions to get the overall reaction:

$$\begin{array}{lcl} 4e^- + 2XeF_2 & \rightarrow & 2Xe + 4F^- \\ 4OH^- & \rightarrow & O_2 + 2H_2O + 4e \\ \hline 2XeF_2 + 4OH^- & \rightarrow & 2Xe + 4F^- + O_2 + 2H_2O \end{array}$$

21.168. From the information given,

$XeO_3 + I^- \rightarrow Xe + I_2$ (acidic solution; not balanced)

Balance by the half-reaction method.

Reduction: $XeO_3 \rightarrow Xe$

Balance O atoms: $XeO_3 \rightarrow Xe + 3H_2O$

Balance H atoms: $6H^+ + XeO_3 \rightarrow Xe + 3H_2O$

Balance charge: $6e^- + 6H^+ + XeO_3 \rightarrow Xe + 3H_2O$

Oxidation: $I^- \rightarrow I_2$

Balance I atoms: $2I^- \rightarrow I_2$

Balance charge: $2I^- \rightarrow I_2 + 2e^-$

Triple the Iodine half-reaction, and add the half-reactions:

$$\begin{array}{lcl} 6e^- + 6H^+ + XeO_3 & \rightarrow & Xe + 3H_2O \\ 6I^- & \rightarrow & 3I_2 + 6e \\ \hline XeO_3 + 6H^+ + 6I^- & \rightarrow & Xe + 3H_2O + 3I_2 \end{array}$$

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■ SOLUTIONS TO GENERAL PROBLEMS

21.169. Sphalerite, ZnS, has the molar mass 97.48 g/mol. Thus

$$1.00 \text{ metric ton} \times 0.870 \text{ ZnS} \times \frac{1 \text{ mol ZnS}}{97.48 \text{ g ZnS}} \times \frac{1 \text{ mol Zn}}{1 \text{ mol ZnS}} \times \frac{65.41 \text{ g Zn}}{1 \text{ mol Zn}}$$

$$= 0.58377 = 0.584 \text{ metric ton Zn}$$

21.170. Galena, PbS, has the molar mass 239.3 g/mol. Thus

$$1.00 \text{ metric ton} \times 0.780 \text{ PbS} \times \frac{1 \text{ mol PbS}}{239.3 \text{ g PbS}} \times \frac{1 \text{ mol Pb}}{1 \text{ mol PbS}} \times \frac{207.2 \text{ g Pb}}{1 \text{ mol Pb}}$$

$$= 0.67536 = 0.675 \text{ metric ton Pb}$$

21.171. The equations are

$$2HCl + Mg(OH)_2(s) \rightarrow MgCl_2 + 2H_2O$$

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Using a 1:1 ratio of HCl to NaOH, calculate the moles of HCl reacting with NaOH:

$$\left[\frac{0.4987 \text{ mol HCl}}{\text{L}} \times 0.05000 \text{ L}\right] - \left[\frac{0.2456 \text{ mol NaOH}}{\text{L}} \times 0.03942 \text{ L}\right] = 0.015253 \text{ mol HCl}$$

The mass of $Mg(OH)_2$ is

$$0.015253 \text{ mol HCl} \times \frac{1 \text{ mol Mg(OH)}_2}{2 \text{ mol HCl}} \times \frac{58.33 \text{ g Mg(OH)}_2}{1 \text{ mol Mg(OH)}_2} = 0.44486 \text{ g Mg(OH)}_2$$

The mass percentage is

$$\frac{0.44486 \text{ g}}{5.436 \text{ g}} \times 100\% = 8.1837 = 8.184\%$$

21.172. The equations are $2HCl + CaCO_3(s) \rightarrow CaCl_2 + H_2O + CO_2$ and $HCl + NaOH \rightarrow NaCl + H_2O$. Using a 1:1 ratio of HCl to NaOH, calculate the moles of HCl reacting with NaOH:

$$\left[\frac{0.5068 \text{ mol HCl}}{\text{L}} \times 0.05000 \text{ L}\right] - \left[\frac{0.2590 \text{ mol NaOH}}{\text{L}} \times 0.04123 \text{ L}\right]$$

$$= 0.014661 \text{ mol HCl}$$

The mass of $CaCO_3$ is

$$0.014661 \text{ mol HCl} \times \frac{1 \text{ mol CaCO}_3}{2 \text{ mol HCl}} \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 0.73380 \text{ g CaCO}_3$$

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The mass percentage is

$$\frac{0.73380\text{ g}}{0.9863\text{ g}} \times 100\% = 74.3\underline{9}9 = 74.40\%$$

21.173. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

	$Fe_2O_3(s)$ +	$2Al(s)$ →	$2Fe(s)$ +	$Al_2O_3(s)$
$\Delta H_f°$:	-825.5	0	0	-1675.7 kJ

$$\Delta H° = [-1675.7 - (-825.5)]\text{ kJ} = -850.2\text{ kJ}$$

For 1 mol of iron,

$$\frac{-850.2\text{ kJ}}{2\text{ mol Fe}} = -425.1\text{ kJ/mol Fe}$$

21.174. The equation, with $\Delta H_f°$'s recorded beneath each substance, is

	$3CaO(s)$ +	$2Al(s)$ →	$3Ca(s)$ +	$Al_2O_3(s)$
$\Delta H_f°$:	3(-635.1)	0	0	-1675.7 kJ

$$\Delta H° = [-1675.7 - 3(-635.1)]\text{ kJ} = 229.6\text{ kJ}$$

For 1 mol of calcium,

$$\frac{229.6\text{ kJ}}{3\text{ mol Ca}} = 76.5\underline{3}3 = 76.53\text{ kJ/mol Ca}$$

21.175. From the ideal gas law, the moles of CO_2 are

$$n = \frac{PV}{RT} = \frac{(745/760\text{ atm})(0.03456\text{ L})}{(0.0821\text{ L}\bullet\text{atm/K}\bullet\text{mol})(294\text{ K})} = 0.0014\underline{0}35\text{ mol } CO_2$$

The equation is $CaCO_3(s) + 2HCl \rightarrow CO_2(g) + CaCl_2(aq) + H_2O(l)$. Using a 1:1 mole ratio of CO_2 to $CaCO_3$, the mass of $CaCO_3$ is

$$0.0014035\text{ mol } CO_2 \times \frac{1\text{ mol } CaCO_3}{1\text{ mol } CO_2} \times \frac{100.1\text{ g } CaCO_3}{1\text{ mol } CaCO_3} = 0.14\underline{0}49\text{ g } CaCO_3$$

The mass percentage of $CaCO_3$ is

$$\frac{0.14049\text{ g}}{0.1662\text{ g}} \times 100\% = 84.\underline{5}3 = 84.5\%\text{ } CaCO_3$$

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21.176. From the ideal gas law, the moles of CO_2 are

$$n = \frac{PV}{RT} = \frac{(758/760 \text{ atm})(0.03771 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})} = 0.0015\underline{5}29 \text{ mol } CO_2$$

The equation is $MgCO_3(s) + 2HCl \rightarrow CO_2(g) + MgCl_2 + H_2O(l)$. Using a 1:1 ratio of CO_2 to $MgCO_3$, the mass of $MgCO_3$ is

$$0.0015529 \text{ mol } CO_2 \times \frac{1 \text{ mol } MgCO_3}{1 \text{ mol } CO_2} \times \frac{84.32 \text{ g } MgCO_3}{1 \text{ mol } MgCO_3} = 0.13\underline{0}94 \text{ g } MgCO_3$$

The mass percentage of $MgCO_3$ is

$$\frac{0.13094 \text{ g}}{0.1504 \text{ g}} \times 100\% = 87.\underline{0}6\% = 87.1\% \text{ } MgCO_3$$

21.177. The equation is $NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl$. Using a 1:1 mole ratio of NaCl to $NaHCO_3$, the mass of NaCl is

$$10.00 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.00 \text{ g } NaHCO_3} \times \frac{1 \text{ mol NaCl}}{1 \text{ mol } NaHCO_3} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}}$$

$$= 6.95\underline{7}1 = 6.957 \text{ g NaCl}$$

21.178. The equation is $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$. Using a 1:2 mole ratio of Cr_2O_3 to Al, the mass of Al is

$$15.00 \text{ g } Cr_2O_3 \times \frac{1 \text{ mol } Cr_2O_3}{152.0 \text{ g } Cr_2O_3} \times \frac{2 \text{ mol Al}}{1 \text{ mol } Cr_2O_3} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

$$= 5.32\underline{5}0 = 5.325 \text{ g Al}$$

21.179. Write the reaction with the $\Delta H_f°$'s and $S°$'s below:

	$SrCO_3(s)$	$\rightarrow$	$SrO(s)$	+	$CO_2(g)$
$\Delta H_f°$:	-1220.1		-592.0		-393.5 kJ
S°:	97.1		55.52		213.7 J/K

$\Delta H° = [-592.0 - 393.5 - (-1220.1)]$ kJ = 234.6 kJ

$\Delta S° = [55.52 + 213.7 - 97.1]$ J/K = 172.$\underline{1}$2 J/K = 0.17212 kJ/K

Finally, determine the temperature.

$$\Delta G° = \Delta H° - T\Delta S°$$

$$0 = 234.6 \text{ kJ} - T(0.17212 \text{ kJ/K})$$

$$T = \frac{234.6 \text{ kJ}}{0.17212 \text{ kJ/K}} = 136\underline{3}.0 = 1363 \text{ K}$$

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21.180. Write the reaction with the $\Delta H_f°$'s and $S°$'s below:

	$BaCO_3(s)$	$\rightarrow$	$BaO(s)$	+	$CO_2(g)$
$\Delta H_f°$:	-1216.3		-548.1		-393.5 kJ
S°:	112.1		72.07		213.7 J/K

$\Delta H° = [-548.1 - 393.5 - (-1216.3)]$ kJ $= 274.7$ kJ

$\Delta S° = [72.07 + 213.7 - 112.1]$ J/K $= 173.\underline{6}7$ J/K $= 0.173\underline{6}7$ kJ/K

Finally, determine the temperature.

$$\Delta G° = \Delta H° - T\Delta S°$$

$$0 = 274.7 \text{ kJ} - T(0.17367 \text{ kJ/K})$$

$$T = \frac{274.7 \text{ kJ}}{0.17367 \text{ kJ/K}} = 158\underline{1}.7 = 1582 \text{ K}$$

21.181. The overall disproportionation reaction can be considered as the sum of the following reactions:

$$2e^- + 2In^+(aq) \rightarrow 2In(s)$$
$$In^+(aq) \rightarrow In^{3+}(aq) + 2e^-$$
$$3In^+(aq) \rightarrow 2In(s) + In^{3+}$$

$E°_{cell} = E°_{cathode} - E°_{anode} = [(-0.21) - (-0.40)]$ V $= 0.19$ V

$\Delta G° = -nFE°_{cell} = -(2)\,(9.65 \times 10^4 \text{ C})\,(0.19 \text{ J/C}) = -3.\underline{6}67 \times 10^4 \text{ J} = -37$ kJ

$\Delta G°$ for the reaction as written is negative, so the disproportionation does occur spontaneously.

21.182. The overall disproportionation can be considered as the sum of the following reactions:

$$2Tl^+(aq) + 2e^- \rightarrow 2Tl(s)$$
$$Tl^+(aq) \rightarrow Tl^{3+} + 2e^-$$
$$3Tl^+(aq) \rightarrow 2Tl(s) + Tl^{3+}(aq)$$

$E°_{cell} = E°_{cathode} - E°_{anode} = [(-0.34) - (1.25)]$ V $= -1.59$ V

$\Delta G° = -nFE°_{cell} = -(2)\,(9.65 \times 10^4 \text{ C})\,(-1.59 \text{ J/C}) = 3.0\underline{6}87 \times 10^5 \text{ J}$ (307 kJ)

$\Delta G°$ is positive for the reaction, so the disproportionation does not occur spontaneously.

21.183. Using the ideal gas law, the amount of CO_2 is

$$n = \frac{PV}{RT} = \frac{(30.0/760 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 1.6\underline{1}4 \times 10^{-3} \text{ mol } CO_2$$

The balanced equation is $2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(s) + H_2O(g)$, so use the mole ratio 1 mol CO_2 to 2 mol LiOH. Therefore, the mass of LiOH is

$$1.614 \times 10^{-3} \text{ mol } CO_2 \times \frac{2 \text{ mol LiOH}}{1 \text{ mol } CO_2} \times \frac{23.95 \text{ g LiOH}}{1 \text{ mol LiOH}}$$

$$= 7.7\underline{3}1 \times 10^{-2} = 7.73 \times 10^{-2} \text{ g LiOH}$$

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21.184. Using the ideal gas law, the amount of Cl_2 is

$$n = \frac{PV}{RT} = \frac{(784/760 \text{ atm})(138 \text{ L})}{(0.0821 \text{ L} \bullet \text{atm/K} \bullet \text{mol})(298 \text{ K})} = 5.8\underline{1}86 \text{ mol } Cl_2$$

The balanced equation is $6KOH(aq) + 3Cl_2(g) \rightarrow KClO_3(s) + 5KCl(aq) + 3H_2O(l)$, so use the mole ratio 3 mol Cl_2 to 1 mol $KClO_3$. Therefore, the mass of $KClO_3$ is

$$5.8186 \text{ mol } Cl_2 \times \frac{1 \text{ mol } KClO_3}{3 \text{ mol } Cl_2} \times \frac{122.55 \text{ g } KClO_3}{1 \text{ mol } KClO_3} = 23\underline{7}.69 = 238 \text{ g } KClO_3$$

21.185. Assume a sample of 100.0 g fertilizer. This contains 17.1 g P. Convert this to the mass of $Ca(H_2PO_4)_2 \bullet H_2O$ in the 100.0 g of fertilizer.

$$17.1 \text{ g P} \times \frac{1 \text{ mol P}}{30.97 \text{ g P}} \times \frac{1 \text{ mol } Ca(H_2PO_4)_2 \bullet H_2O}{2 \text{ mol P}} \times \frac{252.1 \text{ g } Ca(H_2PO_4)_2 \bullet H_2O}{1 \text{ mol } Ca(H_2PO_4)_2 \bullet H_2O}$$
$$= 69.\underline{5}89 \text{ g } Ca(H_2PO_4)_2$$

The mass percent $Ca(H_2PO_4)_2 \bullet H_2O$ in the fertilizer is

$$\text{Mass percent } Ca(H_2PO_4)_2 \bullet H_2O = \frac{69.589 \text{ g } Ca(H_2PO_4)_2 \bullet H_2O}{100 \text{ g fertilizer}} \times 100\%$$

$$= 69.\underline{5}89 = 69.6\%$$

21.186. In 100.0 g of the fertilizer, there are 30.0 g of $Ca(H_2PO_4)_2 \bullet H_2O$ and 10.0 g $CaHPO_4$. The mass of P in the 30.0 g of $Ca(H_2PO_4)_2 \bullet H_2O$ is

$$30.0 \text{ g } Ca(H_2PO_4)_2 \bullet H_2O \times \frac{1 \text{ mol } Ca(H_2PO_4)_2 \bullet H_2O}{252.1 \text{ g } Ca(H_2PO_4)_2 \bullet H_2O} \times \frac{2 \text{ mol P}}{1 \text{ mol } Ca(H_2PO_4)_2 \bullet H_2O}$$
$$\times \frac{30.97 \text{ g P}}{1 \text{ mol P}} = 7.3\underline{7}1 \text{ g P}$$

The mass of P in the 10.0 g of $CaHPO_4$ is

$$10.0 \text{ g } CaHPO_4 \times \frac{1 \text{ mol } CaHPO_4}{136.1 \text{ g } CaHPO_4} \times \frac{1 \text{ mol P}}{1 \text{ mol } CaHPO_4} \times \frac{30.97 \text{ g P}}{1 \text{ mol P}} = 2.2\underline{7}6 \text{ g P}$$

The total mass of P in the 100.0 g sample is (7.371 + 2.276) g = 9.6$\underline{4}$7 g. Therefore, the mass percent P = 9.6$\underline{4}$7% = 9.65%.

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21.187. $2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$ (electrolysis)

$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$ (spontaneous)

One mole of NaClO is produced for every two moles of NaCl. Thus, the reaction requires two electrons per mole of NaClO produced.

Convert the 1.00×10^3 L of NaOCl to time:

$$1.00 \times 10^3 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.00 \text{ g soln}}{1 \text{ mL}} \times \frac{5.25 \text{ g NaOCl}}{100 \text{ g soln}} \times \frac{1 \text{ mol NaOCl}}{74.44 \text{ g NaOCl}}$$

$$\times \frac{2 \text{ mol e}^-}{1 \text{ mol NaOCl}} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{3.00 \times 10^3 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}}$$

$$= 12.\underline{6}0 = 12.6 \text{ h}$$

21.188. The electrode reaction is

$$ClO_3^-(aq) + H_2O(l) \rightarrow ClO_4^-(aq) + 2H^+(aq) + 2e^-$$

The amount of $NaClO_4$ per hour is

$$\frac{2.50 \times 10^3 \text{ C}}{1 \text{ s}} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol } NaClO_4}{2 \text{ mol e}^-} \times \frac{122.4 \text{ g } NaClO_4}{1 \text{ mol } NaClO_4}$$

$$= 5.7\underline{0}7 \times 10^3 \text{ g/h} = 5.71 \text{ kg/h}$$

21.189. The reactions are

$$H_2O + NaOCl + 2I^- \rightarrow I_2 + NaCl + 2OH^-$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The mass of NaOCl is

$$0.0346 \text{ L } Na_2S_2O_3 \times \frac{0.100 \text{ mol } Na_2S_2O_3}{1 \text{ L}} \times \frac{1 \text{ mol } I_2}{2 \text{ mol } Na_2S_2O_3} \times \frac{1 \text{ mol NaOCl}}{1 \text{ mol } I_2}$$

$$\times \frac{74.44 \text{ g NaOCl}}{1 \text{ mol NaOCl}} = 0.12\underline{8}8 \text{ g NaOCl}$$

If the density of bleach is taken as 1.00 g/mL, then 5.00 mL = 5.00 g. Thus, the mass percent is

$$\text{Mass percent NaOCl} = \frac{\text{mass NaOCl}}{\text{mass bleach}} \times 100\% = \frac{0.1288 \text{ g}}{5.00 \text{ g}} \times 100\% = 2.5\underline{7}5 = 2.58\%$$

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21.190. In acid,

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

Find the amount of I_2 initially present:

$$1.000 \times 10^{-2}\ \text{L}\ IO_3^- \times \frac{0.0500\ \text{mol}\ IO_3^-}{1\ \text{L}\ IO_3^-} \times \frac{3\ \text{mol}\ I_2}{1\ \text{mol}\ IO_3^-} = 1.5\underline{0}0 \times 10^{-3}\ \text{mol}\ I_2$$

The reaction for thiosulfate with I_2 is

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

Find the amount of excess I_2:

$$3.12 \times 10^{-2}\ \text{L}\ S_2O_3^{2-} \times \frac{0.0300\ \text{mol}\ S_2O_3^{2-}}{1\ \text{L}\ S_2O_3^{2-}} \times \frac{1\ \text{mol}\ I_2}{2\ \text{mol}\ S_2O_3^{2-}} = 4.6\underline{8}0 \times 10^{-4}\ \text{mol}\ I_2$$

The amount of I_2 consumed by the ascorbic acid is

$$1.5\underline{0}0 \times 10^{-3}\ \text{mol} - 4.6\underline{8}0 \times 10^{-4}\ \text{mol} = 1.0\underline{3}2 \times 10^{-3}\ \text{mol}\ I_2$$

From the stoichiometry of the equation, there must have been $1.0\underline{3}2 \times 10^{-3}$ mol of ascorbic acid present in the original 30.0-g sample. Convert moles to mass:

$$1.0\underline{3}2 \times 10^{-3}\ \text{mol ascorbic acid} \times \frac{176.1\ \text{g ascorbic acid}}{1\ \text{mol ascorbic acid}} = 0.18\underline{1}7\ \text{g ascorbic acid}$$

$$\text{Mass percent ascorbic acid} = \frac{0.1817\ \text{g ascorbic acid}}{30.0\ \text{g drink mix}} \times 100\% = 0.60\underline{5}7 = 0.606\%$$

In 100.0 g of drink mix, there would be 0.606 g of ascorbic acid.

21.191. A superconductor is a material that abruptly loses its resistance to an electric current when cooled to a definite characteristic temperature. This means that an electric current will flow in a superconductor without heat loss, unlike the current in a typical conductor. Once a current has been started in a superconducting circuit, it continues to flow indefinitely. Another intriguing property of a superconductor is its perfect diamagnetism. It became possible to construct superconducting magnets with high magnetic fields by starting an electric current in a superconducting circuit. Such magnets are being used in medical magnetic resonance imaging.

21.192. In 1986, Johannes Georg Bednorz and Karl Alexander Müller of IBM discovered that certain copper oxide ceramic materials became superconducting at 30 K, and within months researchers had found similar materials that became superconducting at 125 K. This means that superconductors can be operated using cheap refrigerants, such as liquid nitrogen, at a few cents a gallon.

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21.193. In 1985, Harold W. Kroto approached Richard E. Smalley and Robert F. Curl to do some experiments to simulate the conditions in certain stars to see what sorts of carbon-containing molecules might be produced. The research group had previously constructed an instrument in which they used an intense laser beam to vaporize solids. The hot vapor produced in this way could then be directed as a molecular beam into a mass spectrometer, where the molecular masses of the species in the vapor could be measured. The experiments on the vaporization of graphite produced surprising results. Molecular clusters of 2 to 30 carbon atoms were found, as expected; but in addition, the mass spectrum of the vapor consistently showed the presence of a particularly abundant molecule, C_{60}.

21.194. The molecule must be like a piece of graphite sheet that somehow closed back on itself to form a closed-dome structure. Smalley set about trying to construct a model of C_{60} by gluing paper polygons together. He discovered that he could obtain a very stable, closed polygon with 60 vertices by starting with a pentagon and attaching hexagons to each of its five edges. To this bowl-shaped structure he attached more pentagons and hexagons, producing a paper soccer ball stable enough to bounce on the floor.

■ SOLUTIONS TO STRATEGY PROBLEMS

21.195. The product of the combustion of sulfur in excess oxygen is sulfur trioxide. The reaction is

$$2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$$

When sulfur trioxide dissolves in water, sulfuric acid forms. The reaction is

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

When aqueous $BaCl_2$ is added to a solution of sulfuric acid, a white precipitate forms, which is barium sulfate. The reaction is

$$BaCl_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$$

To determine the mass of precipitate that forms, first determine the limiting reagent. Since the reactants are in a one-to-one mole ratio, calculate the moles of each reactant. For $BaCl_2$,

$$(0.1028\ M)(75.6 \times 10^{-3}\ \text{L}) = 0.0077\underline{1}6\ \text{mol}\ BaCl_2$$

For sulfuric acid, note that one mole of sulfur corresponds to one mole of sulfuric acid.

$$(0.325\ \text{g S}) \times \frac{1\ \text{mol S}}{32.07\ \text{g}} \times \frac{1\ \text{mol}\ H_2SO_4}{1\ \text{mol S}} = 0.010\underline{1}3\ \text{mol}\ H_2SO_4$$

Therefore, $BaCl_2$ is the limiting reactant. The mass of $BaSO_4$ that forms is

$$0.0077716\ \text{mol} \times \frac{233.40\ \text{g}}{1\ \text{mol}\ BaSO_4} = 1.8\underline{1}3 = 1.81\ \text{g}$$

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21.196.

a. $2Pb(NO_3)_2(s) \rightarrow 4NO_2(g) + 2PbO(s) + O_2(g)$

b. $2NO_2(g) \rightleftharpoons N_2O_4(g)$

c. Use the ideal gas law to determine the total number of moles in the system.

$$n = \frac{PV}{RT} = \frac{(738/760 \text{ atm})(0.456 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.018\underline{1}07 \text{ mol}$$

Let x be the mass of NO_2. Then $1.427 \text{ g} - x$ is the mass of N_2O_4. The total moles can now be written in terms of x as

$$\frac{x}{46.01 \text{ g/mol}} + \frac{1.427 \text{ g} - x}{92.02 \text{ g/mol}} = 0.018107 \text{ mol}$$

Solving for x gives the mass of NO_2 and the mass of N_2O_4.

