

Student Solutions Manual

to accompany

PRINCIPLES OF GENERAL CHEMISTRY



SILBERBERG

Prepared by
Patricia Amateis and Martin Silberberg

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Principles of General Chemistry

Martin S. Silberberg

Prepared by

Patricia Amateis

Virginia Tech

and

Martin S. Silberberg



Higher Education

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PATRICIA AMATEIS AND MARTIN S. SILBERBERG

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PREFACE

Welcome To Your Student Solutions Manual

Your Student Solutions Manual (SSM) includes detailed solutions for the Follow-up Problems and highlighted End-of-Chapter Problems in Martin Silberberg's *Principles of General Chemistry*.

You should use the SSM in your study of chemistry as a study tool to:

- *better understand the reasoning behind problem solutions.* The plan-solution-check format illustrates the problem-solving thought process for the Follow-up problems and for selected End-of-Chapter problems.
- *better understand the concepts through their applications in problems.* Explanations and hints for problems are in response to questions from students in general chemistry courses.
- *check your problem solutions.* Solutions provide comments on the solution process as well as the answer.

To succeed in general chemistry you must develop skills in problem solving. Not only does this mean being able to follow a solution path and reproduce it on your own, but also to analyze problems you have never seen before and develop a solution strategy. Chemistry problems are story problems that bring together chemistry concepts and mathematical reasoning. The analysis of new problems is the most challenging step for general chemistry students. You may face this in the initial few chapters or not until later in the year when the material is less familiar. When you find that you are having difficulty starting problems, do not be discouraged. This is an opportunity to learn new skills that will benefit you in future courses and your future career. The following two strategies, tested and found successful by many students, may help you develop the skills you need.

The first strategy is to become aware of your own thought processes as you solve problems. As you solve a problem, make notes in the margin concerning your thoughts. Why are you doing each step and what questions do you ask yourself during the solution? After you complete the problem, review your notes and make an outline of the process you used in the solution while reviewing the reasoning behind the solution. It may be useful to write a paragraph describing the solution process you used.

The second strategy helps you develop the ability to transfer a solution process to a new problem. After solving a problem, rewrite the problem to ask a different question. One way to rewrite the question is to ask the question backwards—find what has been given in the problem from the answer to the problem. Another approach is to change the conditions—for instance, ask yourself what if the temperature is higher or there is twice as much carbon dioxide present? A third method is to change the reaction or process taking place—what if the substance is melting instead of boiling?

At times, you may find slight differences between your answer and the one in the SSM. Two reasons may account for the differences. First, SSM calculations do not round answers until the final step so this may impact the exact numerical answer. Note that in preliminary calculations extra significant figures are retained and shown in the intermediate answers. The second reason for discrepancies may be that your solution route was different from the one given in the SSM. Valid alternate paths exist for many problems, but the SSM does not have space to show all alternate solutions. So, trust your solution as long as the discrepancy with the SSM answer is small, and use the different solution route to understand the concepts used in the problem.

Some problems have more than one correct answer. For example, if you are asked to name a metal, there are over 80 correct answers. You may also find slight differences between the answer in the textbook appendix and the one in the SSM. These differences occur when questions are open-ended, such as, "Give an example of an acid." The example given in the SSM may differ from the one in the Appendix, but both answers are correct.

Patricia Amateis

Chapter 1 Keys to the Study of Chemistry

Most numerical problems will have two answers, a “calculator” answer and a “true” answer. The calculator answer, as seen on a calculator, will have one or more additional significant figures. These extra digits are retained in all subsequent calculations to avoid intermediate rounding error. Rounding of a calculator answer to the correct number of significant figures gives the true (final) answer.

FOLLOW-UP PROBLEMS

1.1 Plan: The real question is “Does the substance change composition or just change form?”

Solution:

- a) Both the solid and the vapor are iodine, so this must be a physical change.
- b) The burning of the gasoline fumes produces energy and products that are different gases. This is a chemical change.
- c) The scab forms due to a chemical change.

1.2 Plan: We need to know the total area supplied by the bolts of fabric, and the area required for each chair. These two areas need to be in the same units. The area units can be either ft² or m². The conversion of one to the other will use the conversion given in the problem: 1 m = 3.281 ft.

Solution:

$$(3 \text{ bolts}) \left(\frac{200 \text{ m}^2}{1 \text{ bolt}} \right) \left(\frac{(3.281 \text{ ft})^2}{(1 \text{ m})^2} \right) \left(\frac{1 \text{ chair}}{31.5 \text{ ft}^2} \right) = 205.047 = \mathbf{205 \text{ chairs}}$$

Check: 200 chairs require about $200 \times 32 / 10 = 640 \text{ m}^2$ of fabric. (Round 31.5 to 32, and $1 / (3.281)^2$ to $1 / 10$)
Three bolts contain $3 \times 200 = 600 \text{ m}^2$.

1.3 Plan: The volume of the ribosome must be determined using the equation given in the problem. This volume may then be converted to the other units requested in the problem.

Solution:

$$\begin{aligned} V &= \frac{4}{3} \pi r^3 = \frac{4}{3} (3.14159) \left(\frac{21.4 \text{ nm}}{2} \right)^3 = 5131.45 \text{ nm}^3 \\ (5131.45 \text{ nm}^3) &\left(\frac{(10^{-9} \text{ m})^3}{(1 \text{ nm})^3} \right) \left(\frac{(1 \text{ dm})^3}{(0.1 \text{ m})^3} \right) = 5.13145 \times 10^{-21} = \mathbf{5.13 \times 10^{-21} \text{ dm}^3} \\ (5.13145 \times 10^{-21} \text{ dm}^3) &\left(\frac{1 \text{ L}}{(1 \text{ dm})^3} \right) \left(\frac{1 \mu\text{L}}{10^{-6} \text{ L}} \right) = 5.13145 \times 10^{-15} = \mathbf{5.13 \times 10^{-15} \mu\text{L}} \end{aligned}$$

Check: The magnitudes of the answers are reasonable. The units also agree.

1.4 Plan: The time is given in hours and the rate of delivery is in drops per second. A conversion(s) relating seconds to hours is needed. This will give the total number of drops, which may be combined with their mass to get the total mass. The mg of drops will then be changed to kilograms. The other conversions are given in the inside back cover of the book.

Solution:

$$8.0 \text{ h} \left(\frac{60 \text{ min}}{1 \text{ h}} \right) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) \left(\frac{1.5 \text{ drops}}{1 \text{ s}} \right) \left(\frac{65 \text{ mg}}{1 \text{ drop}} \right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 2.808 = \mathbf{2.8 \text{ kg}}$$

Check: Estimating the answer — $(8 \text{ h}) (3600 \text{ s} / \text{h}) (2 \text{ drops} / \text{s}) (0.070 \text{ kg} / 10^3 \text{ drop}) = 4 \text{ kg}$. The final units in the calculation are the desired units.

- 1.5 Plan: The volume unit may be factored away by multiplying by the density. Then it is simply a matter of changing grams to kilograms.

Solution:

$$4.6 \text{ cm}^3 \left(\frac{7.5 \text{ g}}{\text{cm}^3} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 0.0345 = \mathbf{0.034 \text{ kg}}$$

Check: $5 \times 7 / 1000 = 0.035$, and the calculated units are correct.

- 1.6 Plan: Using the relationship between the Kelvin and Celsius scales, change the Kelvin temperature to the Celsius temperature. Then convert the Celsius temperature to the Fahrenheit value using the relationship between these two scales.

$$T (\text{in}^\circ\text{C}) = T (\text{in K}) - 273.15$$

$$T (\text{in}^\circ\text{F}) = \frac{9}{5} T (\text{in}^\circ\text{C}) + 32$$

Solution:

$$T (\text{in}^\circ\text{C}) = 234 \text{ K} - 273.15 = -39.15 = \mathbf{-39^\circ\text{C}}$$

$$T (\text{in}^\circ\text{F}) = \frac{9}{5} (-39.15^\circ\text{C}) + 32 = -38.47 = \mathbf{-38^\circ\text{F}}$$

Check: Since the Kelvin temperature is below 273, the Celsius temperature must be negative. The low Celsius value gives a negative Fahrenheit value.

- 1.7 Plan: Determine the significant figures by determining the digits present, and accounting for the zeros. Only zeros between non-zero digits and zeros on the right, if there is a decimal point, are significant. The units make no difference.

Solution:

a) 31.070 mg; **five** significant figures

b) 0.06060 g; **four** significant figures

c) 850.°C; **three** significant figures — note the decimal point that makes the zero significant.

d) 2.000×10^2 mL; **four** significant figures

e) 3.9×10^{-6} m; **two** significant figures — note that none of the zeros are significant.

f) 4.01×10^{-4} L; **three** significant figures

Check: All significant zeros must come after a significant digit.

- 1.8 Plan: Use the rules presented in the text. Add the two values in the numerator before dividing. The time conversion is an exact conversion, and, therefore, does not affect the significant figures in the answer. The addition of 25.65 and 37.4 gives an answer where the last significant figure is the one after the decimal point (giving three significant figures total). When a four significant figure number divides a three significant figure number, the answer must round to three significant figures. An exact number (1 min / 60 s) will have no bearing on the number of significant figures.

Solution:

$$\frac{25.65 \text{ mL} + 37.4 \text{ mL}}{73.55 \text{ s} \left(\frac{1 \text{ min}}{60 \text{ s}} \right)} = 51.434 = \mathbf{51.4 \text{ mL/min}}$$

Check: $(25 + 35) / (5 / 4) = (60)4/5 = 48$. The approximated value checks well.

END-OF-CHAPTER PROBLEMS

- 1.2 Plan: Apply the definitions of the states of matter to a container. Next, apply these definitions to the examples.

Solution:

Gas molecules fill the entire container; the volume of a gas is the volume of the container. Solids and liquids have a definite volume. The volume of the container does not affect the volume of a solid or liquid.

a) The helium fills the volume of the entire balloon. The addition or removal of helium will change the volume of a balloon. Helium is a **gas**.

b) At room temperature, the mercury does not completely fill the thermometer. The surface of the **liquid** mercury indicates the temperature.

c) The soup completely fills the bottom of the bowl, and it has a definite surface. The soup is a **liquid**, though it is possible that solid particles of food will be present.

1.3 Plan: Define the terms and apply these definitions to the examples.

Solution:

Physical property – A characteristic shown by a substance itself, without interacting with or changing into other substances.

Chemical property – A characteristic of a substance that appears as it interacts with, or transforms into, other substances.

a) The change in color (yellow-green and silvery to white), and the change in physical state (gas and metal to crystals) are examples of **physical properties**. The change in the physical properties indicates that a chemical change occurred. Thus, the interaction between chlorine gas and sodium metal producing sodium chloride is an example of a **chemical property**.

b) The sand and the iron are still present. Neither sand nor iron became something else. Colors along with magnetism are **physical properties**. No chemical changes took place, so there are no chemical properties to observe.

1.5 Plan: Apply the definitions of chemical and physical changes to the examples.

Solution:

a) Not a chemical change, but a **physical change** — simply cooling returns the soup to its original form.

b) There is a **chemical change** — cooling the toast will not “un-toast” the bread.

c) Even though the wood is now in smaller pieces, it is still wood. There has been no change in composition, thus this is a **physical change**, and not a chemical change.

d) This is a **chemical change** converting the wood (and air) into different substances with different compositions. The wood cannot be “unburned.”

1.7 Plan: A system has a higher potential energy before the energy is released (used).

Solution:

a) The exhaust is lower in energy than the fuel by an amount of energy equal to that released as the fuel burns. The **fuel** has a higher potential energy.

b) **Wood**, like the fuel, is higher in energy by the amount released as the wood burns.

1.11 Plan: Re-read the section in the Chapter on experimental design (Experiment step of the scientific method).

Solution:

A well-designed experiment must have the following essential features.

1) There must be two variables that are expected to be related.

2) There must be a way to control all the variables, so that only one at a time may be changed while keeping all others constant.

3) The results must be reproducible.

1.14 Plan: Review the table of conversions in the Chapter or inside the back cover of the book.

Solution:

a) To convert from in^2 to cm^2 , use $\frac{(2.54 \text{ cm})^2}{(1 \text{ in})^2}$.

b) To convert from km^2 to m^2 , use $\frac{(1000 \text{ m})^2}{(1 \text{ km})^2}$.

c) This problem requires two conversion factors: one for distance and one for time. It does not matter which conversion is done first. Alternate methods may be used.

To convert distance, mi to m, use:

$$\left(\frac{1.609 \text{ km}}{1 \text{ mi}} \right) \left(\frac{1000 \text{ m}}{1 \text{ km}} \right) = 1.609 \times 10^3 \text{ m/mi}$$

To convert time, h to s, use:

$$\left(\frac{1 \text{ h}}{60 \text{ min}}\right)\left(\frac{1 \text{ min}}{60 \text{ s}}\right) = \mathbf{1 \text{ h} / 3600 \text{ s}}$$

Therefore, the complete conversion factor is $\left(\frac{1.609 \times 10^3 \text{ m}}{1 \text{ mi}}\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right) = \frac{0.4469 \text{ m h}}{\text{mi s}}$. Do the units cancel when you start with a measurement of mi/h?

d) To convert from pounds (lb) to grams (g), use $\frac{1000 \text{ g}}{2.205 \text{ lb}}$; to convert volume from ft^3 to cm^3

$$\text{use } \left(\frac{(1 \text{ ft})^3}{(12 \text{ in})^3}\right)\left(\frac{(1 \text{ in})^3}{(2.54 \text{ cm})^3}\right) = \mathbf{3.531 \times 10^{-5} \text{ ft}^3/\text{cm}^3}$$

1.16 Plan: Review the definitions of extensive and intensive properties.

Solution:

An extensive property depends on the amount of material present. An intensive property is the same regardless of how much material is present.

a) Mass is an **extensive property**. Changing the amount of material will change the mass.

b) Density is an **intensive property**. Changing the amount of material changes both the mass and the volume, but the ratio (density) remains fixed.

c) Volume is an **extensive property**. Changing the amount of material will change the size (volume).

d) The melting point is an **intensive property**. The melting point depends on the identity of the substance, not on the amount of substance.

1.18 Plan: Anything that increases the mass or decreases the volume will increase the density ($\text{density} = \frac{\text{mass}}{\text{volume}}$)

Solution:

a) Density **increases**. The mass of the chlorine gas is not changed, but its volume is smaller.

b) Density **remains the same**. Neither the mass nor the volume of the solid has changed.

c) Density **decreases**. Water is one of the few substances that expands on freezing. The mass is constant, but the volume increases.

d) Density **increases**. Iron, like most materials, contracts on cooling, thus the volume decreases while the mass does not change.

e) Density **remains the same**. The water does not alter either the mass or the volume of the diamond.

1.21 Plan: Use conversion factors from the inside back cover: $10^{-12} \text{ m} = 1 \text{ pm}$; $10^{-9} \text{ m} = 1 \text{ nm}$

Solution:

$$\text{Radius} = 1430 \text{ pm} \left(\frac{10^{-12} \text{ m}}{1 \text{ pm}}\right)\left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = \mathbf{1.43 \text{ nm}}$$

1.23 a) Plan: Use conversion factors: $(0.01 \text{ m})^2 = (1 \text{ cm})^2$; $(1 \text{ km})^2 = (1000 \text{ m})^2$

Solution:

$$17.7 \text{ cm}^2 \left(\frac{(0.01 \text{ m})^2}{(1 \text{ cm})^2}\right)\left(\frac{(1 \text{ km})^2}{(1000 \text{ m})^2}\right) = \mathbf{1.77 \times 10^{-9} \text{ km}^2}$$

b) Plan: Use conversion factor: $(1 \text{ inch})^2 = (2.54 \text{ cm})^2$

Solution:

$$17.7 \text{ cm}^2 \left(\frac{(1 \text{ in})^2}{(2.54 \text{ cm})^2}\right)\left(\frac{\$3.25}{1 \text{ in}^2}\right) = 8.91639 = \mathbf{\$8.92}$$

- 1.25 Plan: Use the relationships from the inside back cover of the book. The conversions may be performed in any order.

Solution:

$$\begin{aligned} \text{a) } & \left(\frac{5.52 \text{ g}}{\text{cm}^3} \right) \left(\frac{(1 \text{ cm})^3}{(0.01 \text{ m})^3} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = \mathbf{5.52 \times 10^3 \text{ kg/m}^3} \\ \text{b) } & \left(\frac{5.52 \text{ g}}{\text{cm}^3} \right) \left(\frac{(2.54 \text{ cm})^3}{(1 \text{ in})^3} \right) \left(\frac{(12 \text{ in})^3}{(1 \text{ ft})^3} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) \left(\frac{2.205 \text{ lb}}{1 \text{ kg}} \right) = 344.661 = \mathbf{345 \text{ lb/ft}^3} \end{aligned}$$

- 1.27 Plan: The conversions may be done in any order. Use the definitions of the various SI prefixes.

Solution:

$$\begin{aligned} \text{a) Volume} &= \left(\frac{1.72 \mu\text{m}^3}{\text{cell}} \right) \left(\frac{(1 \times 10^{-6} \text{ m})^3}{(1 \mu\text{m})^3} \right) \left(\frac{(1 \text{ mm})^3}{(1 \times 10^{-3} \text{ m})^3} \right) = \mathbf{1.72 \times 10^{-9} \text{ mm}^3/\text{cell}} \\ \text{b) Volume} &= (10^5 \text{ cells}) \left(\frac{1.72 \mu\text{m}^3}{\text{cell}} \right) \left(\frac{(1 \times 10^{-6} \text{ m})^3}{(1 \mu\text{m})^3} \right) \left(\frac{1 \text{ L}}{(1 \times 10^{-3} \text{ m})^3} \right) = 1.72 \times 10^{-10} = \mathbf{10^{-10} \text{ L}} \end{aligned}$$

- 1.29 Plan: The mass of the contents is the mass of the full container minus the mass of the empty container. The volume comes from the mass density relationship. Reversing this process gives the answer to part b.

Solution:

$$\text{a) Mass of mercury} = 185.56 \text{ g} - 55.32 \text{ g} = 130.24 \text{ g}$$

$$\text{Volume of mercury} = \text{volume of vial} = (130.24 \text{ g}) \left(\frac{1 \text{ cm}^3}{13.53 \text{ g}} \right) = 9.626016 = \mathbf{9.626 \text{ cm}^3}$$

$$\text{b) Mass of water} = (9.626016 \text{ cm}^3) \left(\frac{0.997 \text{ g}}{1 \text{ cm}^3} \right) = 9.59714 \text{ g water}$$

$$\text{Mass of vial filled with water} = 55.32 \text{ g} + 9.59714 \text{ g} = 64.91714 = \mathbf{64.92 \text{ g}}$$

- 1.31 Plan: Volume of a cube = (length of side)³

Solution:

The value 15.6 means this is a three significant figure problem.

The final answer, and no other, is rounded to the correct number of significant figures.

$$15.6 \text{ mm} \left(\frac{10^{-3} \text{ m}}{1 \text{ mm}} \right) \left(\frac{1 \text{ cm}}{10^{-2} \text{ m}} \right) = 1.56 \text{ cm} \quad (\text{convert to cm to match density unit})$$

$$\text{Al cube volume} = (1.56 \text{ cm})^3 = 3.7964 \text{ cm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{10.25 \text{ g}}{3.7964 \text{ cm}^3} = 2.69993 = \mathbf{2.70 \text{ g/cm}^3}$$

- 1.33 Plan: Use the equations given in the text for converting between the three temperature scales.

Solution:

$$\text{a) } T (\text{in } ^\circ\text{C}) = [T (\text{in } ^\circ\text{F}) - 32] \frac{5}{9} = (72^\circ\text{F} - 32) \frac{5}{9} = 22.222 = \mathbf{22^\circ\text{C}}$$

$$T (\text{in K}) = T (\text{in } ^\circ\text{C}) + 273.15 = 22.222^\circ\text{C} + 273.15 = 295.372 = \mathbf{295 \text{ K}}$$

$$\text{b) } T (\text{in K}) = T (\text{in } ^\circ\text{C}) + 273.15 = -164^\circ\text{C} + 273.15 = 109.15 = \mathbf{109 \text{ K}}$$

$$T (\text{in } ^\circ\text{F}) = \frac{9}{5} T (\text{in } ^\circ\text{C}) + 32 = \frac{9}{5} (-164^\circ\text{C}) + 32 = -263.2 = \mathbf{-263^\circ\text{F}}$$

$$\text{c) } T (\text{in } ^\circ\text{C}) = T (\text{in K}) - 273.15 = 0 \text{ K} - 273.15 = -273.15 = \mathbf{-273^\circ\text{C}}$$

$$T (\text{in } ^\circ\text{F}) = \frac{9}{5} T (\text{in } ^\circ\text{C}) + 32 = \frac{9}{5} (-273.15^\circ\text{C}) + 32 = -459.67 = \mathbf{-460.^\circ\text{F}}$$

- 1.36 Plan: Use $10^{-9} \text{ m} = 1 \text{ nm}$ to convert wavelength. Use $0.01 \text{ \AA} = 1 \text{ pm}$, $10^{-12} \text{ m} = 1 \text{ pm}$, and $10^{-9} \text{ m} = 1 \text{ nm}$
Solution:
- a) $255 \text{ nm} \left(\frac{10^{-9} \text{ m}}{1 \text{ nm}} \right) = \mathbf{2.55 \times 10^{-7} \text{ m}}$
- b) $683 \text{ nm} \left(\frac{10^{-9} \text{ m}}{1 \text{ nm}} \right) \left(\frac{1 \text{ pm}}{10^{-12} \text{ m}} \right) \left(\frac{0.01 \text{ \AA}}{1 \text{ pm}} \right) = \mathbf{6830 \text{ \AA}}$
- 1.41 Plan: Review the rules for significant figures.
Solution:
 Initial or leading zeros are never significant; internal zeros (occurring between non-zero digits) are always significant; terminal zeros to the right of a decimal point are significant; terminal zeros to the left of a decimal point are significant **only** if they were measured.
- 1.42 Plan: Review the rules for significant zeros.
Solution:
- a) No significant zeros (leading zeros are not significant)
 b) No significant zeros (leading zeros are not significant)
 c) 0.0390 (terminal zeros to the right of the decimal point are significant)
 d) 3.0900 $\times 10^4$ (zeros between nonzero digits are significant; terminal zeros to the right of the decimal point are significant)
- 1.44 Plan: Use a calculator to obtain an initial value. Use the rules for significant figures and rounding to get the final answer.
Solution:
- a) $\frac{(2.795 \text{ m})(3.10 \text{ m})}{6.48 \text{ m}} = 1.3371 = \mathbf{1.34 \text{ m}}$ (maximum of 3 significant figures allowed)
- b) $V = \left(\frac{4}{3} \right) \pi (9.282 \text{ cm})^3 = 3.34976 \times 10^3 = \mathbf{3.350 \times 10^3 \text{ cm}^3}$ (maximum of 4 significant figures allowed)
- c) $1.110 \text{ cm} + 17.3 \text{ cm} + 108.2 \text{ cm} + 316 \text{ cm} = 442.61 = \mathbf{443 \text{ cm}}$ (no digits allowed to the right of the decimal since 316 has no digits to the right of the decimal point)
- 1.46 Plan: Review the procedure for changing a number to scientific notation.
Solution:
- a) $\mathbf{1.310000 \times 10^5}$ (Note that all zeros are significant.)
 b) $\mathbf{4.7 \times 10^{-4}}$ (No zeros are significant.)
 c) $\mathbf{2.10006 \times 10^5}$
 d) $\mathbf{2.1605 \times 10^3}$
- 1.48 Plan: Review the examples for changing a number from scientific notation to standard notation.
Solution:
- a) $\mathbf{5550}$ (Do not use terminal decimal point since the zero is not significant.)
 b) $\mathbf{10070.}$ (Use terminal decimal point since final zero is significant.)
 c) $\mathbf{0.000000885}$
 d) $\mathbf{0.003004}$
- 1.50 Plan: Calculate a temporary by simply entering the numbers into a calculator. Then you will need to round the value to the appropriate number of significant figures. Cancel units as you would cancel numbers, and place the remaining units after your numerical answer.

Solution:

$$a) \frac{(6.626 \times 10^{-34} \text{ Js})(2.9979 \times 10^8 \text{ m/s})}{489 \times 10^{-9} \text{ m}} = 4.06218 \times 10^{-19}$$

$4.06 \times 10^{-19} \text{ J}$ ($489 \times 10^{-9} \text{ m}$ limits the answer to 3 significant figures; units of m and s cancel)

$$b) \frac{(6.022 \times 10^{23} \text{ molecules/mol})(1.19 \times 10^2 \text{ g})}{46.07 \text{ g/mol}} = 1.5555 \times 10^{24}$$

$1.56 \times 10^{24} \text{ molecules}$ ($1.19 \times 10^2 \text{ g}$ limits answer to 3 significant figures; units of mol and g cancel)

$$c) (6.022 \times 10^{23} \text{ atoms/mol}) \left(2.18 \times 10^{-18} \text{ J/atom} \right) \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 1.82333 \times 10^5$$

$1.82 \times 10^5 \text{ J/mol}$ ($2.18 \times 10^{-18} \text{ J/atom}$ limits answer to 3 significant figures; unit of atoms cancels)

- 1.52 Plan: Exact numbers are those that have no uncertainty. Unit definitions and number counts of items in a group are examples of exact numbers.

Solution:

- a) The height of Angel Falls is a measured quantity. This is not an exact number.
b) The number of planets in the solar system is a number count. This is an exact number.
c) The number of grams in a pound is not a unit definition. This is not an exact number.
d) The number of millimeters in a meter is a definition of the prefix “milli-.” This is an exact number.

- 1.54 Plan: Observe the figure, and estimate a reading the best you can.

Solution:

The scale markings are 0.2 cm apart. The end of the metal strip falls between the mark for 7.4 cm and 7.6 cm. If we assume that one can divide the space between markings into fourths, the uncertainty is one-fourth the separation between the marks. Thus, since the end of the metal strip falls between 7.45 and 7.55 we can report its length as **$7.50 \pm 0.05 \text{ cm}$** . (Note: If the assumption is that one can divide the space between markings into halves only, then the result is $7.5 \pm 0.1 \text{ cm}$.)

- 1.56 Plan: Calculate the average of each data set. Remember that accuracy refers to how close a measurement is to the actual or true value while precision refers to how close multiple measurements are to each other.

Solution:

$$a) \quad \begin{aligned} \text{I}_{\text{avg}} &= \frac{8.72 \text{ g} + 8.74 \text{ g} + 8.70 \text{ g}}{3} = 8.7200 = \mathbf{8.72 \text{ g}} \\ \text{II}_{\text{avg}} &= \frac{8.56 \text{ g} + 8.77 \text{ g} + 8.83 \text{ g}}{3} = 8.7200 = \mathbf{8.72 \text{ g}} \\ \text{III}_{\text{avg}} &= \frac{8.50 \text{ g} + 8.48 \text{ g} + 8.51 \text{ g}}{3} = 8.4967 = \mathbf{8.50 \text{ g}} \\ \text{IV}_{\text{avg}} &= \frac{8.41 \text{ g} + 8.72 \text{ g} + 8.55 \text{ g}}{3} = 8.5600 = \mathbf{8.56 \text{ g}} \end{aligned}$$

Sets **I** and **II** are most accurate since their average value, 8.72 g, is closest to the true value, 8.72 g.

- b) To get an idea of precision, calculate the range of each set of values: largest value – smallest value. A small range is an indication of good precision since the values are close to each other.

$$\text{I}_{\text{range}} = 8.74 \text{ g} - 8.70 \text{ g} = 0.040 \text{ g}$$

$$\text{II}_{\text{range}} = 8.83 \text{ g} - 8.56 \text{ g} = 0.27 \text{ g}$$

$$\text{III}_{\text{range}} = 8.51 \text{ g} - 8.48 \text{ g} = 0.030 \text{ g}$$

$$\text{IV}_{\text{range}} = 8.72 \text{ g} - 8.41 \text{ g} = 0.31 \text{ g}$$

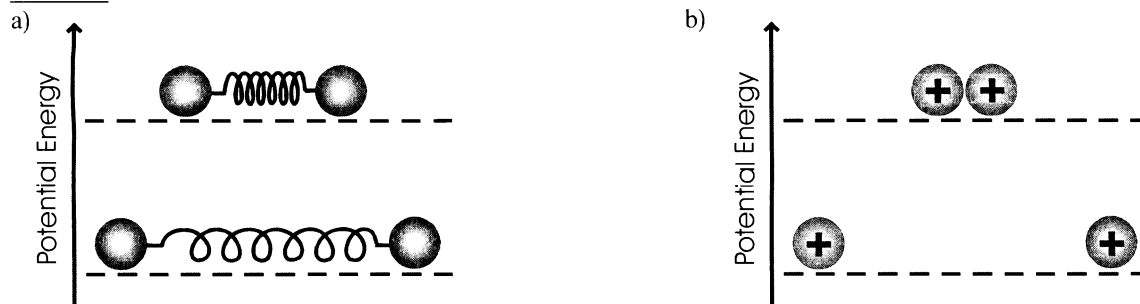
Set III is the most precise (smallest range), but is the least accurate (the average is the farthest from the actual value).

- c) **Set I** has the best combination of high accuracy (average value = actual value) and high precision (relatively small range).

- d) **Set IV** has both low accuracy (average value differs from actual value) and low precision (has the largest range).