Mass of $NO_2 = x = (0.018107 \text{ mol})(92.02 \text{ g/mol}) - 1.427 \text{ g} = 0.23\underline{9}25 \text{ g}$

Mass of $N_2O_4 = 1.427 \text{ g} - 0.23925 \text{ g} = 1.1\underline{8}77 \text{ g}$

The moles of each gas present are

$$\text{Moles of } NO_2 = \frac{0.23925 \text{ g}}{46.01 \text{ g/mol}} = 0.005\underline{1}99 \text{ mol}$$

$$\text{Moles of } N_2O_4 = \frac{1.1877 \text{ g}}{92.02 \text{ g/mol}} = 0.012\underline{9}06 \text{ mol}$$

The partial pressure of each gas is

$$P_{NO_2} = \frac{nRT}{V} = \frac{(0.005199 \text{ mol atm})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{0.456 \text{ L}} = 0.27\underline{8}8 \text{ atm}$$

$$P_{N_2O_4} = \frac{nRT}{V} = \frac{(0.012906 \text{ mol atm})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{0.456 \text{ L}} = 0.69\underline{2}1 \text{ atm}$$

The equilibrium constant can now be determined.

$$K_p = \frac{P_{N_2O_4}}{P_{NO_2}^{\ 2}} = \frac{0.6921}{(0.2788)^2} = 8.9\underline{0}3 = 8.90$$

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21.197.

a. $SO_2(g) + 2H_2S(g) \rightarrow 3S(s) + 2H_2O(g)$

b. First, determine the limiting reagent by calculating the moles of each reactant.

$$\text{Moles of } H_2S = 15.1 \text{ g} \times \frac{1 \text{ mol } H_2S}{34.086 \text{ g}} = 0.44\underline{3}0 \text{ mol}$$

$$\text{Moles of } SO_2 = n = \frac{PV}{RT} = \frac{(748/760 \text{ atm})(5.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(295 \text{ K})} = 0.20\underline{3}2 \text{ mol}$$

Since it takes two moles of H_2S for each mole of SO_2, there is sufficient H_2S to react completely with the SO_2, and SO_2 is the limiting reactant. The mass of sulfur produced is

$$(0.2032 \text{ mol } SO_2) \times \frac{3 \text{ mol S}}{1 \text{ mol } SO_2} \times \frac{32.07 \text{ g}}{1 \text{ mol S}} = 19.\underline{5}4 = 19.5 \text{ g S}$$

21.198. The reaction and enthalpies of formation are

$H_2O(g)$	$\rightarrow$	$2H(g)$	+	$O(g)$	
−241.8		218.0		249.2	kJ/mol

The enthalpy change for the reaction is

$$\Delta H_{rxn}^\circ = [2(218.0) + (249.2) - (-241.8)]\text{kJ} = 927.0 \text{ kJ}$$

Now write the enthaply for the reaction in terms of the bond energies.

$$\Delta H_{rxn}^\circ = [2 \text{ BE(O–H)} - 0] = 927.0 \text{ kJ}$$

$$\text{BE (O–H)} = \frac{927.0 \text{ kJ}}{2 \text{ mol}} = 463.5 \text{ kJ/mol}$$

For hydrogen peroxide, the reaction and enthalpies of formation are

$H_2O_2(g)$	$\rightarrow$	$2H(g)$	+	$2O(g)$	
−136.1		218.0		249.2	kJ/mol

The enthalpy change for the reaction is

$$\Delta H_{rxn}^\circ = [2(218.0) + 2(249.2) - (-136.1)]\text{kJ} = 1070.5 \text{ kJ}$$

Now write the enthalpy for the reaction in terms of the bond energies.

$$\Delta H_{rxn}^\circ = [2 \text{ BE(O–H)} + \text{BE(O–O)} - 0] = 1070.5 \text{ kJ}$$

Use the bond energy from the previous step for the O–H bond and solve.

$$\text{BE (O–O)} = 1070\ 5 \text{ kJ/mol} - 2(463.5 \text{ kJ/mol}) = 143.5 \text{ kJ/mol}$$

The values from Table 9.5 for the bond energies are BE(O–H) = 459 kJ/mol and BE(O–O) = 142 kJ/mol.

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21.199.

a. The difference in mass of the metal sulfide and metal oxide is due to replacement of S with O in the formula of the compound. Use this difference to determine the number of moles of sulfur and moles of oxygen in the compound.

$$\text{Moles} = \frac{\text{mass difference}}{\text{molar mass difference}} = \frac{6.125\text{ g} - 5.714\text{ g}}{32.07\text{ g/mol} - 16.00\text{ g/mol}} = 0.02557\text{ mol}$$

Since sulfide, oxide, and sulfate ions all have a −2 charge, the number of moles of each ion is the same in the compound. Using the mass of the metal sulfide, the mass of the metal present is

$$\text{Mass metal} = 6.125\text{ g} - (0.02557\text{ mol})(32.07\text{ g/mol}) = 5.304\text{ g}$$

Using the mass of SO_4^{2-} (96.07 g/mol), determine the mass of the metal sulfate.

$$\text{Mass metal sulfate} = 5.304\text{ g} + (0.02557\text{ mol})(96.07\text{ g/mol}) = 7.761\text{ g}$$

The mass of the metal sulfate given in the problem is 7.763 g, so the data are consistent with the precipitate being a sulfate.

b. Assume the metal can have a +1, +2, +3, or +4 charge. The formulas of the corresponding sulfides are M_2S, MS, M_2S_3, and MS_2, respectively. Use this information to determine the molar mass of the metal in each case.

$$M_2S: \frac{5.304\text{ g M}}{0.02557\text{ mol S}} \times \frac{1\text{ mol S}}{2\text{ mol M}} = 103.7 = 104\text{ g/mol}$$

$$MS: \frac{5.304\text{ g M}}{0.02557\text{ mol S}} \times \frac{1\text{ mol S}}{1\text{ mol M}} = 207.4 = 207\text{ g/mol}$$

$$M_2S_3: \frac{5.304\text{ g M}}{0.02557\text{ mol S}} \times \frac{3\text{ mol S}}{2\text{ mol M}} = 311.1 = 311\text{ g/mol}$$

$$MS_2: \frac{5.304\text{ g M}}{0.02557\text{ mol S}} \times \frac{2\text{ mol S}}{1\text{ mol M}} = 414.8 = 415\text{ g/mol}$$

The last two are too high; however, 104 g/mol corresponds to rhodium (Rh), and 207 g/mol corresponds to lead (Pb). There is not enough information to decide about rhodium, but for lead, Pb^{2+} is common.

21.200. Sodium sulfate does not react with sodium hydroxide. The reaction of aluminum sulfate with sodium hydroxide is

$$Al_2(SO_4)_3(aq) + 6NaOH(aq) \rightarrow 2Al(OH)_3(s) + 3Na_2SO_4(aq)$$

The reaction for the incineration of the precipitate is

$$2Al(OH)_3(s) \xrightarrow{\Delta} Al_2O_3(s) + 3H_2O(g)$$

Use the mass of aluminum oxide from the final step to calculate the moles of aluminum present.

$$(0.474\text{ g } Al_2O_3) \times \frac{1\text{ mol } Al_2O_3}{101.96\text{ g}} \times \frac{2\text{ mol Al}}{1\text{ mol } Al_2O_3} = 0.009297\text{ mol Al}$$

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Now determine the mass of the aluminum sulfate in the mixture.

$$(0.009297 \text{ mol Al}) \text{ x } \frac{1 \text{ mol } Al_2(SO_4)_3}{2 \text{ mol Al}} \text{ x } \frac{342.17 \text{ g}}{1 \text{ mol } Al_2(SO_4)_3} = 1.590 \text{ g}$$

The percent aluminum sulfate in the mixture is

$$\frac{1.590 \text{ g}}{3.458 \text{ g}} \text{ x } 100\% = 46.00 = 46.0\%$$

21.201.

a. $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

b. When P_4O_{10} is dissolved in water, phosphoric acid forms, which dissociates and produces an acidic solution according to

$$H_3PO_4(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + H_2PO_4^-(aq), \quad K_a = 6.9 \text{ x } 10^{-3}$$

The equilibrium-constant expression is

$$K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)^2}{[H_3PO_4]_o - x}$$

Use the pH to determine the value of x.

$$x = [H_3O^+] = 10^{-pH} = 10^{-2.091} = 8.109 \text{ x } 10^{-3} M$$

Rearrange the equilibrium-constant expression and solve for the initial phosphoric acid concentration.

$$[H_3PO_4]_o = x + \frac{(x)^2}{K_a} = 8.109 \text{ x } 10^{-3} M + \frac{(8.109 \text{ x } 10^{-3})^2}{6.9 \text{ x } 10^{-3}} = 0.01764 M$$

The mass of phosphorus can now be determined.

$$(0.01764 M) \text{ x } (1.258 \text{ L}) \text{ x } \frac{1 \text{ mol P}}{1 \text{ mol } H_3PO_4} \text{ x } \frac{30.97 \text{ g}}{1 \text{ mol P}} = 0.687 = 0.69 \text{ g P}$$

c. $2H_3PO_4(aq) + 3Ca(NO_3)_2(aq) \rightarrow Ca_3(PO_4)_2(s) + 6HNO_3(aq)$

d. The mass of calcium phosphate formed is

$$(0.01764 M) \text{ x } (1.258 \text{ L}) \text{ x } \frac{1 \text{ mol } Ca_3(PO_4)_2}{2 \text{ mol } H_3PO_4} \text{ x } \frac{310.18 \text{ g}}{1 \text{ mol } Ca_3(PO_4)_2} = 3.44 = 3.4 \text{ g}$$

21.202. Of the two compounds, only sodium acetate reacts with water according to

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftarrows HC_2H_3O_2(aq) + OH^-(aq)$$

The equilibrium constant for the reaction is obtained using K_w.

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \text{ x } 10^{-14}}{1.7 \text{ x } 10^{-5}} = 5.882 \text{ x } 10^{-10}$$

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Write out the equilibrium-constant expression.

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{(x)^2}{[C_2H_3O_2^-]_o - x} = 5.882 \times 10^{-10}$$

Use the pOH to determine the value of x.

$$pOH = 14.00 - pH = 14.00 - 9.03 = 4.97$$

$$x = [OH^-] = 10^{-pOH} = 10^{-4.97} = 1.\underline{0}71 \times 10^{-5}\ M$$

Rearrange the equilibrium-constant expression and solve for the initial $C_2H_3O_2^-$ ion concentration.

$$[C_2H_3O_2^-]_o = x + \frac{(x)^2}{K_b} = 1.\underline{0}71 \times 10^{-5}\ M + \frac{(1.071 \times 10^{-5})^2}{5.882 \times 10^{-10}} = 0.1\underline{9}52\ M$$

The mass of sodium acetate present in the sample is

$$(0.1952\ M) \times (25.0 \times 10^{-3}\ L) \times \frac{1\ mol\ NaC_2H_3O_2}{1\ mol\ C_2H_3O_2^-} \times \frac{82.034\ g}{1\ mol\ NaC_2H_3O_2} = 0.4\underline{0}0\ g$$

The percentage sodium acetate in the mixture is

$$\text{Percentage } NaC_2H_3O_2 = \frac{0.400\ g}{0.613\ g} \times 100\% = 6\underline{5}.3 = 65\%$$

21.203. The reaction and corresponding thermodynamic data are summarized as follows.

	$CO_2(g)$	+ C(graphite)	→	$2CO(g)$
ΔH_f°	-393.5	0		-110 kJ/mol
S°	213.7	5.740		197.5 J/mol·K

Calculate the standard enthalpy change and the standard entropy change for the reaction.

$$\Delta H_{rxn}^\circ = [2(-110.5) - (-393.5)]\ kJ = 172.5\ kJ$$

$$\Delta S_{rxn}^\circ = [2(197.5) - (213.7) - (5.740)]\ J/K = 175.\underline{5}6\ J/K = 0.175\underline{5}6\ kJ/K$$

Assume that the enthalpy change and the entropy change do not vary appreciably with temperature, and use them to calculate ΔG at the higher temperature.

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = (172.5\ kJ) - (2273\ K)(0.17556\ kJ/K) = -226.\underline{5}4\ kJ$$

Write out the free-energy change in terms of the equilibrium constant.

$$\Delta G_{rxn} = -RT \ln K = -226.54\ kJ/mol$$

Rearrange and solve for K.

$$\ln K = \frac{-\Delta G}{RT} = \frac{-(-226.54\ kJ/mol)}{(8.314 \times 10^{-3}\ kJ/mol \cdot K)(2273\ K)} = 11.9\underline{8}8$$

$$K = e^{11.988} = 1.\underline{6}0 \times 10^5 = 1.6 \times 10^5$$

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21.204. The following half-reactions and standard electrode potentials will be used in the discussion.

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \quad E° = -0.41\ V$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E° = 0.34\ V$

$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E° = 0.00\ V$

$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l) \quad E° = 0.96\ V$

When iron metal reacts with dilute hydrochloric acid, the following reaction occurs.

$Fe(s)$	$\rightarrow$	$Fe^{2+}(aq) + 2e^-$	$E° = -(-0.41\ V)$
$2H^+(aq) + 2e^-$	$\rightarrow$	$H_2(g)$	$E° = 0.00\ V$
$Fe(s) + 2H^+(aq)$	$\rightarrow$	$Fe^{2+}(aq) + H_2(g)$	$E_{rxn} = 0.41\ V$

Since the potential is positive, the reaction is spontaneous, and iron metal dissolves in hydrochloric acid to form hydrogen gas and a solution of iron(II) chloride.

The reaction of copper metal with dilute nitric acid does not involve the hydrogen ions. The reaction would be

$Cu(s)$	$\rightarrow$	$Cu^{2+}(aq) + 2e^-$	$E° = -(0.34\ V)$
$2H^+(aq) + 2e^-$	$\rightarrow$	$H_2(g)$	$E° = 0.00\ V$
$Cu(s) + 2H^+(aq)$	$\rightarrow$	$Cu^{2+}(aq) + H_2(g)$	$E_{rxn} = 0.34\ V$

Since the potential is negative, the reaction is nonspontaneous, and copper metal does not dissolve in nitric acid to form hydrogen gas.

The reaction involves the nitrate ion as follows:

3 x	$Cu(s)$	$\rightarrow$	$Cu^{2+}(aq) + 2e^-$	$E° = -(0.34\ V)$
2 x	$NO_3^-(aq) + 4H^+(aq) +$	$\rightarrow$	$NO(g) + 2H_2O(l)$	$E° = 0.96\ V$
3e				
	$3Cu(s) + 8H^+(aq) + 2NO_3^-(aq)$	$\rightarrow$	$3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$	$E_{rxn} = 0.62\ V$

21.205. Since the potential is positive, the reaction is spontaneous, and copper metal dissolves in dilute nitric acid to form nitrogen monoxide gas and a solution of copper(II) nitrate.

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CHAPTER 22

The Transition Elements and Coordination Compounds

■ SOLUTIONS TO EXERCISES

22.1.

a. Pentaamminechlorocobalt(III) chloride

b. Potassium aquapentacyanocobaltate(III)

c. Pentaaquahydroxoiron(III) ion

22.2.

a. $K_4[Fe(CN)_6]$

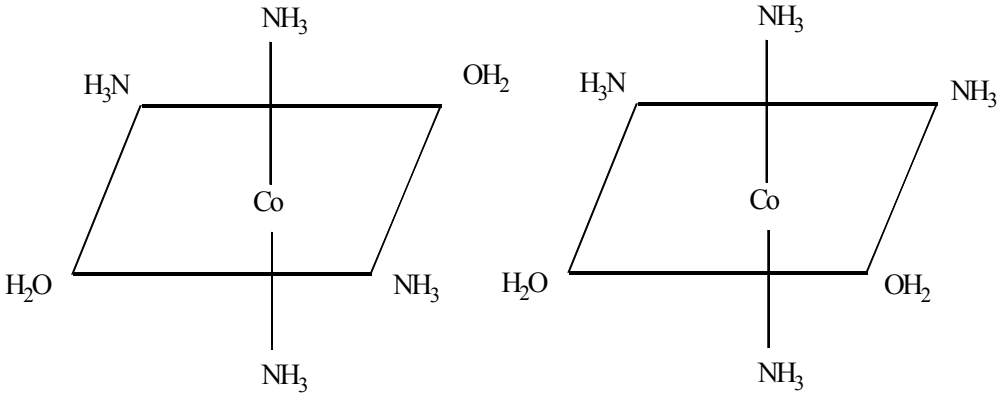
b. $[Co(NH_3)_4Cl_2]Cl$

c. $[PtCl_4]^{2-}$

22.3.

a. No geometric isomers.

b.



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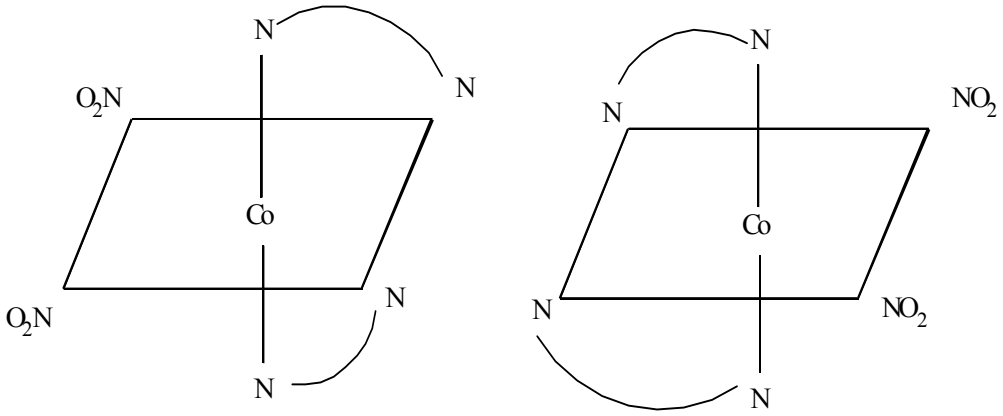
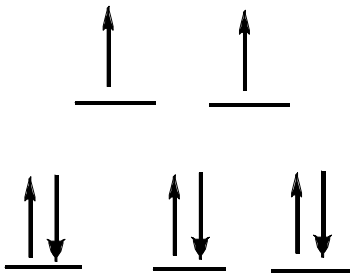
22.4.

a. No optical isomers.

b.

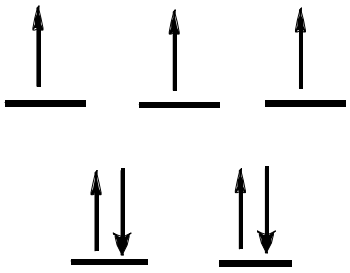


22.5. The electron configuration of Ni^{2+} is $[Ar]3d^8$. The distribution of electrons among the *d* orbitals of Ni in $[Ni(H_2O)_6]^{2+}$ is as follows:



Note that there is only one possible distribution of electrons, giving two unpaired electrons.

22.6. The electron configuration of the Co^{2+} ion is $[Ar]3d^7$. The distribution of the *d* electrons in $[CoCl_4]^{2-}$ is as follows:



22.7. The approximate wavelength of the maximum absorption for $[Fe(H_2O)_6]^{3+}$, which is pale purple, is 530 nm. The approximate wavelength of the maximum absorption for $[Fe(CN)_6]^{3-}$, which is red, is 500 nm. The shift is in the expected direction because CN^- is a more strongly bonding ligand than H_2O. As a result, Δ should increase, and the wavelength of the absorption should decrease, when H_2O is replaced by CN^-.

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■ ANSWERS TO CONCEPT CHECKS

22.1. Because silver nitrate does not precipitate AgCl from the complex, you conclude that chlorine is not present as free chloride ions; the Cl is presumably present as a complex. Potassium ion is likely present as K^+, which would account for two of the ions present in each formula unit. The other would be a complex ion of platinum with six chlorine atoms (a complex of Pt with six Cl^- ions). The charge on this complex ion must be −2 to counter the charges from the K^+ ions, so its formula is $[PtCl_6]^{2-}$. The formula of the complex, then, is $K_2[PtCl_6]$.

22.2. The addition of silver nitrate to the complex precipitates AgCl equivalent to two Cl^- ions per formula unit. Since each formula unit consists of three ions, the complex appears to consist of two Cl^- ions plus a complex ion with a charge of +2. The formula of the complex would then be $[Co(NH_3)_4(H_2O)Br]Cl_2$. The structural formula of a possible constitutional isomer is $[Co(NH_3)_4(H_2O)Cl]BrCl$.

22.3.

a. If you were to place a mirror to the right of complex X, complex A would directly represent what you would see in the mirror, so it is a mirror image. Note that complexes B and C are exactly the same, and A and E are the same; in both cases, they differ only by rotation (spin one of the complexes in each pair 180° to see this). Therefore, A and E are mirror images of X.

b. Optical isomers are nonsuperimposable mirror images of one another. The mirror images of molecule X, which are molecules A and E, are both nonsuperimposable mirror images, and are optical isomers of X.

c. To answer this part, you need to rotate each of the complexes to see if they have the same bonding arrangement in space with each of the ligands. Models A and E are the same complex, neither of which has the same bonding arrangement as complex X, so the complex they represent is a geometric isomer. Models B and C represent the same complex that also has a different bonding arrangement than complex X, so the complex they represent is also a geometric isomer. Complex D is the same complex as complex X, so it is not a geometric isomer.

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

22.1. Characteristics of the transition elements that set them apart from the main-group elements are the following: (1) The transition elements are metals with high melting points (only the IIB elements have low melting points). Most main-group elements have low melting points. (2) Each of the transition metals has several oxidation states (except for the Group IIIB and IIB elements). Most main-group metals have only one oxidation state in addition to zero. (3) Transition-metal compounds are often colored, and many are paramagnetic. Most main-group compounds are colorless and diamagnetic.

22.2. Technetium has the electron configuration [Kr] $4d^5 5s^2$.

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22.3. Molybdenum has the highest melting point of all elements in the fifth period because it has the maximum number of unpaired electrons, which contributes to the strength of the metal bonding.

22.4. One reason why iron, cobalt, and nickel are similar in properties is that these elements have similar covalent radii.

22.5. Nickel falls in the fourth period; accordingly, it has a much smaller covalent radius than the corresponding metals, palladium and platinum, in the fifth and sixth periods. However, palladium and platinum have very similar covalent radii.

22.6. $Cr(s) + 2HCl(aq) + 6H_2O(l) \rightarrow [Cr(H_2O)_6]^{2+} + 2Cl^-(aq) + H_2(g)$

$Cu(s) + HCl(aq) \rightarrow NR$

22.7. $Cr_2O_3(s) + 6HCl(aq) + 9H_2O(l) \rightarrow 2[Cr(H_2O)_6]^{3+} + 6Cl^-(aq)$

22.8. Four of the water molecules are associated with the copper(II) ion, and the fifth is hydrogen-bonded to the sulfate ion as well as to water molecules on the copper(II) ion. Heating changes the blue color to a white color, the color of anhydrous $CuSO_4$. The blue color is associated with $[Cu(H_2O)_4]^{2+}$. When the water molecules leave the copper ion, the blue color is lost.

22.9. Two Cu^{2+} ions gain a total of two electrons in forming one Cu_2O. The HCHO loses two electrons in forming $HCOO^-$ ion. Thus, the final equation is

$$2Cu^{2+}(aq) + HCHO(aq) + 5OH^-(aq) \rightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$$

22.10. Werner showed that the electrical conductance of a solution of $[Pt(NH_3)_4Cl_2]Cl_2$ corresponded to that of three ions in solution and that two of the chloride ions could be precipitated as AgCl, whereas the other two could not.

22.11. A complex ion is a metal atom or ion with Lewis bases attached to it through coordinate covalent bonds. A ligand is a Lewis base attached to a metal ion in a complex; it may be either a molecule or an anion, rarely a cation. The coordination number of a metal atom in a complex ion is the total number of bonds the metal forms with ligands. An example of a complex ion is $[Fe(CN)_6]^{4-}$; an example of a ligand is CN^-; and the coordination number of the preceding complex ion is 6.

22.12. A bidentate ligand is a ligand that bonds to a metal ion through two atoms. Two examples are ethylenediamine, $H_2N–C_2H_4–NH_2$, and the oxalate ion, $^-O_2C–CO_2^-$.

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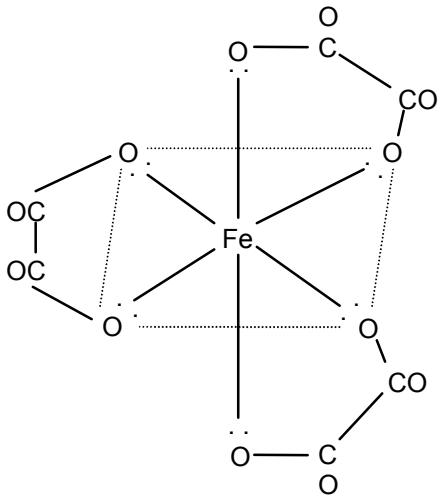
22.13.



22.14. The three properties are isomerism, paramagnetism, and color (or absorption of visible and ultraviolet radiation).

22.15.

a. Ionization isomerism involves isomers that are alike in that the same anions are present in the formula, but different anions are coordinated to the metal ion. For example, the sulfate ion is coordinated to cobalt in $[Co(NH_3)_5(SO_4)]Br$, but the bromide ion is coordinated to cobalt in $[Co(NH_3)_5Br]SO_4$.

b. Hydrate isomerism involves differences in the placement of water molecules in the complex ion. For example, $CrCl_3 \cdot 6H_2O$ exists as $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, and one other isomer.

c. Coordination isomers are those in which both the cation and the anion are complex, and the ligands are distributed between the two metal atoms in different ways. For example,

$$[Cu(NH_3)_4][PtCl_4] \text{ and } [Pt(NH_3)_4][CuCl_4]$$

d. Linkage isomers are those in which two different donor atoms on the ligand may bond to the metal ion. For example, SCN^- can bond to a metal ion through the sulfur atom or through the nitrogen atom.

22.16. Geometric isomers are isomers in which the atoms are joined to one another in the same way but differ because some atoms occupy different relative positions in space. In $[Pt(NH_3)_2Cl_2]$, the two NH_3's (or Cl's) can be arranged *trans* or *cis* to one another. Optical isomers are isomers that are nonsuperimposable mirror images of one another. See Figure 22.16 for an example of two cobalt optical isomers.

22.17. A *d* optical isomer rotates the plane of polarized light to the right (dextrorotatory), and an *l* ioptical isomer rotates the plane to the left (levorotatory).

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22.18. A racemic mixture is a mixture of 50% of the *d* isomer and 50% of the *l* isomer. One method of resolving a racemic mixture is to prepare a salt with an optically active ion of the opposite charge and crystallize the salts. They will no longer be optical isomers and will have different solubilities, so one can be precipitated before the other.

22.19. According to valence bond theory, a ligand orbital containing two electrons overlaps an unoccupied orbital on the metal ion.

22.20.

a. In the high-spin complex ion, all 3*d* orbitals of Fe^{2+} are occupied (four of the 3*d* orbitals each contain only one electron). Because they are occupied, those orbitals cannot be used for ligand bonding. Instead, d^2sp^3 hybrid orbitals form from the 4*s*, the three 4*p*, and two of the 4*d* orbitals. Each of six ligands donates a pair of electrons to one of these sp^3d^2 hybrid orbitals.

b. In the low-spin complex ion, the six electrons in the 3*d* orbitals are paired, so they occupy only three of the 3*d* orbitals. Then sp^3d^2 hybrid orbitals form from two of the 3*d*, the 4*s*, and the three 4*p* orbitals. Each of six ligands donates a pair of electrons to one of these d^2sp^3 hybrid orbitals.

22.21. The *d* orbitals of a transition-metal atom may have different energies in the octahedral field of six negative charges because the electron pairs of the ligands point directly at the d_{z^2} and $d_{x^2-y^2}$ orbitals. These orbitals are raised much more in energy than the other three *d* orbitals because they occupy space between the ligands. Thus, there is a crystal field splitting between the first two *d* orbitals mentioned and the d_{xy}, d_{xz}, and d_{yz} orbitals.

22.22.

a. A high-spin Fe(II) octahedral complex is

b. A low-spin Fe(II) octahedral complex is

22.23. Crystal field splitting is the difference in energy between the two sets of *d* orbitals for a given structure (such as octahedral) in complex ions. It is determined experimentally by measuring the energy of light absorbed by complex ions.

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22.24. The spectrochemical series is the arrangement of ligands in order of the relative size of the crystal field splittings (Δ) they induce in the *d* orbitals of a given oxidation state of a given metal ion. The order is the same, no matter what metal or oxidation state is involved. For Cl^-, H_2O, NH_3, and CN^-, the order of increasing crystal field splitting is

$$Cl^- < H_2O < NH_3 < CN^-$$

where CN^- always acts as a strong-bonding ligand.

22.25. Pairing energy, *P*, is the energy required to place two electrons in the same orbital. If the crystal field splitting (Δ) is small because of weak-bonding ligands, then the pairing energy will be larger, and the complex will be high-spin. If the crystal field splitting (Δ) is large because of strong-bonding ligands, then the pairing energy will be smaller, and the complex will be low-spin.

22.26. The complex absorbing red light would appear as a mixture of blue and green (approximately).

22.27. The answer is e, 6.

22.28. The answer is a, $[Zn(NH_3)_2Cl_2]$.

22.29. The answer is b, dicyanobis(ethylenediamine)chromium(III) chloride.

22.30. The answer is a, 0.

■ ANSWERS TO CONCEPTUAL PROBLEMS

22.31. Because one mole of chloride ion is precipitated per formula unit of the complex, the chlorine atoms must be present as chloride ion. All the other ligands are coordinated to the cobalt. An appropriate formula is $[Co(NH_3)_4(NO_2)_2]Cl$.

22.32. In order to solve this problem, you need to check each of the possible coordination compounds (A−D) to see if they are different from compound X. Compounds B, C, and D, through rotation and flipping over, all turn out to be the same as compound X. The only compound that is different is A, so it is the only geometric isomer of compound X.

22.33. "Hexacyano" means that there are six CN^- ligands bonded to the iron cation. The roman numeral II means the oxidation state of the iron cation is +2, so the overall charge of the complex ion is −4. This requires four potassium ions to counterbalance the −4 charge.

22.34. Compounds A and B are geometric isomers because these isomers have different physical properties, whereas optical isomers do not.

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22.35. The given compound must consist of a chloride ion (which can be precipitated with $AgNO_3$ solution) and a $[Co(NH_3)_4Br_2]^+$ ion, giving $[Co(NH_3)_4Br_2]Cl$. The structural formula of a possible constitutional isomer is $[Co(NH_3)_4BrCl]Br$.

22.36. The *d* orbital energy-level diagram contains six electrons. This indicates that the metal, M, must have the electron configuration $[Ar]3d^6$ and, therefore, a charge of 2+ (M^{2+}). The two complexes that have M in the 2+ oxidation state are $[MF_6]^{4-}$ and $[M(CN)_6]^{4-}$. The *d* orbital energy-level diagram is high-spin, indicating that there is a relatively small amount of crystal field splitting. According to the spectrochemical series, F^- is a less strongly bonding ligand with relatively smaller crystal field splitting, which makes $[MF_6]^{4-}$ the most likely answer.

■ SOLUTIONS TO PRACTICE PROBLEMS

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multistep problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

22.37.

a. The charge on the carbonate ion is −2. For $FeCO_3$ to be neutral, the oxidation number of iron must be +2.

b. The oxidation number of oxygen is −2. For the sum of the oxidation numbers of all atoms to be zero, manganese must be in the +4 oxidation state.

c. The oxidation number of the chlorine is −1, so the oxidation number of copper must be +2.

d. The oxidation number of oxygen is −2. The oxidation number of chlorine is −1. For the sum of the oxidation numbers to be zero, the oxidation number of chromium must be +6.

$$+6 + 2(-2) + 2(-1) = 0$$

22.38.

a. The charge on the sulfate ion is −2. For $CoSO_4$ to be neutral, the oxidation number of Co must be +2.

b. The oxidation number of oxygen is −2. For the sum of the oxidation numbers to be zero, tantalum must have an oxidation number of +5.

$$2(+5) + 5(-2) = 0$$

c. The oxidation number of H is +1; the oxidation number of O is −2; the oxidation number of Cl is −1. Therefore, the oxidation number of Cu is +2.

$$2(+2) + 3(+1) + 3(-2) + 1(-1) = 0$$

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22.39. The half-reactions are

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$4H^+ + NO_3^- + 3e^- \rightarrow NO + 2H_2O$

The balanced equation is

$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$

22.40. The balanced half-reactions are

Oxidation: $H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Multiply the oxidation half-reaction by 3. After adding and cancellation of the water, hydrogen ions, and electrons, the balanced equation is

$Cr_2O_7^{2-} + 3H_2SO_3 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

22.41.

a. Four. There are four cyanide groups coordinated to the gold atom.

b. Six. There are four ammonia molecules and two water molecules coordinated to the cobalt.

c. Four. Each of the ethylenediamine molecules bonds to the gold atom through two nitrogen atoms.

d. Six. Each ethylenediamine molecule bonds to the chromium atom through two nitrogen atoms, and the oxalate ion bonds to the chromium through two oxygen atoms.

22.42.

a. Six. There are six ammonia molecules around the nickel atom.

b. Four. There are four ammonia molecules around the copper atom.

c. Six. Each ethylenediamine molecule bonds to the chromium atom through two nitrogen atoms.

d. Four. There are four cyanide ions around the nickel atom.

22.43.

a. The charge on the $[Ni(CN)_4]^{2-}$ ion is −2 to balance the charge of +2 from the two K^+ ions. Each cyanide ion has a charge of −1. The sum of the oxidation number of nickel and the charge on the cyanide ions must equal the charge, so

$-2 = [4 \times (-1)] + 1 \times [\text{ox. no. (Ni)}]$

$\text{Ox. no. (Ni)} = -2 - (-4) = +2$

b. The charge on ethylenediamine is zero, so the oxidation number of Mo is equal to the charge on the complex ion.

$\text{Ox. no. (Mo)} = +3$

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c. Oxalate ion has a charge of −2, so

Ox. no. of Cr = charge of complex ion −3 x (charge of oxalate ion)
= (−3) − [3 x (−2)] = +3

d. Chloride ion has a charge of −1, so the charge on the complex ion is +2. The NH_3 ligands are neutral and contribute nothing to the charge of the complex ion.

Ox. no. of Co = charge of complex ion − charge of nitrite ligand = +2 − (−1) = +3

22.44.

a. Nitrite ion has a charge of −1, so the charge on the complex ion is +1. The en ligands are neutral. Both the chloride ligand and the nitrite ligand have a charge of −1, so

Ox. no. of Co = charge of complex ion − charge of chloride − charge of nitrite

= +1 − (−1) − (−1) = +3

b. Each chloride ligand has a charge of −1.

Ox. no. of Pt = charge of complex ion − 4 x (charge of chloride ion)

= −2 − [4 x (−1)] = +2

c. Potassium has a charge of +1, so the complex ion has a charge of −3. Each cyanide ligand has a charge of −1.

Ox. no. of Cr = charge of complex ion − 6 x (charge of cyanide)

= −3 − [6 x (−1)] = +3

d. The water ligands are neutral, and the hydroxide ligand has a charge of −1, so

Ox. no. of Fe = charge of complex ion − charge of hydroxide = +2 − (−1) = +3

22.45.

a. The charge on each chloride ligand is −1; the charge on the oxalate ligand is −2. The ammonia ligands are neutral.

Ox. no. of Cr = charge of complex ion − charge of oxalate − 2 x (charge of chloride)
= −1 − (−2) − 2(−1) = +3

b.

Formula	Name
NH_3	Ammine
Cl^-	Chloro
$C_2O_4^{2-}$	Oxalato

c. Six. The chromium atom has one bond to each of the NH_3 ligands and Cl^- ligands and two bonds to the $C_2O_4^{2-}$ ligand.

d. If each NH_3 were replaced by one Cl^-, and the $C_2O_4^{2-}$ ligand were replaced by two Cl^- ligands, there would be a total of six Cl^- ligands bonded to a chromium atom in the +3 oxidation state.

Charge on complex ion = ox. no. of Cr + 6 x (charge on chloride ligand)
= +3 + [6 x (−1)] = −3

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22.46.

a. The only charged ligands are the hydroxo ligands with a charge of −1.

Ox. no. of Mn = charge of complex ion − charge of hydroxo ligand = +2 − (−1) = +3

b.

Formula	Name
H_2O	Aqua
NH_3	Ammine
OH^-	Hydroxo

c. Six. There are two ammonia molecules, three water molecules, and a hydroxide ion, each singly bonded to the manganese atom.

d. If each of the ligands were replaced by chloride ions, there would be six chloride ions bonded to a manganese atom in the +3 oxidation state.

Charge of complex ion = ox. no. of Mn + 6 x (charge of chloride ion)
= +3 + [6 x (−1)] = −3

22.47.

a. Potassium hexafluoroferrate(III)

b. Diamminediaquacopper(II) ion

c. Ammonium aquapentafluoroferrate(III)

d. Dicyanoargentate(I) ion

22.48.

a. Potassium octacyanomolybdate(IV)

b. Hexafluorochromate(III) ion

c. Trioxalatovanadate(IV) ion

d. Potassium tetrachloroferrate(II)

22.49.

a. Pentacarbonyliron(0)

b. Dicyanobis(ethylenediamine)rhodium(III) ion

c. Tetraamminesulfatochromium(III) chloride

d. Tetraoxomanganate(VII) ion (Permanganate is the usual name.)

22.50.

a. Octacarbonyltungsten(0)

b. Diaquabis(ethylenediamine)cobalt(VI) sulfate

c. Potassium octacyanomolybdate(VII)

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d. Tetraoxochromate(VI) ion (Chromate is the usual name.)

22.51.

a. The charge on the complex ion equals

Ox. no. of Mn + 6 x (charge on cyanide ion) = +3 + 6(−1) = −3

Hence, the formula is $K_3[Mn(CN)_6]$.

b. The charge on the complex ion equals

Ox. no. of Zn + 4 x (charge on cyanide ion) = 2 + 4(−1) = −2

Hence, the formula is $Na_2[Zn(CN)_4]$.

c. The charge on the complex ion equals

Ox. no. of Co + 2 x (charge on chloride ion)

Note that the ammine ligand (NH_3) is neutral. You get +3 + 2(−1) = +1. The formula is $[Co(NH_3)_4Cl_2]NO_3$.

d. The charge on the cation equals the oxidation number of Cr (+3). The charge on the anion equals

Ox. no. of Cu + 4 x (charge on chloride ion) = +2 + 4(−1) = −2

The formula is $[Cr(NH_3)_6]_2[CuCl_4]_3$.

22.52.

a. The charge on the complex ion equals

Ox. no. of Cu + 2 x (charge on cyanide ion) = +2 + 2(−1) = 0

The formula is $[Cu(H_2O)_2(CN)_2]$.

b. The charge on the complex ion is

Ox. no. of Pt + 6 x (charge on chloride ion) = +4 + 6(−1) = −2

The formula is $K_2[PtCl_6]$.

c. The charge on the complex ion equals the

Ox. no. of Ni (+2)

The formula is $[Ni(NH_3)_4](ClO_4)_2$.

d. The charge on the cation equals the oxidation number of Pt(+2). The charge on the anion equals

Ox. no. of Cu + 4 x (charge on chloride ion) = +2 + 4(−1) = −2

Therefore, the formula is $[Pt(NH_3)_4][CuCl_4]$.

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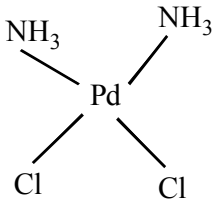
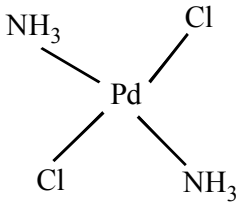
22.53.

a.



cis

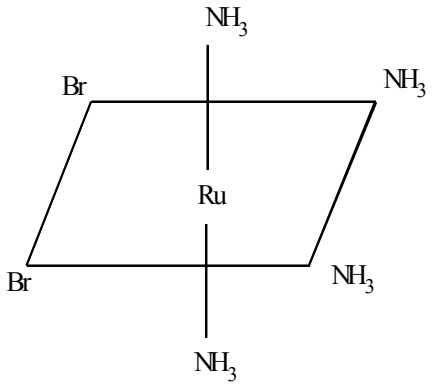


trans

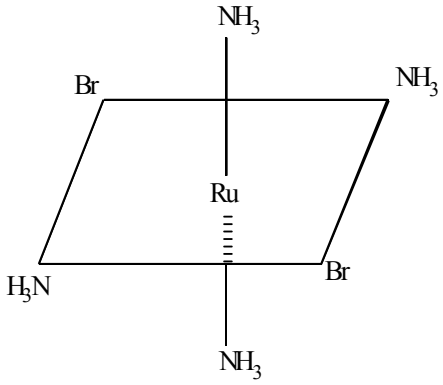
b. No geometric isomerism.

c. No geometric isomerism.

d.



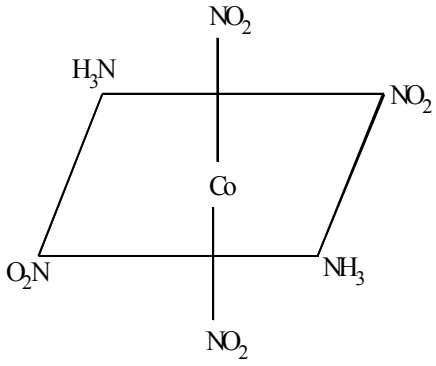
cis



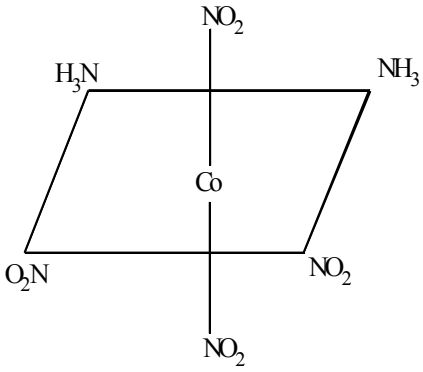
trans

22.54.

a.



trans



cis

b. No geometric isomerism.

c. No Geometric isomerism.

d. No geometric isomerism.

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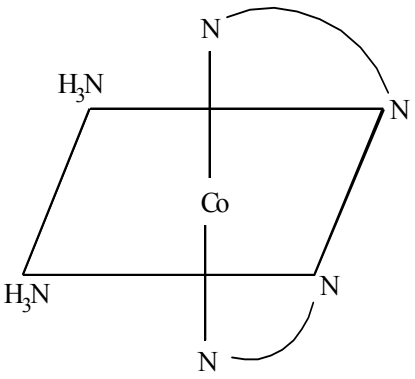
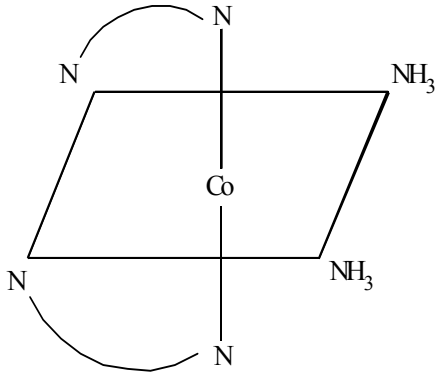
22.55.

a.

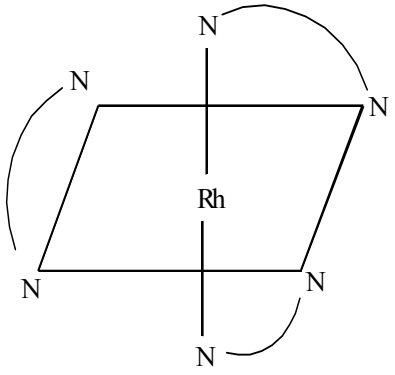


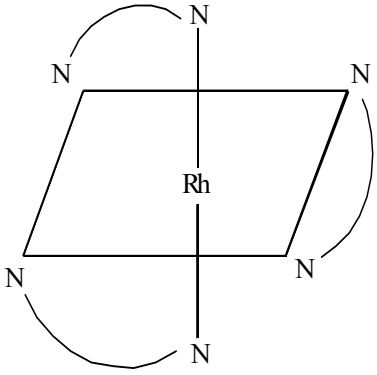


b. No optical isomers.

22.56.

a.

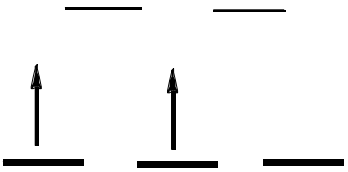




b. No optical isomers.

22.57.

a. V^{3+} has two *d* electrons arranged as shown:



There are two unpaired electrons.

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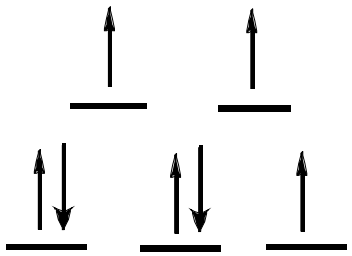
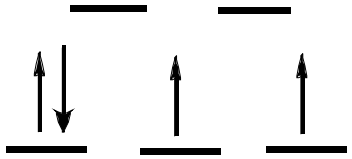
b. Co^{2+} has seven *d* electrons. In the high-spin case, they are arranged as follows:



There are three unpaired e^-.

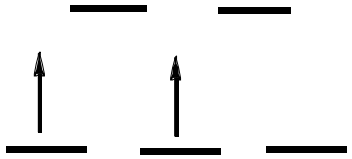
c. Mn^{3+} has four *d* electrons. In the low-spin case, they are arranged as follows:



There are two unpaired e^-.

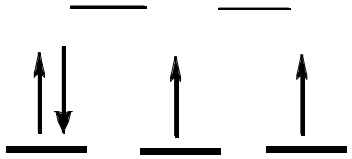
22.58.

a. Zr^{2+} has two electrons in the 4*d* subshell. In the complex, they are arranged as follows:



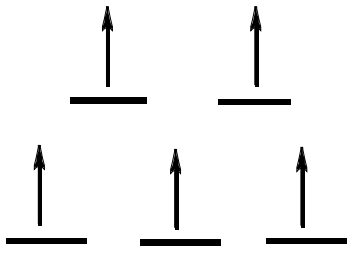
There are two unpaired e^-.

b. Os^{4+} has four electrons in the 5*d* subshell. In the low-spin case, they are arranged as follows:



There are two unpaired e^-.

c. Mn^{2+} has five *d* electrons. In the high-spin case, they are arranged as follows:



There are five unpaired electrons.

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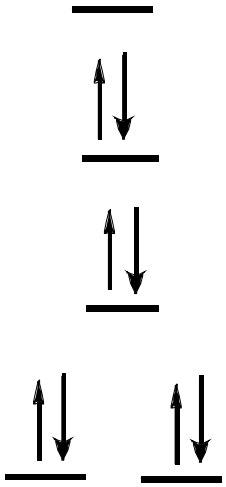
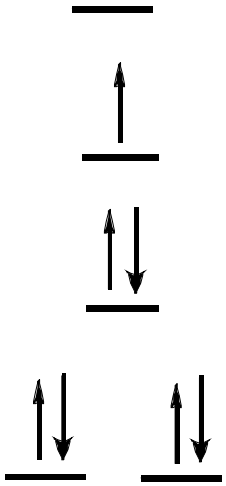
22.59.

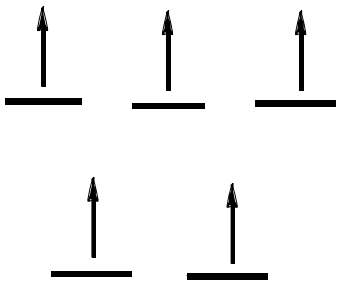
a. Pt^{2+} has eight electrons in the 5*d* subshell. Because the complex is diamagnetic, the crystal field felt by the *d* orbitals is probably square planar (no low-spin tetrahedral complexes are known). The arrangement of the *d* electrons is



b. Co^{2+} has seven *d* electrons. One unpaired electron implies a low-spin complex. A square planar field will lead to low-spin complexes, so the geometry is probably square planar with the *d* electrons arranged as follows:



c. Fe^{3+} has five *d* electrons. If they are all unpaired (that is, a high-spin complex), the field felt by the metal ion is probably tetrahedral with the *d* electrons arranged as follows:



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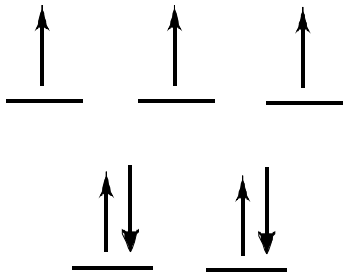
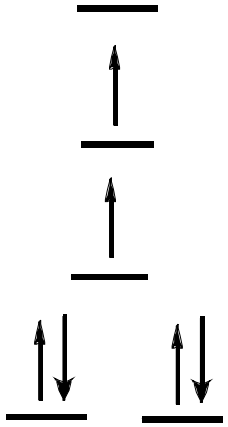
d. Co^{2+} has seven *d* electrons. Three unpaired electrons imply a high-spin complex. A tetrahedral field will lead to high-spin complexes, so the geometry is probably tetrahedral with the *d* electrons arranged as follows:

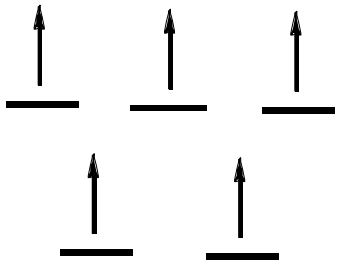


22.60.

a. Pt^{4+} has six electrons in the 5*d* subshell. The presence of only two unpaired electrons can be explained by a square planar field with the *d* electrons arranged as follows:



b. Mn^{2+} has five *d* electrons. Because these are all unpaired, it is a high-spin complex and probably has tetrahedral geometry.