1.59 Plan: If it is necessary to force something to happen, the potential energy will be higher.

Solution:



- a) The balls on the relaxed spring have a lower potential energy and are more stable. The balls on the compressed spring have a higher potential energy, because the balls will move once the spring is released. This configuration is less stable.
- b) The two + charges apart from each other have a lower potential energy and are more stable. The two + charges near each other have a higher potential energy, because they repel one another. This arrangement is less stable.

1.62 Plan: Use the conversions presented in the problem.

Solution:

$$a) (33.436 \text{ g}) \left(\frac{90.0\%}{100.0\%} \right) \left(\frac{1 \text{ tr. oz.}}{31.1 \text{ g}} \right) \left(\frac{\$20.00}{1 \text{ tr. oz.}} \right) = 19.3520 = \text{\$19.4 before price increase.}$$

$$(33.436 \text{ g}) \left(\frac{90.0\%}{100.0\%} \right) \left(\frac{1 \text{ tr. oz.}}{31.1 \text{ g}} \right) \left(\frac{\$35.00}{1 \text{ tr. oz.}} \right) = 33.8660 = \text{\$33.9 after price increase.}$$

$$b) (50.0 \text{ tr. oz.}) \left(\frac{31.1 \text{ g}}{1 \text{ tr. oz.}} \right) \left(\frac{100.0\%}{90.0\%} \right) \left(\frac{1 \text{ Coin}}{33.436 \text{ g}} \right) = 51.674 = \text{51.7 Coins}$$

$$c) (2.00 \text{ in}^3) \left(\frac{(2.54 \text{ cm})^3}{1 \text{ in}^3} \right) \left(\frac{19.3 \text{ g}}{1 \text{ cm}^3} \right) \left(\frac{100.0\%}{90.0\%} \right) \left(\frac{1 \text{ Coin}}{33.436 \text{ g}} \right) = 21.0199 = \text{21.0 Coins}$$

1.64 Plan: In each case, calculate the overall density of the sphere and contents.

Solution:

$$a) \text{ Density of evacuated ball: } d = \frac{\text{mass}}{\text{volume}} = \frac{0.12 \text{ g}}{560 \text{ cm}^3} = 2.1429 \times 10^{-4} \text{ g/cm}^3$$

$$\text{Convert density to units of g/L: } \frac{2.1429 \times 10^{-4} \text{ g}}{\text{cm}^3} \left(\frac{1 \text{ cm}^3}{1 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.21429 = 0.21 \text{ g/L}$$

The evacuated ball will float because its density is less than that of air.

b) Because the density of CO₂ is greater than that of air, a ball filled with CO₂ will **sink**.

$$c) 560 \text{ cm}^3 \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.560 = \text{0.56 L}$$

$$\text{Mass of hydrogen: } (0.56 \text{ L}) \left(\frac{0.0899 \text{ g}}{1 \text{ L}} \right) = 0.0503 \text{ g}$$

The H₂ filled ball will have a total mass of 0.0503 + 0.12 g = 0.17 g, and a resulting density of

$$d = \frac{0.17 \text{ g}}{0.56 \text{ L}} = 0.30 \text{ g/L} \text{ The ball will } \textbf{float} \text{ because density of the ball filled with hydrogen is less than density of air.}$$

Note: The densities are additive because the volume of the ball and the volume of the H₂ gas are the same:
 $0.0899 + 0.21 \text{ g/L} = 0.30 \text{ g/L}$.

d) Because the density of O₂ is greater than that of air, a ball filled with O₂ will **sink**.

e) Density of ball filled with nitrogen: $0.21 \text{ g/L} + 1.165 \text{ g/L} = 1.38 \text{ g/L}$. Ball will **sink** because density of ball filled with nitrogen is greater than density of air.

f) To sink, the total mass of the ball and gas must weigh $\left(\frac{1.189 \text{ g}}{1 \text{ L}}\right)\left(\frac{0.0560 \text{ L}}{1 \text{ L}}\right) = 0.66584 \text{ g}$. For ball filled with hydrogen: $0.66584 - 0.17 \text{ g} = 0.4958 = \mathbf{0.50 \text{ g}}$. More than 0.50 g would have to be added to make the ball sink.

1.67 Plan: Use the surface area and the depth to determine the volume. The volume may then be converted to liters, and finally to the mass using the g/L. Once the mass of the gold is known, other conversions stem from it.

Solution:

$$\text{a) } (3800 \text{ m})(3.63 \times 10^8 \text{ km}^2) \left(\frac{(1000 \text{ m})^2}{(1 \text{ km})^2} \right) \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) \left(\frac{5.8 \times 10^{-9} \text{ g}}{\text{L}} \right) = 8.00052 \times 10^{12} = \mathbf{8.0 \times 10^{12} \text{ g}}$$

b) Use the density of gold to convert mass of gold to volume:

$$(8.00052 \times 10^{12} \text{ g}) \left(\frac{1 \text{ cm}^3}{19.3 \text{ g}} \right) \left(\frac{(0.01 \text{ m})^3}{(1 \text{ cm})^3} \right) = 4.14535 \times 10^5 = \mathbf{4.1 \times 10^5 \text{ m}^3}$$

$$\text{c) } (8.00052 \times 10^{12} \text{ g}) \left(\frac{1 \text{ tr. oz.}}{31.1 \text{ g}} \right) \left(\frac{\$370.00}{1 \text{ tr. oz.}} \right) = 9.51830 \times 10^{13} = \mathbf{\$9.5 \times 10^{13}}$$

1.69 Plan: Use the equations for temperature conversion given in the chapter. The mass and density will then give the volume.

Solution:

$$\text{a) } T (\text{in } ^\circ\text{C}) = T (\text{in K}) - 273.15 = 77.36 \text{ K} - 273.15 = \mathbf{-195.79^\circ\text{C}}$$

$$\text{b) } T (\text{in } ^\circ\text{F}) = \frac{9}{5} T (\text{in } ^\circ\text{C}) + 32 = \frac{9}{5} (-195.79^\circ\text{C}) + 32 = -320.422 = \mathbf{-320.42^\circ\text{F}}$$

c) The mass of nitrogen is conserved, meaning that the mass of the nitrogen gas equals the mass of the liquid nitrogen. We first find the mass of liquid nitrogen and then convert that quantity to volume using the density of the liquid.

$$\text{Mass of liquid nitrogen} = \text{mass of gaseous nitrogen} = (895.0 \text{ L}) \left(\frac{4.566 \text{ g}}{1 \text{ L}} \right) = 4086.57 \text{ g N}_2$$

$$\text{Volume of liquid N}_2 = (4086.57 \text{ g}) \left(\frac{1 \text{ L}}{809 \text{ g}} \right) = 5.0514 = \mathbf{5.05 \text{ L}}$$

1.72 Plan: Determine the volume of a particle, and then convert the volume to a convenient unit (cm³ in this case). Use the density and volume of the particles to determine the mass. In a separate set of calculations, determine the mass of all the particles in the room or in one breath. Use the total mass of particles and the individual mass of the particles to determine the number of particles.

Solution:

$$V (\mu\text{m}^3) = \left(\frac{4}{3} \right) \pi r^3 = \left(\frac{4}{3} \right) \pi \left(\frac{2.5 \mu\text{m}}{2} \right)^3 = 8.1812 = 8.2 \mu\text{m}^3$$

$$V (\text{cm}^3) = 8.1812 \mu\text{m}^3 \left(\frac{(1 \text{ cm})^3}{(10^4 \mu\text{m})^3} \right) = 8.1812 \times 10^{-12} \text{ cm}^3$$

$$\text{Mass (g)} = 8.1812 \times 10^{-12} \text{ cm}^3 \left(\frac{2.5 \text{ g}}{\text{cm}^3} \right) = 2.045 \times 10^{-11} = 2.0 \times 10^{-11} \text{ g each microparticle}$$

Calculate the volume of the room in m³:

$$\text{Volume}_{\text{room}} = 10.0 \text{ ft} \times 8.25 \text{ ft} \times 12.5 \text{ ft} = 1.031 \times 10^3 \text{ ft}^3$$

$$(1.031 \times 10^3 \text{ ft}^3) \left(\frac{(12 \text{ in})^3}{(1 \text{ ft})^3} \right) \left(\frac{(2.54 \text{ cm})^3}{(1 \text{ in})^3} \right) \left(\frac{(10^{-2} \text{ m})^3}{(1 \text{ cm})^3} \right) = 2.9195 \times 10^1 \text{ m}^3$$

$$(2.9195 \times 10^1 \text{ m}^3) \left(\frac{50. \mu\text{g}}{1 \text{ m}^3} \right) \left(\frac{10^{-6} \text{ g}}{1 \mu\text{g}} \right) = 1.460 \times 10^{-3} = 1.5 \times 10^{-3} \text{ g for all the microparticles in the room}$$

$$\begin{aligned} \text{Number of microparticles in room} &= 1.460 \times 10^{-3} \text{ g} \left(\frac{1 \text{ microparticle}}{2.045 \times 10^{-11} \text{ g}} \right) \\ &= 7.1394 \times 10^7 = \mathbf{7.1 \times 10^7 \text{ microparticles in the room}} \end{aligned}$$

$$\text{Mass} = 0.500 \text{ L} \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) \left(\frac{50 \mu\text{g}}{\text{m}^3} \right) \left(\frac{10^{-6} \text{ g}}{1 \mu\text{g}} \right) = 2.5 \times 10^{-8} \text{ g in one 0.500-L breath}$$

$$\begin{aligned} \text{Number of microparticles in one breath} &= 2.5 \times 10^{-8} \text{ g} \left(\frac{1 \text{ microparticle}}{2.045 \times 10^{-11} \text{ g}} \right) \\ &= 1.222 \times 10^3 = \mathbf{1.2 \times 10^3 \text{ microparticles in a breath}} \end{aligned}$$

- 1.73 Plan: Determine the total mass of the Earth's crust in metric tons (t) by combining the depth, surface area and density along with conversions from the inside back cover. The mass of each individual element comes from the concentration of that element multiplied by the mass of the crust.

Solution:

$$(35 \text{ km})(5.10 \times 10^8 \text{ km}^2) \left(\frac{(1000 \text{ m})^3}{(1 \text{ km})^3} \right) \left(\frac{(1 \text{ cm})^3}{(0.01 \text{ m})^3} \right) \left(\frac{2.8 \text{ g}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) \left(\frac{1 \text{ t}}{1000 \text{ kg}} \right) = 4.998 \times 10^{19} \text{ t}$$

$$(4.998 \times 10^{19} \text{ t})(4.55 \times 10^5 \text{ g Oxygen / t}) = 2.2741 \times 10^{25} = \mathbf{2.3 \times 10^{25} \text{ g Oxygen}}$$

$$(4.998 \times 10^{19} \text{ t})(2.72 \times 10^5 \text{ g Silicon / t}) = 1.3595 \times 10^{25} = \mathbf{1.4 \times 10^{25} \text{ g Silicon}}$$

$$(4.998 \times 10^{19} \text{ t})(1 \times 10^{-4} \text{ g Ruthenium / t}) = 4.998 \times 10^{15} = \mathbf{5 \times 10^{15} \text{ g Ruthenium (and Rhodium)}}$$

- 1.75 Plan: In visualizing the problem, the two scales can be set next to each other.

Solution:

There are 50 divisions between the freezing point and boiling point of benzene on the °X scale and 74.6 divisions

$$(80.1^\circ\text{C} - 5.5^\circ\text{C}) \text{ on the } ^\circ\text{C} \text{ scale. So } ^\circ\text{X} = \left(\frac{50^\circ\text{X}}{74.6^\circ\text{C}} \right) ^\circ\text{C}$$

This does not account for the offset of 5.5 divisions in the °C scale from the zero point on the °X scale.

$$\text{So } ^\circ\text{X} = \left(\frac{50^\circ\text{X}}{74.6^\circ\text{C}} \right) (^\circ\text{C} - 5.5^\circ\text{C})$$

Check: Plug in 80.1°C and see if result agrees with expected value of 50°X.

$$\text{So } ^\circ\text{X} = \left(\frac{50^\circ\text{X}}{74.6^\circ\text{C}} \right) (80.1^\circ\text{C} - 5.5^\circ\text{C}) = 50^\circ\text{X}$$

Use this formula to find the freezing and boiling points of water on the °X scale.

$$\text{FP}_{\text{water}} ^\circ\text{X} = \left(\frac{50^\circ\text{X}}{74.6^\circ\text{C}} \right) (0.00^\circ\text{C} - 5.5^\circ\text{C}) = \mathbf{-3.7^\circ\text{X}}$$

$$\text{BP}_{\text{water}} ^\circ\text{X} = \left(\frac{50^\circ\text{X}}{74.6^\circ\text{C}} \right) (100.0^\circ\text{C} - 5.5^\circ\text{C}) = \mathbf{63.3^\circ\text{X}}$$

Chapter 2 The Components of Matter

FOLLOW-UP PROBLEMS

- 2.1 Plan: The mass fraction of uranium in pitchblende was determined in the problem as $(71.4/84.2 = 0.84798)$. The remainder of the sample must be oxygen $(1.00000 - 0.84798 = 0.15202)$. The mass fraction of the uranium will be used to determine the total mass of pitchblende. The total mass of pitchblende and the mass fraction of oxygen may then be used to determine the mass of oxygen.

Solution:

$$\text{Mass of pitchblende} = 2.3 \text{ t Uranium} \left(\frac{1.00 \text{ t pitchblende}}{0.84798 \text{ t uranium}} \right) = 2.7123 = 2.7 \text{ t pitchblende}$$

$$\text{Mass of oxygen} = 2.7123 \text{ t Pitchblende} \left(\frac{0.15202 \text{ t oxygen}}{1.00 \text{ t pitchblende}} \right) = 0.4123 = \mathbf{0.41 \text{ t oxygen}}$$

Check: Adding the amount of oxygen calculated to the mass of uranium gives the calculated 2.7 t of pitchblende.

- 2.2 Plan: The subscript (Atomic Number = Z) gives the number of protons, and for an atom, the number of electrons. The Atomic Number identifies the element. The superscript gives the mass number (A) which is the total of the protons plus neutrons. The number of neutrons is simply the Mass Number minus the Atomic Number ($A - Z$).

Solution:

a) $Z = 5$ and $A = 11$, there are 5 p^+ and 5 e^- and $11 - 5 = 6$ n^0 Atomic number = 5 = **B**.

b) $Z = 20$ and $A = 41$, there are 20 p^+ and 20 e^- and $41 - 20 = 21$ n^0 Atomic number = 20 = **Ca**.

c) $Z = 53$ and $A = 131$, there are 53 p^+ and 53 e^- and $131 - 53 = 78$ n^0 Atomic number = 53 = **I**.

- 2.3 Plan: To find the percent abundance of each B isotope, let x equal the fractional abundance of ^{10}B and $(1 - x)$ equal the fractional abundance of ^{11}B . Remember that atomic mass = isotopic mass of ^{10}B x fractional abundance + (isotopic mass of ^{11}B x fractional abundance).

Solution:

Atomic Mass = (^{10}B mass) (fractional abundance of ^{10}B) + (^{11}B mass) (fractional abundance of ^{11}B)

Amount of ^{10}B + Amount $^{11}\text{B} = 1$ (setting $^{10}\text{B} = x$ gives $^{11}\text{B} = 1 - x$)

$$10.81 \text{ amu} = (10.0129 \text{ amu})(x) + (11.0093 \text{ amu})(1 - x)$$

$$10.81 \text{ amu} = 11.0093 - 11.0093x + 10.0129x$$

$$10.81 \text{ amu} = 11.0093 - 0.9964x$$

$$-0.1993 = -0.9964x$$

$$x = 0.20; \quad 1 - x = 0.80 \quad (10.81 - 11.0093 \text{ limits the answer to 2 significant figures})$$

Fraction x 100% = percent abundance.

% abundance of $^{10}\text{B} = \mathbf{20.0\%}$; % abundance of $^{11}\text{B} = \mathbf{80.0\%}$

Check: The atomic mass of B is 10.81 (close to the mass of ^{11}B , thus the sample must be mostly this isotope.)

- 2.4 Plan: Locate these elements on the periodic table and predict what ions they will form. For A-group cations (metals), ion charge = group number; for anions (nonmetals), ion charge = group number minus 8. Or, relate the element's position to the nearest noble gas. Elements after a noble gas lose electrons to become positive ions, while those before a noble gas gain electrons to become negative ions.

Solution:

a) $_{16}\text{S}^{2-}$ [Group 6A(16); $6 - 8 = -2$]; sulfur needs to gain 2 electrons to match the number of electrons in $_{18}\text{Ar}$.

b) $_{37}\text{Rb}^+$ [Group 1A(1)]; rubidium needs to lose 1 electron to match the number of electrons in $_{36}\text{Kr}$.

c) $_{56}\text{Ba}^{2+}$ [Group 2A(2)]; barium needs to lose 2 electrons to match the number of electrons in $_{54}\text{Xe}$.

- 2.5 Plan: When dealing with ionic binary compounds, the first name belongs to the metal and the second name belongs to the nonmetal. If there is any doubt, refer to the periodic table. The metal name is unchanged, while the nonmetal has an -ide suffix added to the nonmetal root.
Solution:
 a) **Zinc** is in **Group 2B(12)** and **oxygen**, from oxide, is in **Group 6A(16)**.
 b) **Silver** is in **Group 1B(11)** and **bromine**, from bromide, is in **Group 7A(17)**.
 c) **Lithium** is in **Group 1A(1)** and **chlorine**, from chloride, is in **Group 7A(17)**.
 d) **Aluminum** is in **Group 3A(13)** and **sulfur**, from sulfide, is in **Group 6A(16)**.
- 2.6 Plan: Use the charges to predict the lowest ratio leading to a neutral compound.
Solution:
 a) Zinc should form Zn^{2+} and oxygen should form O^{2-} , these will combine to give **ZnO**. The charges cancel ($+2 -2 = 0$), so this is an acceptable formula.
 b) Silver should form Ag^+ and bromine should form Br^- , these will combine to give **AgBr**. The charges cancel ($+1 -1 = 0$), so this is an acceptable formula.
 c) Lithium should form Li^+ and chlorine should form Cl^- , these will combine to give **LiCl**. The charges cancel ($+1 -1 = 0$), so this is an acceptable formula.
 d) Aluminum should form Al^{3+} and sulfur should form S^{2-} , to produce a neutral combination the formula is **Al_2S_3** . This way the charges will cancel [$2(+3) + 3(-2) = 0$], so this is an acceptable formula.
- 2.7 Plan: Determine the names or symbols of each of the species present. Then combine the pieces to produce a name or formula. The metal or positive ions always go first. Review the rules for nomenclature covered in the chapter. For metals like many transition metals, that can form more than one ion each with a different charge, the ionic charge of the metal ion is indicated by a Roman numeral within parentheses immediately following the metal's name.
Solution:
 a) The Roman numerals mean that the lead is Pb^{4+} and oxygen produces the usual O^{2-} . The neutral combination is [$+4 + 2(-2) = 0$], so the formula is **PbO_2** .
 b) Sulfide, like oxide, is -2 . This is split between two copper ions, each of which must be $+1$. This is one of the two common charges for copper ions. The $+1$ charge on the copper is indicated with a Roman numeral. This gives the name **copper(I) sulfide** (common name = cuprous sulfide).
 c) Bromide, like other elements in the same column of the periodic table, forms a -1 ion. Two of these ions requires a total of $+2$ to cancel them out. Thus, the iron must be $+2$ (indicated with a Roman numeral). This is one of the two common charges on iron ions. This gives the name **iron(II) bromide** (or ferrous bromide).
 d) The mercuric ion is Hg^{2+} , and two -1 ions (Cl^-) are needed to cancel the charge. This gives the formula **HgCl_2** .
- 2.8 Plan: Determine the names or symbols of each of the species present. Then combine the pieces to produce a name or formula. The metal or positive ions always go first.
Solution:
 a) The cupric ion, Cu^{2+} , requires two nitrate ions, NO_3^- , to cancel the charges. Trihydrate means three water molecules. These combine to give: **$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$** .
 b) The zinc ion, Zn^{2+} , requires two hydroxide ions, OH^- , to cancel the charges. These combine to give: **$\text{Zn}(\text{OH})_2$** .
 c) Lithium only forms the Li^+ ion, so Roman numerals are unnecessary. The cyanide ion, CN^- , has the appropriate charge. These combine to give **lithium cyanide**.
- 2.9 Plan: Determine the names or symbols of each of the species present. Then combine the pieces to produce a name or formula. The metal or positive ions always go first. Make corrections accordingly.
Solution:
 a) The ammonium ion is NH_4^+ and the phosphate ion is PO_4^{3-} . To give a neutral compound they should combine [$3(+1) + (-3) = 0$] to give the correct formula **$(\text{NH}_4)_3\text{PO}_4$** .
 b) Aluminum gives Al^{3+} and the hydroxide ion is OH^- . To give a neutral compound they should combine [$+3 + 3(-1) = 0$] to give the correct formula **$\text{Al}(\text{OH})_3$** . Parentheses are required around the polyatomic ion.
 c) Manganese is Mn, and Mg, in the formula, is magnesium. Magnesium only forms the Mg^{2+} ion, so Roman numerals are unnecessary. The other ion is HCO_3^- , which is called the hydrogen carbonate (or bicarbonate) ion. The correct name is **magnesium hydrogen carbonate** or **magnesium bicarbonate**.

- d) Either use the “-ic” suffix or the “(III)” but not both. *Nitride* is N^{3-} , and *nitrate* is NO_3^- . This gives the correct name: **chromium(III) nitrate** (the common name is chromic nitrate).
- e) Cadmium is Cd, and Ca, in the formula, is calcium. *Nitrate* is NO_3^- , and *nitrite* is NO_2^- . The correct name is **calcium nitrite**.

- 2.10 **Plan:** Determine the names or symbols of each of the species present. The number of hydrogen atoms equals the charge on the anion. Then combine the pieces to produce a name or formula. The hydrogen always goes first. For the oxoanions, the -ate suffix changes to -ic acid and the -ite suffix changes to -ous acid.

Solution:

- a) Chloric acid is derived from the chlorate ion, ClO_3^- . The -1 charge on the ion requires one hydrogen. These combine to give the formula: **HClO_3** .
- b) As a binary acid, HF requires a “hydro-” prefix and an “ic” suffix on the “fluor” root. These combine to give the name: **hydrofluoric acid**.
- c) Acetic acid is derived from the acetate ion, which may be written as CH_3COO^- or as $\text{C}_2\text{H}_3\text{O}_2^-$. The -1 charge means that one H is needed. These combine to give the formula: **CH_3COOH** or **$\text{HC}_2\text{H}_3\text{O}_2$** .
- d) Sulfurous acid is derived from the sulfite ion, SO_3^{2-} . The -2 charge on the ion requires two hydrogen atoms. These combine to give the formula: **H_2SO_3** .
- e) HBrO is an oxoacid containing the BrO^- ion (hypobromite ion). To name the acid, the “-ite” must be replaced with “-ous.” This gives the name: **hypobromous acid**.

- 2.11 **Plan:** Determine the names or symbols of each of the species present. The number of atoms leads to prefixes, and the prefixes lead to the number of that type of atom.

Solution:

- a) **Sulfur trioxide** — one sulfur and three (tri) oxygens, as oxide, are present. b) **Silicon dioxide** — one silicon and two (di) oxygens, as oxide, are present. c) **N_2O** Nitrogen has the prefix “di” = 2, and oxygen has the prefix “mono” = 1 (understood in the formula). d) **SeF_6** Selenium has no prefix (understood as = 1), and the fluoride has the prefix “hexa” = 6.

- 2.12 **Plan:** Determine the names or symbols of each of the species present. For compounds between nonmetals, the number of atoms of each type is indicated by a prefix.

Solution:

- a) Suffixes are not used in the common names of the nonmetal listed first in the formula. Sulfur does not qualify for the use of a suffix. Chlorine correctly has an “ide” suffix. There are two of each nonmetal atom, so both names require a “di” prefix. This gives the name: **disulfur dichloride**.
- b) Both elements are nonmetals, and there is more than one nitrogen. Two nitrogens require a “di” prefix; the one oxygen could use an optional “mono” prefix. These combine to give the name **dinitrogen monoxide** or **dinitrogen oxide**.
- c) The heavier Br should be named first. The three chlorides are correctly named. The correct name is **bromine trichloride**.

- 2.13 **Plan:** First, write a formula to match the name. Next, multiply the number of each type of atom by the atomic mass of that atom. Sum all the masses to get an overall mass.

Solution:

- a) The peroxide ion is O_2^{2-} , which requires two hydrogen atoms to cancel the charge: **H_2O_2** .
Molecular mass = $(2 \times 1.008 \text{ amu}) + (2 \times 16.00 \text{ amu}) = 34.016 = \mathbf{34.02 \text{ amu}}$.
- b) A Cs^+ ion requires one Cl^- ion to give: **CsCl** ; formula mass = $132.9 \text{ amu} + 35.45 \text{ amu} = 168.35 = \mathbf{168.4 \text{ amu}}$.
- c) Sulfuric acid contains the sulfate ion, SO_4^{2-} , which requires two hydrogen atoms to cancel the charge: **H_2SO_4** ; molecular mass = $(2 \times 1.008 \text{ amu}) + 32.07 \text{ amu} + (4 \times 16.00 \text{ amu}) = 98.086 = \mathbf{98.09 \text{ amu}}$.
- d) The sulfate ion, SO_4^{2-} , requires two $+1$ potassium ions, K^+ , to give **K_2SO_4** ; formula mass = $(2 \times 39.10 \text{ amu}) + 32.07 \text{ amu} + (4 \times 16.00 \text{ amu}) = \mathbf{174.27 \text{ amu}}$.

- 2.14 Plan: Since the compounds only contain two elements, finding the formulas involve simply counting each type of atom and developing a ratio.
Solution:
a) There are two brown atoms (sodium) for every red (oxygen). The compound contains a metal with a nonmetal. Thus, the compound is **sodium oxide**, with the formula Na_2O . The formula mass is twice the mass of sodium plus the mass of oxygen: $2 (22.99 \text{ amu}) + (16.00 \text{ amu}) = \mathbf{61.98 \text{ amu}}$.
b) There is one blue (nitrogen) and two reds (oxygen) in each molecule. The compound only contains nonmetals. Thus, the compound is **nitrogen dioxide**, with the formula NO_2 . The molecular mass is the mass of nitrogen plus twice the mass of oxygen: $(14.01 \text{ amu}) + 2 (16.00 \text{ amu}) = \mathbf{46.01 \text{ amu}}$.

END-OF-CHAPTER PROBLEMS

- 2.1 Plan: Refer to the definitions of an element and a compound.
Solution:
Unlike compounds, elements cannot be broken down by chemical changes into simpler materials. Compounds contain different types of atoms; there is only one type of atom in an element.
- 2.4 Plan: Review the definitions of elements, compounds, and mixtures.
Solution:
a) The presence of more than one element (calcium and chlorine) makes this pure substance a **compound**.
b) There are only atoms from one element, sulfur, so this pure substance is an **element**.
c) The presence of more than one compound makes this a **mixture**.
d) The presence of more than one type of atom means it cannot be an element. The specific, not variable, arrangement means it is a **compound**.
- 2.6 Plan: Restate the three laws in your own words.
Solution:
a) The law of mass conservation applies to all substances — **elements, compounds, and mixtures**. Matter can neither be created nor destroyed, whether it is an element, compound, or mixture.
b) The law of definite composition applies to **compounds** only, because it refers to a constant, or definite, composition of elements within a compound.
c) The law of multiple proportions applies to **compounds** only, because it refers to the combination of elements to form compounds.
- 2.7 Plan: Review the three laws: Law of Mass Conservation, Law of Definite Composition, and Law of Multiple Proportions.
Solution:
a) Law of Definite Composition — The compound potassium chloride, KCl , is composed of the same elements and same fraction by mass, regardless of its source (Chile or Poland).
b) Law of Mass Conservation — The mass of the substance inside the flashbulb did not change during the chemical reaction (formation of magnesium oxide from magnesium and oxygen).
c) Law of Multiple Proportions — Two elements, O and As, can combine to form two different compounds that have different proportions of As present.
- 2.8 Plan: Review the definition of percent by mass.
Solution:
a) **No**, the mass percent of each element in a compound is fixed. The percentage of Na in the compound NaCl is 39.34% ($22.99 \text{ amu} / 58.44 \text{ amu}$), whether the sample is 0.5000 g or 50.00 g.
b) **Yes**, the mass of each element in a compound depends on the mass of the compound. A 0.5000 g sample of NaCl contains 0.1967 g of Na (39.34% of 0.5000 g), whereas a 50.00 g sample of NaCl contains 19.67 g of Na (39.34% of 50.00 g).
c) **No**, the composition of a compound is determined by the elements used, not their amounts. If too much of one element is used, the excess will remain as unreacted element when the reaction is over.