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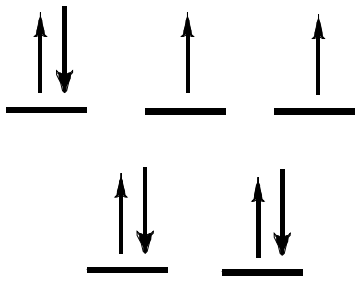
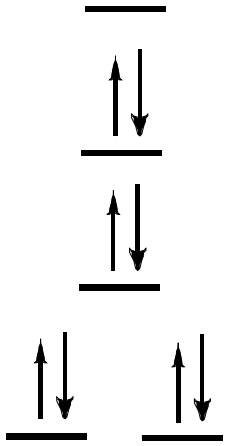
c. Ni^{2+} has eight *d* electrons. In a tetrahedral complex, eight *d* electrons would be arranged as follows:



giving two unpaired electrons, as observed. The complex is probably tetrahedral.

d. Au^{3+} has eight electrons in the 5*d* subshell. In a square planar complex, these would be arranged as follows:



with no unpaired electrons. The complex is probably square planar.

22.61. Purple (from Table 22.7)

22.62. Orange (from Table 22.7)

22.63. Yes. According to the spectrochemical series, H_2O is a more weakly bonding ligand than NH_3, so Δ should decrease. The wavelength of the absorption should increase ($\lambda = hc/\Delta$). The light absorbed by $[Co(NH_3)_6]^{3+}$ is violet-blue, and the replacement of one NH_3 by H_2O shifts this toward blue. Thus, the observed (complementary) color should shift toward red, as is observed.

22.64. Yes. According to the spectrochemical series, F^- is a more weakly bonding ligand than ethylenediamine, so Δ should decrease, and the wavelength of the absorbed light should increase. The wavelength absorbed by $[Co(en)_3]^{3+}$ is violet-blue, and replacement of all the ligands by F^- shifts the absorption toward the red end of the spectrum. The color of the complex (the complement of the absorbed light) should shift toward blue, as is observed.

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22.65. $\Delta = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(2.998 \times 10^{8}\ \text{m/s})}{(500 \times 10^{-9}\ \text{m})} \times 6.02 \times 10^{23}\ \text{/mol}$

$= 2.3\underline{9}17 \times 10^{5} = 2.39 \times 10^{5}\ \text{J/mol}\ \ (239\ \text{kJ/mol})$

22.66. $\Delta = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(2.998 \times 10^{8}\ \text{m/s})}{(680 \times 10^{-9}\ \text{m})} \times 6.02 \times 10^{23}\ \text{/mol}$

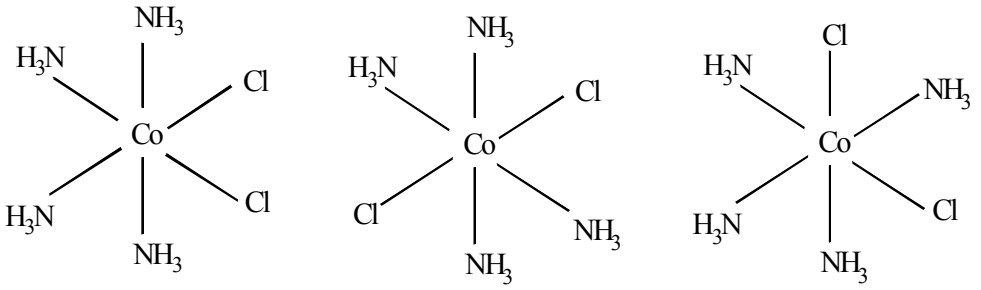
$= 1.7\underline{5}86 \times 10^{5} = 1.76 \times 10^{5}\ \text{J/mol}\ \ (176\ \text{kJ/mol})$

■ SOLUTIONS TO GENERAL PROBLEMS

22.67. The color in transition-metal complexes is due to absorption of light when a *d* electron moves to a higher energy level. Because Sc^{3+} has no *d* electrons, it is expected to be colorless.

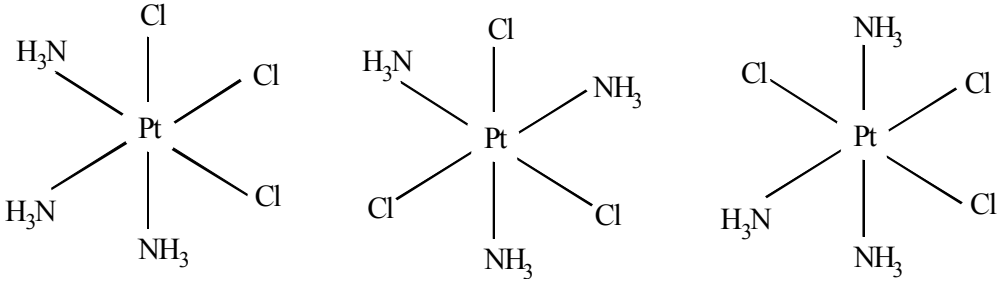
22.68. Zn^{2+} ion has a completely filled *d* subshell, so there are no openings for *d* electrons to be promoted to a higher energy level for which the difference in energy would correspond to the energy of visible light.

22.69. If $[Co(NH_3)_4Cl_2]^+$ had a regular planar hexagonal geometry, three geometric isomers would be expected.



The known existence of three isomers of the complex rules out hexagonal geometry as a possibility.

22.70. If $[Pt(NH_3)_3Cl_3]^+$ had a regular planar hexagonal geometry, two geometric isomers would be expected.



Yes. Same explanation as for Problem 22.69.

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22.71. The reaction and equilibrium-constant equation are

$$K_c = 2.1 \times 10^{-13} = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]}$$

Concentration (M)	$Cu^{2+}(aq)$	+	$4NH_3(aq)$	$\rightleftharpoons$	$[Cu(NH_3)_4]^{2+}(aq)$
Start	0.10		0.40		0
Change	$-x$		$-4x$		$+x$
Equilibrium	$0.10 - x$		$0.40 - 4x$		x

Substituting into the equilibrium expression, you obtain

$$2.1 \times 10^{-13} = \frac{(0.10 - x)[4(0.10 - x)]^4}{x}$$

To simplify, let $y = 0.10 - x$. Then $x = 0.10 - y$. The above equation becomes

$$2.1 \times 10^{-13} = \frac{y(4y)^4}{(0.10 - y)}$$

Assume y is small compared to 0.10. Then $0.10 - y \cong 0.10$.

$$2.1 \times 10^{-13} = \frac{y(4y)^4}{(0.10)}$$

$$y^5 = \frac{(2.1 \times 10^{-13})(0.10)}{4^4} = 8.\underline{2}03 \times 10^{-17}$$

$$y = \sqrt[5]{8.203 \times 10^{-17}} = 6.\underline{0}64 \times 10^{-4}$$

Going back to the above assumption, you find that, to two significant figures, $0.10 - 0.0006\underline{1} = 0.10$. The assumption was valid.

At equilibrium:

$$[Cu^{2+}] = (0.10 - x)\,M = y = 6.\underline{0}64 \times 10^{-4} = 6.1 \times 10^{-4}\,M$$

$$[NH_3] = 4(0.10 - x)\,M = 4y = 4 \times 6.\underline{0}64 \times 10^{-4} = 2.\underline{4}3 \times 10^{-3} = 2.4 \times 10^{-3}\,M$$

$$[Cu(NH_3)_4]^{2+} = x = (0.10 - y) = 0.10\,M$$

22.72. The reaction and formation constant (Table 17.2) are ($K_f = 1/K_d = 1.7 \times 10^7$).

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \quad K_f = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

Since K_f is large, and NH_3 is the limiting reactant, assume the NH_3 reacts completely to form the complex, and then allow the complex to redissociate slightly. The equilibrium concentrations at this point are

Concentration (M)	$Ag^+(aq)$	+	$2NH_3(aq)$	$\rightleftharpoons$	$[Ag(NH_3)_2]^+(aq)$
Start	0.050		0.00		0.050
Change	$+x$		$+2x$		$-x$
Equilibrium	$0.050 + x$		$2x$		$0.050 - x$

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Plug into the equilibrium expression:

$$K_f = 1.7 \times 10^7 = \frac{(0.050 - x)}{(0.050 + x)(2x)^2}$$

Assume x is small compared to 0.050 M, so $0.050 - x = 0.050 + x = 0.050$. This gives

$$1.7 \times 10^7 = \frac{1}{(2x)^2}$$

Solving for x gives

$$x = \frac{1}{2}\sqrt{\frac{1}{1.7 \times 10^7}} = 1.\underline{2}12 \times 10^{-4}\ M$$

Checking the assumption above, you note that 0.050 + 0.0001212 = 0.05$\underline{0}$1, so the assumption was valid.

At equilibrium:

$$[Ag^+] = (0.050 + x) = 0.050\ M$$

$$[NH_3] = 2x = 2.\underline{4}2 \times 10^{-4} = 2.4 \times 10^{-4}\ M$$

$$[Ag(NH_3)_2]^+ = (0.050 - x) = 0.050\ M$$

22.73. Commercial mayonnaise and salad dressing use EDTA to remove traces of metal ions. Metal ions can catalyze undesirable reactions or else provide nutrient for bacteria, resulting in off-flavors and spoilage of the product. EDTA is a polydentate ligand that forms particularly stable chelates with many metal ions, effectively removing those ions from the product. Many commercial products contain chelating agents such as EDTA.

22.74. Their stability stems from the additional entropy obtained when they are formed. This leads to a large negative $\Delta G°$, which is equivalent to a large equilibrium constant for the formation of the chelate. To understand how this happens, consider the formation of the chelate $[Co(en)_3]^{3+}$ from the complex ion $[Co(NH_3)_6]^{3+}$, with monodentate ligands NH_3.

$$[Co(NH_3)_6]^{3+} + 3en \rightleftharpoons [Co(en)_3]^{3+} + 6NH_3$$

Each en molecule replaces two NH_3 molecules. Therefore, the number of particles in the reaction mixture is increased when the reaction goes to the right. In most cases, an increase in number of particles increases the possibilities for randomness or disorder. Therefore, when the reaction goes to the right, there is an increase in entropy; that is, $\Delta S°$ is positive. At the same time, the reaction involves very little change of internal energy ($\Delta U°$) or enthalpy ($\Delta H° = \Delta U° + P\Delta V$), because the bonds are similar; all consist of a nitrogen atom coordinated to a cobalt atom. Therefore, $\Delta H° \cong 0$.

The spontaneity of a reaction depends on $\Delta G°$, which equals $\Delta H° - T\Delta S°$. But because $\Delta H° \cong 0$,

$$\Delta G° = \Delta H° - T\Delta S° = -T\Delta S°$$

The entropy change is positive, so $\Delta G°$ is negative, and the reaction is spontaneous from left to right. The fact that the equilibrium for the reaction favors the chelate $[Co(en)_3]^{3+}$ means that the chelate has thermodynamic stability.

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22.75. Hemoglobin is an iron-containing substance in red blood cells responsible for the transport of O_2 from the lungs to various parts of the body. Myoglobin is a similar substance in muscle tissue, acting as a reservoir for storage of O_2 and as a transporter of O_2 within muscle cells. Hemoglobin is essentially a four-unit structure of myoglobinlike units, but it does not function simply as four independent units of myoglobin. For it to function efficiently as a transporter of O_2 from the lungs and then be able to release that O_2 easily to myoglobin, hemoglobin must be less strongly attached to O_2 in the vicinity of a muscle cell than is myoglobin.

22.76. The mechanism postulated for cooperative release of O_2 depends on a change of iron(II) from a low-spin to a high-spin form, with a corresponding change in radius of the iron atom. In oxyhemoglobin, iron(II) exists in the low-spin form. When O_2 leaves, the iron atom goes to a high-spin form with two electrons in the higher-energy *d* orbital. These higher-energy orbitals are somewhat larger than the lower-energy *d* orbitals. When an O_2 molecule leaves a heme group, the radius of the iron atom increases, and the atom pops out of the heme plane by about 70 pm. In hemoglobin, this change triggers the cooperative release of another O_2 molecule.

■ SOLUTIONS TO STRATEGY PROBLEMS

22.77.

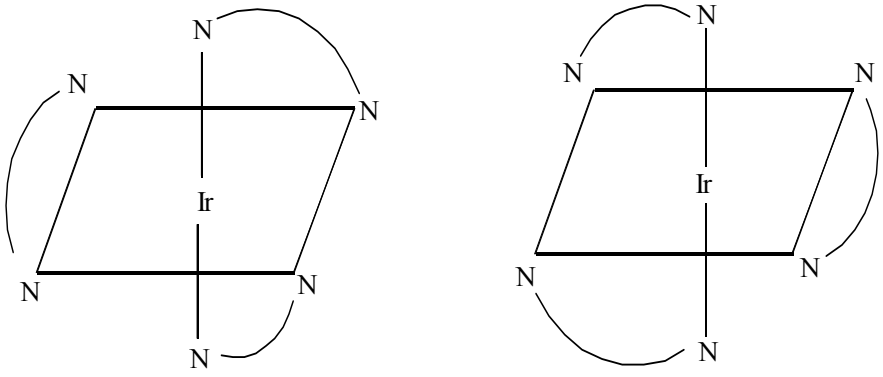
a. Since CO_3^{2-} is bidentate, there are six ligands attached to the cobalt atom, and the complex ion is octahedral.

b. The cobalt must have an oxidation state of +3 since the carbonate ion has a charge of −2, and the complex has a charge of +1 overall.

22.78. Ethylenediamine (en) is a bidentate ligand, so the complex ion $[Co(en)_2Cl_2]^+$ has an octahedral geometry. The two chlorine atoms can be 90° apart (*cis*) or 180° apart (*trans*), so *cis*-*trans* isomerism exists for this complex ion.

22.79.

a. The complex $[Ir(en)_3]^{3+}$ has a nonsuperimposable mirror image, so it has optical isomers.



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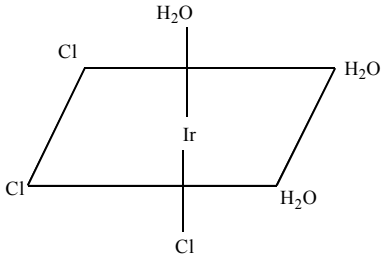
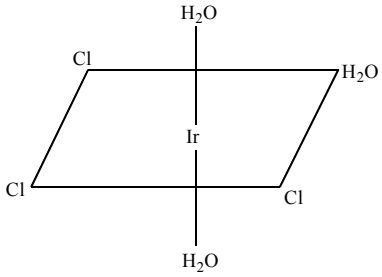
b. The complex $[Ir(H_2O)_3Cl_3]$ can exist in two different geometric forms. However, each form has a superimposable mirror image, so the complex does not have optical isomers.



trans



cis

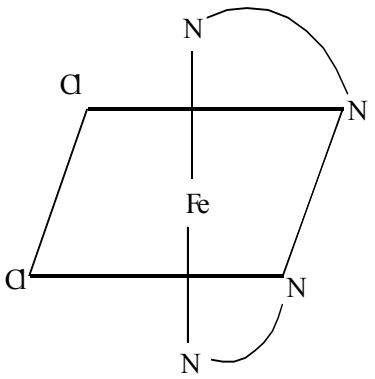
22.80. It is not possible for a square planar complex to have optical isomers because square planar complexes always have superimposible mirror images.

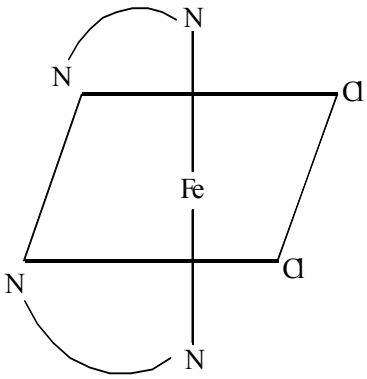
22.81.

a. The complex $[Fe(en)_2Cl_2]Cl$ has an octahedral geometry. The en ligands are bidentate.

b. The oxidation state of the Fe is +3. The complex ion is $[Fe(en)_2Cl_2]^+$ and there are two chloride ions, each with a −1 charge.

c. There are two possible geometric isomers. The two chlorine atoms can be 90° apart (*cis*) or 180° apart (*trans*). In the case of the *trans* isomer, it has a superimposable mirror image and is not optically active. In the case of the *cis* isomer, it has a nonsuperimposable mirror image and is optically active.





22.82.

a. The complex $[CoF_6]^{3+}$ has an octahedral geometry.

b. Fluorine is a weak-bonding ligand and you would expect Δ to be small. This means that the complex would absorb lower-energy photons, which would be red.

c. Since fluorine is a weak-bonding ligand and Δ is small, the complex should be high-spin.

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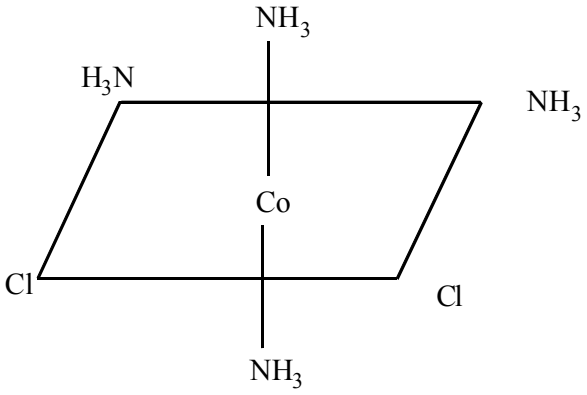
22.83. The name of $K_2[MoOCl_4]$ is potassium tetrachlorooxomolybdate(IV).

22.84. The formula for *cis*-tetraamminedichlorocobalt(III) cation is $[Co(NH_3)_4Cl_2]^+$. The structure of the complex is



22.85. Absorption in the blue region of the spectrum suggests that the value of Δ is probably large, and thus the complex is expected to be low-spin. Low-spin complexes exist when the energy spacing (Δ) is large. It takes more energy to promote an electron to a higher energy level. Blue light has a higher energy than red light, so absorption of blue light suggests a low-spin complex.

22.86.

a. The name of $[Cr(H_2O)_6]^{3+}$ is hexaaquachromium(III) ion, and the name of $[Mn(CN)_6]^{4-}$ is hexacyanomanganese(II) ion.

b. The complex $[Cr(H_2O)_6]^{3+}$ is octahedral with a d^3 electron configuration. All three *d* electrons are unpaired. The complex $[Mn(CN)_6]^{4-}$ is octahedral with a d^5 configuration. In a low-spin complex, this would correspond to one unpaired electron.

c. The highest-frequency light corresponds to the highest energy gap (Δ). According to the spectrochemical series, CN^- is a stronger-bonding ligand than H_2O, and thus the complex $[Mn(CN)_6]^{4-}$ is expected to absorb at the highest frequency.

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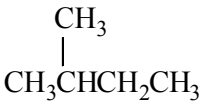
CHAPTER 23

Organic Chemistry

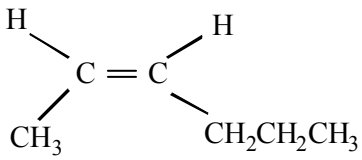
■ SOLUTIONS TO EXERCISES

23.1. The condensed structural formula is

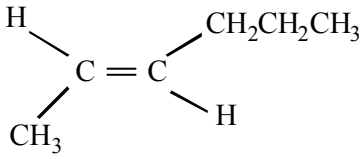


23.2.

a. Geometric isomers are possible.



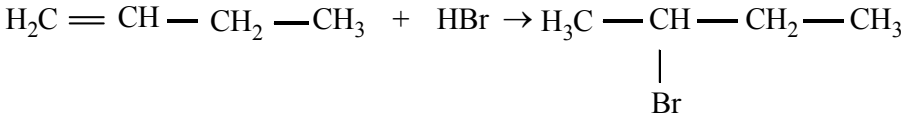
cis-2-Hexene



trans-2-Hexene

b. No geometric isomers are possible because there are two H atoms attached to the second carbon of the double bond.

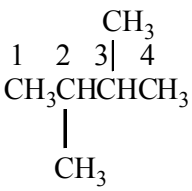
23.3. According to Markownikoff's rule, when HBr is added across the double bond in 1-butene, the H will add to carbon 1 (the C atom with the most bonds to H atoms) and the Br will add to carbon 2.



The product is 2-bromobutane.

23.4.

a. The longest continuous chain is numbered as follows:



The name of the compound is 2,3-dimethylbutane.

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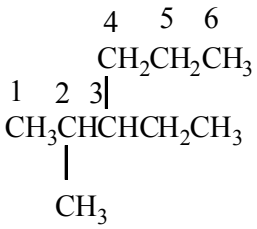
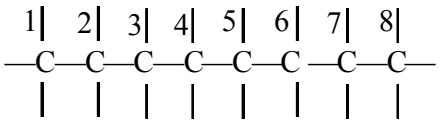
b. To give the substituents the smaller numbers, the longest continuous chain is numbered as follows:

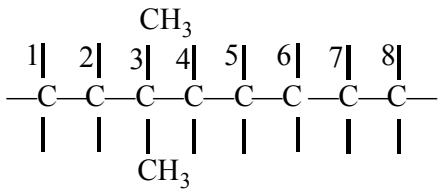


The name of the compound is 3-ethyl-2-methylhexane.

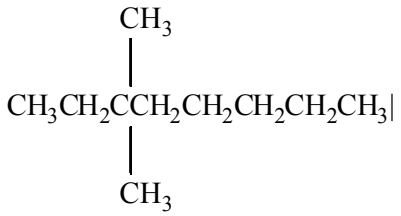
23.5. First write out the carbon skeleton for octane.



Then attach the alkyl groups.

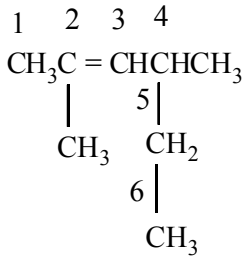


Finally, fill out the structure with H atoms.



23.6.

a. The numbering of the carbon chain is



Because the longest chain containing a double bond has six carbons, this is a hexene. It is a 2-hexene because the double bond is between carbons 2 and 3. The name of the compound is 2,4-dimethyl-2-hexene.

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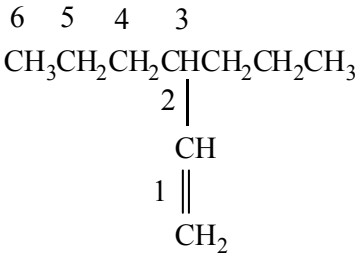
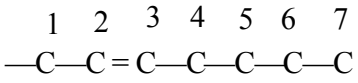
b. The numbering of the longest chain with a double bond is

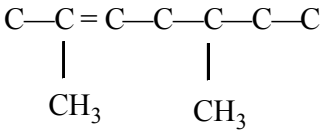


The longest chain containing the double bond has six carbon atoms; therefore, this is a hexene. It is a 1-hexene because the double bond is between carbons 1 and 2. The name of the compound is 3-propyl-1-hexene.

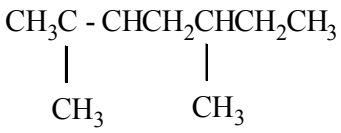
23.7. First write out the carbon skeleton for 2-heptene.



Then add the alkyl groups.



Finally, add the H atoms.