- 2.9 Plan: Review the mass laws: Law of Mass Conservation, Law of Definite Composition, and Law of Multiple Proportions.
Solution:
 Experiments 1 and 2 together demonstrate the Law of Definite Composition. When 3.25 times the amount of blue compound in experiment 1 is used in experiment 2, then 3.25 times the amount of products were made and the relative amounts of each product are the same in both experiments. In experiment 1, the ratio of white compound to colorless gas is 0.64:0.36 or 1.78:1 and in experiment 2, the ratio is 2.08:1.17 or 1.78:1. The two experiments also demonstrate the Law of Conservation of Mass since the total mass before reaction equals the total mass after reaction.
- 2.11 Plan: The difference between the mass of fluorite and the mass of calcium gives the mass of fluorine. The masses of calcium, fluorine, and fluorite combine to give the other values.
Solution:
 Fluorite is a mineral containing only calcium and fluorine.
 a) Mass of fluorine = mass of fluorite – mass of calcium = 2.76 g – 1.42 g = **1.34 g F**
 b) To find the mass fraction of each element, divide the mass of each element by the mass of fluorite:

$$\text{Mass fraction of Ca} = \frac{1.42 \text{ g Ca}}{2.76 \text{ g fluorite}} = 0.51449 = \mathbf{0.514}$$

$$\text{Mass fraction of F} = \frac{1.34 \text{ g F}}{2.76 \text{ g fluorite}} = 0.48551 = \mathbf{0.486}$$
 c) To find the mass percent of each element, multiply the mass fraction by 100:
 Mass % Ca = (0.514) (100) = 51.449 = **51.4%**
 Mass % F = (0.486) (100) = 48.551 = **48.6%**
- 2.13 Plan: Since copper is a metal and sulfur is a nonmetal, the sample contains 88.39 g Cu and 44.61 g S. Calculate the mass fraction of each element in the sample.
Solution:
 Mass of compound = 88.39 g copper + 44.61 g sulfur = 133.00 g compound

$$\text{Mass of copper} = (5264 \text{ kg compound}) \left(\frac{10^3 \text{ g compound}}{1 \text{ kg compound}} \right) \left(\frac{88.39 \text{ g copper}}{133.00 \text{ g compound}} \right) = 3.49838 \times 10^6$$

$$= \mathbf{3.498 \times 10^6 \text{ g copper}}$$

$$\text{Mass of sulfur} = (5264 \text{ kg compound}) \left(\frac{10^3 \text{ g compound}}{1 \text{ kg compound}} \right) \left(\frac{44.61 \text{ g sulfur}}{133.00 \text{ g compound}} \right) = 1.76562 \times 10^6$$

$$= \mathbf{1.766 \times 10^6 \text{ g sulfur}}$$
- 2.15 Plan: The law of multiple proportions states that if two elements form two different compounds, the relative amounts of the elements in the two compounds form a whole number ratio. To illustrate the law we must calculate the mass of one element to one gram of the other element for each compound and then compare this mass for the two compounds. The law states that the ratio of the two masses should be a small whole number ratio such as 1:2, 3:2, 4:3, etc.
Solution:
 Compound 1: $\frac{47.5 \text{ mass \% S}}{52.5 \text{ mass \% Cl}} = 0.90476 = 0.904$
 Compound 2: $\frac{31.1 \text{ mass \% S}}{68.9 \text{ mass \% Cl}} = 0.451379 = 0.451$
 Ratio: $\frac{0.904}{0.451} = 2.0044 = 2.00 / 1.00$
 Thus, the ratio of the mass of sulfur per gram of chlorine in the two compounds is a small whole number ratio of 2 to 1, which agrees with the law of multiple proportions.

- 2.18 Plan: Determine the mass percent of sulfur in each sample by dividing the grams of sulfur in the sample by the total mass of the sample. The coal type with the smallest mass percent of sulfur has the smallest environmental impact.

Solution:

$$\text{Mass \% in Coal A} = \left(\frac{11.3 \text{ g sulfur}}{378 \text{ g sample}} \right) (100 \%) = 2.9894 = 2.99\% \text{ S (by mass)}$$

$$\text{Mass \% in Coal B} = \left(\frac{19.0 \text{ g sulfur}}{495 \text{ g sample}} \right) (100 \%) = 3.8384 = 3.84\% \text{ S (by mass)}$$

$$\text{Mass \% in Coal C} = \left(\frac{20.6 \text{ g sulfur}}{675 \text{ g sample}} \right) (100 \%) = 3.0519 = 3.05\% \text{ S (by mass)}$$

Coal A has the smallest environmental impact.

- 2.19 Plan: This question is based on the Law of Definite Composition. If the compound contains the same types of atoms, they should combine in the same way to give the same mass percentages of each of the elements.

Solution:

Potassium nitrate is a compound composed of three elements — potassium, nitrogen, and oxygen — in a specific ratio. If the ratio of elements changed, then the compound would be different, for example to potassium nitrite, with different physical and chemical properties. Dalton postulated that atoms of an element are identical, regardless of whether that element is found in India or Italy. Dalton also postulated that compounds result from the chemical combination of specific ratios of different elements. Thus, Dalton's theory explains why potassium nitrate, a compound comprised of three different elements in a specific ratio, has the same chemical composition regardless of where it is mined or how it is synthesized.

- 2.20 Plan: Review the discussion of the experiments in this chapter.

Solution:

- a) Millikan determined the minimum *charge* on an oil drop and that the minimum charge was equal to the charge on one electron. Using Thomson's value for the *mass-to-charge ratio* of the electron and the determined value for the charge on one electron, Millikan calculated the mass of an electron (charge/(charge/mass)) to be

$$9.109 \times 10^{-28} \text{ g.}$$

- b) The value $-1.602 \times 10^{-19} \text{ C}$ is a common factor, determined as follows:

$$-3.204 \times 10^{-19} \text{ C} / -1.602 \times 10^{-19} \text{ C} = 2.000$$

$$-4.806 \times 10^{-19} \text{ C} / -1.602 \times 10^{-19} \text{ C} = 3.000$$

$$-8.010 \times 10^{-19} \text{ C} / -1.602 \times 10^{-19} \text{ C} = 5.000$$

$$-1.442 \times 10^{-18} \text{ C} / -1.602 \times 10^{-19} \text{ C} = 9.000$$

- 2.23 Plan: The superscript is the mass number. Consult the periodic table to get the atomic number (the number of protons). The mass number – the number of protons = the number of neutrons. For atoms, the number of protons and electrons are equal.

Solution:

Isotope	Mass Number	# of Protons	# of Neutrons	# of Electrons
^{36}Ar	36	18	18	18
^{38}Ar	38	18	20	18
^{40}Ar	40	18	22	18

- 2.25 Plan: The superscript is the mass number (A) and the subscript is the atomic number (Z, number of protons). The mass number – the number of protons = the number of neutrons. For atoms, the number of protons = the number of electrons.

Solution:

a) $^{16}_8\text{O}$ and $^{17}_8\text{O}$ have the same number of protons and electrons (8), but different numbers of neutrons.

$^{16}_8\text{O}$ and $^{17}_8\text{O}$ are isotopes of oxygen, and $^{16}_8\text{O}$ has $16 - 8 = 8$ neutrons whereas $^{17}_8\text{O}$ has $17 - 8 = 9$ neutrons. **Same Z value**

b) $^{40}_{18}\text{Ar}$ and $^{41}_{19}\text{K}$ have the same number of neutrons ($\text{Ar}: 40 - 18 = 22$; $\text{K}: 41 - 19 = 22$) but different numbers of protons and electrons ($\text{Ar} = 18$ protons and 18 electrons; $\text{K} = 19$ protons and 19 electrons). **Same N value**

c) $^{60}_{27}\text{Co}$ and $^{60}_{28}\text{Ni}$ have different numbers of protons, neutrons, and electrons. Co : 27 protons, 27 electrons and $60 - 27 = 33$ neutrons; Ni : 28 protons, 28 electrons and $60 - 28 = 32$ neutrons. However, both have a mass number of 60. **Same A value**

- 2.27 Plan: Combine the particles in the nucleus (protons + neutrons) to give the mass number (superscript, A). The number of protons gives the atomic number (subscript, Z) and identifies the element.

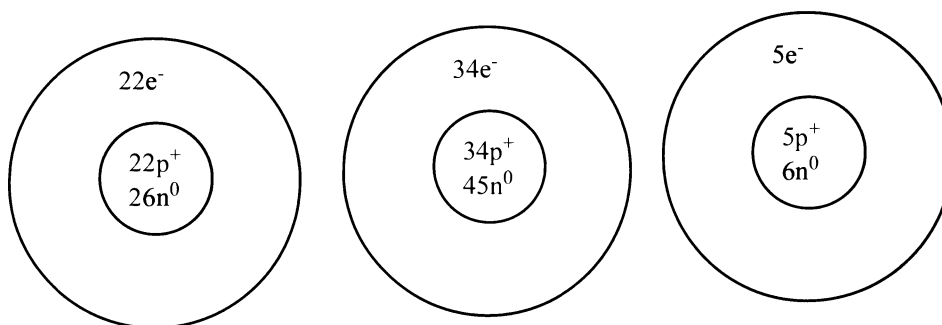
Solution:

a) $^{38}_{18}\text{Ar}$ b) $^{55}_{25}\text{Mn}$ c) $^{109}_{47}\text{Ag}$

- 2.29 Plan: The subscript (Z) is the atomic number and gives the number of protons and the number of electrons. The superscript (A) is the mass number and represents the number of protons + the number of neutrons. Therefore, mass number – number of protons = number of neutrons.

Solution:

a) $^{48}_{22}\text{Ti}$ b) $^{79}_{34}\text{Se}$ c) $^{11}_5\text{B}$
 $48 - 22 = 26$ $79 - 34 = 45$ $11 - 5 = 6$



- 2.31 Plan: To calculate the atomic mass of an element, take a weighted average based on the natural abundance of the isotopes: (isotopic mass of isotope 1 x fractional abundance) + (isotopic mass of isotope 2 x fractional abundance)

Solution:

$$\text{Atomic mass of gallium} = (68.9256 \text{ amu})\left(\frac{60.11\%}{100\%}\right) + (70.9247 \text{ amu})\left(\frac{39.89\%}{100\%}\right) = 69.7230 = \mathbf{69.72 \text{ amu}}$$

- 2.33 Plan: To find the percent abundance of each Cl isotope, let x equal the fractional abundance of ^{35}Cl and $(1 - x)$ equal the fractional abundance of ^{37}Cl . Remember that atomic mass = isotopic mass of ^{35}Cl x fractional abundance + (isotopic mass of ^{37}Cl x fractional abundance).

Solution:

Atomic mass of Cl = 35.4527 amu

$$35.4527 = 34.9689x + 36.9659(1 - x)$$

$$35.4527 = 34.9689x + 36.9659 - 36.9659x$$

$$35.4527 = 36.9659 - 1.9970x$$

$$1.9970x = 1.5132$$

$$x = 0.75774 \text{ and } 1 - x = 0.24226$$

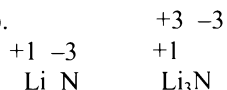
$$\% \text{ abundance } ^{35}\text{Cl} = \mathbf{75.774\%} \quad \% \text{ abundance } ^{37}\text{Cl} = \mathbf{24.226\%}$$

- 2.35 Plan: Review the section in the chapter on the periodic table.
Solution:
 a) In the modern periodic table, the elements are arranged in order of increasing atomic **number**.
 b) Elements in a **column or group** (or family) have similar chemical properties, not those in the same period or row.
 c) Elements can be classified as **metals**, metalloids, or nonmetals.
- 2.38 Plan: Locate each element on the periodic table. The Z value is the atomic number of the element. Metals are to the left of the “staircase”, nonmetals are to the right of the “staircase” and the metalloids are the elements that lie along the “staircase” line.
Solution:
 a) Germanium Ge 4A(14) metalloid
 b) Sulfur S 6A(16) nonmetal
 c) Helium He 8A(18) nonmetal
 d) Lithium Li 1A(1) metal
 e) Molybdenum Mo 6B(6) metal
- 2.40 Plan: Review the section in the chapter on the periodic table. Remember that alkaline earth metals are in Group 2A(2) and the halogens are in Group 7A(17); periods are horizontal rows.
Solution:
 a) The symbol and atomic number of the heaviest alkaline earth metal are **Ra** and **88**.
 b) The symbol and atomic number of the lightest metalloid in Group 5A(15) are **As** and **33**.
 c) The symbol and atomic mass of the coinage metal whose atoms have the fewest electrons are **Cu** and **63.55 amu**.
 d) The symbol and atomic mass of the halogen in Period 4 are **Br** and **79.90 amu**.
- 2.42 Plan: Review the section of the chapter on the formation of ionic compounds.
Solution:
 These atoms will form **ionic** bonds, in which one or more electrons are transferred from the metal atom to the nonmetal atom to form a cation and an anion, respectively. The oppositely charged ions attract, forming the ionic bond.
- 2.44 Plan: Assign charges to each of the ions. Since the sizes are similar, there are no differences due to the sizes.
Solution:
 Coulomb’s law states the energy of attraction in an ionic bond is directly proportional to the *product of charges* and inversely proportional to the *distance between charges*. The *product of charges* in MgO ($+2 \times -2 = -4$) is greater than the *product of charges* in LiF ($+1 \times -1 = -1$). Thus, MgO has stronger ionic bonding.
- 2.47 Plan: Locate these elements on the periodic table and predict what ions they will form. For A-group cations (metals), ion charge = group number; for anions (nonmetals), ion charge = group number minus 8.
Solution:
 Potassium (K) is in Group 1A(1) and forms the **K⁺** ion. Iodine (I) is in Group 7A(17) and forms the **I⁻** ion ($7 - 8 = -1$).
- 2.49 Plan: Use the number of protons (atomic number) to identify the element. Add the number of protons and neutrons together to get the mass number. Locate the element on the periodic table and assign its group and period number.
Solution:
 a) Oxygen (atomic number = 8) mass number = $8p + 9n = 17$ Group 6A(16) Period 2
 b) Fluorine (atomic number = 9) mass number = $9p + 10n = 19$ Group 7A(17) Period 2
 c) Calcium (atomic number = 20) mass number = $20p + 20n = 40$ Group 2A(2) Period 4

- 2.51 Plan: Determine the charges of the ions based on their position on the periodic table. Next, determine the ratio of the charges to get the ratio of the ions.
Solution:
 Lithium [Group 1A(1)] forms the Li^+ ion; oxygen [Group 6A(16)] forms the O^{2-} ion ($6 - 8 = -2$). The ionic compound that forms from the combination of these two ions must be electrically neutral, so two Li^+ ions combine with one O^{2-} ion to form the compound Li_2O . There are twice as many Li^+ ions as O^{2-} ions in a sample of Li_2O .
- $$\text{Number of } \text{O}^{2-} \text{ ions} = (5.3 \times 10^{20} \text{ Li}^+ \text{ ions}) \left(\frac{1 \text{ O}^{2-} \text{ ion}}{2 \text{ Li}^+ \text{ ions}} \right) = 2.65 \times 10^{20} = \mathbf{2.6 \times 10^{20} \text{ O}^{2-} \text{ ions}}$$
- 2.53 Plan: The key is the size of the two alkali ions. The charges on the sodium and potassium ions are the same as both are in Group 1A(1), so there will be no difference due to the charge. The chloride ions are the same, so there will be no difference due to the chloride.
Solution:
 Coulomb's law states that the energy of attraction in an ionic bond is directly proportional to the *product of charges* and inversely proportional to the *distance between charges*. (See also problem 2.44.) The *product of the charges* is the same in both compounds because both sodium and potassium ions have a +1 charge. Attraction increases as distance decreases, so the ion with the smaller radius, Na^+ , will form a stronger ionic interaction (**NaCl**).
- 2.55 Plan: Review the definitions of empirical and molecular formulas.
Solution:
 An empirical formula describes the type and **simplest ratio** of the atoms of each element present in a compound whereas a molecular formula describes the type and **actual number** of atoms of each element in a molecule of the compound. The empirical formula and the molecular formula can be the same. For example, the compound formaldehyde has the molecular formula, CH_2O . The carbon, hydrogen, and oxygen atoms are present in the ratio of 1:2:1. The ratio of elements cannot be further reduced, so formaldehyde's empirical formula and molecular formula are the same. Acetic acid has the molecular formula, $\text{C}_2\text{H}_4\text{O}_2$. The carbon, hydrogen, and oxygen atoms are present in the ratio of 2:4:2, which can be reduced to 1:2:1. Therefore, acetic acid's empirical formula is CH_2O , which is different from its molecular formula. Note that the empirical formula does not *uniquely* identify a compound, because acetic acid and formaldehyde share the same empirical formula but are not the same compound.
- 2.56 Plan: Review the concepts of atoms and molecules.
Solution:
 The mixture is similar to the sample of hydrogen peroxide in that both contain 20 billion oxygen atoms and 20 billion hydrogen atoms since both O_2 and H_2O_2 contain 2 oxygen atoms per molecule and both H_2 and H_2O_2 contain 2 hydrogen atoms per molecule. They differ in that they contain different types of molecules: H_2O_2 molecules in the hydrogen peroxide sample and H_2 and O_2 molecules in the mixture. In addition, the mixture contains 20 billion molecules (10 billion H_2 and 10 billion O_2) while the hydrogen peroxide sample contains 10 billion molecules.
- 2.57 Plan: Examine the subscripts and see if there is a common divisor. If one exists, divide all subscripts by this value.
Solution:
 a) To find the empirical formula for N_2H_4 , divide the subscripts by the highest common divisor, 2: N_2H_4 becomes **NH_2**
 b) To find the empirical formula for $\text{C}_6\text{H}_{12}\text{O}_6$, divide the subscripts by the highest common divisor, 6: $\text{C}_6\text{H}_{12}\text{O}_6$ becomes **CH_2O**
- 2.59 Plan: Locate each of the individual elements on the periodic table, and assign charges to each of the ions. For A-group cations (metals), ion charge = group number; for anions (nonmetals), ion charge = group number minus 8. Find the smallest number of each ion that gives a neutral compound.

Solution:

a) Lithium is a metal that forms a +1 (group 1A) ion and nitrogen is a nonmetal that forms a -3 ion (group 5A, $5 - 8 = -3$).



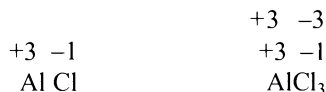
The compound is **Li₃N, lithium nitride**.

b) Oxygen is a nonmetal that forms a -2 ion (group 6A, $6 - 8 = -2$) and strontium is a metal that forms a +2 ion (group 2A).



The compound is **SrO, strontium oxide**.

c) Aluminum is a metal that forms a +3 ion (group 3A) and chlorine is a nonmetal that forms a -1 ion (group 7A, $7 - 8 = -1$).



The compound is **AlCl₃, aluminum chloride**.

- 2.61 Plan: Based on the atomic numbers (the subscripts) locate the elements on the periodic table. Once the atomic numbers are located, identify the element and based on its position, assign a charge. For A-group cations (metals), ion charge = group number; for anions (nonmetals), ion charge = group number minus 8. Find the smallest number of each ion that gives a neutral compound.

Solution:

a) $_{12}\text{L}$ is the element Mg ($Z = 12$). Magnesium [group 2A(2)] forms the Mg^{2+} ion. $_{9}\text{M}$ is the element F ($Z = 9$). Fluorine [group 7A(17)] forms the F^{-} ion ($7 - 8 = -1$). The compound formed by the combination of these two elements is **MgF₂, magnesium fluoride**.

b) $_{11}\text{L}$ is the element Na ($Z = 11$). Sodium [group 1A(1)] forms the Na^{+} ion. $_{16}\text{M}$ is the element S ($Z = 16$). Sulfur [group 6A(16)] will form the S^{2-} ion ($6 - 8 = -2$). The compound formed by the combination of these two elements is **Na₂S, sodium sulfide**.

c) $_{17}\text{L}$ is the element Cl ($Z = 17$). Chlorine [group 7A(17)] forms the Cl^{-} ion ($7 - 8 = -1$). $_{38}\text{M}$ is the element Sr ($Z = 38$). Strontium [group 2A(2)] forms the Sr^{2+} ion. The compound formed by the combination of these two elements is **SrCl₂, strontium chloride**.

- 2.63 Plan: Review the rules for nomenclature covered in the chapter. For metals, like many transition metals, that can form more than one ion each with a different charge, the ionic charge of the metal ion is indicated by a Roman numeral within parentheses immediately following the metal's name.

Solution:

a) Tin (IV) chloride = **SnCl₄** The (IV) indicates that the metal ion is Sn^{4+} which requires 4 Cl^{-} ions for a neutral compound.

b) FeBr_3 = **iron(III) bromide** (common name is ferric bromide); the charge on the iron ion is +3 to match the -3 charge of 3 Br^{-} ions. The +3 charge of the Fe is indicated by (III)



c) cuprous bromide = **CuBr** (cuprous is +1 copper ion, cupric is +2 copper ion)



d) Mn_2O_3 = **manganese(III) oxide** Use (III) to indicate the +3 ionic charge of Mn: Mn_2O_3

- 2.65 Plan: Review the rules for nomenclature covered in the chapter. Compounds must be neutral.

Solution:

a) Barium [Group 2a(2)] forms Ba^{2+} and oxygen [Group 6A(16)] forms O^{2-} ($6 - 8 = -2$) so the neutral compound forms from one barium ion and one oxygen ion. Correct formula is **BaO**.

b) Iron(II) indicates Fe^{2+} and nitrate is NO_3^{-} so the neutral compound forms from one iron(II) ion and two nitrate ions. Correct formula is **Fe(NO₃)₂**.

c) Mn is the symbol for manganese. Mg is the correct symbol for magnesium. Correct formula is **MgS**. Sulfide is the S^{2-} ion and sulfite is the SO_3^{2-} ion.

- 2.67 Plan: Acids donate H^{+} ion to solution, so the acid is a combination of H^{+} and a negatively charged ion. Binary acids (H plus one other nonmetal) are named hydro + nonmetal root + ic acid. Oxoacids (H + an oxoanion) are named by changing the suffix of the oxoanion: -ate becomes -ic acid and -ite becomes -ous acid.

Solution:

a) Hydrogen sulfate is HSO_4^{-} , so its source acid is **H₂SO₄**. Name of acid is **sulfuric acid**.

b) **HIO₃, iodic acid** (IO_3^{-} is the iodate ion)

- c) Cyanide is CN^- ; its source acid is **HCN hydrocyanic acid**.
 d) **H_2S , hydrosulfuric acid**

2.69 **Plan:** This compound is composed of two nonmetals. Rule 1 (“Names and Formulas of Binary Covalent Compounds”) indicates that the element with the lower group number is named first. Greek numerical prefixes are used to indicate the number of atoms of each element in the compound.

Solution:

Disulfur tetrafluoride S_2F_4 di- indicates two S atoms and tetra- indicates four F atoms.

2.71 **Plan:** Break down each formula to the individual elements and count the number of each. The molecular (formula) mass is the sum of the atomic masses of all of the atoms.

Solution:

a) There are **12 atoms of oxygen** in $\text{Al}_2(\text{SO}_4)_3$. The molecular mass is:

Al	=	2(26.98 amu)	=	53.96 amu
S	=	3(32.07 amu)	=	96.21 amu
O	=	12(16.00 amu)	=	192.0 amu

342.2 amu

b) There are **9 atoms of hydrogen** in $(\text{NH}_4)_2\text{HPO}_4$. The molecular mass is:

N	=	2(14.01 amu)	=	28.02 amu
H	=	9(1.008 amu)	=	9.072 amu
P	=	1(30.97 amu)	=	30.97 amu
O	=	4(16.00 amu)	=	64.00 amu

132.06 amu

c) There are **8 atoms of oxygen** in $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$. The molecular mass is:

Cu	=	3(63.55 amu)	=	190.6 amu
O	=	8(16.00 amu)	=	128.0 amu
H	=	2(1.008 amu)	=	2.016 amu
C	=	2(12.01 amu)	=	24.02 amu

344.6 amu

2.73 **Plan:** Review the rules of nomenclature and then assign a name. The molecular (formula) mass is the sum of the atomic masses of all of the atoms.

Solution:

a) **$(\text{NH}_4)_2\text{SO}_4$**

N	=	2(14.01 amu)	=	28.02 amu
H	=	8(1.008 amu)	=	8.064 amu
S	=	1(32.07 amu)	=	32.07 amu
O	=	4(16.00 amu)	=	64.00 amu

132.15 amu

b) **NaH_2PO_4**

Na	=	1(22.99 amu)	=	22.99 amu
H	=	2(1.008 amu)	=	2.016 amu
P	=	1(30.97 amu)	=	30.97 amu
O	=	4(16.00 amu)	=	64.00 amu

119.98 amu

c) **KHCO_3**

K	=	1(39.10 amu)	=	39.10 amu
H	=	1(1.008 amu)	=	1.008 amu
C	=	1(12.01 amu)	=	12.01 amu
O	=	3(16.00 amu)	=	48.00 amu

100.12 amu

- 2.75 Plan: Use the chemical symbols and count the atoms of each type to give a molecular formula. Divide the molecular formula by the largest factor to give the empirical formula. Use the nomenclature rules in the chapter to derive the name. This compound is composed of two nonmetals. Rule 1 ("Names and Formulas of Binary Covalent Compounds") indicates that the element with the lower group number is named first. Greek numerical prefixes are used to indicate the number of atoms of each element in the compound. The molecular (formula) mass is the sum of the atomic masses of all of the atoms.
Solution:
The compound's name is **disulfur dichloride**. (Note: Are you unsure when and when not to use a prefix? If you leave off a prefix, can you definitively identify the compound? The name *sulfur* dichloride would not exclusively identify the molecule in the diagram because sulfur dichloride could be any combination of sulfur atoms with two chlorine atoms. Use prefixes when the name may not uniquely identify a compound.) The empirical formula is $S_{2/2}Cl_{2/2}$ or **SCl**. The molecular mass is $2(32.07 \text{ amu}) + 2(35.45 \text{ amu}) = \mathbf{135.04 \text{ amu}}$.
- 2.77 Plan: Use the chemical symbols and count the atoms of each type to give a molecular formula. Divide the molecular formula by the largest factor to give the empirical formula. Use the nomenclature rules in the chapter to derive the name. This compound is composed of two nonmetals. Rule 1 ("Names and Formulas of Binary Covalent Compounds") indicates that the element with the lower group number is named first. Greek numerical prefixes are used to indicate the number of atoms of each element in the compound. The molecular (formula) mass is the sum of the atomic masses of all of the atoms.
Solution:
a) Formula is **SO₃**. Name is **sulfur trioxide**. (1 S atom and three O atoms)
Molecular mass = $(32.07 \text{ amu}) + 3(16.00 \text{ amu}) = \mathbf{80.07 \text{ amu}}$
b) Formula is **N₂O**. Name is **dinitrogen monoxide**. (2 N atoms and 1 O atom)
Molecular mass = $2(14.01 \text{ amu}) + (16.00 \text{ amu}) = \mathbf{44.02 \text{ amu}}$
- 2.79 Plan: Review the discussion on separations.
Solution:
Separating the components of a mixture requires physical methods only; that is, no chemical changes (no changes in composition) take place and the components maintain their chemical identities and properties throughout. Separating the components of a compound requires a chemical change (change in composition).
- 2.82 Plan: Review the definitions in the chapter.
Solution:
a) Distilled water is a **compound** that consists of H₂O molecules only. How would you classify tap water?
b) Gasoline is a **homogeneous mixture** of hydrocarbon compounds of uniform composition that can be separated by physical means (distillation).
c) Beach sand is a **heterogeneous mixture** of different size particles of minerals and broken bits of shells.
d) Wine is a **homogenous mixture** of water, alcohol, and other compounds that can be separated by physical means (distillation).
e) Air is a **homogeneous mixture** of different gases, mainly N₂, O₂, and Ar.
- 2.84 Plan: Use the equation for the volume of a sphere in Part a) to find the volume of the nucleus and the volume of the atom. Calculate the fraction of the atom volume that is occupied by the nucleus. For Part b), calculate the total mass of the two electrons; subtract the electron mass from the mass of the atom to find the mass of the nucleus. Then calculate the fraction of the atom's mass contributed by the mass of the nucleus.
Solution:

$$\text{a) Fraction of volume} = \frac{\text{Volume of Nucleus}}{\text{Volume of Atom}} = \frac{\left(\frac{4}{3}\right)\pi(2.5 \times 10^{-15} \text{ m})^3}{\left(\frac{4}{3}\right)\pi(3.1 \times 10^{-11} \text{ m})^3} = 5.2449 \times 10^{-13} = \mathbf{5.2 \times 10^{-13}}$$

b) Mass of nucleus = mass of atom – mass of electrons
 $= 6.64648 \times 10^{-24} \text{ g} - 2(9.10939 \times 10^{-28} \text{ g}) = 6.64466 \times 10^{-24} \text{ g}$

$$\text{Fraction of mass} = \frac{\text{Mass of Nucleus}}{\text{Mass of Atom}} = \frac{(6.64466 \times 10^{-24} \text{ g})}{(6.64648 \times 10^{-24} \text{ g})} = 0.99972617 = \mathbf{0.999726}$$

As expected, the volume of the nucleus relative to the volume of the atom is small while its relative mass is large.

2.86 Plan: Determine the percent oxygen in each oxide by subtracting the percent nitrogen from 100%. Express the percentage in grams and divide by the atomic mass of the appropriate elements. Then divide by the smaller ratio and convert to a whole number.

Solution:

a) I $(100.00 - 46.69 \text{ N})\% = 53.31\% \text{ O}$
 $(46.69 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 3.3326 \text{ mol N} \quad (53.31 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 3.3319 \text{ mol O}$

$$\frac{3.3326 \text{ mol N}}{3.3319} = 1.0002 \text{ mol N}$$

$$\frac{3.3319 \text{ mol O}}{3.3319} = 1.0000 \text{ mol O}$$

1:1 N:O gives the empirical formula: **NO**

II $(100.00 - 36.85 \text{ N})\% = 63.15\% \text{ O}$
 $(36.85 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 2.6303 \text{ mol N} \quad (63.15 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 3.9469 \text{ mol O}$

$$\frac{2.6303 \text{ mol N}}{2.6303} = 1.0000 \text{ mol N}$$

$$\frac{3.9469 \text{ mol O}}{2.6303} = 1.5001 \text{ mol O}$$

1:1.5 N:O gives the empirical formula: **N₂O₃**

III $(100.00 - 25.94 \text{ N})\% = 74.06\% \text{ O}$
 $(25.94 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 1.8515 \text{ mol N} \quad (74.06 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 4.6288 \text{ mol O}$

$$\frac{1.8515 \text{ mol N}}{1.8515} = 1.0000 \text{ mol N}$$

$$\frac{4.6288 \text{ mol O}}{1.8515} = 2.5000 \text{ mol O}$$

1:2.5 N:O gives the empirical formula: **N₂O₅**

b) I $(1.00 \text{ g N}) \left(\frac{53.31 \text{ g O}}{46.69 \text{ g N}} \right) = 1.1418 = \mathbf{1.14 \text{ g O}}$

II $(1.00 \text{ g N}) \left(\frac{63.15 \text{ g O}}{36.85 \text{ g N}} \right) = 1.7137 = \mathbf{1.71 \text{ g O}}$

III $(1.00 \text{ g N}) \left(\frac{74.06 \text{ g O}}{25.94 \text{ g N}} \right) = 2.8550 = \mathbf{2.86 \text{ g O}}$

- 2.88 Plan: The mass percent comes from determining the kilograms of each substance in a kilogram of seawater. The percent of an ion is simply the mass of that ion divided by the total mass of ions.

Solution:

a) For chloride ions:

$$\text{Mass\% Cl}^- = \left(\frac{18980. \text{mg Cl}^-}{1 \text{ kg seawater}} \right) \left(\frac{0.001 \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) (100\%) = 1.898\% \text{ Cl}^-$$

Cl⁻: 1.898%

Na⁺: 1.056%

SO₄²⁻: 0.265%

Mg²⁺: 0.127%

Ca²⁺: 0.04%

K⁺: 0.038%

HCO₃⁻: 0.014%

Comment: Should the mass percent add up to 100? No, the majority of seawater is H₂O.

b) Total mass of ions in 1 kg of seawater

$$= 18980 \text{ mg} + 10560 \text{ mg} + 2650 \text{ mg} + 1270 \text{ mg} + 400 \text{ mg} + 380 \text{ mg} + 140 \text{ mg} = 34380 \text{ mg}$$

$$\% \text{ Na}^+ = (10560 \text{ mg Na}^+ / 34380 \text{ mg total ions}) (100) = 30.71553 = \mathbf{30.72\%}$$

c) Alkaline earth metal ions are Mg²⁺ and Ca²⁺. Total mass% = 0.127 + 0.04 = 0.167 = **0.17%**

Alkali metal ions are K⁺ and Na⁺. Total mass% = 1.056 + 0.038 = **1.094%**

Total mass percent for alkali metal ions is 6.6 times greater than the total mass percent for alkaline earth metal ions. Sodium ions (alkali metal ions) are dominant in seawater.

d) Anions are Cl⁻, SO₄²⁻, and HCO₃⁻. Total mass% = 1.898 + 0.265 + 0.014 = **2.177%**

Cations are Na⁺, Mg²⁺, Ca²⁺, and K⁺. Total mass% = 1.056 + 0.127 + 0.04 + 0.038 = 1.2610 = **1.26%**

The mass fraction of **anions** is larger than the mass fraction of cations. Is the solution neutral since the mass of anions exceeds the mass of cations? Yes, although the mass is larger the number of positive charges equals the number of negative charges.

- 2.90 Plan: First, count each type of atom present to produce a molecular formula. Divide the molecular formula by the largest divisor to produce the empirical formula. The molecular mass comes from the sum of each of the atomic masses times the number of each atom. The atomic mass times the number of each type of atom divided by the molecular mass times 100 percent gives the mass percent of each element.

Solution:

The molecular formula of succinic acid is **C₄H₆O₄**.

Dividing the subscripts by 2 yields the empirical formula **C₂H₃O₂**.

The molecular mass of succinic acid is 4(12.01 amu) + 6(1.008 amu) + 4(16.00 amu) = 118.088 = **118.09 amu**.

$$\% \text{ C} = \left(\frac{4(12.01 \text{ amu C})}{118.088 \text{ amu}} \right) 100\% = 40.6815 = \mathbf{40.68\% \text{ C}}$$

$$\% \text{ H} = \left(\frac{6(1.008 \text{ amu H})}{118.088 \text{ amu}} \right) 100\% = 5.1216 = \mathbf{5.122\% \text{ H}}$$

$$\% \text{ O} = \left(\frac{4(16.00 \text{ amu O})}{118.088 \text{ amu}} \right) 100\% = 54.1969 = \mathbf{54.20\% \text{ O}}$$

Check: Total = (40.68 + 5.122 + 54.20)% = 100.00% The answer checks.

- 2.92 Plan: To find the formula mass of potassium fluoride, add the atomic masses of potassium and fluorine. Fluorine has only one naturally occurring isotope, so the mass of this isotope equals the atomic mass of fluorine. The atomic mass of potassium is the weighted average of the two isotopic masses: (isotopic mass of isotope 1 x fractional abundance) + (isotopic mass of isotope 2 x fractional abundance)

Solution:

$$\text{Average atomic mass of K} = (38.9637 \text{ amu}) \left(\frac{93.258\%}{100\%} \right) + (40.9618 \text{ amu}) \left(\frac{6.730\%}{100\%} \right) = 39.093 \text{ amu}$$

The formula for potassium fluoride is KF, so its molecular mass is (39.093 + 18.9984) = **58.091 amu**

- 2.94 Plan: First, count each type of atom present to produce a molecular formula. Determine the mass percent of each element. Mass percent = $\left(\frac{\text{total mass of the element}}{\text{molecular mass of TNT}} \right) 100$. The mass of TNT times the mass percent of each element gives the mass of that element.

Solution:

The molecular formula for TNT is $\text{C}_7\text{H}_5\text{O}_6\text{N}_3$. (What is its empirical formula?) The molecular mass of TNT is:

C	=	7(12.01 amu)	=	84.07 amu
H	=	5(1.008 amu)	=	5.040 amu
O	=	6(16.00 amu)	=	96.00 amu
N	=	3(14.01 amu)	=	<u>42.03 amu</u>
				227.14 amu

The mass percent of each element is:

$$\text{C} = \left(\frac{84.07 \text{ amu}}{227.14 \text{ amu}} \right) 100 = 37.01\% \text{ C} \qquad \text{H} = \left(\frac{5.040 \text{ amu}}{227.14 \text{ amu}} \right) 100 = 2.219\% \text{ H}$$

$$\text{O} = \left(\frac{96.00 \text{ amu}}{227.14 \text{ amu}} \right) 100 = 42.26\% \text{ O} \qquad \text{N} = \left(\frac{42.03 \text{ amu}}{227.14 \text{ amu}} \right) 100 = 18.50\% \text{ N}$$

Masses:

$$\text{kg C} = \left(\frac{37.01\% \text{ C}}{100\% \text{ TNT}} \right) (1.00 \text{ lbs}) = \mathbf{0.370 \text{ lb C}}$$

$$\text{kg H} = \left(\frac{2.219\% \text{ H}}{100\% \text{ TNT}} \right) (1.00 \text{ lbs}) = \mathbf{0.0222 \text{ lb H}}$$

$$\text{kg O} = \left(\frac{42.26\% \text{ O}}{100\% \text{ TNT}} \right) (1.00 \text{ lbs}) = \mathbf{0.4223 \text{ lb O}}$$

$$\text{kg N} = \left(\frac{18.50\% \text{ N}}{100\% \text{ TNT}} \right) (1.00 \text{ lbs}) = \mathbf{0.185 \text{ lb N}}$$

Note: The percent ratio yields the mass of a substance in the compound.

- 2.104 Plan: Remember that a change is physical when there has been a change in physical form but not a change in composition. In a chemical change, a substance is converted into a different substance

Solution:

- 1) Initially, all the molecules are present in blue-blue or red-red pairs. After the change, there are no red-red pairs, and there are now red-blue pairs. Changing some of the pairs means there has been a **chemical change**.
- 2) There are two blue-blue pairs and four red-blue pairs both before and after the change, thus no chemical change occurred. The different types of molecules are separated into different boxes. This is a **physical change**.
- 3) The identity of the box contents has changed from pairs to individuals. This requires a **chemical change**.
- 4) The contents have changed from all pairs to all triplets. This is a change in the identity of the particles, thus, this is a **chemical change**.
- 5) There are four red-blue pairs both before and after, thus there has been no change in the identity of the individual units. There has been a **physical change**.

Chapter 3 Stoichiometry of Formulas and Equations

FOLLOW-UP PROBLEMS

- 3.1 a) Plan: The mass of carbon must be changed from mg to g. The molar mass of carbon can then be used to determine the number of moles.

Solution:

$$315 \text{ mg C} \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 2.6228 \times 10^{-2} = \mathbf{2.62 \times 10^{-2} \text{ mol C}}$$

Check: 315 mg is less than a gram, which is less than 1/12 mol of C.

- b) Plan: Avogadro's number is needed to convert the number of atoms to moles. The molar mass of manganese can then be used to determine the number of grams.

Solution:

$$3.22 \times 10^{20} \text{ Mn Atoms} \left(\frac{1 \text{ mol Mn}}{6.022 \times 10^{23} \text{ Mn Atoms}} \right) \left(\frac{54.94 \text{ g Mn}}{1 \text{ mol Mn}} \right) = 2.9377 \times 10^{-2} \\ = \mathbf{2.94 \times 10^{-2} \text{ g Mn}}$$

Check: The exponent, 20, from the Mn atoms is much smaller than that for Avogadro's number, 23, thus the mass is much smaller than the molar mass of Mn.

- 3.2 a) Plan: Avogadro's number is used to change the number of molecules to moles. Moles may be changed to mass using the molar mass. The molar mass of tetraphosphorus decaoxide requires the chemical formula.

Solution:

Tetra = 4, and deca = 10 to give P_4O_{10} .

The molar mass, \mathcal{M} , is the sum of the atomic weights, expressed in g/mol:

$$\begin{aligned} \text{P} &= 4(30.97) &= 123.88 \text{ g/mol} \\ \text{O} &= 10(16.00) &= \underline{160.00 \text{ g/mol}} \\ &&= 283.88 \text{ g/mol of } \text{P}_4\text{O}_{10} \end{aligned}$$

$$4.65 \times 10^{22} \text{ molecules } \text{P}_4\text{O}_{10} \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \right) \left(\frac{283.88 \text{ g}}{1 \text{ mol}} \right) = 21.9203 = \mathbf{21.9 \text{ g } \text{P}_4\text{O}_{10}}$$

Check: The exponents indicate there is less than 1/10 mole of P_4O_{10} . Thus the grams must be less than 1/10 the molar mass.

- b) Plan: Each molecule has four phosphorus atoms, so the total number of atoms is four times the number of molecules.

Solution:

$$(4.65 \times 10^{22} \text{ } \text{P}_4\text{O}_{10} \text{ molecules}) \left(\frac{4 \text{ atoms P}}{1 \text{ } \text{P}_4\text{O}_{10} \text{ molecule}} \right) = \mathbf{1.86 \times 10^{23} \text{ P atoms}}$$

Check: There are more phosphorus atoms than molecules so the answer should be larger than the original number.

- 3.3 Plan: The formula of ammonium nitrate and the molar mass are needed. The total mass of nitrogen over the molar mass times 100% gives the answer.

Solution:

The formula for ammonium nitrate is NH_4NO_3 . There are 2 atoms of N per each formula.

- a) Molar mass $\text{NH}_4\text{NO}_3 = (2 \times 14.01) + (4 \times 1.008) + (3 \times 16.00) = 80.05 \text{ g/mol}$

$$\frac{\text{total mass of N}}{\text{molar mass of } \text{NH}_4\text{NO}_3} (100) = \frac{2 \times 14.01 \text{ g/mol}}{80.05 \text{ g/mol}} (100) = 35.0031 = \mathbf{35.00\% \text{ N}}$$

b) Plan: Convert kg to grams. Use the mass percent found in (a) to find the mass of N in the sample.

Solution:

$$(35.8 \text{ kg}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{35.00 \text{ g N}}{100 \text{ g NH}_4\text{NO}_3} \right) = 1.2530 \times 10^4 = \mathbf{1.25 \times 10^4 \text{ g Nitrogen}}$$

Note: The percent ratio yields the mass of nitrogen in the compound.

Check: Nitrogen and oxygen are about the same mass. The difference is very slight and is neglected. Now 40% of the atoms remaining are N, so the answer should be about 40%.

- 3.4 Plan: The moles of sulfur may be calculated from the mass of sulfur and the molar mass of sulfur. The moles of sulfur and the chemical formula will give the moles of M. The mass of M divided by the moles of M will give the molar mass of M.

Solution:

$$(2.88 \text{ g S}) \left(\frac{1 \text{ mol S}}{32.07 \text{ g S}} \right) \left(\frac{2 \text{ mol M}}{3 \text{ mol S}} \right) = 0.0599 \text{ mol M}$$

$$(3.12 \text{ g M}) / (0.0599 \text{ mol M}) = 52.1 = 52.1 \text{ g M} / \text{mol M}$$

The element is Cr (52.00 g/mol); M is **Chromium** and M_2S_3 is **chromium(III) sulfide**.

Check: Given that, the starting masses are similar, but the final formula has 1.5 times as many S ions as M ions. M should have a molar mass near 1.5 times the molar mass of sulfur: $32 \times 1.5 = 48$

- 3.5 Plan: Two calculations are needed — one for carbon and one for hydrogen. This is because these are the only elements present in benzo[a]pyrene. If we assume there are 100 grams of this compound, then the masses of carbon and hydrogen, in grams, are numerically equivalent to the percentages. Using the atomic masses of these two elements, the moles of each may be calculated. Dividing each of the moles by the smaller value gives the simplest ratio of C and H. The smallest multiplier to convert the ratios to whole numbers gives the empirical formula. Comparing the molar mass of the empirical formula to the molar mass given in the problem allows the molecular formula to be determined.

Solution:

Assuming 100 g of compound gives 95.21 g C and 4.79 g H. Then find the moles of each element using their molar masses.

$$95.21 \text{ g C} \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 7.92756 \text{ mol C}$$

$$4.79 \text{ g H} \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 4.75198 \text{ mol H}$$

Divide each of the moles by 4.75198, the smaller value.

$$\frac{7.92756 \text{ mol C}}{4.75198} = 1.6683 \text{ mol C}; \frac{4.75198 \text{ mol H}}{4.75198} = 1.000 \text{ mol H}$$

The value 1.668 is $5/3$, so the moles of C and H must each be multiplied by 3. If it is not obvious that the value is near $5/3$, use a trial and error procedure whereby the value is multiplied by the successively larger integer until a value near an integer results. This gives C_5H_3 as the empirical formula. The molar mass of this formula is:

$$(5 \times 12.01 \text{ g/mol}) + (3 \times 1.008 \text{ g/mol}) = 63.074 \text{ g/mol}$$

Dividing 252.30 g/mol by 63.074 g/mol gives 4.000. Thus, the empirical formula must be multiplied by 4 to give **C₂₀H₁₂** as the molecular formula of benzo[a]pyrene.

Check: Determine the molar mass of the formula given and compare it to the value given in the problem:

$\mathcal{M} = (20 \times 12.01 \text{ g/mol}) + (12 \times 1.008 \text{ g/mol}) = 252.296 \text{ g/mol}$. This is very close to the given value.

- 3.6 Plan: The carbon in the sample is converted to carbon dioxide, the hydrogen is converted to water, and the remaining material is chlorine. The grams of carbon dioxide and the grams of water are both converted to moles. One mole of carbon dioxide gives one mole of carbon, while one mole of water gives two moles of hydrogen. Using the molar masses of carbon and hydrogen, the grams of each of these elements in the original sample may be determined. The original mass of sample minus the masses of carbon and hydrogen gives the mass of chlorine. The mass of chlorine and the molar mass of chlorine will give the moles of chlorine. Once the moles of each of the elements have been calculated, divide by the smallest value, and, if necessary, multiply by the smallest number required to give a set of whole numbers for the empirical formula. Compare the molar mass of the empirical formula to the molar mass given in the problem to find the molecular formula.

Solution:

Determine the moles and the masses of carbon and hydrogen produced by combustion of the sample.

$$0.451 \text{ g CO}_2 \left(\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) \left(\frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right) = 0.010248 \text{ mol C} \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 0.12307 \text{ g C}$$

$$0.0617 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} \right) \left(\frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right) = 0.0068495 \text{ mol H} \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 0.006904 \text{ g H}$$

The mass of chlorine is given by: $0.250 \text{ g sample} - (0.12307 \text{ g C} + 0.006904 \text{ g H}) = 0.120 \text{ g Cl}$

The moles of chlorine are:

$$0.120 \text{ g Cl} \left(\frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} \right) = 0.0033850 \text{ mol Cl. This is the smallest number of moles.}$$

Dividing each mole value by the lowest value, 0.0033850:

$$\frac{0.010248 \text{ mol C}}{0.0033850} = 3.03 \text{ mol C}; \quad \frac{0.0068495 \text{ mol H}}{0.0033850} = 2.02 \text{ mol H}; \quad \frac{0.0033850 \text{ mol Cl}}{0.0033850} = 1.00 \text{ mol Cl}$$

These values are all close to whole numbers, thus the empirical formula is $\text{C}_3\text{H}_2\text{Cl}$.

The empirical formula has the following molar mass:

$$(3 \times 12.01 \text{ g/mol}) + (2 \times 1.008 \text{ g/mol}) + (35.45 \text{ g/mol}) = 73.496 \text{ g/mol C}_3\text{H}_2\text{Cl}$$

Dividing the given molar mass by the empirical formula mass: $(146.99 \text{ g/mol}) / (73.496 \text{ g/mol}) = 2.00$ Thus, the molecular formula is two times the empirical formula, $\text{C}_6\text{H}_4\text{Cl}_2$.

Check: Carbon is about one-fourth the mass of carbon dioxide, or 0.11 grams of C in the compound. The mass of hydrogen is very small, thus, most of the remaining mass of the compound ($0.250 - 0.11 = 0.14$) must be chlorine. Chlorine is about three times as heavy as carbon, thus, there must be three carbons for each chlorine.

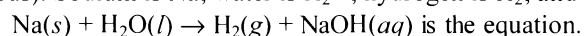
Also, check that the molar mass of the molecular formula agrees with the given molar mass.

$$(6 \times 12.01 \text{ g/mol}) + (4 \times 1.008 \text{ g/mol}) + (2 \times 35.45 \text{ g/mol}) = 146.992 \text{ g/mol}$$

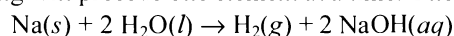
- 3.7 Plan: In each part it is necessary to determine the chemical formulas, including the physical states, for both the reactants and products. The formulas are then placed on the appropriate sides of the reaction arrow. The equation is then balanced.

a) Solution:

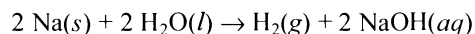
Sodium is a metal (solid) that reacts with water (liquid) to produce hydrogen (gas) and a solution of sodium hydroxide (aqueous). Sodium is Na; water is H_2O ; hydrogen is H_2 ; and sodium hydroxide is NaOH.



Balancing will precede one element at a time. One way to balance hydrogen gives:



Next, the sodium will be balanced:

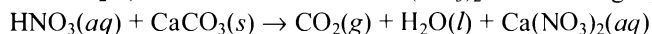


On inspection, we see that the oxygens are already balanced.

Check: Reactants (2 Na, 4 H, 2 O) = Products (2 Na, 4 H, 2 O)

b) Solution:

Aqueous nitric acid reacts with calcium carbonate (solid) to produce carbon dioxide (gas), water (liquid), and aqueous calcium nitrate. Nitric acid is HNO_3 ; calcium carbonate is CaCO_3 ; carbon dioxide is CO_2 ; water is H_2O ; and calcium nitrate is $\text{Ca}(\text{NO}_3)_2$. The starting equation is



Initially, Ca and C are balanced. Proceeding to another element, such as N, or better yet the group of elements in NO_3^- gives the following partially balanced equation:

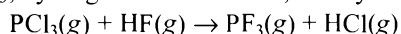


Now, all the elements are balanced.

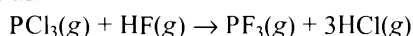
Check: Reactants (2 H, 2 N, 9 O, 1 Ca, 1 C) = Products (2 H, 2 N, 9 O, 1 Ca, 1 C)

c) Solution:

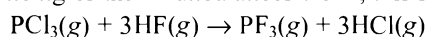
We are told all the substances involved are gases. The reactants are phosphorus trichloride and hydrogen chloride, while the products are phosphorus trifluoride and hydrogen chloride. Phosphorus trifluoride is PF_3 ; phosphorus trichloride is PCl_3 ; hydrogen fluoride is HF ; and hydrogen chloride is HCl . The initial equation is:



Initially, P and H are balanced. Proceed to another element (either F or Cl); if we will choose Cl, it balances as:



The balancing of the Cl unbalances the H, this should be corrected by balancing the H as:

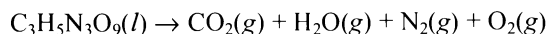


Now, all the elements are balanced.

Check: Reactants (1 P, 3 Cl, 3 H, 3 F) = Products (1 P, 3 Cl, 3 H, 3 F)

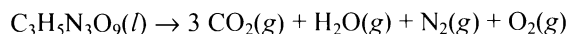
d) Solution:

We are told that nitroglycerine is a liquid reactant, and that all the products are gases. The formula for nitroglycerine is given. Carbon dioxide is CO_2 ; water is H_2O ; nitrogen is N_2 ; and oxygen is O_2 . The initial equation is:

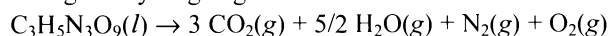


Counting the atoms shows no atoms are balanced.

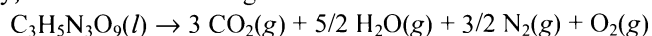
One element should be picked and balanced. Any element except oxygen will work. Oxygen will not work in this case because it appears more than once on one side of the reaction arrow. We will start with carbon. Balancing C gives:



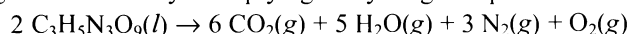
Now balancing the hydrogen gives:



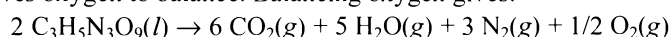
Similarly, if we balance N we get:



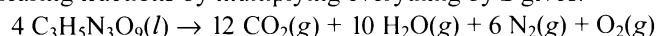
Clearing the fractions by multiplying everything except the unbalanced oxygen by 2 gives:



This leaves oxygen to balance. Balancing oxygen gives:



Again clearing fractions by multiplying everything by 2 gives:



Now all the elements are balanced.

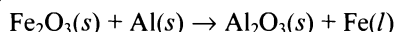
Check: Reactants (12 C 20 H 12 N 36 O) = Products (12 C 20 H 12 N 36 O)

3.8

a) Plan: The reaction, like all reactions, needs a balanced chemical equation. The atomic mass of aluminum is used to determine the moles of aluminum. The mole ratio, from the balanced chemical equation, converts the moles of aluminum to moles of iron. Finally, the atomic mass of iron is used to change the moles of iron to the grams of iron.

Solution:

The names and formulas of the substances involved are: iron(III) oxide, Fe_2O_3 , and aluminum, Al , as reactants, and aluminum oxide, Al_2O_3 , and iron, Fe . The iron is formed as a liquid; all other substances are solids. The equation begins as:



There are 2 Fe, 3 O, and 1 Al on the reactant side and 1 Fe, 3 O, and 2 Al on the product side.

Balancing aluminum: $\text{Fe}_2\text{O}_3(s) + 2 \text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(s) + \text{Fe}(l)$

Balancing iron: $\text{Fe}_2\text{O}_3(s) + 2 \text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2 \text{Fe}(l)$

Check: reactants: (2 Fe, 3 O, 2 Al) = products: (2 Fe, 3 O, 2 Al)

Using the balanced equation and the atomic masses, calculate the grams of iron:

$$(135 \text{ g Al}) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{2 \text{ mol Fe}}{2 \text{ mol Al}} \right) \left(\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \right) = 279.457 = \mathbf{279 \text{ g Fe}}$$

Check: The number of moles of aluminum produces an equal number of moles of iron. Iron has about double the mass of Al ($2 \times 27 = 54$). Thus, the initial mass of aluminum should give approximately $2 \times 135 \text{ g} (= 270)$ of iron.

b) Plan: The grams of aluminum oxide must be converted to moles. The formula shows there are two moles of aluminum for every mole of aluminum oxide. Avogadro's number will then convert the moles of aluminum to the number of atoms.

Solution:

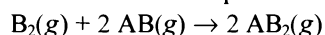
$$(1.00 \text{ g Al}_2\text{O}_3) \left(\frac{1 \text{ mol Al}_2\text{O}_3}{101.96 \text{ g Al}_2\text{O}_3} \right) \left(\frac{2 \text{ mol Al}}{1 \text{ mol Al}_2\text{O}_3} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms Al}}{1 \text{ mol Al}} \right) = 1.18125 \times 10^{22} = \mathbf{1.18 \times 10^{22} \text{ atoms Al}}$$

Check: The molar mass of aluminum oxide is about 100, so one mole of aluminum oxide is about 1/100 the mass of aluminum oxide. Doubling the moles of aluminum oxide gives the moles of aluminum atoms. Multiplying Avogadro's number by 2/100 gives about 1.2×10^{22} atoms.

- 3.9 Plan: (a) Count the molecules of each type, and find the simplest ratio. The simplest ratio leads to a balanced chemical equation. The substance with no remaining particles is the limiting reagent. (b) Use the balanced chemical equation to determine the mole ratio for the reaction.

Solution:

(a) The balanced chemical equation is



The limiting reagent is **AB** since there is a B_2 molecule left over (excess).

(b) Moles of AB_2 from AB: $(1.5 \text{ mol AB}) \left(\frac{2 \text{ mol AB}_2}{2 \text{ mol AB}} \right) = 1.5 \text{ mol AB}_2$

Moles of AB_2 from B_2 : $(1.5 \text{ mol B}_2) \left(\frac{2 \text{ mol AB}_2}{1 \text{ mol B}_2} \right) = 3.0 \text{ mol AB}_2$

Thus AB is the Limiting reagent and only **1.5 mol of AB_2** will form.

Check: The balanced chemical equation says twice as many moles of AB are needed for every mole of B_2 . Equal numbers of moles means AB is not twice as great as B_2 . Thus, AB should be limiting.

- 3.10 Plan: First, determine the formulas of the materials in the reaction and begin a chemical equation. Balance the equation. Using the molar mass of each reactant, determine the moles of each reactant. Use mole ratios from the balanced equation to determine the moles of aluminum sulfide that may be produced from each reactant. The reactant that generates the smaller number of moles is limiting. Change the moles of aluminum sulfide from the limiting reactant to the grams of product using the molar mass of aluminum sulfide. To find the excess reactant amount, find the amount of excess reactant required to react with the limiting reagent and subtract that amount from the amount given in the problem.

Solution:

The balanced equation is: $2\text{Al}(s) + 3\text{S}(s) \rightarrow \text{Al}_2\text{S}_3(s)$

Determining the moles of product from each reactant:

$$(10.0 \text{ g Al}) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{1 \text{ mol Al}_2\text{S}_3}{2 \text{ mol Al}} \right) = 0.18532 \text{ mol Al}_2\text{S}_3$$

$$(15.0 \text{ g S}) \left(\frac{1 \text{ mol S}}{32.07 \text{ g S}} \right) \left(\frac{1 \text{ mol Al}_2\text{S}_3}{3 \text{ mol S}} \right) = 0.155909 \text{ mol Al}_2\text{S}_3$$

Sulfur produces less product, thus it is limiting. The moles of product formed are calculated from the moles and the molar mass.

$$(0.155909 \text{ mol Al}_2\text{S}_3) \left(\frac{150.17 \text{ g Al}_2\text{S}_3}{1 \text{ mol Al}_2\text{S}_3} \right) = 23.413 = \mathbf{23.4 \text{ g Al}_2\text{S}_3}$$

The mass of aluminum used in the reaction is now determined:

$$(15.0 \text{ g S}) \left(\frac{1 \text{ mol S}}{32.07 \text{ g S}} \right) \left(\frac{2 \text{ mol Al}}{3 \text{ mol S}} \right) \left(\frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \right) = 8.41258 \text{ g Al used}$$

Subtracting the mass of aluminum used from the initial aluminum gives the mass remaining.

Un-reacted aluminum = $10.0 \text{ g} - 8.41285 \text{ g} = 1.5872 = \mathbf{1.6 \text{ g Al excess}}$

Check: The reactant ratios in the balanced chemical equation are the same as the mass ratio given in the problem. Thus, the substance with the larger molar mass should be limiting. This is the sulfur. An additional check is based on the aluminum calculation. If the sulfur were not the limiting reactant, the "remaining" aluminum would have been a negative number.

- 3.11 Plan: Determine the formulas, and then balance the chemical equation. The grams of marble are converted to moles, a mole ratio (from the balanced equation) gives the moles of CO_2 , and finally the theoretical yield of CO_2 is determined from the moles of CO_2 and its molar mass.