23.8. The two isomers of $CH_3CH_2CH{=}CHCH_2CH_3$ are *cis*-3-hexene and *trans*-3-hexene.

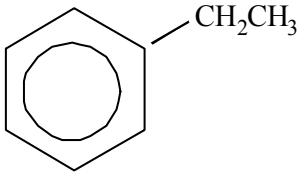
23.9.

a. There are only three carbons in the chain. The compound is propyne.

b. The longest continuous chain containing the triple bond has five carbon atoms. The compound is 3-methyl-1-pentyne.

23.10.

a. This compound has an ethyl group attached to a benzene ring.



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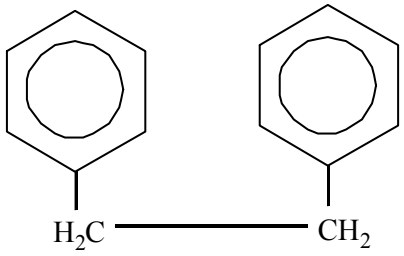
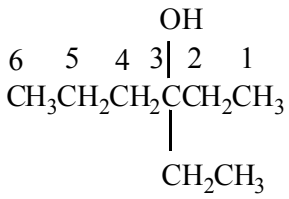
b. This compound has one phenyl group attached to each carbon atom in the ethane molecule.



23.11. Because the compound has an –OH group, it is an alcohol. The longest carbon chain in the molecule has six carbons.



The name of the compound is 3-ethyl-3-hexanol.

23.12.

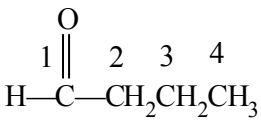
a. Dimethyl ether

b. Methyl ethyl ether

23.13.

a. There are two alkyl groups attached to the carbonyl; therefore, the compound is a ketone. There are five carbon atoms in the chain. The name of the compound is 2-pentanone.

b. There is a hydrogen atom attached to the carbonyl, so the compound is an aldehyde. The numbering of the stem carbon chain is



The name of the compound is butanal.

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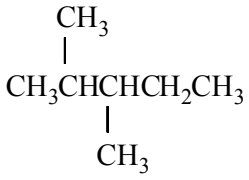
■ ANSWERS TO CONCEPT CHECKS

23.1.

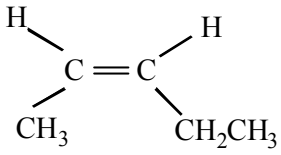
a. C_7H_{16}

b. 

23.2. Since, by definition, heptane is zero octane and 2,2,4-trimethylpentane is 100 octane, a mixture of 10% heptane and 90% 2,2,4-trimethylpentane would produce a 90 octane mixture.

23.3.

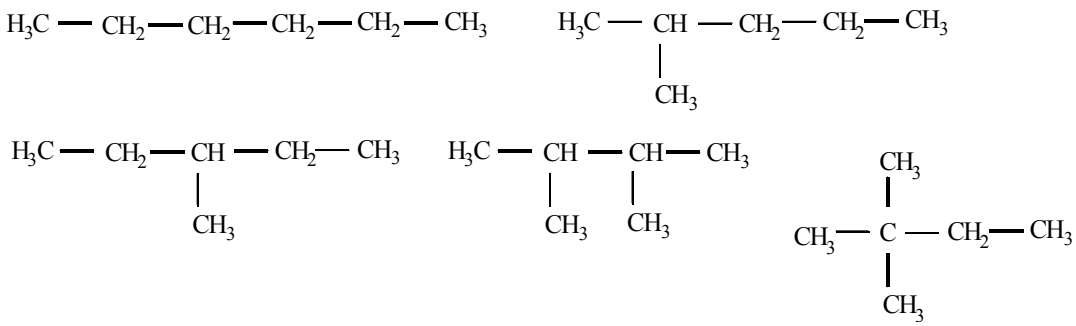
a. C_5H_{10}

b. 

c. *cis*-2-pentene

■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

23.1. The formula of an alkane with 30 carbon atoms is $C_{30}H_{62}$.

23.2. 

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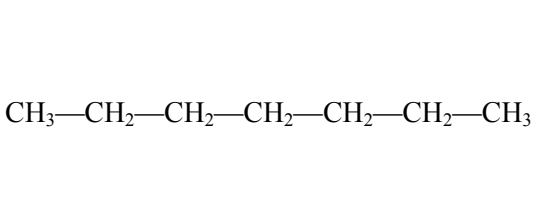
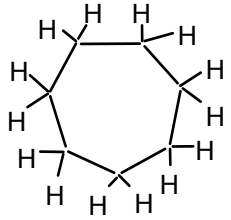
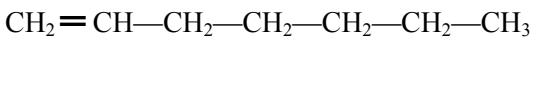
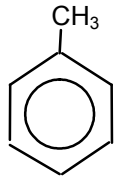
23.3. The structures of a seven-carbon alkane, cycloalkane, alkene, and aromatic hydrocarbon are



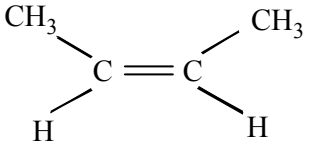




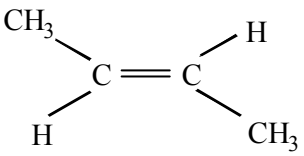


(toluene)

23.4. The two isomers of 2-butene are the *cis* and *trans* geometric isomers:



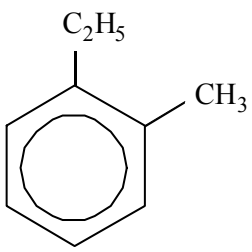
cis-2-Butene

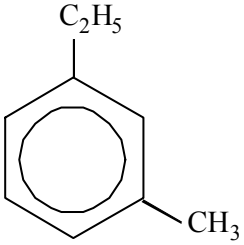


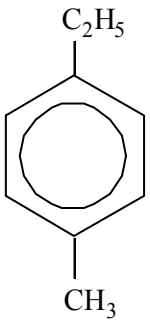
trans-2-Butene

In the *cis*-2-butene, the two methyl groups are on the same side of the double bond; in the *trans* isomer, they are on opposite sides.

23.5. The structural formulas for the isomers of ethyl-methylbenzene are







23.6. Methane: source–natural gas; use–home fuel.

Octane: source–petroleum; use–auto fuel.

Ethylene: source–petroleum refining; use–chemical industry raw material.

Acetylene: source–methane; use–acetylene torch.

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23.7.

CH_3CH_2Cl	CH_2ClCH_2Cl	$CHCl_2CHCl_2$	CCl_3CCl_3
CH_3CHCl_2	$CH_2ClCHCl_2$	$CHCl_2CCl_3$	
CH_3CCl_3	CH_2ClCCl_3		

23.8. A substitution reaction is a reaction in which part of the reagent molecule is substituted for a hydrogen atom on a hydrocarbon or hydrocarbon group. For example,

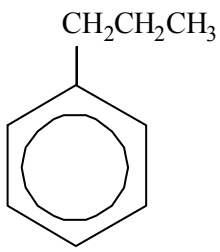
$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

An addition reaction is a reaction in which parts of the reagent are added to each carbon atom of a carbon-carbon multiple bond, which then becomes a C—C single bond. For example,

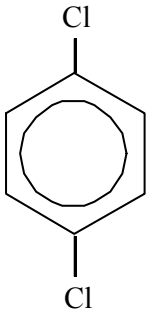
$$CH_2 = CH_2 + Br_2 \rightarrow CH_2Br–CH_2Br$$

23.9. The major product of HCl plus acetylene should be $Cl_2HC–CH_3$ because Markownikoff's rule predicts this.

23.10. The structures are



Propylbenzene



Paradichlorobenzene

23.11. A functional group is a reactive portion of a molecule that undergoes predictable reactions no matter what the rest of the molecule is like. An example is a C=C bond, which always reacts with bromine or other addition reagents to add part of each reagent to each carbon atom.

23.12. An aldehyde is different from a ketone, a carboxylic acid, and an ester in that a hydrogen atom is always attached to the carbonyl group in addition to a hydrocarbon group.

23.13. Methanol: source–$CO + H_2$; use–solvent.

Ethanol: source–fermentation of glucose; use–solvent.

Ethylene glycol: source–ethylene; use–antifreeze.

Glycerol: source–from soap making; use–foods.

Formaldehyde: source–oxidation of methanol; use–plastics and resins.

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23.14.

a. CO is a carbonyl group (ketone).

b. CH_3O—C is an ether group.

c. C═C is a double bond.

d. COOH is a carboxylic acid group.

e. CHO is an aldehyde (carbonyl).

f. CH_2OH, or –OH, is a hydroxyl group (primary alcohol).

23.15. The answer is e, 6.

23.16. The answer is d, $CH_3CH{=}CHCH_3$.

23.17. The answer is d, C_4H_{10}.

23.18. The answer is c, 3-methyl-2-pentanol.

■ ANSWERS TO CONCEPTUAL PROBLEMS

23.19.

a. The molecules with carbon chains in the $C_5 - C_{11}$ range will no longer be present because they have all boiled off. Additionally, some of the heavily branched C_{12} chains will boil off.

b. The molecules with carbon chains greater than C_{11} will be left in the barrel because they boil at temperatures above 200°C. (Keep in mind that the heavily branched C_{12} chains will have boiled off at or slightly below 200°C.)

c. Low-molecular-mass hydrocarbons have fewer polarizable electrons; therefore, they have weaker London forces than the longer chains and, as a result, boil at a lower temperature.

d. The more compact 2,3-dimethylbutane would boil at a lower temperature.

23.20.

a. He is incorrect. The longest chain of carbon atoms is seven, making the compound a heptane. The correct name would be 4-ethylheptane.

b. The condensed formula for the compound can be redrawn as follows.

$$\begin{array}{l} \qquad\qquad\quad CH_2CH_3 \\ \qquad\qquad\quad | \\ CH_3CH_2CH_2CHCH_2CH_2CH_3 \end{array}$$

23.21. Since carbon would have more than four bonds in this case, CH_5 would be in violation of the octet rule.

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23.22. 1-Octene: $CH_2=CHCH_2CH_2CH_2CH_2CH_2CH_3$

The other product formula is C_9H_{20}.

23.23.

a. The molecular formulas are trimethylamine, C_3H_9N; acetaldehyde, C_2H_4O; 2-propanol, C_3H_8O; and acetic acid, $C_2H_4O_2$.

b. The condensed structural formulas are

trimethylamine: $N(CH_3)_3$

acetaldehyde: $CH_3\overset{\overset{O}{\|}}{C}H$

2-propanol: $CH_3\overset{\overset{OH}{\|}}{C}HCH_3$

acetic acid: $CH_3\overset{\overset{O}{\|}}{C}OH$

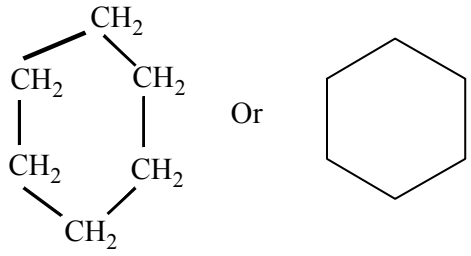
c. The functional groups in the molecules are trimethylamine, amine (tertiary); acetaldehyde, aldehyde; 2-propanol, alcohol; and acetic acid, carboxylic acid.

23.24.

a. The molecular formulas are 2-butene, C_4H_8; cyclohexane, C_6H_{12}; and 2,2,4-trimethylpentane, C_8H_{18}.

b. The condensed structural formulas are

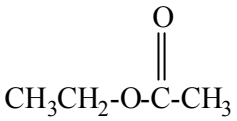
2-butene: $CH_3CH=CHCH_3$

cyclohexane  Or

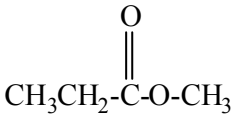
2,2,4-trimethyl pentane: $CH_3\overset{\overset{CH_3}{|}}{C}CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$
$\quad\quad\quad

23.25. The molecules increase regularly in molecular mass. Therefore, you expect their intermolecular forces and thus their melting points to increase.

23.26. Ethyl ethanoate (acetate) is



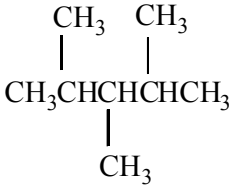
Methyl propanoate is



■ SOLUTIONS TO PRACTICE PROBLEMS

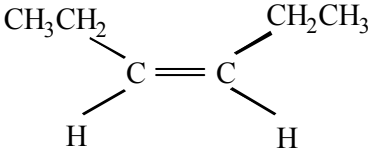
23.27. The condensed structural formula is $CH_3CH_2CH_2CH_3$.

23.28. The condensed structural formula is

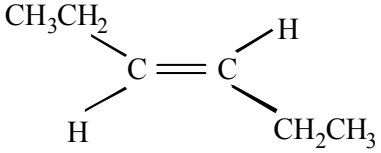


23.29.

a.

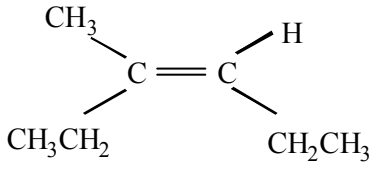


cis-3-Hexene

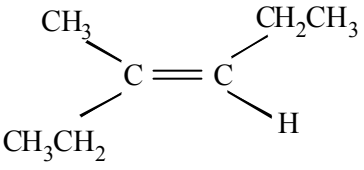


trans-3-Hexene

b.



cis-3-Methyl-3-hexene



trans-3-Methyl-3-hexene

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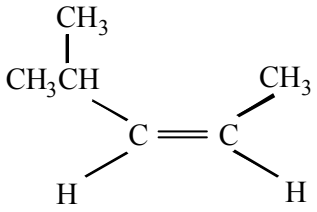
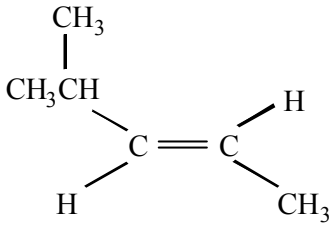
23.30.



a. *cis*-4-Methyl-2-pentene

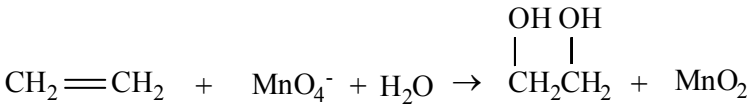


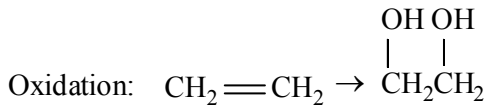
b. *trans*-4-Methyl-2-pentene

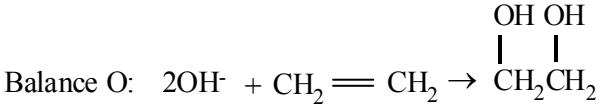
c. This compound (2-methyl-2-pentene) has no geometric isomers because the second carbon in the chain has two identical groups (CH_3) attached to it.

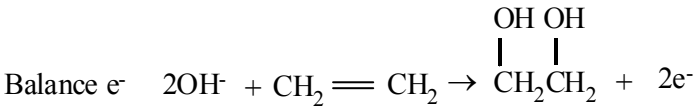
23.31.

a. $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$









b.

Reduction: $MnO_4^- \rightarrow MnO_2$

Balance O: $MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$

Balance e^-: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

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Add half-reactions:

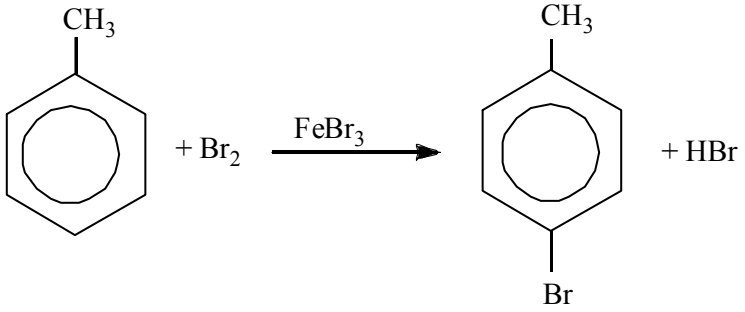
$$3\left(2OH^- + CH_2{=}CH_2 \rightarrow \overset{OH\ OH}{\overset{|\quad|}{CH_2CH_2}} + 2e^-\right)$$

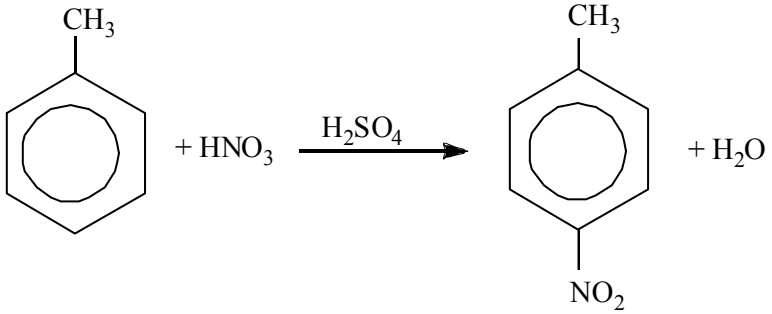
$$2\left(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-\right)$$

$$\cancel{6}OH^- + 3CH_2{=}CH_2 + 2MnO_4^- + 4H_2O \rightarrow 3\ \overset{OH\ OH}{\overset{|\quad|}{CH_2CH_2}} + 2MnO_2 + \cancel{8}^{2}OH^-$$

$$3CH_2{=}CH_2 + 2MnO_4^- + 4H_2O \rightarrow 3\ \overset{OH\ OH}{\overset{|\quad|}{CH_2CH_2}} + 2MnO_2 + 2OH^-$$

c. $$CH_2{=}CH_2 + Br_2 \rightarrow \overset{Br\ Br}{\overset{|\quad|}{CH_2CH_2}}$$

d. 

e. 

23.32.

a. $C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O$

Remove the fraction:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

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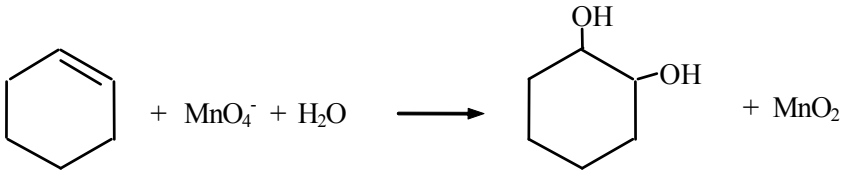
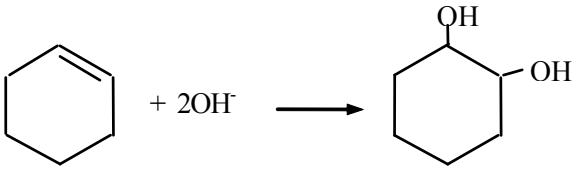
b.

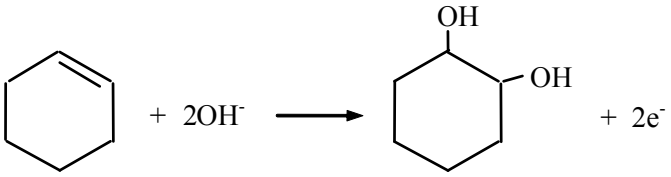


Oxidation:

Balance O



Balance charge:

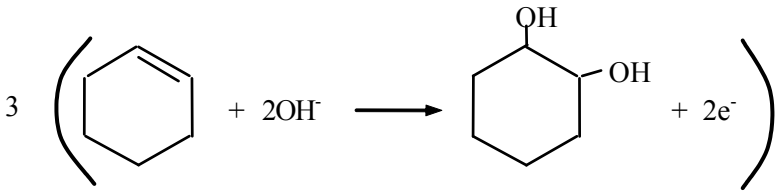


Reduction: $MnO_4^- \rightarrow MnO_2$

Balance O: $MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$

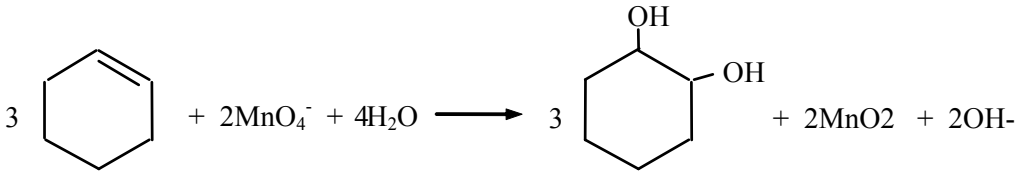
Balance charge: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Add half-reactions:



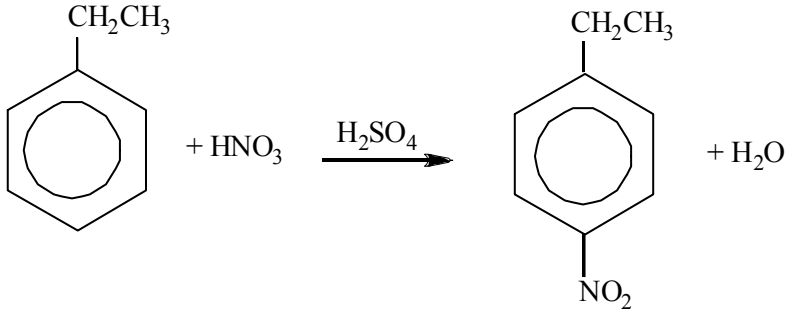
$2(MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-)$

The result is



c. $CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$

d.



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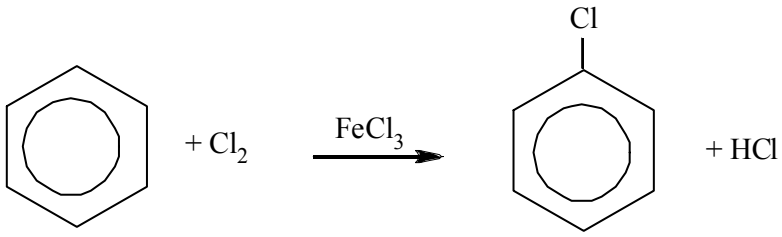
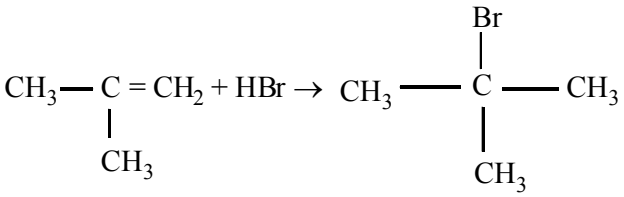
e. 

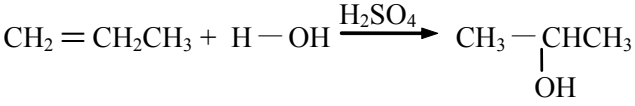
23.33. $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$

23.34. $CH_3CH_2CH_3 + Br_2 \rightarrow CH_3CHBrCH_3 + HBr$

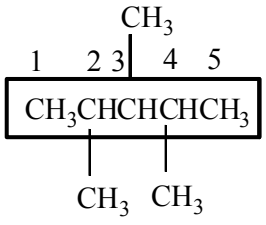
23.35. According to Markownikoff's rule, the major product is the one obtained when the H atom adds to the carbon atom of the double bond that already has more hydrogen atoms attached to it. Therefore, 2-bromo-2-methylpropane is the major product.



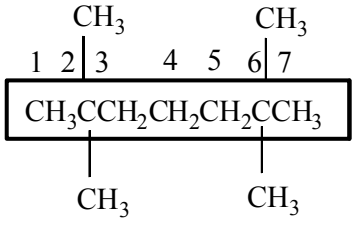
23.36. According to Markownikoff's rule, the major product is the one obtained when the H atom adds to the carbon atom of the double bond that already has more hydrogen atoms attached to it. The product is 2-propanol.



23.37.

a. 

longest chain 2,3,4-trimethylpentane

b. 

longest chain 2,2,6,6-tetramethylheptane

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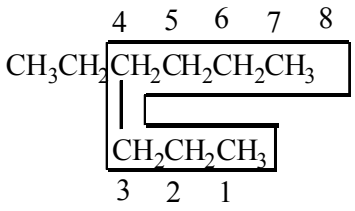
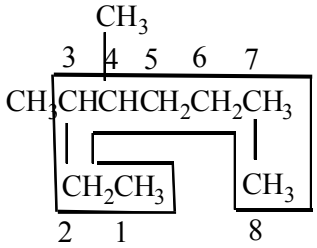
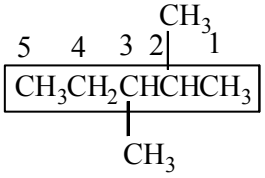
c. 

longest chain 4-ethyloctane

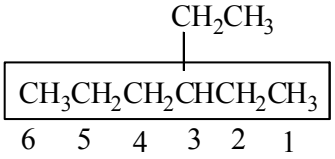
d. 

longest chain 3,4-dimethyloctane

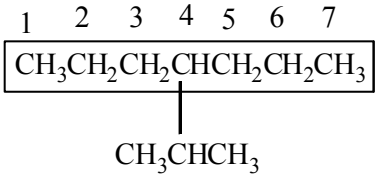
23.38.

a. 