Solution:

The balanced equation: $\text{CaCO}_3(s) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$

The theoretical yield of carbon dioxide:

$$(10.0 \text{ g CaCO}_3) \left(\frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \right) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol CaCO}_3} \right) \left(\frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) = 4.39704 \text{ g CO}_2$$

The percent yield:

$$\left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) (100\%) = \left(\frac{3.65 \text{ g CO}_2}{4.39704 \text{ g CO}_2} \right) (100\%) = 83.0104 = \mathbf{83.0\%}$$

Check: Initially, there are about 10/100 moles of marble (mass of marble/molar mass). Theoretically, about 1/10 the molar mass of carbon dioxide should form.

- 3.12 Plan: Multiply the molarity by the liters to determine the moles.

Solution:

$$\left(\frac{0.50 \text{ mol KI}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (84 \text{ mL}) = \mathbf{0.042 \text{ mol KI}}$$

Check: The molarity is 0.5, this ratio implies the moles should be $0.5 (84 \text{ mL}) = 42 \text{ mmole} (0.042)$

- 3.13 Plan: Use the molar mass to change the grams to moles. The molarity may then be used to convert to volume.

Solution:

$$(135 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}) \left(\frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} \right) \left(\frac{1 \text{ L}}{3.30 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \right) = 0.11951 = \mathbf{0.120 \text{ L}}$$

Check: All units cancel except the volume units requested. The mass given is about 1/3 mole and the molarity term gives another 1/3 ratio, thus the answer should be about $(1/3) (1/3) = 1/9 \text{ L}$.

- 3.14 Plan: Determine the new concentration from the dilution equation $(M_{\text{conc}})(V_{\text{conc}}) = (M_{\text{dil}})(V_{\text{dil}})$. Convert the molarity (mol/L) to g/mL in two steps (one-step is moles to grams, and the other step is L to mL.)
Solution:

$$M_{\text{dil}} = \frac{M_{\text{conc}} V_{\text{conc}}}{V_{\text{dil}}} = \frac{(7.50 \text{ M})(25.0 \text{ m}^3)}{500. \text{m}^3} = 0.375 \text{ M}$$

$$\left(\frac{0.375 \text{ mol H}_2\text{SO}_4}{1 \text{ L}} \right) \left(\frac{98.09 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.036784 = \mathbf{3.68 \times 10^{-2} \text{ g/mL solution}}$$

Check: The dilution will give a concentration lower by $25/500 = 1/20$. Checking the calculation by doing a rough calculation gives $(8) (1/20) (100) (0.001) = 0.04$.

- 3.15 Plan: The problem should be solved like Sample Problem 3.15 to facilitate the comparison. A new balanced chemical equation is needed. A 0.10 g sample of aluminum hydroxide, for direct comparison, is converted to moles. The mole ratio from the balanced equation converts from moles of $\text{Al}(\text{OH})_3$ to moles of HCl . Finally, the moles of acid reacting with the $\text{Al}(\text{OH})_3$ are compared to the 3.4×10^{-3} mol of HCl that was shown in the Sample Problem to react with 0.10 g of $\text{Mg}(\text{OH})_2$.

Solution:

Balanced equation: $3 \text{ HCl}(aq) + \text{Al}(\text{OH})_3(s) \rightarrow \text{AlCl}_3(aq) + 3 \text{ H}_2\text{O}(l)$

$$(0.10 \text{ g Al}(\text{OH})_3) \left(\frac{1 \text{ mol Al}(\text{OH})_3}{78.00 \text{ g Al}(\text{OH})_3} \right) \left(\frac{3 \text{ mol HCl}}{1 \text{ mol Al}(\text{OH})_3} \right) = 3.84615 \times 10^{-3} = 3.8 \times 10^{-3} \text{ mol HCl}$$

Magnesium hydroxide is less effective than aluminum hydroxide because it reacts with fewer (3.4×10^{-3}) moles of HCl .

Check: The greater molar mass of $\text{Al}(\text{OH})_3$ is about 6/8, and this compound has a 3/2 larger mole ratio from the balanced equations. This gives $(3.4 \times 10^{-3}) (6/8) (1.5) = 3.8 \times 10^{-3}$.

- 3.16 a) Plan: The formula of lead(II) acetate is needed. The moles of compound are converted to moles of lead; this value times the inverse of the molarity gives the volume of the solution.

Solution:

The formula is $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ which may be written as $\text{Pb}(\text{CH}_3\text{COO})_2$.

$$(0.400 \text{ mol Pb}^{2+}) \left(\frac{1 \text{ mol Pb}(\text{C}_2\text{H}_3\text{O}_2)_2}{1 \text{ mol Pb}^{2+}} \right) \left(\frac{1 \text{ L}}{1.50 \text{ mol Pb}(\text{C}_2\text{H}_3\text{O}_2)_2} \right) = 0.266667 = \mathbf{0.267 \text{ L}}$$

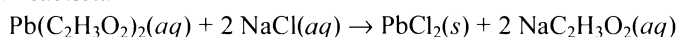
Check: A reverse calculation may serve as a check (complete units are unnecessary):

$$(0.267 \text{ L}) \left(\frac{1.5 \text{ mol}}{\text{L}} \right) \left(\frac{1 \text{ mol}}{1 \text{ mol}} \right) = 0.4005 = 0.400 \text{ mol}$$

b) Plan: The formulas are used for the balanced chemical equation. The molarity and the volume of the sodium chloride solution are used to determine the moles of NaCl . Either the lead or the chloride ion is limiting — the one producing the fewer moles of product is limiting. Convert the lower number of moles of product to grams of product.

Solution:

Balanced reaction:



Because of the 1:1 ratio, there will be 0.400 mol of PbCl_2 produced from 0.400 mol of Pb^{2+} .

The moles of PbCl_2 produced from the NaCl are:

$$\left(\frac{3.40 \text{ mol NaCl}}{1 \text{ L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (125 \text{ mL}) \left(\frac{1 \text{ mol PbCl}_2}{2 \text{ mol NaCl}} \right) = 0.2125 \text{ mol PbCl}_2$$

The NaCl is limiting. The mass of PbCl_2 may now be determined using the molar mass.

$$(0.2125 \text{ mol PbCl}_2) \left(\frac{278.1 \text{ g PbCl}_2}{1 \text{ mol PbCl}_2} \right) = 59.0962 = \mathbf{59.1 \text{ g PbCl}_2}$$

Check: There are 0.400 mol of lead ions; they will require $2 \times 0.400 = 0.800$ mol of chloride ion. The volume of NaCl solution needed to supply the chloride ions is $(0.800/3.4) = 0.235$ L (235 mL). The NaCl must be limiting because less than 235 mL are supplied.

END-OF-CHAPTER PROBLEMS

- 3.2 Plan: The formulas are based on the mole ratios of the constituents. Avogadro's number allows the change from moles to atoms.

Solution:

$$\text{a) Moles of C atoms} = (1 \text{ mol Sucrose}) \left(\frac{12 \text{ mol C}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \right) = \mathbf{12 \text{ mol C}}$$

$$\text{b) C atoms} = (1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}) \left(\frac{12 \text{ mol C}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \right) \left(\frac{6.022 \times 10^{23} \text{ C atoms}}{1 \text{ mol C}} \right) = \mathbf{7.226 \times 10^{24} \text{ C atoms}}$$

- 3.6 Plan: It is possible to relate the relative atomic masses by counting the number of atoms.

Solution:

a) The element on the **left** (green) has the higher molar mass because only 5 green balls are necessary to counterbalance the mass of 6 yellow balls. Since the green ball is heavier, its atomic mass is larger, and therefore its molar mass is larger.

b) The element on the **left** (red) has more atoms per gram. This figure requires more thought because the number of red and blue balls is unequal and their masses are unequal. If each pan contained 3 balls, then the red balls would be lighter. The presence of six red balls means that they are that much lighter. Because the red ball is lighter, more red atoms are required to make 1 gram.

c) The element on the **left** (orange) has fewer atoms per gram. The orange balls are heavier, and it takes fewer orange balls to make 1 gram.

d) **Neither** element has more atoms per mole. Both the left and right elements have the same number of atoms per mole. The number of atoms per mole (6.022×10^{23}) is constant and so is the same for every element.

- 3.7 Plan: Locate each of the elements on the periodic table and record its atomic mass. The atomic mass of the element times the number of atoms present in the formula gives the mass of that element in one mole of the substance. The molar mass is the sum of the masses of the elements in the substance.

Solution:

a) The molar mass, \mathcal{M} , is the sum of the atomic weights, expressed in g/mol:

$$\begin{aligned} \text{Sr} &= &= 87.62 \text{ g Sr/mol Sr(OH)}_2 \\ \text{O} = (2 \text{ mol O}) (16.00 \text{ g O/mol O}) &= 32.00 \text{ g O/mol Sr(OH)}_2 \\ \text{H} = (2 \text{ mol H}) (1.008 \text{ g H/mol H}) &= \underline{2.016 \text{ g H/mol Sr(OH)}_2} \\ &= \mathbf{121.64 \text{ g/mol of Sr(OH)}_2} \end{aligned}$$

$$\text{b) } \mathcal{M} = (2 \text{ mol N}) (14.01 \text{ g N/mol N}) + (1 \text{ mol O}) (16.00 \text{ g O/mol O}) = \mathbf{44.02 \text{ g/mol of N}_2\text{O}}$$

$$\begin{aligned} \text{c) } \mathcal{M} &= (1 \text{ mol Na}) (22.99 \text{ g Na/mol Na}) + (1 \text{ mol Cl}) (35.45 \text{ g Cl/mol Cl}) \\ &\quad + (3 \text{ mol O}) (16.00 \text{ g O/mol O}) = \mathbf{106.44 \text{ g/mol of NaClO}_3} \end{aligned}$$

$$\text{d) } \mathcal{M} = (2 \text{ mol Cr}) (52.00 \text{ g Cr/mol Cr}) + (3 \text{ mol O}) (16.00 \text{ g O/mol O}) = \mathbf{152.00 \text{ g/mol of Cr}_2\text{O}_3}$$

- 3.9 Plan: Locate each of the elements on the periodic table and record its atomic mass. The atomic mass of the element times the number of atoms present in the formula gives the mass of that element in one mole of the substance. The molar mass is the sum of the masses of the elements in the substance.

Solution:

$$\text{a) } \mathcal{M} = (1 \text{ mol Sn}) (118.7 \text{ g Sn/mol Sn}) + (2 \text{ mol O}) (16.00 \text{ g O/mol O}) = \mathbf{150.7 \text{ g/mol of SnO}_2}$$

$$\text{b) } \mathcal{M} = (1 \text{ mol Ba}) (137.3 \text{ g Ba/mol Ba}) + (2 \text{ mol F}) (19.00 \text{ g F/mol F}) = \mathbf{175.3 \text{ g/mol of BaF}_2}$$

$$\begin{aligned} \text{c) } \mathcal{M} &= (2 \text{ mol Al}) (26.98 \text{ g Al/mol Al}) + (3 \text{ mol S}) (32.07 \text{ g S/mol S}) + (12 \text{ mol O}) (16.00 \text{ g O/mol O}) \\ &= \mathbf{342.17 \text{ g/mol of Al}_2(\text{SO}_4)_3} \end{aligned}$$

$$\text{d) } \mathcal{M} = (1 \text{ mol Mn}) (54.94 \text{ g Mn/mol Mn}) + (2 \text{ mol Cl}) (35.45 \text{ g Cl/mol Cl}) = \mathbf{125.84 \text{ g/mol of MnCl}_2}$$

- 3.11 Plan: The mass of a substance and its number of moles are related through the conversion factor of \mathcal{M} , the molar mass expressed in g/mol. The moles of a substance and the number of entities per mole are related by the conversion factor, Avogadro's number.

Solution:

a) \mathcal{M} of $\text{KMnO}_4 = 39.10 + 54.94 + (4 \times 16.00) = 158.04 \text{ g/mol of KMnO}_4$

$$\text{Mass of KMnO}_4 = (0.57 \text{ mol KMnO}_4) \left(\frac{158.04 \text{ g KMnO}_4}{1 \text{ mol KMnO}_4} \right) = 90.08 = \mathbf{9.0 \times 10^1 \text{ g KMnO}_4}$$

b) \mathcal{M} of $\text{Mg}(\text{NO}_3)_2 = 24.31 + (2 \times 14.01) + (6 \times 16.00) = 148.33 \text{ g/mol Mg}(\text{NO}_3)_2$

$$\begin{aligned} \text{Moles of O atoms} &= (8.18 \text{ g Mg}(\text{NO}_3)_2) \left(\frac{1 \text{ mol Mg}(\text{NO}_3)_2}{148.33 \text{ g Mg}(\text{NO}_3)_2} \right) \left(\frac{6 \text{ mol O atoms}}{1 \text{ mol Mg}(\text{NO}_3)_2} \right) \\ &= 0.33088 = \mathbf{0.331 \text{ mol O atoms}} \end{aligned}$$

c) \mathcal{M} of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 63.55 + 32.07 + (9 \times 16.00) + (10 \times 1.008) = 249.70 \text{ g/mol}$

(Note that the waters of hydration are included in the molar mass.)

$$\begin{aligned} \text{O atoms} &= (8.1 \times 10^{-3} \text{ g Cu Cmpd}) \left(\frac{1 \text{ mol Cu Cmpd}}{249.70 \text{ g Cu Cmpd}} \right) \left(\frac{9 \text{ mol O atoms}}{1 \text{ mol Cu Cmpd}} \right) \left(\frac{6.022 \times 10^{23} \text{ O atoms}}{1 \text{ mol O atoms}} \right) \\ &= 1.7581 \times 10^{20} = \mathbf{1.8 \times 10^{20} \text{ O atoms}} \end{aligned}$$

- 3.13 Plan: Determine the molar mass of each substance, then perform the appropriate molar conversions.

Solution:

a) \mathcal{M} of $\text{MnSO}_4 = (54.94 \text{ g Mn/mol Mn}) + (32.07 \text{ g S/mol S}) + [(4 \text{ mol O}) (16.00 \text{ g O/mol O})]$
 $= 151.01 \text{ g/mol of MnSO}_4$

$$\text{Mass of MnSO}_4 = (0.64 \text{ mol MnSO}_4) \left(\frac{151.01 \text{ g MnSO}_4}{1 \text{ mol MnSO}_4} \right) = 96.65 = \mathbf{97 \text{ g MnSO}_4}$$

b) \mathcal{M} of $\text{Fe}(\text{ClO}_4)_3 = (55.85 \text{ g Fe/mol Fe}) + [(3 \text{ mol Cl}) (35.45 \text{ g Cl/mol Cl})] + [(12 \text{ mol O}) (16.00 \text{ g O/mol O})]$
 $= 354.20 \text{ g/mol of Fe}(\text{ClO}_4)_3$

$$\begin{aligned} \text{Moles Fe}(\text{ClO}_4)_3 &= (15.8 \text{ g Fe}(\text{ClO}_4)_3) \left(\frac{1 \text{ mol Fe}(\text{ClO}_4)_3}{354.20 \text{ g Fe}(\text{ClO}_4)_3} \right) \\ &= 0.044608 = \mathbf{4.46 \times 10^{-2} \text{ mol Fe}(\text{ClO}_4)_3} \end{aligned}$$

c) \mathcal{M} of $\text{NH}_4\text{NO}_2 = [(2 \text{ mol N}) (14.01 \text{ g N/mol N})] + [(4 \text{ mol H}) (1.008 \text{ g H/mol H})]$
 $+ [(2 \text{ mol O}) (16.00 \text{ g O/mol O})] = 64.05 \text{ g/mol of NH}_4\text{NO}_2$

$$\begin{aligned} \text{N atoms} &= 92.6 \text{ g NH}_4\text{NO}_2 \left(\frac{1 \text{ mol}}{64.05 \text{ g}} \right) \left(\frac{2 \text{ mol N}}{1 \text{ mol NH}_4\text{NO}_2} \right) \left(\frac{6.022 \times 10^{23} \text{ N atoms}}{1 \text{ mol N}} \right) \\ &= 1.74126 \times 10^{24} = \mathbf{1.74 \times 10^{24} \text{ N atoms}} \end{aligned}$$

- 3.15 Plan: The formula of each compound must be determined from its name. The molar mass for each formula comes from the formula and atomic masses from the periodic table. Avogadro's number is also necessary to find the number of particles.

Solution:

a) Carbonate is a polyatomic anion with the formula, CO_3^{2-} . Copper (I) indicates Cu^+ . The correct formula for this ionic compound is Cu_2CO_3 .

$$\mathcal{M} \text{ of } \text{Cu}_2\text{CO}_3 = (2 \times 63.55) + 12.01 + (3 \times 16.00) = 187.11 \text{ g/mol}$$

$$\text{Mass Cu}_2\text{CO}_3 = (8.41 \text{ mol Cu}_2\text{CO}_3) \left(\frac{187.11 \text{ g Cu}_2\text{CO}_3}{1 \text{ mol Cu}_2\text{CO}_3} \right) = 1573.595 = \mathbf{1.57 \times 10^3 \text{ g Cu}_2\text{CO}_3}$$

b) Dinitrogen pentaoxide has the formula N_2O_5 . Di- indicates 2 N atoms and penta- indicates 5 O atoms.

$$\mathcal{M} \text{ of } \text{N}_2\text{O}_5 = (2 \times 14.01) + (5 \times 16.00) = 108.02 \text{ g/mol}$$

$$\begin{aligned} \text{Mass N}_2\text{O}_5 &= (2.04 \times 10^{21} \text{ N}_2\text{O}_5 \text{ molecules}) \left(\frac{1 \text{ mol N}_2\text{O}_5}{6.022 \times 10^{23} \text{ N}_2\text{O}_5 \text{ molecules}} \right) \left(\frac{108.02 \text{ g N}_2\text{O}_5}{1 \text{ mol N}_2\text{O}_5} \right) \\ &= 0.365926 = \mathbf{0.366 \text{ g N}_2\text{O}_5} \end{aligned}$$

c) The correct formula for this ionic compound is NaClO_4 . There are Avogadro's number of entities (in this case, formula units) in a mole of this compound.

$$M \text{ of } \text{NaClO}_4 = 22.99 + 35.45 + (4 \times 16.00) = 122.44 \text{ g/mol}$$

$$\text{Moles } \text{NaClO}_4 = (57.9 \text{ g } \text{NaClO}_4) \left(\frac{1 \text{ mol } \text{NaClO}_4}{122.44 \text{ g } \text{NaClO}_4} \right) = 0.47288 = \mathbf{0.473 \text{ mol } \text{NaClO}_4}$$

FU = formula units

$$\text{FU } \text{NaClO}_4 = (57.9 \text{ g } \text{NaClO}_4) \left(\frac{1 \text{ mol } \text{NaClO}_4}{122.44 \text{ g } \text{NaClO}_4} \right) \left(\frac{6.022 \times 10^{23} \text{ FU } \text{NaClO}_4}{1 \text{ mol } \text{NaClO}_4} \right) =$$

$$2.8477115 \times 10^{23} = \mathbf{2.85 \times 10^{23} \text{ FU } \text{NaClO}_4}$$

d) The number of ions or atoms is calculated from the formula units given in part c. Note the unrounded initially calculated value is used to avoid intermediate rounding.

$$2.8477115 \times 10^{23} \text{ mol } \text{NaClO}_4 \left(\frac{1 \text{ Na}^+ \text{ Ion}}{1 \text{ FU } \text{NaClO}_4} \right) = \mathbf{2.85 \times 10^{23} \text{ Na}^+ \text{ ions}}$$

$$2.8477115 \times 10^{23} \text{ mol } \text{NaClO}_4 \left(\frac{1 \text{ ClO}_4^- \text{ Ion}}{1 \text{ FU } \text{NaClO}_4} \right) = \mathbf{2.85 \times 10^{23} \text{ ClO}_4^- \text{ ions}}$$

$$2.8477115 \times 10^{23} \text{ mol } \text{NaClO}_4 \left(\frac{1 \text{ Cl atom}}{1 \text{ FU } \text{NaClO}_4} \right) = \mathbf{2.85 \times 10^{23} \text{ Cl atoms}}$$

$$2.8477115 \times 10^{23} \text{ mol } \text{NaClO}_4 \left(\frac{4 \text{ O atoms}}{1 \text{ FU } \text{NaClO}_4} \right) = \mathbf{1.14 \times 10^{24} \text{ O atoms}}$$

3.17 Plan: Determine the formula and the molar mass of each compound. The formula gives the number of atoms of each type of element present. Masses come from the periodic table. Mass percent = (total mass of element in the substance/molar mass of substance) x 100.

Solution:

a) Ammonium bicarbonate is an ionic compound consisting of ammonium ions, NH_4^+ and bicarbonate ions, HCO_3^-

The formula of the compound is NH_4HCO_3 .

$$M \text{ of } \text{NH}_4\text{HCO}_3 = (14.01 \text{ g/mol}) + (5 \times 1.008 \text{ g/mol}) + (12.01 \text{ g/mol}) + (3 \times 16.00 \text{ g/mol})$$

$$= 79.06 \text{ g/mol } \text{NH}_4\text{HCO}_3$$

In 1 mole of ammonium bicarbonate, with a mass of 79.06 g, there are 5 H atoms with a mass of 5.040 g.

$$\frac{(5 \text{ mol H})(1.008 \text{ g/mol H})}{79.06 \text{ g/mol } \text{NH}_4\text{HCO}_3} \times 100\% = 6.374905 = \mathbf{6.375\% \text{ H}}$$

b) Sodium dihydrogen phosphate heptahydrate is a salt that consists of sodium ions, Na^+ , dihydrogen phosphate ions, H_2PO_4^- , and seven waters of hydration. The formula is $\text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O}$. Note that the waters of hydration are included in the molar mass.

$$M \text{ of } \text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O} = (22.99 \text{ g/mol}) + (16 \times 1.008 \text{ g/mol}) + (30.97 \text{ g/mol}) + (11 \times 16.00 \text{ g/mol})$$

$$= 246.09 \text{ g/mol } \text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O}$$

In each mole of $\text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O}$ (with mass of 246.09 g), there are 11 x 16.00 g/mol or 176.00 g of oxygen.

$$\frac{(11 \text{ mol O})(16.00 \text{ g/mol O})}{246.09 \text{ g/mol}} \times 100\% = 71.51855 = \mathbf{71.52\% \text{ O}}$$

- 3.19 Plan: Determine the formula of cisplatin from the figure, and then calculate the molar mass from the formula. The molar mass is necessary for the subsequent calculations.

Solution:

The formula for cisplatin is $\text{Pt}(\text{Cl})_2(\text{NH}_3)_2$

$$\mathcal{M} \text{ of } \text{Pt}(\text{Cl})_2(\text{NH}_3)_2 = 195.1 + (2 \times 35.45) + (2 \times 14.01) + (6 \times 1.008) = 300.1 \text{ g/mol}$$

$$\text{a) Moles cisplatin} = (285.3 \text{ g cisplatin}) \left(\frac{1 \text{ mol cisplatin}}{300.1 \text{ g cisplatin}} \right) = 0.9506831 = \mathbf{0.9507 \text{ mol cisplatin}}$$

$$\begin{aligned} \text{b) H atoms} &= (0.98 \text{ mol cisplatin}) \left(\frac{6 \text{ mol H}}{1 \text{ mol cisplatin}} \right) \left(\frac{6.022 \times 10^{23} \text{ H atoms}}{1 \text{ mol H}} \right) \\ &= 3.540936 \times 10^{24} = \mathbf{3.5 \times 10^{24} \text{ H atoms}} \end{aligned}$$

- 3.21 Plan: Determine the formulas for the compounds where needed. Determine the molar mass of each formula. Calculate the percent nitrogen by dividing the mass of nitrogen in a mole of compound by the molar mass of the compound, and multiply the result by 100%. Then rank the values.

Solution:

Name	Formula	Molar Mass (g/mol)
Potassium nitrate	KNO_3	101.11
Ammonium nitrate	NH_4NO_3	80.05
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	132.15
Urea	$\text{CO}(\text{NH}_2)_2$	60.06

Calculating the nitrogen percentages:

$$\text{Potassium nitrate} \quad \frac{(1 \text{ mol N})(14.01 \text{ g/mol N})}{101.11 \text{ g/mol}} \times 100 = 13.856196 = \mathbf{13.86\% \text{ N}}$$

$$\text{Ammonium nitrate} \quad \frac{(2 \text{ mol N})(14.01 \text{ g/mol N})}{80.05 \text{ g/mol}} \times 100 = 35.003123 = \mathbf{35.00\% \text{ N}}$$

$$\text{Ammonium sulfate} \quad \frac{(2 \text{ mol N})(14.01 \text{ g/mol N})}{132.15 \text{ g/mol}} \times 100 = 21.20318 = \mathbf{21.20\% \text{ N}}$$

$$\text{Urea} \quad \frac{(2 \text{ mol N})(14.01 \text{ g/mol N})}{60.06 \text{ g/mol}} \times 100 = 46.6533 = \mathbf{46.65\% \text{ N}}$$

Rank is $\text{CO}(\text{NH}_2)_2 > \text{NH}_4\text{NO}_3 > (\text{NH}_4)_2\text{SO}_4 > \text{KNO}_3$

- 3.22 Plan: The volume must be converted from cubic feet to cubic centimeters (or vice versa). The volume and the density will give you mass, and the mass with the molar mass gives you moles. Part (b) requires a conversion from cubic decimeters, instead of cubic feet, to cubic centimeters. The density allows you to change these cubic centimeters to mass, the molar mass allows you to find moles, and finally Avogadro's number allows you to make the last step.

Solution:

The molar mass of galena is 239.3 g/mol.

$$\begin{aligned} \text{a) Moles PbS} &= (1.00 \text{ ft}^3 \text{ PbS}) \left(\frac{(12 \text{ in})^3}{(1 \text{ ft})^3} \right) \left(\frac{(2.54 \text{ cm})^3}{(1 \text{ in})^3} \right) \left(\frac{7.46 \text{ g PbS}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol PbS}}{239.3 \text{ g PbS}} \right) \\ &= 882.7566886 = \mathbf{883 \text{ mol PbS}} \end{aligned}$$

b) Lead atoms =

$$\begin{aligned} &(1.00 \text{ dm}^3 \text{ PbS}) \left(\frac{(0.1 \text{ m})^3}{(1 \text{ dm})^3} \right) \left(\frac{(1 \text{ cm})^3}{(10^{-2} \text{ m})^3} \right) \left(\frac{7.46 \text{ g PbS}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol PbS}}{239.3 \text{ g PbS}} \right) \left(\frac{1 \text{ mol Pb}}{1 \text{ mol PbS}} \right) \left(\frac{6.022 \times 10^{23} \text{ Pb atoms}}{1 \text{ mol Pb}} \right) \\ &= 1.87731 \times 10^{25} = \mathbf{1.88 \times 10^{25} \text{ Pb atoms}} \end{aligned}$$

- 3.24 Plan: Remember that the molecular formula tells the *actual* number of moles of each element in one mole of compound.
Solution:
 a) No, you can obtain the empirical formula from the number of moles of each type of atom in a compound, but not the molecular formula.
 b) Yes, you can obtain the molecular formula from the mass percentages and the total number of atoms.
Solution Plan:
 1) Assume a 100.0 g sample and convert masses (from the mass% of each element) to moles using molar mass.
 2) Identify the element with the lowest number of moles and use this number to divide into the number of moles for each element. You now have at least one elemental mole ratio (the one with the smallest number of moles) equal to 1.00 and the remaining mole ratios that are larger than one.
 3) Examine the numbers to determine if they are whole numbers. If not, multiply each number by a whole number factor to get whole numbers for each element. You will have to use some judgment to decide when to round.
 4) Write the empirical formula using the whole numbers from step 3.
 5) Check the total number of atoms in the empirical formula. If it equals the total number of atoms given then the empirical formula is also the molecular formula. If not, then divide the total number of atoms given by the total number of atoms in the empirical formula. This should give a whole number. Multiply the number of atoms of each element in the empirical formula by this whole number to get the molecular formula. If you do not get a whole number when you divide, return to step 3 and revise how you multiplied and rounded to get whole numbers for each element.
 c) Yes, you can determine the molecular formula from the mass percent and the number of atoms of one element in a compound. Solution plan:
 1) Follow steps 1–4 in part b.
 2) Compare the number of atoms given for the one element to the number in the empirical formula. Determine the factor the number in the empirical formula must be multiplied by to obtain the given number of atoms for that element. Multiply the empirical formula by this number to get the molecular formula.
 d) No, the mass % will only lead to the empirical formula.
 e) Yes, a structural formula shows all the atoms in the compound. Solution plan: Count the number of atoms of each type of element and record as the number for the molecular formula.
- 3.25 Plan: Examine the number of atoms of each type in the compound. Divide all atom numbers by any common factor. The final answers must be the lowest whole-number values.
Solution:
 a) C_2H_4 has a ratio of 2 carbon atoms to 4 hydrogen atoms, or 2:4. This ratio can be reduced to 1:2, so that the empirical formula is **CH_2** . The empirical formula mass is $12.01 + 2(1.008) = \mathbf{14.03 \text{ g/mol}}$.
 b) The ratio of atoms is 2:6:2, or 1:3:1. The empirical formula is **CH_3O** and its empirical formula mass is $12.01 + 3(1.008) + 16.00 = \mathbf{31.03 \text{ g/mol}}$.
 c) Since, the ratio of elements cannot be further reduced, the molecular formula and empirical formula are the same, **N_2O_5** . The formula mass is $2(14.01) + 5(16.00) = \mathbf{108.02 \text{ g/mol}}$.
 d) The ratio of elements is 3 atoms of barium to 2 atoms of phosphorus to 8 atoms of oxygen, or 3:2:8. This ratio cannot be further reduced, so the empirical formula is also **$\text{Ba}_3(\text{PO}_4)_2$** , with a formula mass of $3(137.3) + 2(30.97) + 8(16.00) = \mathbf{601.8 \text{ g/mol}}$.
 e) The ratio of atoms is 4:16, or 1:4. The empirical formula is **TeI_4** , and the formula mass is $127.6 + 4(126.9) = \mathbf{635.2 \text{ g/mol}}$.
- 3.27 Plan: Determine the molar mass of each empirical formula. The molar mass of each compound divided by its empirical formula mass gives the number of times the empirical formula is within the molecule. Multiply the empirical formula by the number of times the empirical formula appears to get the molecular formula.

Solution:

Only approximate whole number values are needed.

a) CH₂ has empirical mass equal to 14.03 g/mol

$$\left(\frac{42.08 \text{ g/mol}}{14.03 \text{ g/mol}} \right) = 3$$

Multiplying the subscripts in CH₂ by 3 gives C₃H₆

b) NH₂ has empirical mass equal to 16.03 g/mol

$$\left(\frac{32.05 \text{ g/mol}}{16.03 \text{ g/mol}} \right) = 2$$

Multiplying the subscripts in NH₂ by 2 gives N₂H₄

c) NO₂ has empirical mass equal to 46.01 g/mol

$$\left(\frac{92.02 \text{ g/mol}}{46.01 \text{ g/mol}} \right) = 2$$

Multiplying the subscripts in NO₂ by 2 gives N₂O₄

d) CHN has empirical mass equal to 27.03 g/mol

$$\left(\frac{135.14 \text{ g/mol}}{27.03 \text{ g/mol}} \right) = 5$$

Multiplying the subscripts in CHN by 5 gives C₅H₅N₅

- 3.29 **Plan:** The empirical formula is the smallest whole-number ratio of the atoms or moles in a formula. All data must be converted to moles of an element. Using the smallest number of moles present, convert the mole ratios to whole numbers.

Solution:

$$\text{a) } \left(\frac{0.063 \text{ mol Cl}}{0.063 \text{ mol Cl}} \right) = 1 \qquad \left(\frac{0.22 \text{ mol O}}{0.063 \text{ mol Cl}} \right) = 3.5$$

The formula is Cl₁O_{3.5}, which in whole numbers (x 2) is Cl₂O₇

$$\text{b) } (2.45 \text{ g Si}) \left(\frac{1 \text{ mol Si}}{28.09 \text{ g Si}} \right) = 0.08722 \text{ mol Si} \qquad (12.4 \text{ g Cl}) \left(\frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} \right) = 0.349788 \text{ mol Cl}$$

$$\left(\frac{0.08722 \text{ mol Si}}{0.08722 \text{ mol Si}} \right) = 1 \qquad \left(\frac{0.349788 \text{ mol Cl}}{0.08722 \text{ mol Si}} \right) = 4$$

The empirical formula is SiCl₄.

c) Assume a 100 g sample and convert the masses to moles.

$$(100 \text{ g}) \left(\frac{27.3\% \text{ C}}{100\%} \right) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 2.2731 \text{ mol C} \qquad (100 \text{ g}) \left(\frac{72.7\% \text{ O}}{100\%} \right) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 4.5438 \text{ mol O}$$

$$\left(\frac{2.2731 \text{ mol C}}{2.2731 \text{ mol C}} \right) = 1 \qquad \left(\frac{4.5438 \text{ mol O}}{2.2731 \text{ mol C}} \right) = 2$$

The empirical formula is CO₂.

- 3.31 **Plan:** The balanced equation for this reaction is: M(s) + F₂(g) → MF₂(s) since fluorine, like other halogens, exists as a diatomic molecule. The moles of the metal are known, and the moles of everything else may be found from these moles using the balanced chemical equation.

Solution:

a) Determine the moles of fluorine.

$$\text{Moles F} = (0.600 \text{ mol M}) \left(\frac{2 \text{ mol F}}{1 \text{ mol M}} \right) = 1.20 \text{ mol F}$$

b) The grams of M are the grams of MF_2 minus the grams of F present.

$$\text{Grams M} = 46.8 \text{ g (M + F)} - (1.20 \text{ mol F}) \left(\frac{19.00 \text{ g F}}{1 \text{ mol F}} \right) = \mathbf{24.0 \text{ g M}}$$

c) The molar mass is needed to identify the element.

$$\text{Molar mass of M} = 24.0 \text{ g M} / 0.600 \text{ mol M} = 40.0 \text{ g/mol}$$

The metal with the closest molar mass to 40.0 g/mol is **calcium**.

- 3.33 Plan: Assume 100 grams of cortisol so the percentages are numerically equivalent to the masses of each element. Convert each of the masses to moles by using the molar mass of each element involved. Divide all moles by the lowest number of moles and convert to whole numbers to determine the empirical formula. The empirical formula mass and the given molar mass will then relate the empirical formula to the molecular formula.

Solution:

$$\text{Moles C} = (69.6 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 5.7952 \text{ mol C}$$

$$\text{Moles H} = (8.34 \text{ g H}) \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 8.2738 \text{ mol H}$$

$$\text{Moles O} = (22.1 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 1.38125 \text{ mol O}$$

$$\left(\frac{5.7952 \text{ mol C}}{1.38125 \text{ mol O}} \right) = 4.20 \quad \left(\frac{8.2738 \text{ mol H}}{1.38125 \text{ mol O}} \right) = 6.00 \quad \left(\frac{1.38125 \text{ mol O}}{1.38125 \text{ mol O}} \right) = 1.00$$

The carbon value is not close enough to a whole number to round the value. The smallest number that 4.20 may be multiplied by to get close to a whole number is 5. (You may wish to prove this to yourself.) All three ratios need to be multiplied by five to get the empirical formula of $\text{C}_{21}\text{H}_{30}\text{O}_5$.

The empirical formula mass is:

$$21 (12.01 \text{ g C/mol}) + 30 (1.008 \text{ g H/mol}) + 5 (16.00 \text{ g O/mol}) = 362.45 \text{ g/mol}$$

The empirical formula mass and the molar mass given are the same, so the empirical and the molecular formulas are the same. The molecular formula is **$\text{C}_{21}\text{H}_{30}\text{O}_5$** .

- 3.34 Plan: In combustion analysis, finding the moles of carbon and hydrogen is relatively simple because all of the carbon present in the sample is found in the carbon of CO_2 , and all of the hydrogen present in the sample is found in the hydrogen of H_2O . The moles of oxygen are more difficult to find, because additional O_2 was added to cause the combustion reaction. The masses of CO_2 and H_2O are used to find both the mass of C and H and the moles of C and H. Subtracting the masses of C and H from the mass of the sample gives the mass of O. Convert the mass of O to moles of O. Take the moles of C, H, and O and divide by the smallest value, and convert to a whole number to get the empirical formula. Determine the empirical formula mass and compare it to the molar mass given in the problem to see how the empirical and molecular formulas are related. Finally, determine the molecular formula.

Solution: (There is no intermediate rounding.)

Initial mole determination:

$$\text{Moles C} = (0.449 \text{ g CO}_2) \left(\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) \left(\frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right) = 0.010202 \text{ mol C}$$

$$\text{Moles H} = (0.184 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) \left(\frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right) = 0.020422 \text{ mol H}$$

Now determine the masses of C and H:

$$\text{Grams C} = (0.010202 \text{ mol C}) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 0.122526 \text{ g C}$$

$$\text{Grams H} = (0.020422 \text{ mol H}) \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 0.020585 \text{ g H}$$

Determine the mass and then the moles of O:

$$0.1595 \text{ g (C, H, and O)} - 0.122526 \text{ g C} - 0.020585 \text{ g H} = 0.016389 \text{ g O}$$

$$\text{Moles O} = (0.016389 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 0.0010243 \text{ mol O}$$

Divide by the smallest number of moles: (Rounding is acceptable for these answers.)

$$\left(\frac{0.010202 \text{ mol C}}{0.0010243 \text{ mol O}} \right) = 9.96 = 10 \quad \left(\frac{0.020422 \text{ mol H}}{0.0010243 \text{ mol O}} \right) = 19.9 = 20 \quad \left(\frac{0.0010243 \text{ mol O}}{0.0010243 \text{ mol O}} \right) = 1$$

Empirical formula = $\text{C}_{10}\text{H}_{20}\text{O}$

Empirical formula mass = $10 (12.01 \text{ g C/mol}) + 20 (1.008 \text{ g H/mol}) + 1 (16.00 \text{ g O/mol}) = 156.26 \text{ g/mol}$

The empirical formula mass matches the given molar mass so the empirical and molecular formulas are the same.

The molecular formula is $\text{C}_{10}\text{H}_{20}\text{O}$.

- 3.36 **Plan:** Examine the diagram and label each formula. We will use A for red atoms and B for green atoms.

Solution:

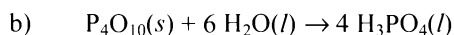
The reaction shows A_2 and B_2 molecules forming AB molecules. Equal numbers of A_2 and B_2 combine to give twice as many molecules of AB. Thus, the reaction is $\text{A}_2 + \text{B}_2 \rightarrow 2 \text{AB}$. This is the answer to part b.

- 3.37 **Plan:** Balancing is a trial and error procedure. Do one blank/one element at a time.

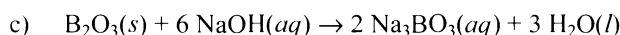
Solution:



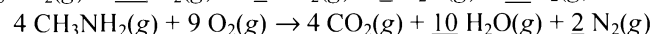
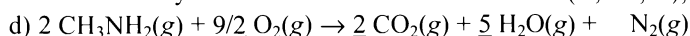
Hint: Balance the S first, because there is an obvious deficiency of S on the right side of the equation. Then balance the Cu.



Hint: Balance the P first, because there is an obvious deficiency of P on the right side of the equation. Balance the H next, because H is present in only one reactant and only one product. Balance the O last, because it appears in both reactants and is harder to balance.



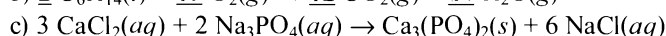
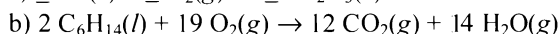
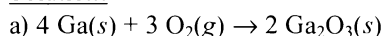
Hint: Oxygen is again the hardest element to balance because it is present in more than one place on each side of the reaction. If you balance the easier elements first (B, Na, H), the oxygen will automatically be balanced.



Hint: You should balance odd/even numbers of oxygen using the "half" method, and then multiply all coefficients by two.

- 3.39 **Plan:** The names must first be converted to chemical formulas. The balancing is a trial and error procedure. Do one blank/one element at a time. Remember that oxygen is diatomic.

Solution:



- 3.41 **Plan:** Convert the kilograms of oxygen to the moles of oxygen. Use the moles of oxygen and the mole ratios from the balanced chemical equation to determine the moles of KNO_3 . The moles of KNO_3 and its molar mass will give the grams.

Solution:

a) Moles $\text{KNO}_3 = (88.6 \text{ kg O}_2) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left(\frac{4 \text{ mol KNO}_3}{5 \text{ mol O}_2} \right) = 2215 = 2.22 \times 10^3 \text{ mol KNO}_3$

b) Grams $\text{KNO}_3 = (88.6 \text{ kg O}_2) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left(\frac{4 \text{ mol KNO}_3}{5 \text{ mol O}_2} \right) \left(\frac{101.11 \text{ g KNO}_3}{1 \text{ mol KNO}_3} \right)$
 $= 223958.65 = 2.24 \times 10^5 \text{ g KNO}_3$

The beginning of the calculation is repeated to emphasize that the second part of the problem is simply an extension of the first part. There is no need to repeat the entire calculation, as only the final step times the answer of the first part will give the final answer to this part.

- 3.43 **Plan:** First, balance the equation. Convert the grams of diborane to moles of diborane using its molar mass. Use mole ratios from the balanced chemical equation to determine the moles of the products. Use the moles and molar mass of each product to determine the mass formed.

Solution:

The balanced equation is: $\text{B}_2\text{H}_6(\text{g}) + 6 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_3\text{BO}_3(\text{s}) + 6 \text{H}_2(\text{g})$.

$$\text{Mass H}_3\text{BO}_3 = (33.61 \text{ g B}_2\text{H}_6) \left(\frac{1 \text{ mol B}_2\text{H}_6}{27.67 \text{ g B}_2\text{H}_6} \right) \left(\frac{2 \text{ mol H}_3\text{BO}_3}{1 \text{ mol B}_2\text{H}_6} \right) \left(\frac{61.83 \text{ g H}_3\text{BO}_3}{1 \text{ mol H}_3\text{BO}_3} \right)$$

$$= 150.206 = \mathbf{150.2 \text{ g H}_3\text{BO}_3}$$

$$\text{Mass H}_2 = (33.61 \text{ g B}_2\text{H}_6) \left(\frac{1 \text{ mol B}_2\text{H}_6}{27.67 \text{ g B}_2\text{H}_6} \right) \left(\frac{6 \text{ mol H}_2}{1 \text{ mol B}_2\text{H}_6} \right) \left(\frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} \right)$$

$$= 14.69268 = \mathbf{14.69 \text{ g H}_2}$$

- 3.45 **Plan:** Write the balanced equation by first writing the formulas for the reactants and products. Reactants: formula for phosphorus is given as P_4 and formula for chlorine gas is Cl_2 (chlorine occurs as a diatomic molecule). Products: formula for phosphorus pentachloride — the name indicates one phosphorus atom and five chlorine atoms to give the formula PCl_5 . Convert the mass of phosphorus to moles, use the mole ratio from the balanced chemical equation, and finally use the molar mass of chlorine to get the mass of chlorine.

Solution:

Formulas give the equation: $\text{P}_4 + \text{Cl}_2 \rightarrow \text{PCl}_5$

Balancing the equation: $\text{P}_4 + 10 \text{Cl}_2 \rightarrow 4 \text{PCl}_5$

$$\text{Grams Cl}_2 = (355 \text{ g P}_4) \left(\frac{1 \text{ mol P}_4}{123.88 \text{ g P}_4} \right) \left(\frac{10 \text{ mol Cl}_2}{1 \text{ mol P}_4} \right) \left(\frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) = 2031.76 = \mathbf{2.03 \times 10^3 \text{ g Cl}_2}$$

- 3.47 **Plan:** Convert the given masses to moles and use the mole ratio from the balanced chemical equation to find the moles of CaO that will form. The reactant that produces the least moles of CaO is the limiting reactant. Convert the moles of CaO from the limiting reactant to grams using the molar mass.

Solution:

$$\text{a) Moles CaO from Ca} = (4.20 \text{ g Ca}) \left(\frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} \right) \left(\frac{2 \text{ mol CaO}}{2 \text{ mol Ca}} \right) = 0.104790 = \mathbf{0.105 \text{ mol CaO}}$$

$$\text{b) Moles CaO from O}_2 = (2.80 \text{ g O}_2) \left(\frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left(\frac{2 \text{ mol CaO}}{1 \text{ mol O}_2} \right) = 0.17500 = \mathbf{0.175 \text{ mol CaO}}$$

c) **Calcium** is the limiting reactant since it will form less calcium oxide.

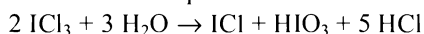
d) The mass of CaO formed is determined by the limiting reactant, Ca.

$$\text{Grams CaO} = (4.20 \text{ g Ca}) \left(\frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} \right) \left(\frac{2 \text{ mol CaO}}{2 \text{ mol Ca}} \right) \left(\frac{56.08 \text{ g CaO}}{1 \text{ mol CaO}} \right) = 5.8766 = \mathbf{5.88 \text{ g CaO}}$$

- 3.49 **Plan:** First, balance the chemical equation. Determine which of the reactants is the limiting reagent. Use the limiting reagent and the mole ratio from the balanced chemical equation to determine the amount of material formed and the amount of the other reactant used. The difference between the amount of reactant used and the initial reactant supplied gives the amount of excess reactant remaining.

Solution:

The balanced chemical equation for this reaction is:



Hint: Balance the equation by starting with oxygen. The other elements are in multiple reactants and/or products and are harder to balance initially.

Next, find the limiting reactant by using the molar ratio to find the smaller number of moles of HIO_3 that can be produced from each reactant given and excess of the other:

$$\text{Moles HIO}_3 \text{ from ICl}_3 = (685 \text{ g ICl}_3) \left(\frac{1 \text{ mol ICl}_3}{233.2 \text{ g ICl}_3} \right) \left(\frac{1 \text{ mol HIO}_3}{2 \text{ mol ICl}_3} \right) = 1.468696 = 1.47 \text{ mol HIO}_3$$

$$\text{Moles HIO}_3 \text{ from H}_2\text{O} = (117.4 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) \left(\frac{1 \text{ mol HIO}_3}{3 \text{ mol H}_2\text{O}} \right) = 2.17166 = 2.17 \text{ mol HIO}_3$$

ICl_3 is the limiting reagent and will produce **1.47 mol HIO_3** . Use the limiting reagent to find the grams of HIO_3 formed.

$$\text{Grams HIO}_3 = (685 \text{ g ICl}_3) \left(\frac{1 \text{ mol ICl}_3}{233.2 \text{ g ICl}_3} \right) \left(\frac{1 \text{ mol HIO}_3}{2 \text{ mol ICl}_3} \right) \left(\frac{175.9 \text{ g HIO}_3}{1 \text{ mol HIO}_3} \right) = 258.355 = \mathbf{258 \text{ g HIO}_3}$$

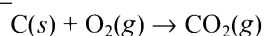
The remaining mass of the excess reagent can be calculated from the amount of H_2O combining with the limiting reagent.

$$\begin{aligned} \text{Grams H}_2\text{O required to react with 685 g ICl}_3 &= (685 \text{ g ICl}_3) \left(\frac{1 \text{ mol ICl}_3}{233.2 \text{ g ICl}_3} \right) \left(\frac{3 \text{ mol H}_2\text{O}}{2 \text{ mol ICl}_3} \right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) \\ &= 79.398 = 79.4 \text{ g H}_2\text{O reacted} \end{aligned}$$

$$\text{Remaining H}_2\text{O} = 117.4 \text{ g} - 79.4 \text{ g} = \mathbf{38.0 \text{ g H}_2\text{O}}$$

- 3.51 Plan: Write the balanced equation: formula for carbon is C, formula for oxygen is O_2 and formula for carbon dioxide is CO_2 . Determine the limiting reagent by seeing which reactant will yield the smaller amount of product. The limiting reagent is used for all subsequent calculations.

Solution:



$$\text{Moles CO}_2 \text{ from C} = (0.100 \text{ mol C}) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol C}} \right) = 0.100 \text{ mol CO}_2$$

$$\text{Moles CO}_2 \text{ from O}_2 = (8.00 \text{ g O}_2) \left(\frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol O}_2} \right) = 0.25000 = 0.250 \text{ mol CO}_2$$

The C is the limiting reactant and will be used to determine the amount of CO_2 that will form.

$$\text{Grams CO}_2 = (0.100 \text{ mol C}) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol C}} \right) \left(\frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) = 4.401 = \mathbf{4.40 \text{ g CO}_2}$$

Since the C is limiting, the **O_2 is in excess**. The amount remaining depends on how much combines with the limiting reagent.

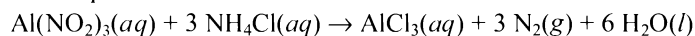
$$\text{O}_2 \text{ required to react with 0.100 mol of C} = (0.100 \text{ mol C}) \left(\frac{1 \text{ mol O}_2}{1 \text{ mol C}} \right) \left(\frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \right) = 3.20 \text{ g O}_2$$

$$\text{Remaining O}_2 = 8.00 \text{ g} - 3.20 \text{ g} = \mathbf{4.80 \text{ g O}_2}$$

- 3.53 Plan: The question asks for the mass of each substance present at the end of the reaction. "Substance" refers to both reactants and products. Solve this problem using multiple steps. Recognizing that this is a limiting reactant problem, first write a balanced chemical equation. Using the molar relationships from the balanced equation, determine which reactant is limiting. Any product can be used to predict the limiting reactant; in this case, AlCl_3 is used. Additional significant figures are retained until the last step.

Solution:

The balanced chemical equation is:



Now determine the limiting reagent. We will use the moles of AlCl_3 produced to determine which is limiting.

$$\begin{aligned} \text{Mole AlCl}_3 \text{ from Al(NO}_2)_3 &= (62.5 \text{ g Al(NO}_2)_3) \left(\frac{1 \text{ mol Al(NO}_2)_3}{165.01 \text{ g Al(NO}_2)_3} \right) \left(\frac{1 \text{ mol AlCl}_3}{1 \text{ mol Al(NO}_2)_3} \right) \\ &= 0.37876 = 0.379 \text{ mol AlCl}_3 \end{aligned}$$

$$\text{Mole AlCl}_3 \text{ from NH}_4\text{Cl} = (54.6 \text{ g NH}_4\text{Cl}) \left(\frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \right) \left(\frac{1 \text{ mol AlCl}_3}{3 \text{ mol NH}_4\text{Cl}} \right) = 0.34025 = 0.340 \text{ mol AlCl}_3$$

Ammonium chloride is the limiting reactant, and it is important for all subsequent calculations.

Mass of substances after the reaction:

$\text{Al}(\text{NO}_2)_3$:

$\text{Al}(\text{NO}_2)_3$ required to react with 54.6 g of NH_4Cl :

$$(54.6 \text{ g NH}_4\text{Cl}) \left(\frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \right) \left(\frac{1 \text{ mol Al}(\text{NO}_2)_3}{3 \text{ mol NH}_4\text{Cl}} \right) \left(\frac{165.01 \text{ g Al}(\text{NO}_2)_3}{1 \text{ mol Al}(\text{NO}_2)_3} \right) \\ = 56.14474 = 56.1 \text{ g Al}(\text{NO}_2)_3$$

$\text{Al}(\text{NO}_2)_3$ remaining: $62.5 \text{ g} - 56.1 \text{ g} = \mathbf{6.4 \text{ g Al}(\text{NO}_2)_3}$

NH_4Cl : **none left** since it is the limiting reagent.

AlCl_3 :

$$(54.6 \text{ g NH}_4\text{Cl}) \left(\frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \right) \left(\frac{1 \text{ mol AlCl}_3}{3 \text{ mol NH}_4\text{Cl}} \right) \left(\frac{133.33 \text{ g AlCl}_3}{1 \text{ mol AlCl}_3} \right) = 45.3656 = \mathbf{45.4 \text{ g AlCl}_3}$$

N_2 :

$$(54.6 \text{ g NH}_4\text{Cl}) \left(\frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \right) \left(\frac{3 \text{ mol N}_2}{3 \text{ mol NH}_4\text{Cl}} \right) \left(\frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} \right) = 28.601 = \mathbf{28.6 \text{ g N}_2}$$

H_2O :

$$(54.6 \text{ g NH}_4\text{Cl}) \left(\frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \right) \left(\frac{6 \text{ mol H}_2\text{O}}{3 \text{ mol NH}_4\text{Cl}} \right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 36.7879 = \mathbf{36.8 \text{ g H}_2\text{O}}$$

3.55 Plan: Multiply the yield of the first step by that of the second step to get the overall yield.

Solution:

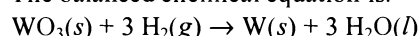
It is simpler to use the decimal equivalents of the percent yields, and then convert to percent using 100%.

$$(0.82)(0.65)(100\%) = 53.3 = \mathbf{53\%}$$

3.57 Plan: Balance the chemical equation using the formulas of the substances. Determine the yield (theoretical yield) for the reaction from the mass of tungsten(VI) oxide. Use the density of water to determine the actual yield of water in grams. The actual yield divided by the yield just calculated (with the result multiplied by 100%) gives the percent yield.

Solution: (Rounding to the correct number of significant figures will be postponed until the final result.)

The balanced chemical equation is:



Theoretical yield of H_2O :

$$(41.5 \text{ g WO}_3) \left(\frac{1 \text{ mol WO}_3}{231.9 \text{ g WO}_3} \right) \left(\frac{3 \text{ mol H}_2\text{O}}{1 \text{ mol WO}_3} \right) \left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \right) = 9.67439 \text{ g H}_2\text{O}$$

Actual yield, in grams, of H_2O :

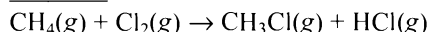
$$(9.50 \text{ mL H}_2\text{O}) \left(\frac{1.00 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \right) = 9.50 \text{ g H}_2\text{O}$$

Calculate the percent yield:

$$\left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}} \right) \times 100\% = \left(\frac{9.50 \text{ g H}_2\text{O}}{9.67439 \text{ g H}_2\text{O}} \right) \times 100\% = 98.1974 = \mathbf{98.2\%}$$

- 3.59 Plan: Write the balanced chemical equation. Since quantities of reactants are present, we must determine which is limiting. Only 80.0% of the calculated amounts of products will form. (Rounding to the correct number of significant figures will be postponed until the final result.)

Solution:



$$\text{Mole HCl from CH}_4 = (18.5 \text{ g CH}_4) \left(\frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) \left(\frac{1 \text{ mol CH}_3\text{Cl}}{1 \text{ mol CH}_4} \right) = 1.153367 \text{ mol CH}_3\text{Cl}$$

$$\text{Mole HCl from Cl}_2 = (43.0 \text{ g Cl}_2) \left(\frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} \right) \left(\frac{1 \text{ mol CH}_3\text{Cl}}{1 \text{ mol Cl}_2} \right) = 0.606488 \text{ mol CH}_3\text{Cl}$$

Chlorine is the limiting reactant.

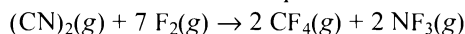
$$\begin{aligned} \text{Grams CH}_3\text{Cl} &= (43.0 \text{ g Cl}_2) \left(\frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} \right) \left(\frac{1 \text{ mol CH}_3\text{Cl}}{1 \text{ mol Cl}_2} \right) \left(\frac{50.48 \text{ g CH}_3\text{Cl}}{1 \text{ mol CH}_3\text{Cl}} \right) \left(\frac{80.0\%}{100\%} \right) \\ &= 24.4924 = \mathbf{24.5 \text{ g CH}_3\text{Cl}} \end{aligned}$$

The beginning of the calculation is repeated to emphasize that the second part of the problem is simply an extension of the first part. There is no need to repeat the entire calculation as only the final step(s) times the answer of the first part will give the final answer to this part.

- 3.61 Plan: The first step is to determine the chemical formulas so a balanced chemical equation can be written. The limiting reactant must be determined. Finally, the mass of CF_4 is determined from the limiting reactant.

Solution: (Rounding to the correct number of significant figures will be postponed until the final result.)

The balanced chemical equation is:



$$\text{Mole CF}_4 \text{ from } (\text{CN})_2 = (80.0 \text{ g } (\text{CN})_2) \left(\frac{1 \text{ mol } (\text{CN})_2}{52.04 \text{ g } (\text{CN})_2} \right) \left(\frac{2 \text{ mol CF}_4}{1 \text{ mol } (\text{CN})_2} \right) = 3.074558 \text{ mol CF}_4$$

$$\text{Mole CF}_4 \text{ from F}_2 = (80.0 \text{ g F}_2) \left(\frac{1 \text{ mol F}_2}{38.00 \text{ g F}_2} \right) \left(\frac{2 \text{ mol CF}_4}{7 \text{ mol F}_2} \right) = 0.60150 \text{ mol CF}_4$$

F_2 is the limiting reactant, and will be used to calculate the yield.

$$\text{Grams CF}_4 = (80.0 \text{ g F}_2) \left(\frac{1 \text{ mol F}_2}{38.00 \text{ g F}_2} \right) \left(\frac{2 \text{ mol CF}_4}{7 \text{ mol F}_2} \right) \left(\frac{88.01 \text{ g CF}_4}{1 \text{ mol CF}_4} \right) = 52.9383 = \mathbf{52.9 \text{ g CF}_4}$$

- 3.64 Plan: The spheres represent particles of solute and the amount of *solute* per given volume of *solution* determines its concentration. Molarity = moles of solute/volume (L) of solution.

Solution:

- Box C** has more solute added because it contains 2 more spheres than Box A contains.
- Box B** has more solvent because solvent molecules have displaced two solute molecules.
- Box C** has a higher molarity, because it has more moles of solute per volume of solution.
- Box B** has a lower concentration (and molarity), because it has fewer moles of solute per volume of solution.

- 3.65 Plan: In all cases, the definition of molarity ($M = \frac{\text{moles solute}}{\text{L of solution}}$) will be important. Volume must be expressed in

liters. The molar mass is used to convert moles to grams. The chemical formulas must be written to determine the molar mass.

Solution:

$$\begin{aligned} \text{a) Grams Ca(C}_2\text{H}_3\text{O}_2)_2 &= (175.8 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.207 \text{ mol Ca(C}_2\text{H}_3\text{O}_2)_2}{1 \text{ L}} \right) \left(\frac{158.17 \text{ g Ca(C}_2\text{H}_3\text{O}_2)_2}{1 \text{ mol Ca(C}_2\text{H}_3\text{O}_2)_2} \right) \\ &= 5.7559 = \mathbf{5.76 \text{ g Ca(C}_2\text{H}_3\text{O}_2)_2} \end{aligned}$$

$$\text{b) Moles KI} = (21.1 \text{ g KI}) \left(\frac{1 \text{ mol KI}}{166.0 \text{ g KI}} \right) = 0.127108 \text{ moles KI}$$

$$\text{Volume} = (500. \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.500 \text{ L}$$

$$\text{Molarity KI} = \frac{0.127108 \text{ mol KI}}{0.500 \text{ L}} = 0.254216 = \mathbf{0.254 \text{ M KI}}$$

$$\text{c) Moles NaCN} = \left(\frac{0.850 \text{ mol NaCN}}{1 \text{ L}} \right) (145.6 \text{ L}) = 123.76 = \mathbf{124 \text{ mol NaCN}}$$

3.67 Plan: These are dilution problems. Dilution problems can be solved by converting to moles and using the new volume, however, it is much easier to use $M_1V_1 = M_2V_2$. Part (c) may be done as two dilution problems or as a mole problem. The dilution equation does not require a volume in liters; it only requires that the volume units match.