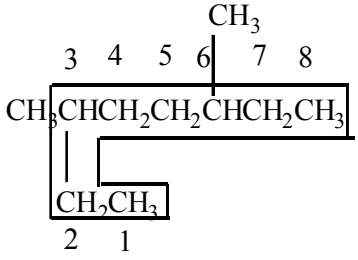
longest chain 2,3-dimethylpentane

b. 

longest chain 3-ethylhexane

c. 

longest chain 4-isopropylheptane

d. 

longest chain 3,6-dimethyloctane

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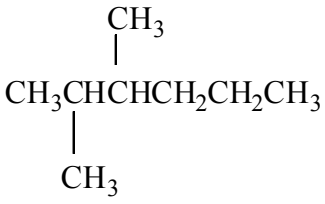
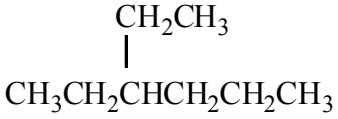
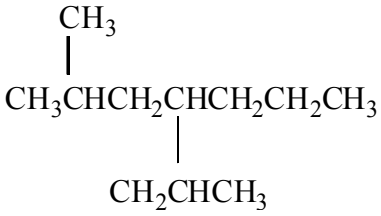
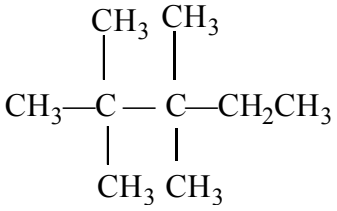
23.39.

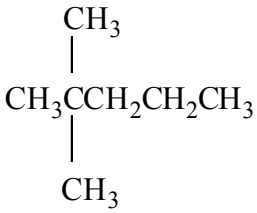
a. 

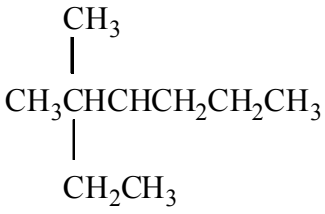
b. 

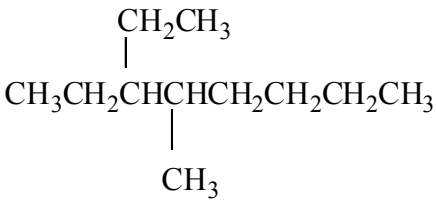
c. 

d. 

23.40.

a. 

b. 

c. 

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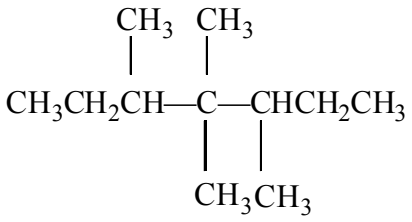
d. 

23.41.

a. 2-pentene

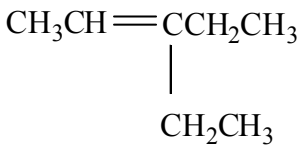
b. 2,5-dimethyl-2-hexene

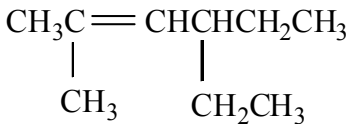
23.42.

a. 3-ethyl-3-hexene

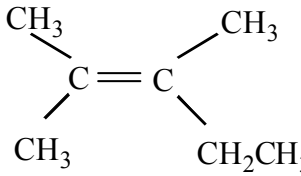
b. 2-ethyl-1-pentene

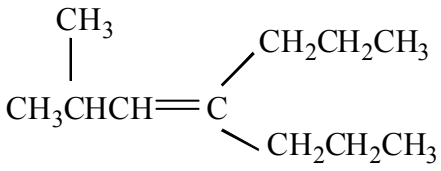
23.43.

a. 

b. 

23.44.

a. 

b. 

23.45. The two isomers are *cis*-2-pentene and *trans*-2-pentene.

23.46. The two isomers are *cis*-2-butene and *trans*-2-butene.

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23.47.

a. 2-butyne

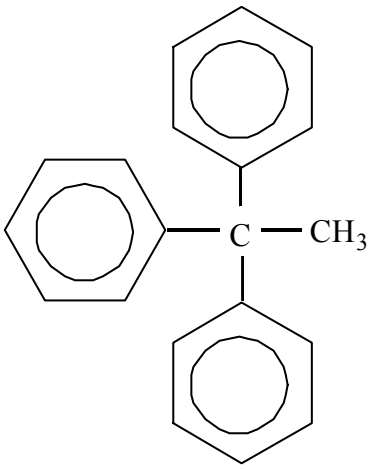
b. 3-methyl-1-pentyne

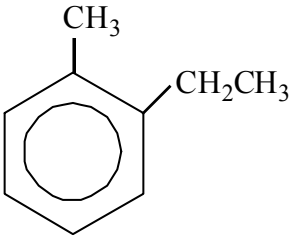
23.48.

a. 3-methyl-1-butyne

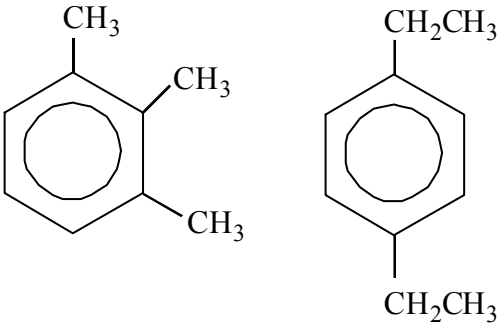
b. 2-pentyne

23.49.

a. 

b. 

23.50.

a. 

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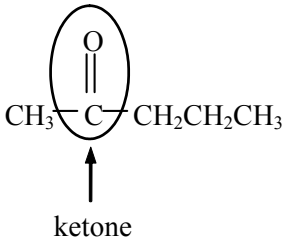
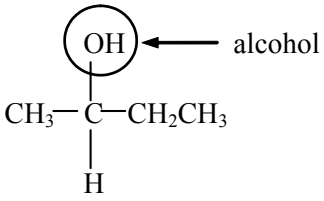
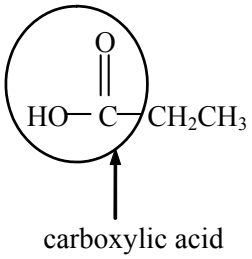
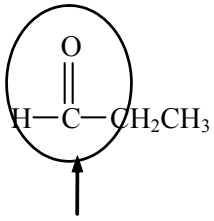
23.51.

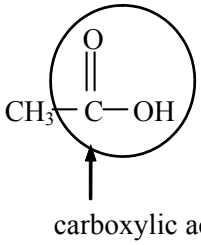
a. 

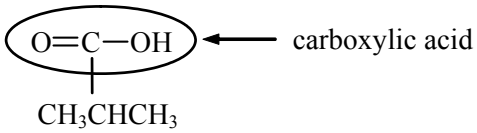
b. 

c. 

d. 

23.52.

a. 

b. 

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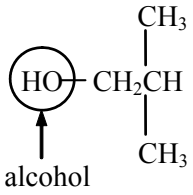
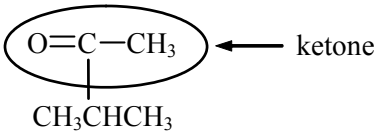
c. 

d. 

23.53.

a. 1-pentanol
b. 2-pentanol
c. 2-propyl-1-pentanol
d. 6-methyl-4-octanol

23.54.

a. 2-ethyl-1-pentanol
b. 4-methyl-1-pentanol
c. 3-methyl-2-pentanol
d. 2-methyl-1-butanol

23.55.

a. secondary alcohol
b. secondary alcohol
c. primary alcohol
d. primary alcohol

23.56.

a. secondary alcohol
b. tertiary alcohol
c. primary alcohol
d. tertiary alcohol

23.57.

a. ethyl propyl ether
b. methyl isopropyl ether

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23.58.

a. *t*-butyl methyl ether
b. diphenyl ether

23.59.

a. butanone
b. butanal
c. 4,4-dimethylpentanal
d. 3-methyl-2-pentanone

23.60.

a. 2-methylpropanal
b. 3-methyl-2-butanone
c. butanal
d. 5-methyl-3-hexanone

23.61.

a. secondary amine
b. secondary amine

23.62.

a. amide
b. primary amine

■ SOLUTIONS TO GENERAL PROBLEMS

23.63.

a. 3-methylbutanoic acid
b. *trans*-5-methyl-2-hexene
c. 2,5-dimethyl-4-heptanone
d. 4-methyl-2-pentyne

23.64.

a. 2,2-dimethylbutanal
b. 2,2-dimethylbutanoic acid

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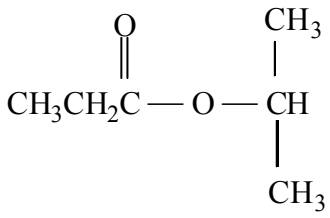
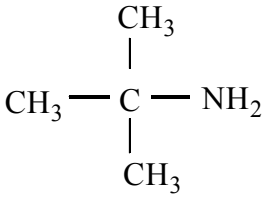
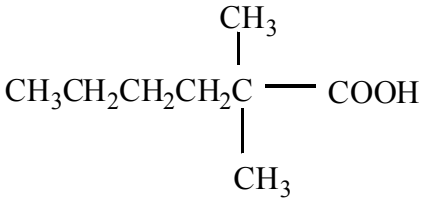
c. 3,3-dimethyl-2-pentanone

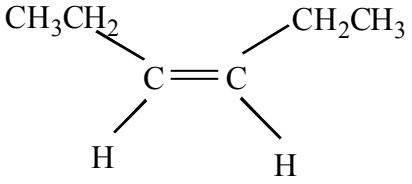
d. 2,2-dimethylbutane

23.65.

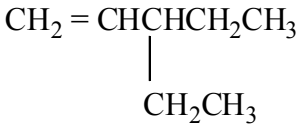
a. 

b. 

c. 

d. 

23.66.

a. 

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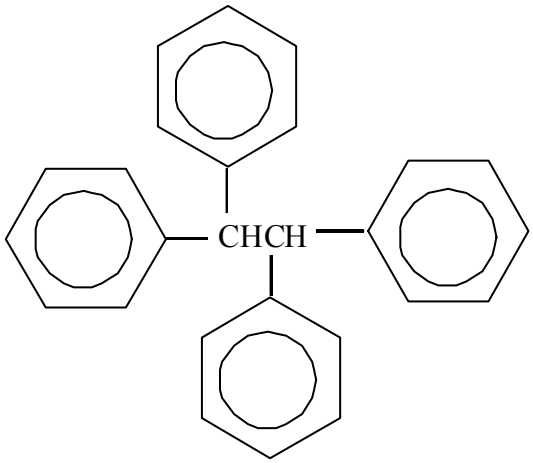
b.



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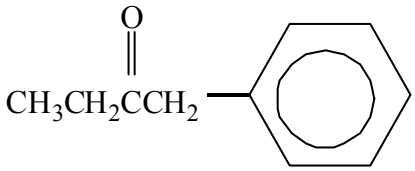

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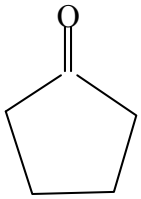

23.67.

a. Addition of dichromate ion in acidic solution to propionaldehyde will cause the reagent to change from orange to green as the aldehyde is oxidized. Under similar conditions, acetone (a ketone) would not react.

b. Addition of a solution of Br_2 in CCl_4 to $CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$ would cause the bromine color to disappear as the Br_2 was added to the multiple bonds. Addition of benzene to Br_2 in CCl_4 results in no reaction. Aromatic rings are not susceptible to attack by Br_2 in the absence of a catalyst.

23.68.

a. Addition of an acidic solution of dichromate ion to acetaldehyde will cause the reagent to change from orange to green as the aldehyde is oxidized. Under similar conditions, acetic acid will not be oxidized.

b. Addition of a solution of Br_2 in CCl_4 to 2-methyl-cyclohexene will cause the bromine color to disappear as the dibromomethylcyclohexene is formed. Toluene will not react instantaneously with Br_2 in CCl_4, as does the alkene.

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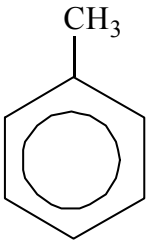
23.69.

a. ethylene, $CH_2 = CH_2$

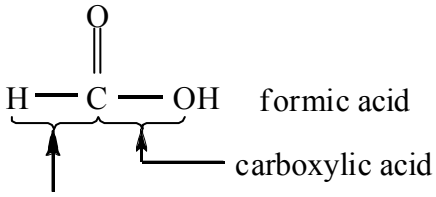
b. There must be an aromatic ring in the compound or the double bonds would react with Br_2. The compound is toluene, and the correct formula is



c. methylamine, CH_3NH_2

d. methanol, CH_3OH

23.70.



a. aldehyde

b. formaldehyde

c. $CH_3CH_2CH_2CH_3$, butane

d. CH_4, methane

23.71. Assume 100.0 g of the unknown. This contains 85.6 g C and 14.4 g H. Convert these amounts to moles.

$$85.6 \text{ g} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.1\underline{2}7 \text{ mol C}$$

$$14.4 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 14.\underline{2}857 \text{ mol H}$$

The molar ratio of H to C is 14.2857:7.12, or 2.00:1. The empirical formula is therefore CH_2. This formula unit has a mass of [12.01 + 2 x (1.008)] amu = 14.026 amu.

$$\frac{56.1 \text{ amu}}{1 \text{ molecule}} \times \frac{1 \text{ formula unit}}{14.026 \text{ amu}} = \frac{4.00 \text{ formula units}}{1 \text{ molecule}}$$

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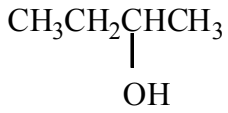
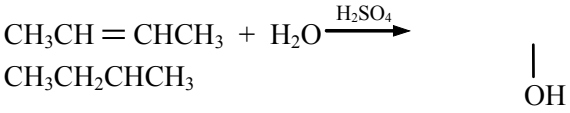
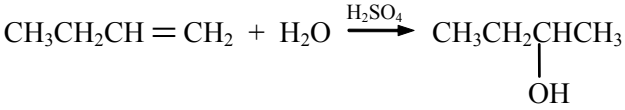
The molecular formula is $(CH_2)_4$, or C_4H_8. The formula (C_nH_{2n}) indicates that the compound is either an alkene or a cycloalkane. Because it reacts with water and H_2SO_4, it must be an alkene. The product of the addition of H_2O to a double bond is an alcohol. Because the alcohol produced can be oxidized to a ketone, it must be a secondary alcohol. The only secondary alcohol with four carbon atoms is 2-butanol.



The original hydrocarbon from which it was produced is either 1-butene or 2-butene.



or



23.72. The fragrant odor suggests an ester, which is consistent with the reaction with acid. Esters are hydrolyzed in acid to give an alcohol and an acid. The only alcohol with a molecular mass of 32.0 amu is methanol, CH_3OH. Carboxylic acids can be reduced to give primary alcohols. In a 100.0-g sample of the alcohol, there are 60.0 g C, 13.4 g H, and 26.6 g O. Convert these masses to moles.

$$60.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.995 \text{ mol C}$$

$$13.4 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 13.29 \text{ mol H}$$

$$26.6 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.662 \text{ mol O}$$

Divide each by 1.662 (smallest number of moles).

$$\frac{4.995}{1.662} = 3.005 = 3 \text{ mol C}$$

$$\frac{13.29}{1.662} = 7.996 = 8 \text{ mol H}$$

$$\frac{1.662}{1.662} = 1.00 = 1 \text{ mol O}$$

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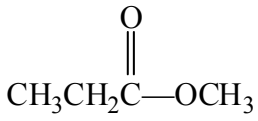
The empirical formula of the alcohol is C_3H_8O, which has a formula mass of 60.1 amu, equal to the molecular mass of the alcohol. The only primary alcohol with this formula is 1-propanol, $CH_3CH_2CH_2OH$. The acid that gives 1-propanol when it is reduced is propanoic acid. Therefore, the original compound was the ester of methanol and propanoic acid:



Methyl propanoate

(The common name for propanoic acid is propionic acid, so the ester could also be named methyl propionate.)

■ SOLUTIONS TO STRATEGY PROBLEMS

23.73.

a. The functional group present is an alcohol.

b. The IUPAC name is 2-methyl-3-hexanol.

23.74.

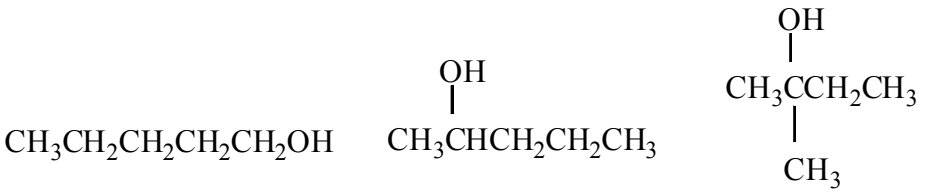
a. The correct condensed structural formula is $CH_3CH_2CH{=}CH_2$.

b. The correct condensed structural formula is $CH{\equiv}CCH_2CH_3$.

c. The correct condensed structural formula is $CH_3CH_2CH{=}CHCH_3$.

23.75. The molecule has three functional groups: aldehyde, alcohol, and carboxylic acid.

23.76. The condensed structural formulas for a primary, secondary, and tertiary alcohol containing five carbons are



Primary alcohol | Secondary alcohol | Tertiary alcohol

23.77.

a. The molecular formula of the compound is C_6H_{12}.

b. The condensed structural formula is $CH_3CH{=}CHCH_2CH_2CH_3$.

c. The IUPAC name of the compound is *trans*-2-hexene.

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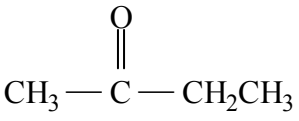
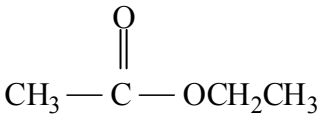
23.78. The condensed structural formula for the compounds are



Ketone

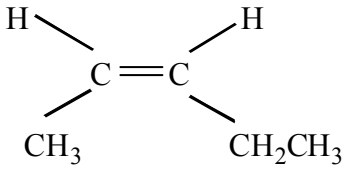


Ester

23.79. The name given is incorrect. The correct IUPAC name for the compound is 3,4-dimethylheptane.

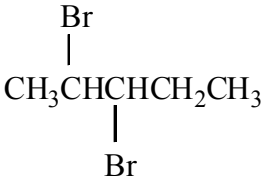
23.80.

a. The structural formula of the *cis* isomer is



b. The name of the molecule is *cis*-2-pentene.

c. The condensed structural formula of the product is



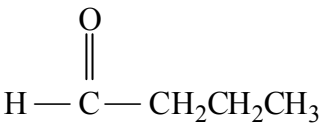
23.81.

a. 3,4-dimethylpentanal

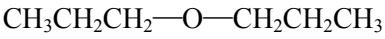
b. 3-methylpentanoic acid

23.82.

a. The condensed structural formula is



b. The condensed structural formula is



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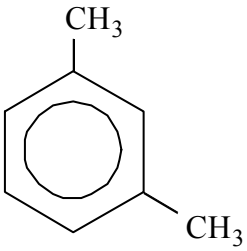
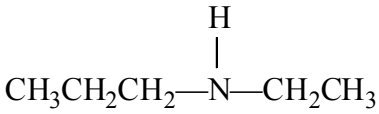
c. The condensed structural formula is



d. The condensed structural formula is



e. The condensed structural formula is

$HC{\equiv}CCH_2CH_3$

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CHAPTER 24

Polymer Materials: Synthetic and Biological

■ SOLUTIONS TO EXERCISES

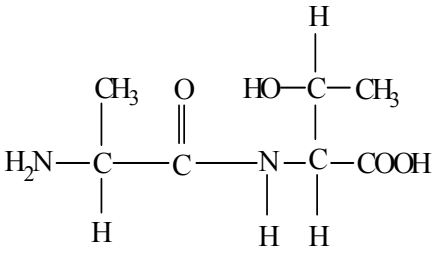
24.1. This addition polymer is formed when vinylidene chloride adds to itself across the double bond.

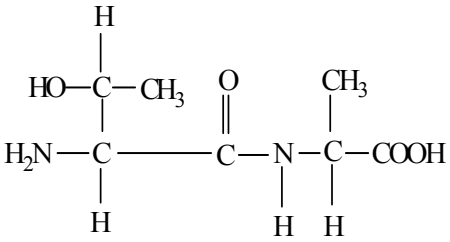
$$\cdots + CH_2{=}CCl_2 + CH_2{=}CCl_2 + CH_2{=}CCl_2 + \cdots \rightarrow$$

$$-CH_2-CCl_2-CH_2-CCl_2-CH_2-CCl_2-$$

■ ANSWERS TO CONCEPT CHECKS

24.1. The carboxyl group, –COOH, of either of the amino acids could be bonded through a peptide bond to the amino group, $-NH_2$,of the other. The structures of these two dipeptides are





24.2. In RNA, the bases are adenine (A), guanine (G), cytosine (C), and uracil (U), but not thymine (T). The complimentary bases are A and T, A and U, and G and C. So, A in DNA would have U as a compliment in RNA; T in DNA would have A as a compliment in RNA; G in DNA would have C in RNA as a compliment; and C in DNA would have G in RNA as a compliment. Here, then, is the RNA sequence complimentary to the DNA sequence given in the problem statement:

UACGAUGCCUAAGUU.

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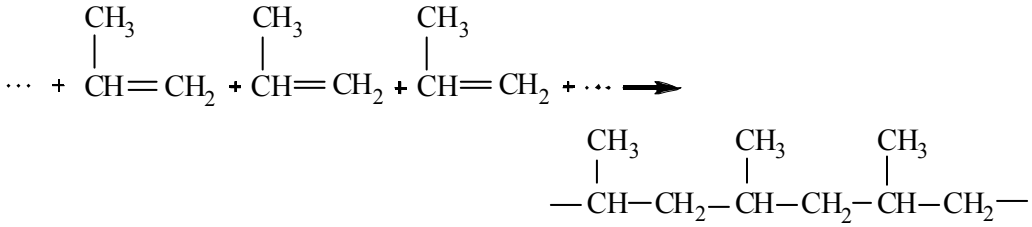
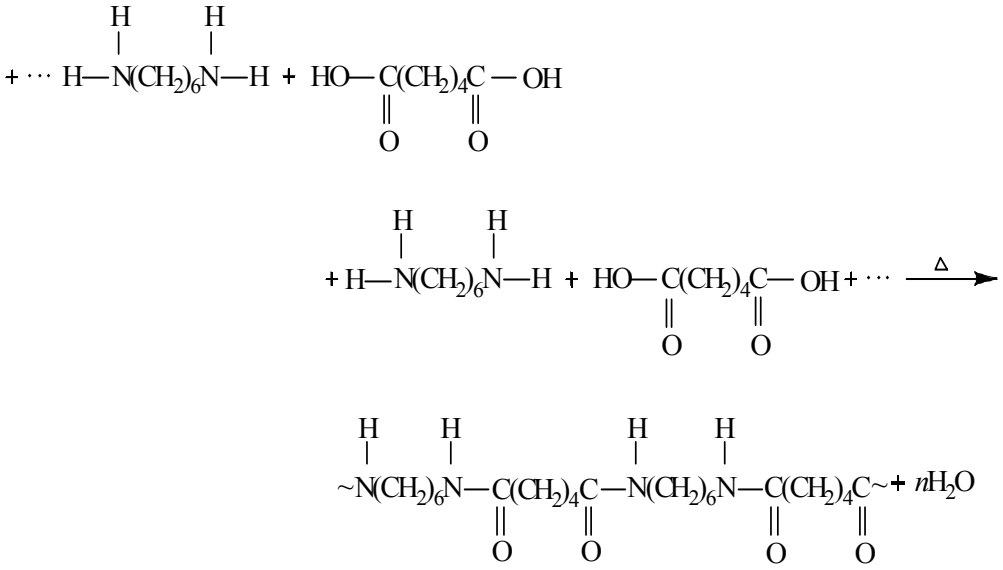
■ ANSWERS TO SELF-ASSESSMENT AND REVIEW QUESTIONS

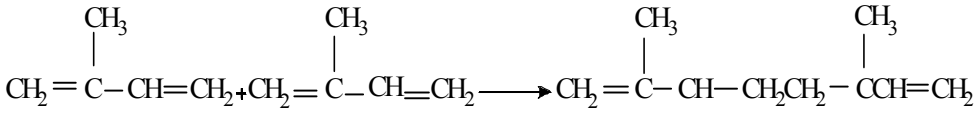
24.1. An addition reaction is a polymer formed by linking together many molecules by addition reactions. The monomers have multiple bonds that will undergo addition reactions. An example is the formation of polypropylene from propene.