Solution:

$$\begin{array}{llll} \text{a) } M_1 = 0.250 \text{ M KCl} & V_1 = 37.00 \text{ mL} & M_2 = ? & V_2 = 150.00 \text{ mL} \\ M_1V_1 = M_2V_2 & (0.250 \text{ M})(37.00 \text{ mL}) = (M_2)(150.0 \text{ mL}) & & \\ \frac{(0.250 \text{ M})(37.00 \text{ mL})}{150.0 \text{ mL}} = M_2 & & M_2 = 0.061667 = \mathbf{0.0617 \text{ M KCl}} & \end{array}$$

$$\begin{array}{llll} \text{b) } M_1 = 0.0706 \text{ M (NH}_4)_2\text{SO}_4 & V_1 = 25.71 \text{ mL} & M_2 = ? & V_2 = 500.00 \text{ mL} \\ M_1V_1 = M_2V_2 & (0.0706 \text{ M})(25.71 \text{ mL}) = (M_2)(500.0 \text{ mL}) & & \\ \frac{(0.0706 \text{ M})(25.71 \text{ mL})}{500.0 \text{ mL}} = M_2 & & M_2 = 0.003630 = \mathbf{0.00363 \text{ M (NH}_4)_2\text{SO}_4} & \end{array}$$

c) When working this as a mole problem it is necessary to find the individual number of moles of sodium ions in each separate solution. (Rounding to the proper number of significant figures will only be done for the final answer.)

$$\begin{aligned} \text{Moles Na}^+ \text{ from NaCl solution} &= \left(\frac{0.288 \text{ mol NaCl}}{1 \text{ L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (3.58 \text{ mL}) \left(\frac{1 \text{ mol Na}^+}{1 \text{ mol NaCl}} \right) \\ &= 0.00103104 \text{ mol Na}^+ \end{aligned}$$

$$\begin{aligned} \text{Moles Na}^+ \text{ from Na}_2\text{SO}_4 \text{ solution} &= \left(\frac{6.51 \times 10^{-3} \text{ mol Na}_2\text{SO}_4}{1 \text{ L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (500. \text{ mL}) \left(\frac{2 \text{ mol Na}^+}{1 \text{ mol Na}_2\text{SO}_4} \right) \\ &= 0.006510 \text{ mol Na}^+ \end{aligned}$$

$$\text{Molarity of Na}^+ = \left(\frac{(0.00103104 + 0.006510) \text{ mol Na}^+}{(3.58 + 500.) \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.01497486 = \mathbf{0.0150 \text{ M Na}^+ \text{ ions}}$$

3.69 Plan: Use the density of the solution to find the mass of 1 L of solution. The 70.0% by mass translates to 70.0 g solute/100 g solution and is used to find the mass of HNO₃ in 1 L of solution. Convert mass of HNO₃ to moles to obtain moles/L, molarity.

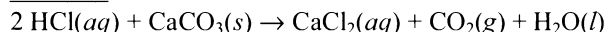
Solution:

$$\text{a) Mass HNO}_3 \text{ per liter} = \left(\frac{1.41 \text{ g Solution}}{1 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{70.0 \text{ g HNO}_3}{100 \text{ g Solution}} \right) = \mathbf{987 \text{ g HNO}_3 / \text{L}}$$

$$\begin{aligned} \text{b) Molarity of HNO}_3 &= \left(\frac{1.41 \text{ g Solution}}{1 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{70.0 \text{ g HNO}_3}{100 \text{ g Solution}} \right) \left(\frac{1 \text{ mol HNO}_3}{63.02 \text{ g HNO}_3} \right) \\ &= 15.6617 = \mathbf{15.7 \text{ M HNO}_3} \end{aligned}$$

- 3.71 **Plan:** Convert the mass of calcium carbonate to moles, and use the balanced chemical equation to find the moles of hydrochloric acid required. The moles of acid along with the molarity of the acid will give the volume required. The molarity of the solution is given in the calculation as mol/L.

Solution:

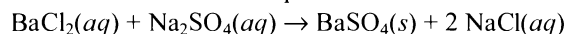


$$\begin{aligned} \text{Volume required} &= (16.2 \text{ g CaCO}_3) \left(\frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \right) \left(\frac{2 \text{ mol HCl}}{1 \text{ mol CaCO}_3} \right) \left(\frac{1 \text{ L}}{0.383 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 845.1923 = \mathbf{845 \text{ mL HCl solution}} \end{aligned}$$

- 3.73 **Plan:** The first step is to write and balance the chemical equation for the reaction. Use the molarity and volume of each of the reactants to determine the moles of each as a prelude to determining which is the limiting reactant. Use the limiting reactant to determine the mass of barium sulfate that will form.

Solution:

The balanced chemical equation is:



The mole and limiting reactant calculations are:

$$\text{Moles BaSO}_4 \text{ from BaCl}_2 = (25.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.160 \text{ mol BaCl}_2}{1 \text{ L}} \right) \left(\frac{1 \text{ mol BaSO}_4}{1 \text{ mol BaCl}_2} \right) = 0.00400 \text{ mol BaSO}_4$$

$$\text{Moles BaSO}_4 \text{ from Na}_2\text{SO}_4 = (68.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.055 \text{ mol Na}_2\text{SO}_4}{1 \text{ L}} \right) \left(\frac{1 \text{ mol BaSO}_4}{1 \text{ mol Na}_2\text{SO}_4} \right) = 0.00374 \text{ mol BaSO}_4$$

Sodium sulfate is the limiting reactant.

$$\begin{aligned} \text{Grams BaSO}_4 &= (68.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.055 \text{ mol Na}_2\text{SO}_4}{1 \text{ L}} \right) \left(\frac{1 \text{ mol BaSO}_4}{1 \text{ mol Na}_2\text{SO}_4} \right) \left(\frac{233.4 \text{ g BaSO}_4}{1 \text{ mol BaSO}_4} \right) \\ &= 0.872916 = \mathbf{0.87 \text{ g BaSO}_4} \end{aligned}$$

- 3.75 **Plan:** The first part of the problem is a simple dilution problem ($M_1V_1 = M_2V_2$). The second part requires the molar mass of the HCl along with the molarity.

Solution:

$$\text{a) } M_1 = 11.7 \text{ M} \quad V_1 = ? \quad M_2 = 3.5 \text{ M} \quad V_2 = 5.0 \text{ gal}$$

$$M_1V_1 = M_2V_2 \quad (11.7 \text{ M})(V_1) = (3.5 \text{ M})(5.0 \text{ gal})$$

$$\frac{(3.5 \text{ M})(5.0 \text{ gal})}{11.7 \text{ M}} = V_1 \quad V_1 = 1.4957 \text{ gallons (unrounded)}$$

Instructions: Be sure to wear goggles to protect your eyes! Pour approximately 3.0 gallons of water into the container. Add slowly and with mixing 1.5 gallon of 11.7 M HCl into the water. Dilute to 5.0 gallons with water.

$$\begin{aligned} \text{b) Volume needed} &= (9.55 \text{ g HCl}) \left(\frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} \right) \left(\frac{1 \text{ L}}{11.7 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 22.38725 = \mathbf{22.4 \text{ mL muriatic acid solution}} \end{aligned}$$

- 3.76 **Plan:** The moles of narceine and the moles of water are required. We can assume any mass of narceine hydrate (we will use 100 g), and use this mass to determine the mass of water present and convert the mass to moles of the hydrate. The mass of water will be converted to moles. Finally, the ratio of the moles of hydrate to moles of water will give the amount of water present.

Solution:

$$\begin{aligned} \text{Moles narceine hydrate} &= (100 \text{ g narceine hydrate}) \left(\frac{1 \text{ mol narceine hydrate}}{499.52 \text{ g narceine hydrate}} \right) \\ &= 0.20019 \text{ mol narceine hydrate} \end{aligned}$$

$$\text{Moles H}_2\text{O} = (100 \text{ g narceine hydrate}) \left(\frac{10.8\% \text{ H}_2\text{O}}{100\% \text{ narceine hydrate}} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right)$$

$$= 0.59933 \text{ mol H}_2\text{O}$$

The ratio of water to hydrate is: $(0.59933 \text{ mol}) / (0.20019 \text{ mol}) = 3$

Thus, there are three water molecules per mole of hydrate. The formula for narceine hydrate is **narceine•3H₂O**

- 3.77 Plan: Determine the formula, then the molar mass of each compound. Determine the mass of hydrogen in each formula. The mass of hydrogen divided by the molar mass of the compound (with the result multiplied by 100%) will give the mass percent hydrogen. Ranking, based on the percents, is easy.

Solution:

Name	Chemical formula	Molar mass (g/mol)	Mass percent H [(mass H) / (molar mass)] x 100%
Ethane	C ₂ H ₆	30.07	[(6 x 1.008) / (30.07)] x 100% = 20.11% H
Propane	C ₃ H ₈	44.09	[(8 x 1.008) / (44.09)] x 100% = 18.29% H
Cetyl palmitate	C ₃₂ H ₆₄ O ₂	480.83	[(64 x 1.008) / (480.83)] x 100% = 13.42% H
Ethanol	C ₂ H ₅ OH	46.07	[(6 x 1.008) / (46.07)] x 100% = 13.13% H
Benzene	C ₆ H ₆	78.11	[(6 x 1.008) / (78.11)] x 100% = 7.743% H

The hydrogen percentage decreases in the following order:

Ethane > Propane > Cetyl palmitate > Ethanol > Benzene

- 3.81 Plan: If 100.0 g of dinitrogen tetroxide reacts with 100.0 g of hydrazine (N₂H₄), what is the theoretical yield of nitrogen if no side reaction takes place? First, we need to identify the limiting reactant. The limiting reactant can be used to calculate the theoretical yield. Determine the amount of limiting reactant required to produce 10.0 grams of NO. Reduce the amount of limiting reactant by the amount used to produce NO. The reduced amount of limiting reactant is then used to calculate an “actual yield.” The “actual” and theoretical yields will give the maximum percent yield.

Solution:

Determining the limiting reactant:

$$\text{N}_2 \text{ from N}_2\text{O}_4 = (100.0 \text{ g N}_2\text{O}_4) \left(\frac{1 \text{ mol N}_2\text{O}_4}{92.02 \text{ g N}_2\text{O}_4} \right) \left(\frac{3 \text{ mol N}_2}{1 \text{ mol N}_2\text{O}_4} \right) = 3.26016 \text{ mol N}_2$$

$$\text{N}_2 \text{ from N}_2\text{H}_4 = (100.0 \text{ g N}_2\text{H}_4) \left(\frac{1 \text{ mol N}_2\text{H}_4}{32.05 \text{ g N}_2\text{H}_4} \right) \left(\frac{3 \text{ mol N}_2}{2 \text{ mol N}_2\text{H}_4} \right) = 4.68019 \text{ mol N}_2$$

N₂O₄ is the limiting reactant.

$$\begin{aligned} \text{Theoretical yield of N}_2 &= (100.0 \text{ g N}_2\text{O}_4) \left(\frac{1 \text{ mol N}_2\text{O}_4}{92.02 \text{ g N}_2\text{O}_4} \right) \left(\frac{3 \text{ mol N}_2}{1 \text{ mol N}_2\text{O}_4} \right) \left(\frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} \right) \\ &= 91.3497 \text{ g N}_2 \text{ (unrounded)} \end{aligned}$$

How much limiting reactant used to produce 100.0 g NO?

$$\text{Grams N}_2\text{O}_4 \text{ used} = (10.0 \text{ g NO}) \left(\frac{1 \text{ mol NO}}{30.01 \text{ g NO}} \right) \left(\frac{2 \text{ mol N}_2\text{O}_4}{6 \text{ mol NO}} \right) \left(\frac{92.02 \text{ g N}_2\text{O}_4}{1 \text{ mol N}_2\text{O}_4} \right) = 10.221 \text{ g N}_2\text{O}_4 \text{ (unrounded)}$$

Determine the “actual yield.”

Amount of N₂O₄ available to produce N₂ = 100.0 g N₂O₄ – mass of N₂O₄ required to produce 10.0 g NO
100.0 g – 10.221 g = 89.779 g N₂O₄ (unrounded)

$$\text{“Actual yield” of N}_2 = (89.779 \text{ g N}_2\text{O}_4) \left(\frac{1 \text{ mol N}_2\text{O}_4}{92.02 \text{ g N}_2\text{O}_4} \right) \left(\frac{3 \text{ mol N}_2}{1 \text{ mol N}_2\text{O}_4} \right) \left(\frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} \right)$$

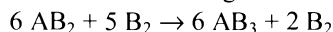
Theoretical yield = [“Actual yield” / theoretical yield] x 100%

$$[(82.01285 \text{ g N}_2) / (91.3497 \text{ g N}_2)] \times 100\% = 89.7790 = \mathbf{89.8\%}$$

- 3.82 Plan: Count the number of each type of molecule in the reactant box and in the product box. Subtract any molecules of excess reagent (molecules appearing in both boxes). The remaining material is the overall equation. This will need to be simplified if there is a common factor among the substances in the equation. The balanced chemical equation is necessary for the remainder of the problem.

Solution:

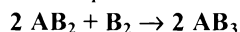
a) The contents of the boxes give:



B_2 is in excess, so two molecules need to be removed from each side. This gives:



Three is a common factor among the coefficients, and all coefficients need to be divided by this value to give the final balanced equation:



b) B_2 was in excess, thus AB_2 is the limiting reactant.

$$\text{c) Moles of AB}_3 \text{ from AB}_2 = (5.0 \text{ mol AB}_2) \left(\frac{2 \text{ mol AB}_3}{2 \text{ mol AB}_2} \right) = 5.0 \text{ mol AB}_3$$

$$\text{Moles of AB}_3 \text{ from B}_2 = (3.0 \text{ mol B}_2) \left(\frac{2 \text{ mol AB}_3}{1 \text{ mol B}_2} \right) = 6.0 \text{ mol AB}_3$$

AB_2 is the limiting reagent and maximum is **5.0 mol AB_3** .

$$\text{d) Moles of B}_2 \text{ that reacts with 5.0 mol AB}_2 = (5.0 \text{ mol AB}_2) \left(\frac{1 \text{ mol B}_2}{2 \text{ mol AB}_2} \right) = 2.5 \text{ mol B}_2$$

The un-reacted B_2 is $3.0 \text{ mol} - 2.5 \text{ mol} = \mathbf{0.5 \text{ mol B}_2}$.

- 3.85 Plan: Count the total number of spheres in each box. The number in box A divided by the volume change in each part will give the number we are looking for and allow us to match boxes.

Solution:

The number in each box is: A = 12, B = 6, C = 4, and D = 3.

- a) When the volume is tripled, there should be $12/3 = 4$ spheres in a box. This is box **C**.
 b) When the volume is doubled, there should be $12/2 = 6$ spheres in a box. This is box **B**.
 c) When the volume is quadrupled, there should be $12/4 = 3$ spheres in a box. This is box **D**.

- 3.89 Plan: This problem may be done as two dilution problems with the two final molarities added, or, as done here, it may be done by calculating, then adding the moles and dividing by the total volume.

Solution:

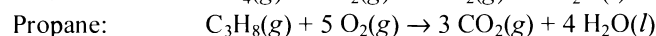
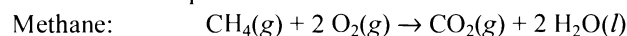
$$M \text{ KBr} = \frac{\text{Total Moles KBr}}{\text{Total Volume}} = \frac{\text{Moles KBr from Solution 1} + \text{Moles KBr from Solution 2}}{\text{Volume Solution 1} + \text{Volume Solution 2}}$$

$$M \text{ KBr} = \frac{\left(\frac{0.053 \text{ mol KBr}}{1 \text{ L}} \right) (0.200 \text{ L}) + \left(\frac{0.078 \text{ mol KBr}}{1 \text{ L}} \right) (0.550 \text{ L})}{0.200 \text{ L} + 0.550 \text{ L}} = 0.071333 = \mathbf{0.071 \text{ M KBr}}$$

- 3.92 Plan: Deal with the methane and propane separately, and combine the results. Balanced equations are needed for each hydrocarbon. The total mass and the percentages will give the mass of each hydrocarbon. The mass of each hydrocarbon is changed to moles, and through the balanced chemical equation the amount of CO_2 produced by each gas may be found. Summing the amounts of CO_2 gives the total from the mixture.

Solution:

The balanced chemical equations are:



Mass of CO_2 from each:

$$\text{Methane: } (200. \text{ g Mixture}) \left(\frac{25.0\%}{100\%} \right) \left(\frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} \right) \left(\frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) = 137.188 \text{ g CO}_2$$

$$\text{Propane: } (200. \text{ g Mixture}) \left(\frac{75.0\%}{100\%} \right) \left(\frac{1 \text{ mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \right) \left(\frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \right) \left(\frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \right) = 449.183 \text{ g CO}_2$$

$$\text{Total CO}_2 = 137.188 \text{ g} + 449.183 \text{ g} = 586.318 = \mathbf{586 \text{ g CO}_2}$$

- 3.93 Plan: If we assume a 100-gram sample of fertilizer, then the 30:10:10 percentages become the masses, in grams, of N, P₂O₅, and K₂O. These masses may be changed to moles of substance, and then to moles of each element. To get the desired x:y:1.0 ratio, divide the moles of each element by the moles of potassium.

Solution:

A 100-gram sample of 30:10:10 fertilizer contains 30 g N, 10 g P₂O₅, and 10 g K₂O.

$$\text{Moles N} = (30 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 2.1413 \text{ mol N (unrounded)}$$

$$\text{Moles P} = (10 \text{ g P}_2\text{O}_5) \left(\frac{1 \text{ mol P}_2\text{O}_5}{141.94 \text{ g P}_2\text{O}_5} \right) \left(\frac{2 \text{ mol P}}{1 \text{ mol P}_2\text{O}_5} \right) = 0.14090 \text{ mol P (unrounded)}$$

$$\text{Moles K} = (10 \text{ g K}_2\text{O}) \left(\frac{1 \text{ mol K}_2\text{O}}{94.20 \text{ g K}_2\text{O}} \right) \left(\frac{2 \text{ mol K}}{1 \text{ mol K}_2\text{O}} \right) = 0.21231 \text{ mol K (unrounded)}$$

This gives a ratio of 2.1413:0.14090:0.21231

The ratio must be divided by the moles of K and rounded.

$$(2.1413/0.21231):(0.14090/0.21231):(0.21231/0.21231)$$

$$10.086:0.66365:1.000$$

$$10:0.66:1.0$$

- 3.95 Plan: Assume 100 grams of mixture. This means the mass of each compound, in grams, is the same as its percentage. Find the mass of C from CO and from CO₂ and add these masses together.

Solution:

100 g of mixture = 35 g CO and 65 g CO₂.

$$\text{C from CO} = (35.0 \text{ g CO}) \left(\frac{1 \text{ mol CO}}{28.01 \text{ g CO}} \right) \left(\frac{1 \text{ mol C}}{1 \text{ mol CO}} \right) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 15.007 \text{ g C (unrounded)}$$

$$\text{C from CO}_2 = (65.0 \text{ g CO}_2) \left(\frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) \left(\frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 17.738 \text{ g C (unrounded)}$$

$$\text{Mass percent C} = \left(\frac{(15.007 + 17.738) \text{ g}}{100 \text{ g Sample}} \right) \times 100\% = 32.745 = \mathbf{32.7\% \text{ C}}$$

- 3.97 Plan: Determine the molecular formula from the figure. Once the molecular formula is known, use the periodic table to determine the molar mass. Convert the volume in (b) from quarts to mL and use the density to convert from mL to mass in grams. Take 6.82% of that mass and use the molar mass to convert to moles.

Solution:

a) The formula of citric acid obtained by counting the number of carbon atoms, oxygen atoms, and hydrogen atoms is **C₆H₈O₇**.

$$\text{Molar mass} = (6 \times 12.01) + (8 \times 1.008) + (7 \times 16.00) = \mathbf{192.12 \text{ g/mol}}$$

b) Determine the mass of citric acid in the lemon juice, and then use the molar mass to find the moles.

$$\begin{aligned} \text{Moles C}_6\text{H}_8\text{O}_7 &= (1.50 \text{ qt}) \left(\frac{1 \text{ L}}{1.057 \text{ qt}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1.09 \text{ g}}{\text{mL}} \right) \left(\frac{6.82\%}{100\%} \right) \left(\frac{1 \text{ mol C}_6\text{H}_8\text{O}_7}{192.12 \text{ g acid}} \right) \\ &= 0.549104 = \mathbf{0.549 \text{ mol C}_6\text{H}_8\text{O}_7} \end{aligned}$$

- 3.99 Plan: Use the mass percent to find the mass of heme in the sample; use the molar mass to convert the mass of heme to moles. Then find the mass of Fe in the sample.

Solution:

$$\text{a) Grams of heme} = (0.45 \text{ g hemoglobin}) \left(\frac{6.0\% \text{ heme}}{100\% \text{ hemoglobin}} \right) = 0.0270 = \mathbf{0.027 \text{ g heme}}$$

$$\text{b) Mole of heme} = (0.027 \text{ g heme}) \left(\frac{1 \text{ mol heme}}{616.49 \text{ g heme}} \right) = 4.37963 \times 10^{-5} = \mathbf{4.4 \times 10^{-5} \text{ mol heme}}$$

$$\begin{aligned} \text{c) Grams of Fe} &= (4.37963 \times 10^{-5} \text{ mol heme}) \left(\frac{1 \text{ mol Fe}}{1 \text{ mol heme}} \right) \left(\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \right) \\ &= 2.44602 \times 10^{-3} = \mathbf{2.4 \times 10^{-3} \text{ g Fe}} \end{aligned}$$

$$\begin{aligned} \text{d) Grams of hemin} &= (4.37963 \times 10^{-5} \text{ mol heme}) \left(\frac{1 \text{ mol hemin}}{1 \text{ mol heme}} \right) \left(\frac{651.94 \text{ g hemin}}{1 \text{ mol hemin}} \right) \\ &= 2.85526 \times 10^{-2} = \mathbf{2.9 \times 10^{-2} \text{ g hemin}} \end{aligned}$$

- 3.102 Plan: Determine the molecular formula and the molar mass of each of the compounds. From the amount of nitrogen present and the molar mass, the percent nitrogen may be determined. The moles need to be determined for part (b).

Solution:

a) To find mass percent of nitrogen, first determine molecular formula, then the molar mass of each compound. Mass percent is then calculated from the mass of nitrogen in the compound divided by the molar mass of the compound, and multiply by 100%.

Urea: $\text{CH}_4\text{N}_2\text{O}$, $\mathcal{M} = 60.06 \text{ g/mol}$

$$\% \text{ N} = \left(\frac{2(14.01 \text{ g/mol N})}{60.06 \text{ g/mol CH}_4\text{N}_2\text{O}} \right) 100\% = 46.6533 = \mathbf{46.65\% \text{ N in urea}}$$

Arginine: $\text{C}_6\text{H}_{15}\text{N}_4\text{O}_2$, $\mathcal{M} = 175.22 \text{ g/mol}$

$$\% \text{ N} = \left(\frac{4(14.01 \text{ g/mol N})}{175.22 \text{ g/mol C}_6\text{H}_{15}\text{N}_4\text{O}_2} \right) 100\% = 31.98265 = \mathbf{31.98\% \text{ N in arginine}}$$

Ornithine: $\text{C}_5\text{H}_{13}\text{N}_2\text{O}_2$, $\mathcal{M} = 133.17 \text{ g/mol}$

$$\% \text{ N} = \left(\frac{2(14.01 \text{ g/mol N})}{133.17 \text{ g/mol C}_5\text{H}_{13}\text{N}_2\text{O}_2} \right) 100\% = 21.04077 = \mathbf{21.04\% \text{ N in ornithine}}$$

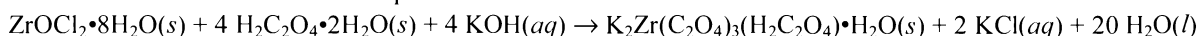
b) Grams of N =

$$\begin{aligned} (143.2 \text{ g C}_5\text{H}_{13}\text{N}_2\text{O}_2) &\left(\frac{1 \text{ mol C}_5\text{H}_{13}\text{N}_2\text{O}_2}{133.17 \text{ g C}_5\text{H}_{13}\text{N}_2\text{O}_2} \right) \left(\frac{1 \text{ mol CH}_4\text{N}_2\text{O}}{1 \text{ mol C}_5\text{H}_{13}\text{N}_2\text{O}_2} \right) \left(\frac{2 \text{ mol N}}{1 \text{ mol CH}_4\text{N}_2\text{O}} \right) \left(\frac{14.01 \text{ g N}}{1 \text{ mol N}} \right) \\ &= 30.130390 = \mathbf{30.13 \text{ g N}} \end{aligned}$$

- 3.106 Plan: The balanced chemical equation is needed. From the balanced chemical equation and the masses we can calculate the limiting reagent. The limiting reagent will be used to calculate the theoretical yield, and finally the percent yield.

Solution:

Determine the balanced chemical equation:



Determine the limiting reactant:

$$\begin{aligned} \text{Moles product from ZrOCl}_2 \cdot 8\text{H}_2\text{O} &= (1.60 \text{ g Zr cmpd}) \left(\frac{1 \text{ mol Zr cmpd}}{322.25 \text{ g Zr cmpd}} \right) \left(\frac{1 \text{ mol product}}{1 \text{ mol Zr cmpd}} \right) \\ &= 0.0049651 \text{ mol product (unrounded)} \end{aligned}$$

Moles product from $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ =

$$(5.20 \text{ g } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}) \left(\frac{1 \text{ mol } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}}{126.07 \text{ g } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}} \right) \left(\frac{1 \text{ mol Product}}{4 \text{ mol } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}} \right)$$
$$= 0.0103117 \text{ mol product (unrounded)}$$

Moles product from KOH = irrelevant because KOH is stated to be in excess.

The $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is limiting, and will be used to calculate the theoretical yield:

$$\text{Grams product} = (1.60 \text{ g Zr cmpd}) \left(\frac{1 \text{ mol Zr cmpd}}{322.25 \text{ g Zr cmpd}} \right) \left(\frac{1 \text{ mol product}}{1 \text{ mol Zr cmpd}} \right) \left(\frac{541.53 \text{ g product}}{1 \text{ mol product}} \right)$$
$$= 2.68874 \text{ g product (unrounded)}$$

Finally, calculating the percent yield:

$$\text{Percent yield} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}} \right) \times 100\% = \left(\frac{1.20 \text{ g}}{2.68874 \text{ g}} \right) \times 100\% = 44.631 = \mathbf{44.6\% \text{ yield}}$$

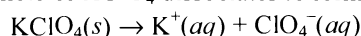
Chapter 4 The Major Classes of Chemical Reactions

FOLLOW-UP PROBLEMS

- 4.1 Plan: We must write an equation showing the dissociation of one mole of compound into its ions. The number of moles of compound times the total number of ions formed gives the moles of ions in solution. If the moles of compound are not given directly, they must be calculated from the information given.

Solution:

a) One mole of KClO_4 dissociates to form one mole of potassium ions and one mole of perchlorate ions.



Therefore, 2 moles of solid KClO_4 produce **2 mol of K^+** ions and **2 mol of ClO_4^-** ions.

b) $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2 \text{C}_2\text{H}_3\text{O}_2^-(aq)$

First convert grams of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ to moles of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ and then use molar ratios to determine the moles of each ion produced.

$$(354 \text{ g Mg}(\text{C}_2\text{H}_3\text{O}_2)_2) \left(\frac{1 \text{ mol Mg}(\text{C}_2\text{H}_3\text{O}_2)_2}{142.40 \text{ g Mg}(\text{C}_2\text{H}_3\text{O}_2)_2} \right) = 2.48596 \text{ mol (unrounded)}$$

The dissolution of 2.48596 mol $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2(s)$ produces **2.49 mol Mg^{2+}** and (2×2.48596) = **4.97 mol $\text{C}_2\text{H}_3\text{O}_2^-$**

c) $(\text{NH}_4)_2\text{CrO}_4(s) \rightarrow 2 \text{NH}_4^+(aq) + \text{CrO}_4^{2-}(aq)$

First convert formula units to moles and then use molar ratios as in part b).

$$(1.88 \times 10^{24} \text{ Formula Units}) \left(\frac{1 \text{ mol } (\text{NH}_4)_2\text{CrO}_4}{6.022 \times 10^{23} \text{ Formula Units}} \right) = 3.121886 \text{ mol (unrounded)}$$

The dissolution of 3.121886 mol $(\text{NH}_4)_2\text{CrO}_4(s)$ produces (2×3.121886) = **6.24 mol NH_4^+** and **3.12 mol CrO_4^{2-}** .