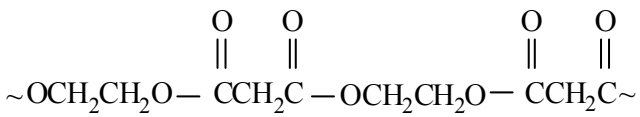
A condensation polymer is formed by linking together many molecules by condensation reactions. An example is the formation of nylon.



24.2. The addition reaction for one isoprene molecule to another is



24.3. The chain polymer obtained by the reaction of ethylene glycol with malonic acid can be represented by



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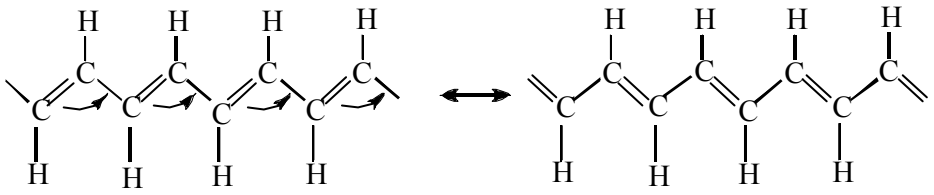
24.4. The pi electrons in polyacetylene would have to shift as follows.



24.5. Experiments show that iodine inserts itself into the plastic between polyacetylene molecules, where it forms triiodide ion. Each ion carries a negative charge that was abstracted from a pi orbital of the polymer molecule. The polymer material is left with a positive charge, or hole. The triiodide ion can facilitate the movement of an electron from an uncharged polymer molecule to a positively charged molecule (a hole). In effect, the hole moves. The movement of holes through the material constitutes an electric current.

24.6. The primary structure of a protein consists of the order, or sequence, of the amino-acid units in the protein polymer. What makes one protein different from another of the same size is the arrangement of the various possible amino acids in the sequence. For example, there are 120 different sequences possible for a polypeptide with just five different amino acids. The basis of the unique conformation of a protein is the folding and coiling into a three-dimensional conformation in aqueous solution due to the different side-chain amino-acid units. In stable conformations, the nonpolar side chains are buried within the structure away from water, and the polar groups are on the surface of the conformation, where they can hydrogen-bond with water.

24.7. The secondary structure of a protein is the simpler coiled or parallel arrangement of the protein chain. The tertiary structure consists of the folded nature of the structure.

24.8. An enzyme is a specific body catalyst, usually a globular protein, that possesses active sites. The specificity of an enzyme is explained by the active sites at which substrates will bind. Substrates fit into the active sites as a key fits into a lock.

24.9. D-ribose and 2-deoxy-D-ribose have identical structures except that D-ribose has an –OH group on carbon two whereas 2-deoxy-D-ribose has an –H instead.

24.10. It is possible for glucose to exist in three forms in any solution such as blood: the straight-chain form, the α-D-glucopyranose form, and the β-D-glucopyranose form.

24.11. The complementary base pairs are the nucleotide bases that form strong hydrogen bonds with one another: adenine and thymine, adenine and uracil, and guanine and cytosine. A DNA molecule consists of two polynucleotide chains with base pairing along their entire lengths. The two chains are coiled about each other to form a double helix.

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24.12. The only difference between ribonucleotides and deoxyribonucleotides is the sugar: Ribonucleotides contain β-D-ribose, and deoxyribonucleotides contain 2-deoxy-β-D-ribose, with both sugars having furanose rings. Both form polymers by condensation (loss of H_2O).

24.13. The genetic code is the relationship between the nucleotide sequence in DNA and the amino-acid sequence in proteins. Genetic information is coded into the linear sequence of nucleotides in the DNA molecule, and this coding then directs the synthesis of the specific proteins that make a cell unique.

24.14. A codon is a code structure in messenger RNA; each such structure has a particular sequence of three nucleotides and is usually denoted simply by its bases. An anticodon is a triplet sequence in transfer RNA complementary to the codon in DNA; the transfer RNA uses the anticodon to carry an amino acid to a ribosome. The messenger RNA and transfer RNA bond to each other through the codon and anticodon, respectively.

24.15. There are four RNA bases, and three of these are arranged in a specific order in each codon. Since there are four different possibilities for each base in the codon, there are 4 x 4 x 4 = 64 different triplet codons.

24.16. A polypeptide is produced as follows: Imagine you have a ribosome with messenger RNA attached in the proper way for translation, and the first codon is in position to be read. (The messenger RNA has been synthesized with a sequence of bases complementary to that of the gene before attachment.) Transfer RNAs bring up various amino acids to be bonded to each other until a termination codon appears to signal the end of the chain, which is then released from the ribosome.

24.17. The answer is d, amino and carboxyl.

24.18. The answer is c, rubber.

24.19. The answer is d, hydrogen.

24.20. The answer is d, adenine.

■ ANSWERS TO CONCEPTUAL PROBLEMS

24.21.

a. Since a homopolymer consists of the same monomer units linked together, examples are −A−A−, −B−B−, and −C−C−

b. Since a copolymer contains different monomer units linked together, an example is −A−B−.

c. A ratio of one C unit to every two A units would produce the desired copolymer: −A−C−A−.

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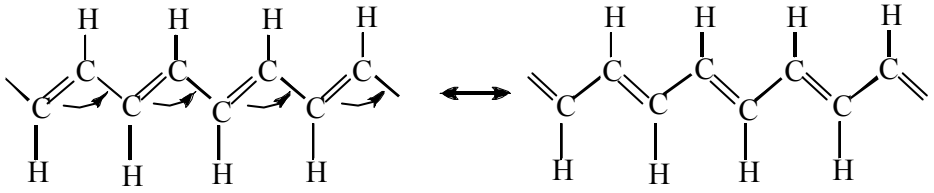
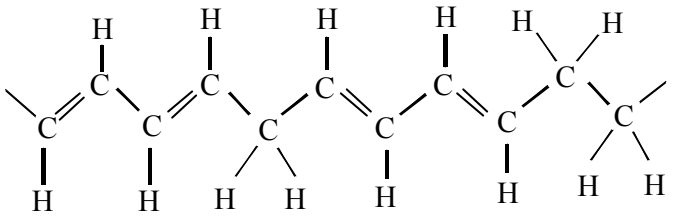
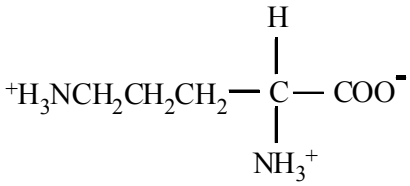
24.22. Polyacetylene has delocalized molecular orbitals extending over the length of the molecule because double bonds alternate with single bonds over the length of the molecule. Each carbon atom in the chain has one single bond and one double bond to an adjacent carbon atom. The resonance structures are



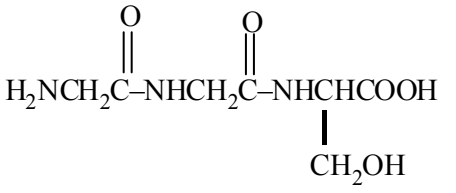
For the molecule in the problem, the pattern of double bonds and single bonds does not alternate regularly over the entire length of the molecule. Some of the carbon atoms do not have a double bond, and there is no delocalization of electrons in these regions.



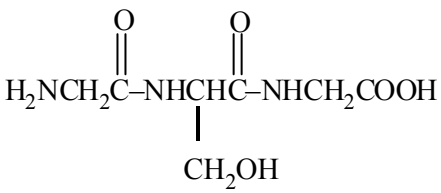
24.23. The fully ionized form of ornithine is



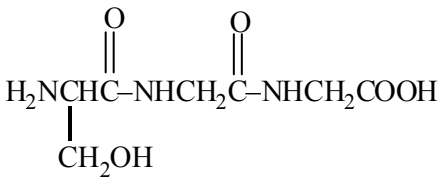
24.24. The possible tripeptides with two glycines and one serine are gly−gly−ser, gly−ser−gly, and ser−gly−gly. Here are the structural formulas



gly-gly-ser



gly-ser-gly



ser-gly-gly

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24.25. Mark off the message into triplets beginning at the left. Then refer to Table 24.3 to determine which amino acid is represented by each triplet.

AGA | GUC | CGA | GAC | UUG | ACG | UGA

The corresponding amino-acid sequence is Arg−Val−Arg−Asp−Leu−Thr. The triplet UGA is the code to end the sequence.

24.26. Refer to Table 24.3 for the sequences that translate to the different amino acids.

lys−pro−ala−phe−trp−glu−his−gly

One possible nucleotide sequence is

AAA CCU GCU UUU UGG GAA CAU GGU UAA.

The triplet UAA indicates the end of the sequence.

■ SOLUTIONS TO PRACTICE PROBLEMS

24.27. $nCF_2{=}CF_2 \rightarrow -CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-$

24.28. $nCH_2{=}CHCl \rightarrow —CH_2CH(Cl)–CH_2CH(Cl)–CH_2CH(Cl)—$

24.29. The two monomer units for this polymer are

$HOCH_2CH_2OH$ and $HOC(=O)CH_2CH_2C(=O)OH$

24.30. The two monomer units for this polymer are

$H_2N(CH_2)_6NH_2$ and $HOC(=O)(CH_2)_{10}C(=O)OH$

24.31.

a. When this monomer undergoes an addition reaction, the triple bond is converted into a double bond, just as it is with acetylene. The resulting polymer contains alternating single and double bonds and, therefore, could produce a conducting polymer.

b. When this monomer (propylene) undergoes an addition reaction, the double bond is converted into a single bond. Since the polymer does not contain any double bonds, this monomer cannot produce a conducting polymer.

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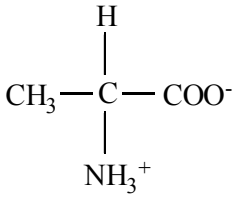
24.32.

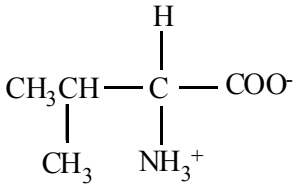
a. When this monomer undergoes an addition reaction, the double bond is converted into a single bond. Since the polymer does not contain any double bonds, this monomer cannot produce a conducting polymer.

b. When this monomer undergoes an addition reaction, the triple bond is converted into a double bond, just as it is with acetylene. The resulting polymer contains alternating single and double bonds and, therefore, could produce a conducting polymer.

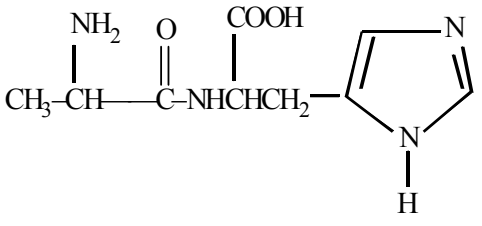
24.33. The zwitterion for alanine is



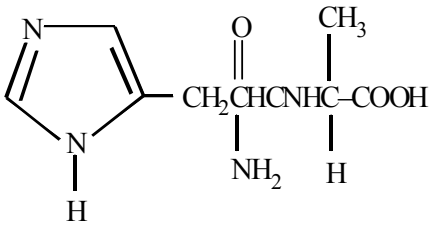
24.34. The zwitterion for valine is



24.35. There are two possible dipeptides containing one molecule each of L-alanine and L-histidine, ala−his and his−ala.



ala-his



his-ala

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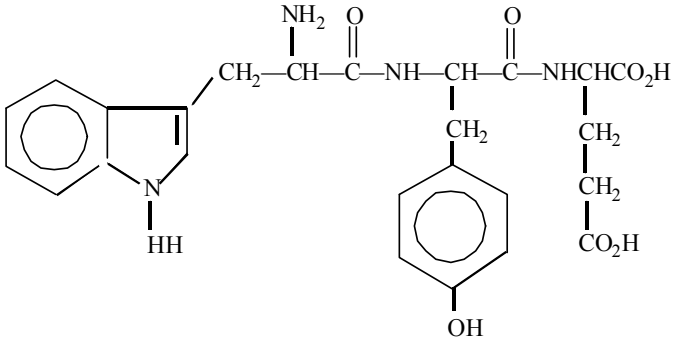
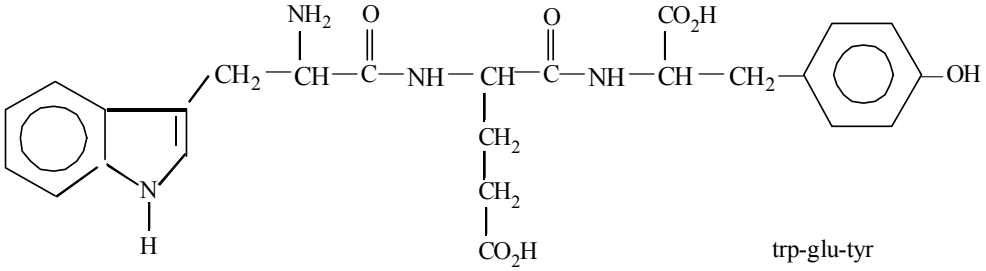
24.36. The number of possible tripeptides is six (3 x 2 x 1). Two possibilities are



trp-tyr-glu

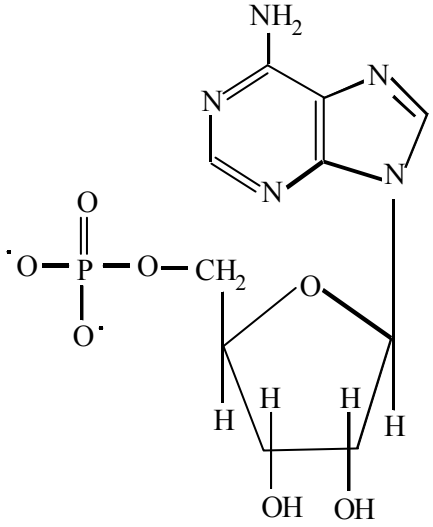


trp-glu-tyr

24.37. DNA consists of two strands of polynucleotides with the adenine units in one strand paired to the thymine units in the other. Similarly, guanine units are paired with cytosine units. Thus, the adenine-thymine molar ratio is 1:1, and the molar ratio of guanine to cytosine is 1:1.

24.38. The ratio of guanine to thymine is the same as that of cytosine to adenosine (3:1). Thus, the sample contains 1.5 mol of guanine and 0.5 mol of thymine.

24.39. Adenosine consists of ribose and adenine.



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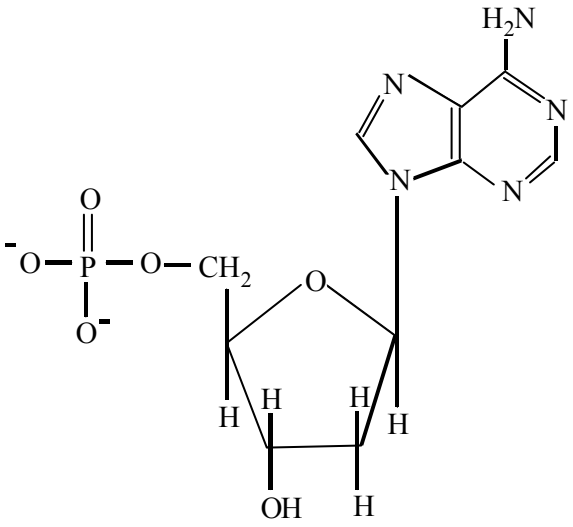
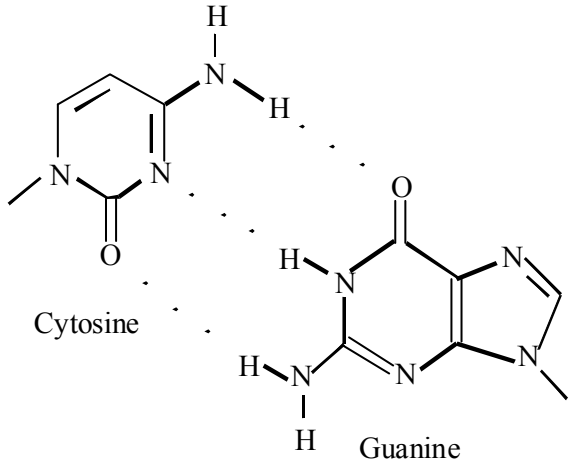
24.40. Deoxyadenosine consists of deoxyribose and adenine.



24.41. Three hydrogen bonds link a guanine-cytosine base pair.



Because only two hydrogen bonds link an adenine-uracil base pair, the bonding would be expected to be stronger in the guanine-cytosine pair.

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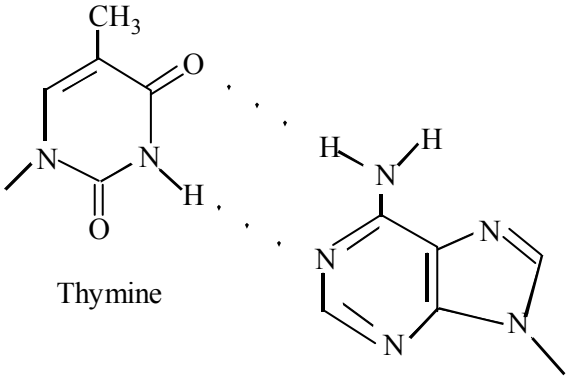
24.42. Two hydrogen bonds link an adenine-thymine base pair. The hydrogen bonding in a uracil-adenine base pair is the same as in a thymine-adenine base pair, so the strength of the bonding should be the same.



Thymine

Adenine

There are three hydrogen bonds in a guanine-cytosine base pair, so the bonding should be stronger between guanine and cytosine than between adenine and thymine.

24.43. If a codon consisted of two nucleotides, there would be 4 x 4, or 16, possible codons using the four nucleotides. Because there are 20 amino acids that must be represented uniquely by a codon for protein synthesis, the codon must be longer than two nucleotides. A two-nucleotide codon would not be workable as an amino-acid code.

24.44. If the codon were four nucleotides, there would be 4 x 4 x 4 x 4, or 256, possible codons using the four nucleotides. This is more than the minimum of 20 codons required for all the amino acids used in protein synthesis. A four-nucleotide codon would be workable as an amino-acid code.

24.45. When DNA is denatured, the hydrogen bonds between base pairs are broken. DNA with a greater percentage composition of guanine and cytosine would be denatured less readily than DNA with a greater percentage composition of adenine and thymine, because there are more hydrogen bonds between the former than between the latter.

24.46. RNA of a greater percentage composition of guanine and cytosine would be denatured less readily than RNA with a lower percentage composition because denaturation involves disruption of hydrogen bonds, and the higher the percentage composition of guanine and cytosine, the more hydrogen bonds there are in the RNA.

24.47. Mark off the message into triplets beginning at the left.

GGA | UCC | CGC | UUU | GGG | CUG | AAA | UAG

Gly–Ser–Arg–Phe–Gly–Leu–Lys

Note that the UAG at the right codes for the end of the sequence.

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24.48. Mark the message off into triplets beginning at the left.

AUU | GGC | GCG | AGA | UCG | AAU | GAG | CCC | AGU

Ile–Gly–Ala–Arg–Ser–Asn–Glu–Pro–Ser

■ SOLUTIONS TO GENERAL PROBLEMS

24.49. The codons have bases that are complementary to those in the anticodon.

Anticodons	GAC	UGA	GGG	ACC
Codons	CUG	ACU	CCC	UGG

24.50.

Codons	UUG	CAC	ACU	GAA
Anticodons	AAC	GUG	UGA	CUU

24.51. Consult Table 24.3 to find which nucleotides correspond to the amino acids in the sequence.

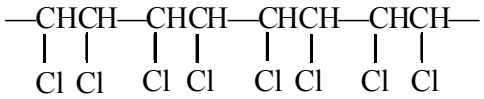
leu–ala–val–glu–asp–cys–met–trp–lys

CUU GCU GUU GAA GAU UGU AUG UGG AAA

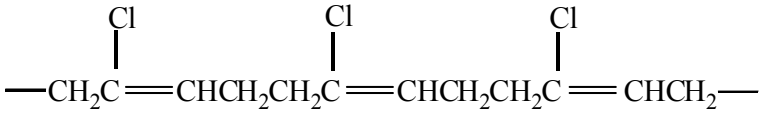
24.52. tyr–ile–pro–his–leu–his–thr–ser–phe–met

UAU AUU CCU CAU CUU CAU ACU UCU UUU AUG

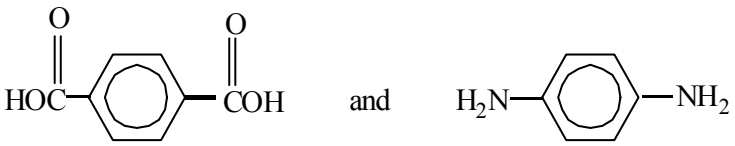
24.53. The addition polymer that forms from *cis* −1,2-dichloroethene is



24.54. The structural formula of neoprene is



24.55. The monomer units that make up Kevlar are



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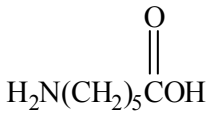
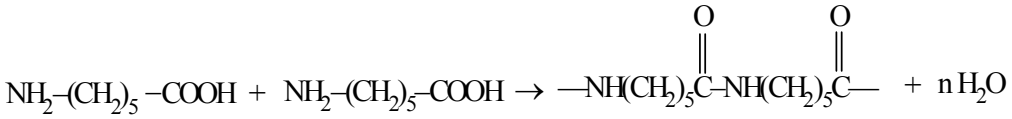
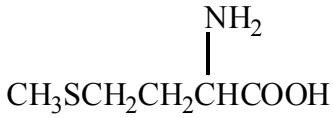
24.56. The monomer unit that makes up nylon 6 is



The reaction is

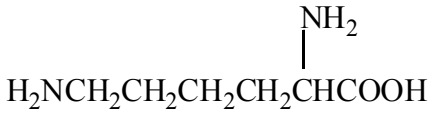


24.57. The amino acid with the nonpolar side chain is

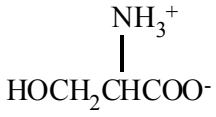


The other amino acid has a polar SH group in the side chain.

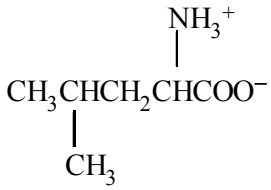
24.58. The amino acid with the polar side chain is



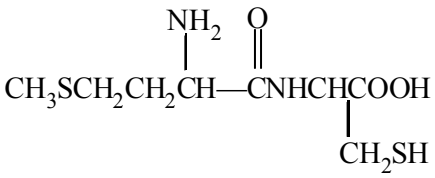
24.59. The zwitterion for serine is



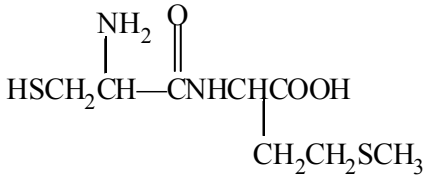
24.60. The zwitterion for leucine is



24.61. The two possibilities are



and



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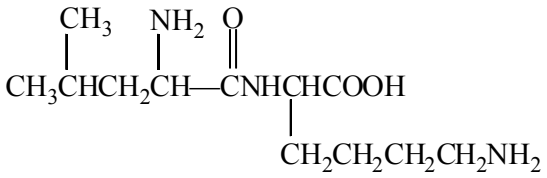
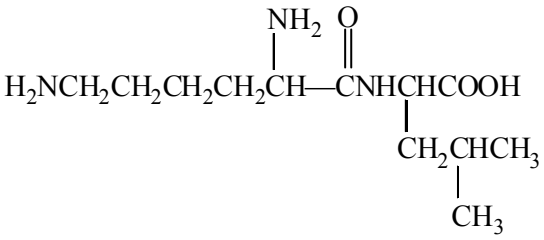
24.62. The two possibilities are



and



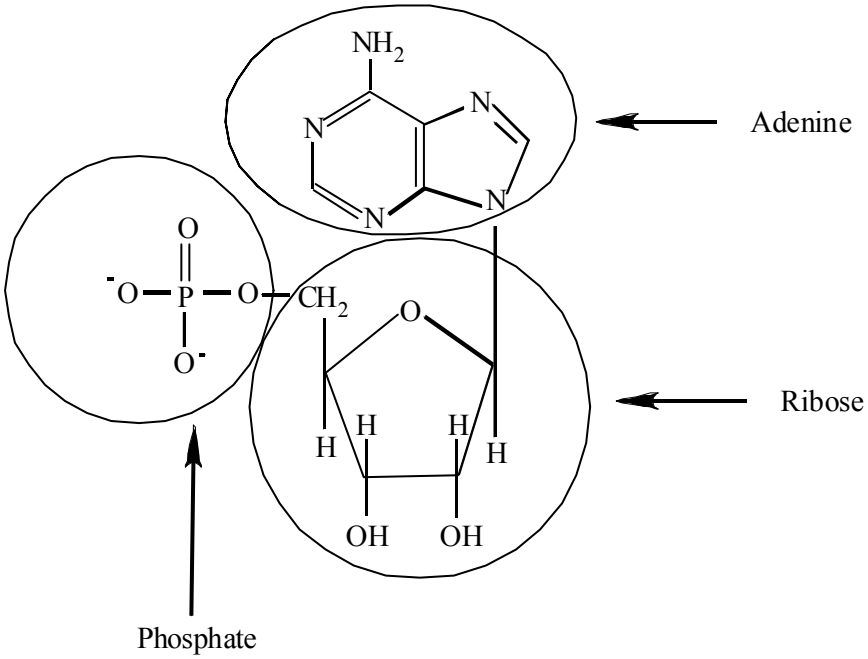
24.63. The number of possible sequences is 6 x 5 x 4 x 3 x 2 x 1, or 720.

24.64. arg–pro–glu–gly–asn–gln

arg–pro–glu–gly–gln–asn

arg–pro–glu–gln–gly–asn

24.65.



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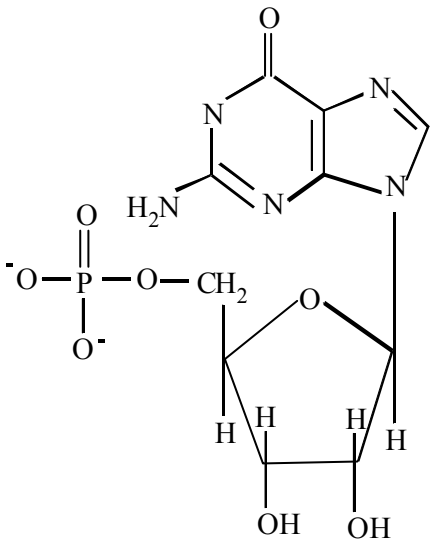
24.66.



24.67. Polymers are actually macromolecules consisting of long chains of similar groups of atoms. Carothers's idea is to consider two functional groups that chemically link together. This was represented as the linking of a hook and an eye. Carothers further suggested finding a molecule having two of the same functional groups at the ends of the molecule; this would be equivalent to a molecule with hooks at both ends. Then the reaction of several such molecules would result in a larger molecule. With many such molecules, the product would be a long-chain molecule: a macromolecule.

24.68. Carothers's synthesis of nylon, neoprene rubber, and polyesters showed that a synthetic polymer could be made with the properties of fibers, like natural silk, rubber, or wool.

24.69. The atomic force microscope is a cousin of a scanning tunneling microscope. Both microscopes use a probe to scan a surface; but whereas the scanning tunneling microscope measures an electric current between the probe tip and the sample, the atomic microscope measures the attractive van der Waals force between the probe tip and the sample.

24.70. The advantage of the atomic force microscope is that it can be used with almost any surface, whereas a scanning tunneling microscope requires a conductive surface.

■ SOLUTIONS TO STRATEGY PROBLEMS

24.71. First, determine the number of moles of NaOH used in the titration.

$$(0.2183\ M)\ \text{x}\ (98.6\ \text{x}\ 10^{-3}\ \text{L}) = 0.02152\ \text{mol NaOH}$$

Since the compound is a dicarboxylic acid, the moles of acid in the titration are

$$0.02152\ \text{mol NaOH}\ \text{x}\ \frac{1\ \text{mol acid}}{2\ \text{mol NaOH}} = 0.01076\ \text{mol acid}$$

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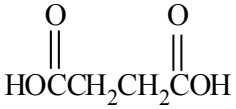
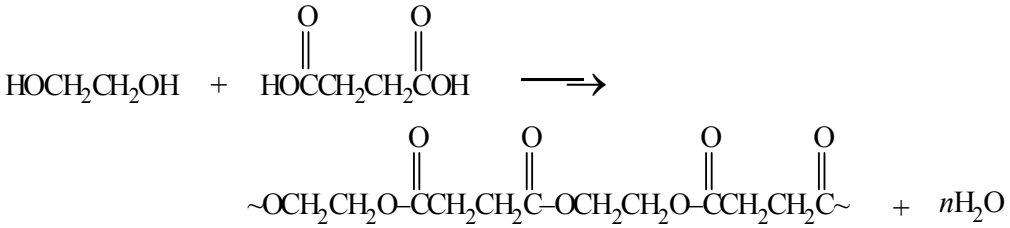
The molar mass of the compound is

$$\frac{1.273\text{ g}}{0.01076\text{ mol acid}} = 11\underline{8}.28\text{ g/mol}$$

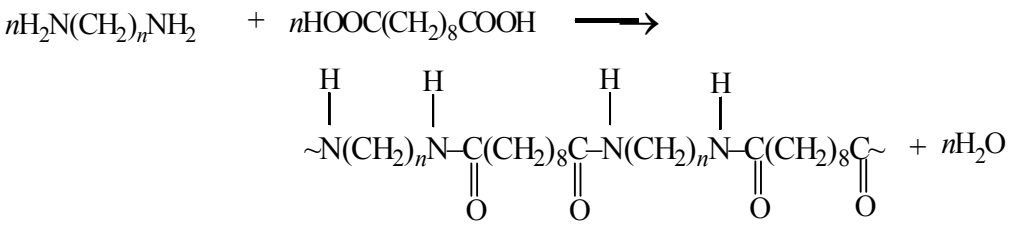
A dicarboxylic acid has two COOH units, each of which weighs 45 g/mol. This accounts for 45 x 2 = 90g/mol so far. The other 28 g/mol could be C_2H_4, giving a dicarboxylic acid with the following possible structural formula.



The condensation reaction with ethylene glycol will produce the following polyester.



24.72. The reaction to produce the polyamide is



The general formula of the monomer unit is $C_{n+10}H_{2n+18}N_2O_2$. Now use the percentage composition to determine the empirical formula. Assume a 100-g sample. Then, the moles of each element in the sample are

$$67.2\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g}} = 5.5\underline{9}5\text{ mol C}$$

$$10.5\text{ g H} \times \frac{1\text{ mol H}}{1.008\text{ g}} = 10.\underline{4}1\text{ mol H}$$

$$10.4\text{ g N} \times \frac{1\text{ mol N}}{14.01\text{ g}} = 0.74\underline{2}3\text{ mol N}$$

$$11.9\text{ g O} \times \frac{1\text{ mol O}}{16.00\text{ g}} = 0.74\underline{3}7\text{ mol O}$$

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Divide each molar quantity by the smallest number of moles, 0.7423 mol N. Divide each molar quantity by the smallest number of moles, 0.7423 mol N.

$$\frac{5.595 \text{ mol C}}{0.7423 \text{ mol}} = 7.5\underline{3}7 \cong 7.5$$

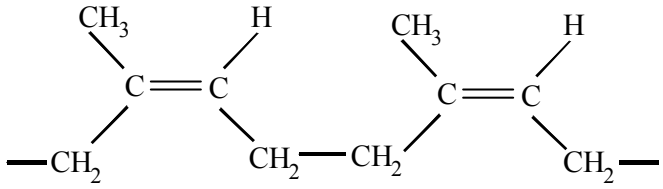
$$\frac{10.41 \text{ mol H}}{0.7423 \text{ mol}} = 14.\underline{0}2 \cong 14$$

$$\frac{0.7423 \text{ mol N}}{0.7423 \text{ mol}} = 1.000 \cong 1$$

$$\frac{0.7437 \text{ mol O}}{0.7423 \text{ mol}} = 1.0\underline{0}1 \cong 1$$

Multiplying each mole ratio by 2 gives $C_{15}H_{28}N_2O_2$ as the formula for the monomer unit of the polyamide, so $n = 5$.

24.73. The structure of rubber (poly-*cis*-isoprene) is



The monomer unit of isoprene has the formula C_5H_8 and contains one double bond that is available to react with Br_2. Each C_5H_8 unit weighs 68.11 g/mol. For each mole of monomer units that react, one mole of Br_2 also reacts. In the process, for one monomer unit, one carbon-carbon double bond is broken, one bromine-bromine bond is broken, one carbon-carbon single bond is formed, and two carbon-bromine bonds are formed. The enthalpy change for the reaction can be estimated using the bond energy values from Table 9.5.The monomer unit of isoprene has the formula C_5H_8 and contains one double bond that is available to react with Br_2. Each C_5H_8 unit weighs 68.11 g/mol. For each mole of monomer units that react, one mole of Br_2 also reacts. In the process, for one monomer unit, one carbon-carbon double bond is broken, one bromine-bromine bond is broken, one carbon-carbon single bond is formed, and two carbon-bromine bonds are formed. The enthalpy change for the reaction can be estimated using the bond energy values from Table 9.5.

$$\Delta H°_{rxn} \cong \text{BE(C=C)} + \text{BE(Br−Br)} - \text{BE(C−C)} - 2\text{BE(C−Br)}$$

$$= (602 \text{ kJ}) + (190 \text{ kJ}) - (346 \text{ kJ}) - 2(285 \text{ kJ}) = -124 \text{ kJ}$$

This is the energy released per mole of monomer units. Thus, for 10.0 g of rubber, the heat released is

$$10.0 \text{ g} \times \frac{1 \text{ mol monomer units}}{68.11 \text{ g}} \times \frac{-124 \text{ kJ}}{1 \text{ mol monomer units}} = -18.\underline{2}0 = -18.2 \text{ kJ}$$

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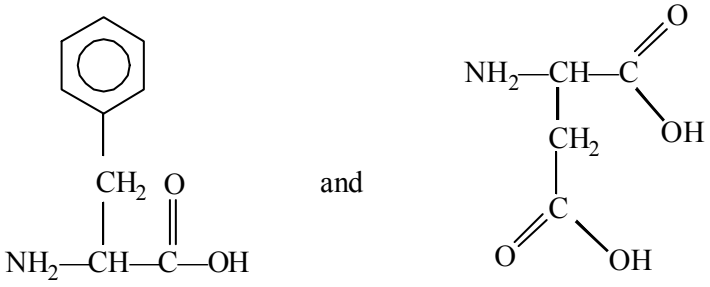
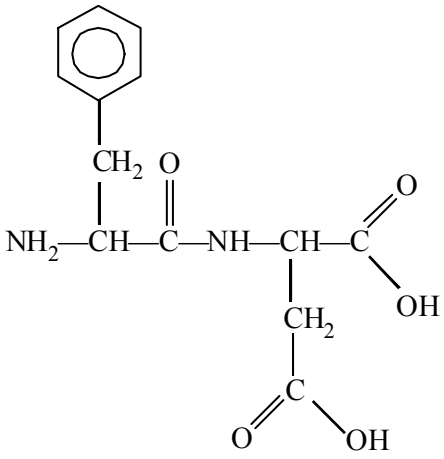
24.74.

a. When aspartame hydrolyzes, the two amino acids that form are aspartic acid and phenylalanine. Their structures are



b. Aspartame is the dipeptide asp−phe. Another dipeptide that could be prepared from these amino acids is phe−asp. It has the following structure.



c. There are $2^3 = 8$ possible tripeptides that can be formed using the amino acids valine (val) and alanine (ala). These are

val−val−val	val−val−ala	val−ala−val
ala−val−val	vla−ala−ala	ala−val−ala
ala−ala−val	ala−ala−ala	

24.75.

a. The number of tripeptides that are possible when four bases are used is 4 x 4 x 4 = 64.The number of tripeptides that are possible when four bases are used is 4 x 4 x 4 = 64.

b. Yes, this is enough to establish a code for all of the 20 amino acids.

c. The number of possible tetrapeptides when two bases are used is 2 x 2 x 2 x 2 x = 16.

d. No, this is not enough to establish the code for the 20 amino acids.

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e. If the bases are taken in groups of five, then 32 combinations are possible. Therefore, develop a hypothetical code using these combinations. For example, using the bases U and T, the 32 possible combinations are

UUUUU	UTUUU	TUUUU	TTUUU
UUUUT	UTUUT	TUUUT	TTUUT
UUUTU	UTUTU	TUUTU	TTUTU
UUTUU	UTTUU	TUTUU	TTTUU
UUUTT	UTUTT	TUUTT	TTUTT
UUTUT	UTTUT	TUTUT	TTTUT
UUTTU	UTTTU	TUTTU	TTTTU
UUTTT	UTTTU	TUTTT	TTTTT

Now, arbitrarily assign amino acids to 20 of these possible code sequences.

UUUUU (gly)	UTUUU (glu)	TUUUU (met)	TTUUU (leu)
UUUUT (ala)	UTUUT (his)	TUUUT (ser)	TTUUT (ile)
UUUTU (val)	UTUTU (lys)	TUUTU (cys)	TTUTU (pro)
UUTUU (leu)	UTTUU (arg)	TUTUU (thr)	TTTUU (phe)
UUUTT (ile)	UTUTT (end)	TUUTT (asp)	TTUTT (trp)
UUTUT (pro)	UTTUT (gly)	TUTUT (glu)	TTTUT (met)
UUTTU (phe)	UTTTU (ala)	TUTTU (tyr)	TTTTU (ser)
UUTTT (trp)	UTTTT (val)	TUTTT (asn)	TTTTT (cys)

The base sequence for the tripeptide leu−ala−val would be

UUTUU UTTTU UUUTU

24.76. First, use the percentage composition to obtain the molecular formula.

$$66.24 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g}} = 5.51\underline{5}4 \text{ mol C}$$

$$5.23 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g}} = 5.1\underline{8}8 \text{ mol H}$$

$$9.06 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} = 0.16\underline{2}2 \text{ mol Fe}$$

$$9.09 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g}} = 0.64\underline{8}8 \text{ mol N}$$

$$10.38 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g}} = 0.648\underline{7}5 \text{ mol O}$$

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Divide each molar quantity by the smallest number of moles of Fe, 0.1622 mol.

$$\frac{5.5154 \text{ mol C}}{0.1622 \text{ mol}} = 34.\underline{0}0 \cong 34$$

$$\frac{5.188 \text{ mol H}}{0.1622 \text{ mol}} = 31.\underline{9}8 \cong 32$$

$$\frac{0.1622 \text{ mol Fe}}{0.1622 \text{ mol}} = 1.000 \cong 1$$

$$\frac{0.6488 \text{ mol N}}{0.1623 \text{ mol}} = 3.9\underline{9}7 \cong 4$$

$$\frac{0.64875 \text{ mol O}}{0.1623 \text{ mol}} = 3.9\underline{9}7 \cong 4$$

Therefore, the molecular formula of heme is $C_{34}H_{32}FeN_4O_4$, with a molecular mass of 616.49 amu. The hemoglobin molecule contains four globin units and four heme units and weighs 64,500 amu. Therefore,

$$64{,}500 \text{ amu} = 4(616.49 \text{ amu}) + 4(\text{weight of globin})$$

$$\text{Weight of globin} = \frac{64{,}500 \text{ amu} - 4(616.49 \text{ amu})}{4} = 15{,}50\underline{8}.5 = 15{,}509 \text{ amu}$$

24.77. Rearrange the boiling-point-depression formula and solve for the molality of the solution.

$$c_m = \frac{\Delta T_b}{K_b} = \frac{0.0556°\text{C}}{0.512 \text{ °C/m}} = 0.10\underline{8}5 \ m$$

The molar mass of ribose ($C_5H_{10}O_5$) is 150.13 g/mol, and for deoxyribose ($C_5H_{10}O_4$) the molar mass is 134.13 g/mol. Let x be the mass of ribose; then 1.500 g − x is the mass of deoxyribose. In 100.0 g of water, the total moles of solute is

$$\text{Moles solute} = c_m \text{ x kg solvent} = 0.1085 \ m \text{ x } 0.1000 \text{ kg} = 0.010\underline{8}50 \text{ mol}$$

Also

$$\text{Moles solute} = \frac{x}{150.13 \text{ g/mol}} + \frac{1.500 \text{ g} - x}{134.13 \text{ g/mol}} = 0.01085 \text{ mol}$$

Solve in the normal way.

$$(134.13\,x) + (150.13)(1.500 \text{ g} - x) = (0.01085 \text{ g})(150.13)(134.13)$$

$$134.13\,x + 225.\underline{1}95 \text{ g} - 150.13\,x = 218.\underline{4}8 \text{ g}$$

$$x = 0.4\underline{1}9 \text{ g}$$

The percentage of ribose in the mixture is

$$\frac{0.419 \text{ g}}{1.500 \text{ g}} \text{ x } 100\% = 2\underline{7}.9 = 28\%$$

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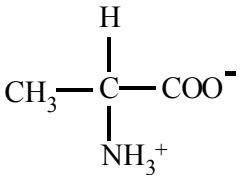
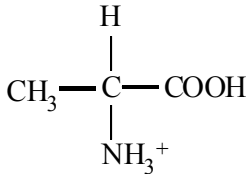
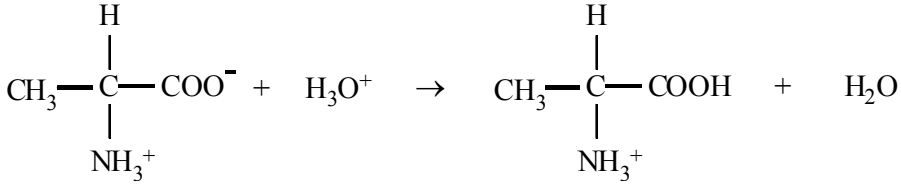
24.78. The zwitterion form of alanine is



When the zwitterion picks up a proton, the resulting ion has the following structure.



The chemical equation for the reaction is



When the pH is 4.0, the Henderson-Hasselbalch equation can be used to get the ratio of the substances present.

$$\text{pH} = \text{p}K_a = \log\frac{[\text{base}]}{[\text{acid}]}$$

Rearranging gives

$$\log\frac{[\text{base}]}{[\text{acid}]} = \text{pH} - \text{p}K_a = 4.0 - 2.3 = 1.7$$

In this equation, the zwitterion is the base and the protonated form is the acid. Let HA represent the zwitterion, and let H_2A^+ represent the protonated form. Thus

$$\frac{[\text{HA}]}{[\text{H}_2\text{A}^+]} = 10^{1.7} = \underline{5}0.1 = 5 \times 10^1$$

Therefore, the predominant form at this pH is HA, which is the zwitterion form.

24.79. From the description, it appears that the monomer units of the material must be a dicarboxylic acid and a dialcohol. When the dialcohol is oxidized, it produces another dicarboxylic acid, with a molecular mass of 90.0 amu. A carboxylic acid group (COOH) has a molecular mass of 45.02 amu, so the dicarboxylic acid obtained from the alcohol must be HOOCCOOH, which is oxalic acid ($H_2C_2O_4$). When oxalic acid reacts with NaOH, the following reaction occurs.

$$H_2C_2O_4(aq) + 2\text{NaOH}(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

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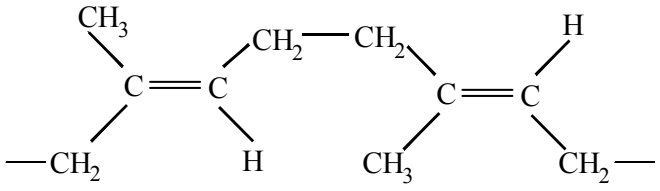
The mass of oxalic acid that would react with 30.5 mL of 0.1056 *M* NaOH is

$$(0.1056\ M)\ \text{x}\ (30.5\ \text{x}\ 10^{-3}\ \text{L})\ \text{x}\ \frac{1\ \text{mol}\ H_2C_2O_4}{2\ \text{mol NaOH}}\ \text{x}\ \frac{90.0\ \text{g}}{1\ \text{mol}\ H_2C_2O_4} = 0.1449 = 0.145\ \text{g}$$

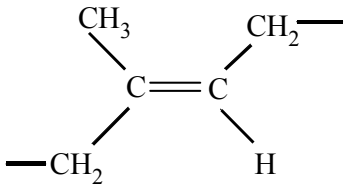
This agrees with the data given in the problem. When calcium chloride solution is added to the acid solution, a white precipitate forms, which is calcium oxalate, CaC_2O_4.

24.80.

a. Gutta percha (poly-*trans*-isoprene) has the following structure.



b. The monomer unit of gutta percha is



The formula of this monomer unit is C_5H_8, which has a molecular mass of 68.11 amu. The number of isoprene units in the sample is

$$\frac{250{,}000\ \text{amu}}{68.11\ \text{amu/unit}} = 3670.3 = 3.7\ \text{x}\ 10^3\ \text{isoprene units}$$

c. Stretching a rubber band evolves heat, so ΔH for the stretching process is negative. A stretched rubber band spontaneously contracts, so ΔG is negative for the contraction process. For the stretching process, ΔG would be positive (nonspontaneous).

Use these two quantities to determine the sign of the entropy change.

$$\Delta G = \Delta H - T\Delta S$$

Rearrange and solve for the entropy change for the stretching process.

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

The denominator (temperature) is always positive. Since ΔH is negative and ΔG is positive, the numerator is negative. Thus, overall, ΔS is negative, and there is a decrease in entropy when the rubber band is stretched.

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APPENDIX A

Mathematical Skills

■ SOLUTIONS TO EXERCISES

1.

a. Either leave it as 4.38 or write it as 4.38×10^{0}.

b. Shift the decimal point left, and count the number of positions shifted (3). The answer is 4.380×10^{3}, assuming the terminal zero is significant.

c. Shift the decimal point right, and count the number of positions shifted (4). The answer is 4.83×10^{-4}.

2.

a. Shift the decimal point right three places. The answer is 7025.

b. Shift the decimal point left four places. The answer is 0.000897.

3. Express 2.8×10^{-6} as 0.028×10^{-4}. Then, the sum can be written

$(3.142 \times 10^{-4}) + (0.028 \times 10^{-4})$ or $(3.142 + 0.028) \times 10^{-4} = 3.170 \times 10^{-4}$.

4.

a. $(5.4 \times 10^{-7}) \times (1.8 \times 10^{8}) = (5.4 \times 1.8) \times 10^{-7} \times 10^{8} = 9.72 \times 10^{1}$. This rounds to 9.7×10^{1}.

b. $$\frac{5.4 \times 10^{-7}}{6.0 \times 10^{-5}} = \frac{5.4}{6.0} \times 10^{-7} \times 10^{5} = 0.90 \times 10^{-2} = 9.0 \times 10^{-3}$$

5.

a. $(3.56 \times 10^{3})^{4} = (3.56)^{4} \times (10^{3})^{4} = 161 \times 10^{12} = 1.61 \times 10^{14}$

b. $\sqrt[3]{4.81 \times 10^{2}} = \sqrt[3]{0.481 \times 10^{3}} = \sqrt[3]{0.481} \times \sqrt[3]{10^{3}} = 0.784 \times 10^{1} = 7.84 \times 10^{0}$

6.

a. $\log 0.00582 = -2.235$

b. $\log 689 = 2.838$

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7.

a. antilog $5.728 = 5.35 \times 10^{5}$

b. antilog $(-5.728) = 1.87 \times 10^{-6}$

8.

a. $\ln 9.93 = 2.295 = 2.296$

b. $e^{1.10} = 3.004 = 3.0$

9. $$x = \frac{-0.850 \pm \sqrt{(0.850)^2 - 4(1.80)(-9.50)}}{2(1.80)} = \frac{-0.850 \pm 8.314}{3.60}$$

The positive root is

$$\frac{7.46}{3.60} = 2.07$$

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