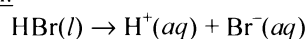
d) $\text{NaHSO}_4(s) \rightarrow \text{Na}^+(aq) + \text{HSO}_4^-(aq)$

The solution contains (1.32 L solution) (0.55 mol NaHSO_4/L solution) = 0.726 mol of NaHSO_4 and therefore **0.73 mol of Na^+** and **0.73 mol HSO_4^-** .

Check: The ratio of the moles of each ion in the solution should equal the ratio in the original formula.

- 4.2 Plan: Each mole of acid will produce one mole of hydrogen ions. It is convenient to express molarity as its definition (moles/L).

Solution:



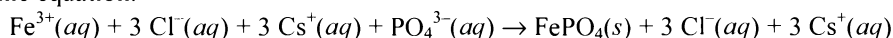
$$\text{Moles H}^+ = (451 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{3.20 \text{ mol HBr}}{\text{L}} \right) \left(\frac{1 \text{ mol H}^+}{1 \text{ mol HBr}} \right) = 1.4432 = \mathbf{1.44 \text{ mol H}^+}$$

- 4.3 Plan: Determine the ions present in each substance on the reactant side. Use Table 4.1 to determine if any combination of ions is not soluble. If a precipitate forms there will be a reaction and chemical equations may be written. The molecular equation simply includes the formulas of the substances, and balancing. In the total ionic equation, all soluble substances are written as separate ions. The net ionic equation comes from the total ionic equation by eliminating all substances appearing in identical form (spectator ions) on each side of the reaction arrow.

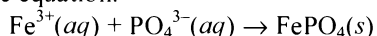
Solution:

a) The resulting ion combinations that are possible are iron(III) phosphate and cesium chloride. According to Table 4.1, iron(III) phosphate is a common phosphate and insoluble, so a reaction occurs. We see that cesium chloride is soluble.

Total ionic equation:

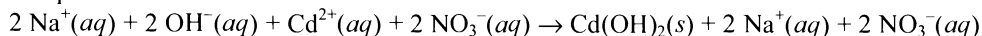


Net ionic equation:



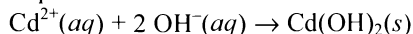
b) The resulting ion combinations that are possible are sodium nitrate (soluble) and cadmium hydroxide (insoluble). A reaction occurs.

Total ionic equation:



Note: The coefficients for Na^{+} and OH^{-} are necessary to balance the reaction and must be included.

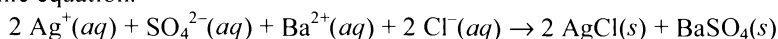
Net ionic equation:



c) The resulting ion combinations that are possible are magnesium acetate (soluble) and potassium bromide (soluble). No reaction occurs.

d) The resulting ion combinations that are possible are silver chloride (insoluble, an exception) and barium sulfate (insoluble, an exception). A reaction occurs.

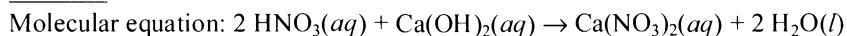
Total ionic equation:



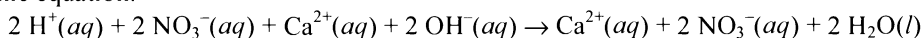
The total and net ionic equations are identical because there are no spectator ions in this reaction.

- 4.4 Plan: According to Table 4.2, both reactants are strong. Thus, the key reaction is the formation of water. The other product of the reaction is soluble.

Solution:



Total ionic equation:

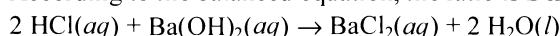


Net ionic equation: $2 \text{H}^{+}(aq) + 2 \text{OH}^{-}(aq) \rightarrow 2 \text{H}_2\text{O}(l)$ which simplifies to: $\text{H}^{+}(aq) + \text{OH}^{-}(aq) \rightarrow \text{H}_2\text{O}(l)$

- 4.5 Plan: A balanced chemical equation is necessary. Determine the moles of HCl, and, through the balanced chemical equation, determine the moles of $\text{Ba}(\text{OH})_2$ required for the reaction. The moles of base and the molarity may be used to determine the volume necessary.

Solution:

The molarity of the HCl solution is 0.1016 M. However, the molar ratio is not 1:1 as in the example problem. According to the balanced equation, the ratio is 2 moles of acid per 1 mole of base:



$$\begin{aligned} \text{Volume} &= (50.00 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.1016 \text{ mol HCl}}{\text{L}} \right) \left(\frac{1 \text{ mol Ba}(\text{OH})_2}{2 \text{ mol HCl}} \right) \left(\frac{\text{L}}{0.1292 \text{ mol Ba}(\text{OH})_2} \right) \\ &= 0.0196594 = \mathbf{0.01966 \text{ L Ba}(\text{OH})_2 \text{ solution}} \end{aligned}$$

- 4.6 Plan: Apply Table 4.3 to the compounds. Do not forget that the sum of the O.N.'s (oxidation numbers) for a compound must sum to zero, and for a polyatomic ion, the sum must equal the charge on the ion.

Solution:

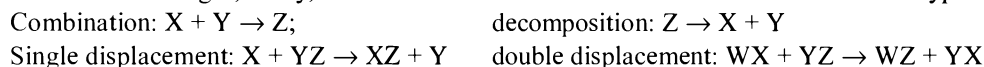
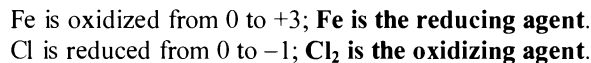
a) **Sc = +3 O = -2** In most compounds, oxygen has a -2 O.N., so oxygen is often a good starting point. If each oxygen atom has a -2 O.N., then each scandium must have a +3 oxidation state so that the sum of O.N.'s equals zero: $2(+3) + 3(-2) = 0$.

b) **Ga = +3 Cl = -1** In most compounds, chlorine has a -1 O.N., so chlorine is a good starting point. If each chlorine atom has a -1 O.N., then the gallium must have a +3 oxidation state so that the sum of O.N.'s equals zero: $1(+3) + 3(-1) = 0$.

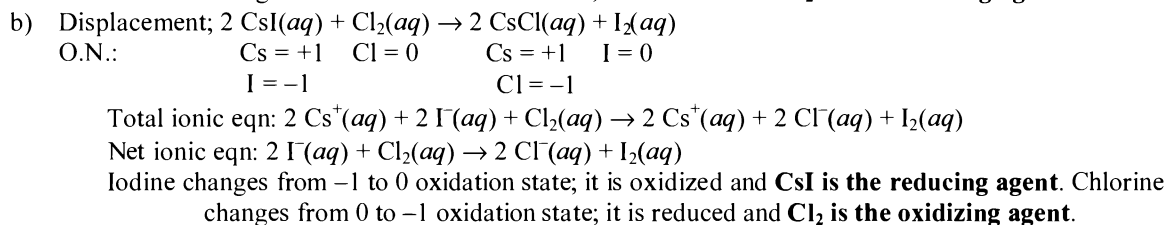
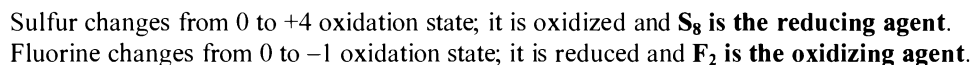
c) **H = +1 P = +5 O = -2** The hydrogen phosphate ion is HPO_4^{2-} . Again, oxygen has a -2 O.N. Hydrogen has a +1 O.N. because it is combined with nonmetals. The sum of the O.N.'s must equal the ionic charge, so the following algebraic equation can be solved for P: $1(+1) + 1(\text{P}) + 4(-2) = -2$; O.N. for P = +5.

d) **I = +3 F = -1** The formula of iodine trifluoride is IF_3 . In all compounds, fluorine has a -1 O.N., so fluorine is often a good starting point. If each fluorine atom has a -1 O.N., then the iodine must have a +3 oxidation state so that the sum of O.N.'s equal zero: $1(+3) + 3(-1) = 0$.

Solution:



Solution:



END-OF-CHAPTER PROBLEMS

- 4.2 Plan: Review the definition of electrolytes.

Solution:

Ions must be present in an aqueous solution for it to conduct an electric current. Ions come from ionic compounds or from other electrolytes such as acids and bases.

Ions must be present in an aqueous solution for it to conduct an electric current. Ions come from ionic compounds or from other electrolytes such as acids and bases.

- 4.5 Plan: Write the formula for magnesium nitrate and note the ratio of magnesium ions to nitrate ions.

Solution:

The box in (2) best represents a volume of magnesium nitrate solution. Upon dissolving the salt in water, magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, would dissociate to form one Mg^{2+} ion for every two NO_3^- ions, thus forming twice as many nitrate ions. Only box (2) has twice as many nitrate ions (red circles) as magnesium ions (blue circles).

- 4.8 Plan: Compounds that are soluble in water tend to be ionic compounds or covalent compounds that have polar bonds.

Solution:

a) Benzene is likely to be insoluble in water because it is non-polar and water is polar.

b) Sodium hydroxide, an ionic compound, is likely to be soluble in water since the ions from sodium hydroxide will be held in solution through ion-dipole attractions with water.

c) Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) will likely be soluble in water because the alcohol group ($-\text{OH}$) will hydrogen bond with the water.

d) Potassium acetate, an ionic compound, will likely dissolve in water to form sodium ions and acetate ions that are held in solution through ion-dipole attractions to water.

- 4.10 Plan: Substances whose aqueous solutions conduct an electric current are electrolytes such as ionic compounds and acids and bases.

Solution:

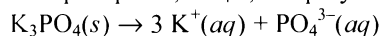
a) An aqueous solution that contains ions conducts electricity. CsI is a soluble ionic compound, and a solution of this salt in water contains Cs^+ and I^- ions. Its solution conducts electricity.

b) HBr is a strong acid that dissociates completely in water. Its aqueous solution contains H^+ and Br^- ions, so it conducts electricity.

- 4.12 Plan: To determine the total moles of ions released, write a dissolution equation showing the correct molar ratios, and convert the given amounts to moles if necessary.

Solution:

a) Recall that phosphate, PO_4^{3-} , is a polyatomic anion and does not dissociate further in water.



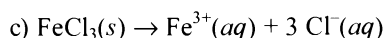
4 moles of ions are released when one mole of K_3PO_4 dissolves, so the total number of moles released is $(0.83 \text{ mol } \text{K}_3\text{PO}_4)(4 \text{ mol ions/mol } \text{K}_3\text{PO}_4) = 3.32 = \mathbf{3.3 \text{ mol of ions}}$

b) $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}(s) \rightarrow \text{Ni}^{2+}(aq) + 2 \text{Br}^-(aq)$

Three moles of ions are released when 1 mole of $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ dissolves.

The waters of hydration become part of the larger bulk of water. Convert the grams of $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ to moles using the molar mass (be sure to include the mass of the water):

$$\begin{aligned} & \left(8.11 \times 10^{-3} \text{ g } \text{NiBr}_2 \cdot 3\text{H}_2\text{O} \right) \left(\frac{1 \text{ mol } \text{NiBr}_2 \cdot 3\text{H}_2\text{O}}{272.54 \text{ g } \text{NiBr}_2 \cdot 3\text{H}_2\text{O}} \right) \left(\frac{3 \text{ mol Ions}}{1 \text{ mol } \text{NiBr}_2 \cdot 3\text{H}_2\text{O}} \right) \\ & = 8.9271 \times 10^{-5} = \mathbf{8.93 \times 10^{-5} \text{ mol of ions}} \end{aligned}$$



Recall that a mole contains 6.022×10^{23} entities, so a mole of FeCl_3 contains 6.022×10^{23} units of FeCl_3 , (more easily expressed as formula units). Since the problem specifies only 1.23×10^{21} formula units, we know that the amount is some fraction of a mole. 4 moles of ions are released when one mole of FeCl_3 dissolves.

$$\left(1.23 \times 10^{21} \text{ F.U. FeCl}_3\right) \left(\frac{1 \text{ mol FeCl}_3}{6.022 \times 10^{23} \text{ F.U. FeCl}_3}\right) \left(\frac{4 \text{ mol Ions}}{1 \text{ mol FeCl}_3}\right) = 8.17004 \times 10^{-3} = \mathbf{8.17 \times 10^{-3} \text{ mol of ions}}$$

4.14 Plan: To determine the moles of each type of ion released, write a dissolution equation showing the correct molar ratios, and convert the given amounts to moles if necessary.

Solution:

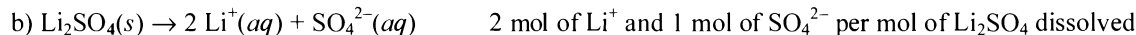


$$\text{Moles Al}^{3+} = (100. \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{2.45 \text{ mol AlCl}_3}{\text{L}}\right) \left(\frac{1 \text{ mol Al}^{3+}}{1 \text{ mol AlCl}_3}\right) = \mathbf{0.245 \text{ mol Al}^{3+}}$$

$$\text{Moles Cl}^- = (100. \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{2.45 \text{ mol AlCl}_3}{\text{L}}\right) \left(\frac{3 \text{ mol Cl}^-}{1 \text{ mol AlCl}_3}\right) = \mathbf{0.735 \text{ mol Cl}^-}$$

$$\text{Al}^{3+} \text{ ions} = (0.245 \text{ mol Al}^{3+}) \left(\frac{6.022 \times 10^{23} \text{ Al}^{3+}}{1 \text{ mol Al}^{3+}}\right) = 1.47539 \times 10^{23} = \mathbf{1.48 \times 10^{23} \text{ Al}^{3+} \text{ ions}}$$

$$\text{Cl}^- \text{ ions} = (0.735 \text{ mol Cl}^-) \left(\frac{6.022 \times 10^{23} \text{ Cl}^-}{1 \text{ mol Cl}^-}\right) = 4.42617 \times 10^{23} = \mathbf{4.43 \times 10^{23} \text{ Cl}^- \text{ ions}}$$

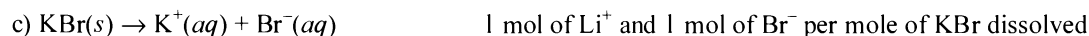


$$\text{Moles Li}^+ = (1.80 \text{ L}) \left(\frac{2.59 \text{ g Li}_2\text{SO}_4}{1 \text{ L}}\right) \left(\frac{1 \text{ mol Li}_2\text{SO}_4}{109.95 \text{ g Li}_2\text{SO}_4}\right) \left(\frac{2 \text{ mol Li}^+}{1 \text{ mol Li}_2\text{SO}_4}\right) = 0.08480 = \mathbf{0.0848 \text{ mol Li}^+}$$

$$\text{Moles SO}_4^{2-} = (1.80 \text{ L}) \left(\frac{2.59 \text{ g Li}_2\text{SO}_4}{1 \text{ L}}\right) \left(\frac{1 \text{ mol Li}_2\text{SO}_4}{109.95 \text{ g Li}_2\text{SO}_4}\right) \left(\frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol Li}_2\text{SO}_4}\right) = 0.04240 = \mathbf{0.0424 \text{ mol SO}_4^{2-}}$$

$$\text{Li}^+ \text{ ions} = (0.084802 \text{ mol Li}^+) \left(\frac{6.022 \times 10^{23} \text{ Li}^+}{1 \text{ mol Li}^+}\right) = 5.106787 \times 10^{22} = \mathbf{5.11 \times 10^{22} \text{ Li}^+ \text{ ions}}$$

$$\text{SO}_4^{2-} \text{ ions} = (0.042401 \text{ mol SO}_4^{2-}) \left(\frac{6.022 \times 10^{23} \text{ SO}_4^{2-}}{1 \text{ mol SO}_4^{2-}}\right) = 2.55339 \times 10^{22} = \mathbf{2.55 \times 10^{22} \text{ SO}_4^{2-} \text{ ions}}$$



$$\text{K}^+ \text{ ions} = (225 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{1.68 \times 10^{22} \text{ F.U. KBr}}{\text{L}}\right) \left(\frac{1 \text{ K}^+}{1 \text{ F.U. KBr}}\right) = \mathbf{3.78 \times 10^{21} \text{ K}^+ \text{ ions}}$$

$$\text{Br}^- \text{ ions} = (225 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) \left(\frac{1.68 \times 10^{22} \text{ F.U. KBr}}{\text{L}}\right) \left(\frac{1 \text{ Br}^-}{1 \text{ F.U. KBr}}\right) = \mathbf{3.78 \times 10^{21} \text{ Br}^- \text{ ions}}$$

$$\text{Moles K}^+ = (3.78 \times 10^{21} \text{ K}^+) \left(\frac{1 \text{ mol K}^+}{6.022 \times 10^{23} \text{ K}^+}\right) = 6.27698 \times 10^{-3} = \mathbf{6.28 \times 10^{-3} \text{ mol K}^+}$$

$$\text{Moles Br}^- = (3.78 \times 10^{21} \text{ Br}^-) \left(\frac{1 \text{ mol Br}^-}{6.022 \times 10^{23} \text{ Br}^-}\right) = 6.27698 \times 10^{-3} = \mathbf{6.28 \times 10^{-3} \text{ mol Br}^-}$$

- 4.16 Plan: The acids in this problem are all strong acids, so you can assume that all acid molecules dissociate completely to yield H^+ ions and associated anions. One mole of HClO_4 , HNO_3 and HCl each produce one mole of H^+ upon dissociation, so moles H^+ = moles acid. Molarity is expressed as moles/L instead of as M .

Solution:

$$\text{a) Moles } \text{H}^+ = \text{mol } \text{HClO}_4 = (1.40 \text{ L}) \left(\frac{0.25 \text{ mol}}{1 \text{ L}} \right) = \mathbf{0.35 \text{ mol } \text{H}^+}$$

$$\text{b) Moles } \text{H}^+ = \text{mol } \text{HNO}_3 = (1.8 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.72 \text{ mol}}{1 \text{ L}} \right) = 1.296 \times 10^{-3} = \mathbf{1.3 \times 10^{-3} \text{ mol } \text{H}^+}$$

$$\text{c) Moles } \text{H}^+ = \text{mol } \text{HCl} = (7.6 \text{ L}) \left(\frac{0.056 \text{ mol}}{1 \text{ L}} \right) = 0.4256 = \mathbf{0.43 \text{ mol } \text{H}^+}$$

- 4.23 Plan: Use Table 4.1 to predict the products of this reaction. Ions not involved in the precipitate are spectator ions and are not included in the net ionic equation.

Solution:

Assuming that the left beaker is AgNO_3 (because it has gray Ag^+ ion) and the right must be NaCl , then the NO_3^- is blue, the Na^+ is brown, and the Cl^- is green. (Cl^- must be green since it is present with Ag^+ in the precipitate in the beaker on the right.)

Molecular equation: $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

Total ionic equation: $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

Net ionic equation: $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$

- 4.24 Plan: Check to see if any of the ion pairs are not soluble according to the solubility rules in Table 4.1 Ions not involved in the precipitate are spectator ions and are omitted from the net ionic equation.

a) Molecular: $\text{Hg}_2(\text{NO}_3)_2(\text{aq}) + 2 \text{KI}(\text{aq}) \rightarrow \text{Hg}_2\text{I}_2(\text{s}) + 2 \text{KNO}_3(\text{aq})$

Total ionic: $\text{Hg}_2^{2+}(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) + 2 \text{K}^+(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{Hg}_2\text{I}_2(\text{s}) + 2 \text{K}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq})$

Net ionic: $\text{Hg}_2^{2+}(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{Hg}_2\text{I}_2(\text{s})$

Spectator ions are K^+ and NO_3^- .

b) Molecular: $\text{FeSO}_4(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow \text{Fe}(\text{OH})_2(\text{s}) + \text{BaSO}_4(\text{s})$

Total ionic: $\text{Fe}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{Ba}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_2(\text{s}) + \text{BaSO}_4(\text{s})$

Net ionic: This is the same as the total ionic equation, because there are no spectator ions.

- 4.26 Plan: A precipitate forms if reactant ions can form combinations that are insoluble, as determined by the solubility rules in Table 4.1. Create cation-anion combinations other than the original reactants and determine if they are insoluble. Any ions not involved in a precipitate are spectator ions and are omitted from the net ionic equation.

Solution:

a) $\text{NaNO}_3(\text{aq}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{Cu}(\text{NO}_3)_2(\text{aq})$

No precipitate will form. The ions Na^+ and SO_4^{2-} will not form an insoluble salt according to solubility rule

#1: *All common compounds of Group 1A ions are soluble.* The ions Cu^{2+} and NO_3^- will not form an insoluble salt according to the solubility rule #2: *All common nitrates are soluble.* There is no reaction.

b) A precipitate will form because silver ions, Ag^+ , and iodide ions, I^- , will combine to form a solid salt, silver iodide, AgI . The ammonium and nitrate ions do not form a precipitate.

Molecular: $\text{NH}_4\text{I}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{NH}_4\text{NO}_3(\text{aq})$

Total ionic: $\text{NH}_4^+(\text{aq}) + \text{I}^-(\text{aq}) + \text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$

Net ionic: $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

- 4.28 Plan: Write a balanced equation for the chemical reaction described in the problem. By applying the solubility rules to the two possible products (NaNO_3 and PbI_2), determine that PbI_2 is the precipitate. By using molar relationships, determine how many moles of $\text{Pb}(\text{NO}_3)_2$ (and thus Pb^{2+} ion) are required to produce 0.628 g of PbI_2 .

Solution:

The reaction is: $\text{Pb}(\text{NO}_3)_2(aq) + 2 \text{NaI}(aq) \rightarrow \text{PbI}_2(s) + 2 \text{NaNO}_3(aq)$.

$$M \text{ Pb}^{2+} = (0.628 \text{ g PbI}_2) \left(\frac{1 \text{ mol PbI}_2}{461.0 \text{ g PbI}_2} \right) \left(\frac{1 \text{ mol Pb}^{2+}}{1 \text{ mol PbI}_2} \right) \left(\frac{1}{35.0 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ = 0.0389216 = \mathbf{0.0389 \text{ M Pb}^{2+}}$$

4.30

Plan: The balanced equation for this reaction is $\text{AgNO}_3(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s) + \text{NO}_3^-(aq)$.

First, find the moles of AgNO_3 and thus the moles of Cl^- present in the 25.00 mL sample by using the molar ratio in the balanced equation. Second, convert moles of Cl^- into grams, and convert the sample volume into grams using the given density. The mass percent of Cl^- is found by dividing the mass of Cl^- by the mass of the sample volume and multiplying by 100.

Solution:

$$(43.63 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.3020 \text{ mol AgNO}_3}{\text{L}} \right) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol AgNO}_3} \right) \left(\frac{35.45 \text{ g Cl}}{1 \text{ mol Cl}^-} \right) = 0.467098 \text{ g Cl (unrounded)}$$

$$\text{Mass of sample} = (25.00 \text{ mL}) \left(\frac{1.04 \text{ g}}{\text{mL}} \right) = 26.0 \text{ g sample}$$

$$\text{Mass\% Cl} = \frac{\text{Mass Cl}}{\text{Mass Sample}} \times 100\% = \frac{0.467098 \text{ g Cl}}{26.0 \text{ g Sample}} \times 100\% = 1.79653 = \mathbf{1.80\% \text{ Cl}}$$

4.36

Plan: Remember that strong acids and bases can be written as ions in the total ionic equation but weak acids and bases cannot be written as ions. Omit spectator ions from the net ionic equation.

Solution:

a) KOH is a strong base and HI is a strong acid; both may be written in dissociated form. KI is a soluble compound since all Group 1A(1) compounds are soluble.

Molecular equation: $\text{KOH}(aq) + \text{HI}(aq) \rightarrow \text{KI}(aq) + \text{H}_2\text{O}(l)$

Total ionic equation: $\text{K}^+(aq) + \text{OH}^-(aq) + \text{H}^+(aq) + \text{I}^-(aq) \rightarrow \text{K}^+(aq) + \text{I}^-(aq) + \text{H}_2\text{O}(l)$

Net ionic equation: $\text{OH}^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l)$

The spectator ions are $\text{K}^+(aq)$ and $\text{I}^-(aq)$

b) NH_3 is a weak base and is written in the molecular form. HCl is a strong acid and is written in the dissociated form (as ions). NH_4Cl is a soluble compound, because all ammonium compounds are soluble.

Molecular equation: $\text{NH}_3(aq) + \text{HCl}(aq) \rightarrow \text{NH}_4\text{Cl}(aq)$

Total ionic equation: $\text{NH}_3(aq) + \text{H}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq)$

Net ionic equation: $\text{NH}_3(aq) + \text{H}^+(aq) \rightarrow \text{NH}_4^+(aq)$

Cl^- is the only spectator ion.

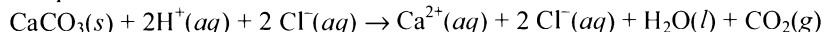
4.38

Plan: Write an acid-base reaction between CaCO_3 and HCl .

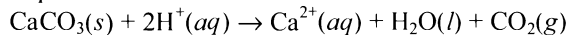
Solution:

Calcium carbonate dissolves in $\text{HCl}(aq)$ because the carbonate ion, a base, reacts with the acid to form $\text{CO}_2(g)$.

Total ionic equation:



Net ionic equation:



4.40

Plan: Write a balanced equation and use the molar ratios to convert the amount of KOH to the amount of CH_3COOH .

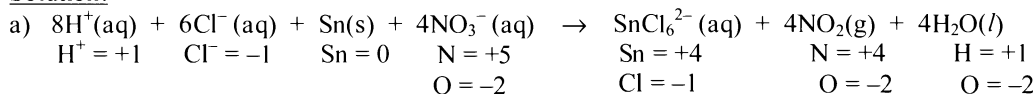
Solution:

The reaction is: $\text{KOH}(aq) + \text{CH}_3\text{COOH}(aq) \rightarrow \text{KCH}_3\text{COO}(aq) + \text{H}_2\text{O}(l)$

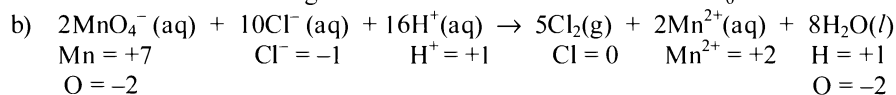
$$M = \left(\frac{0.1180 \text{ mol KOH}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (25.98 \text{ mL}) \left(\frac{1 \text{ mol CH}_3\text{COOH}}{1 \text{ mol KOH}} \right) \left(\frac{1}{52.50 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ = 0.05839314 = \mathbf{0.05839 \text{ M CH}_3\text{COOH}}$$

- 4.45 Plan: An oxidizing agent has an atom whose oxidation number decreases during the reaction.
Solution:
 a) The S in SO_4^{2-} (i.e., H_2SO_4) has O.N. = +6, and in SO_2 , O.N. (s) = +4, so the S has been reduced (and the I^- oxidized), so the H_2SO_4 is an oxidizing agent.
 b) The oxidation numbers remain constant throughout; H_2SO_4 transfers a proton to F^- to produce HF, so it acts as an acid.
- 4.46 Plan: Consult Table 4.3 for the rules for assigning oxidation numbers.
Solution:
 a) NH_2OH : (O.N. for N) + 3(+1 for H) + 1(-2 for O) = 0 O.N. for N = -1
 b) N_2H_4 : 2(O.N. for N) + 4(+1 for H) = 0 O.N. for N = -2
 c) NH_4^+ : (O.N. for N) + 4(+1 for H) = +1 O.N. for N = -3
 d) HNO_2 : (O.N. for N) + 1(+1 for H) + 2(-2 for O) = 0 O.N. for N = +3
- 4.48 Plan: Consult Table 4.3 for the rules for assigning oxidation numbers.
Solution:
 a) AsH_3 . H is combined with a nonmetal, so its O.N. is +1 (Rule 3). The O.N. for As is -3.
 b) H_3AsO_4 . The O.N. of H in this compound is +1, or +3 for 3 H's. Oxygen's O.N. is -2, with total O.N. of -8 (4 times -2), so As needs to have an O.N. of +5: +3 + (+5) + (-8) = 0
 c) AsCl_3 . Cl has an O.N. of -1, total of -3, so As must have an O.N. of +3.
 a) **As = -3** b) **As = +5** c) **As = +3**
- 4.50 Plan: Consult Table 4.3 for the rules for assigning oxidation numbers.
Solution:
 a) MnO_4^{2-} : (O.N. for Mn) + 4(-2 for O) = -2 O.N. for Mn = +6
 b) Mn_2O_3 : {2(O.N. for Mn)} + 3(-2 for O) = 0 O.N. for Mn = +3
 c) KMnO_4 : 1(+1 for K) + (O.N. for Mn) + 4(-2 for O) = 0 O.N. for Mn = +7
- 4.52 Plan: Oxidizing agent: substance that accepts the electrons released by the substance that is oxidized; the oxidation number of the atom accepting electrons decreases. The oxidizing agent undergoes reduction.
 Reducing agent: substance that provides the electrons accepted by the substance that is reduced; the oxidation number of the atom providing the electrons increases. The reducing agent undergoes oxidation.
 First, assign oxidation numbers to all atoms. Second, recognize that the agent is the compound that contains the atom that is gaining or losing electrons, not just the atom itself.
Solution:
 a) $5 \text{H}_2\text{C}_2\text{O}_4(\text{aq}) + 2 \text{MnO}_4^-(\text{aq}) + 6 \text{H}^+(\text{aq}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 10 \text{CO}_2(\text{g}) + 8 \text{H}_2\text{O}(\text{l})$
 H = +1 Mn = +7 H = +1 Mn = +2 C = +4 H = +1
 C = +3 O = -2 O = -2 O = -2
 O = -2
 Hydrogen and oxygen do not change oxidation state. The Mn changes from +7 to +2 (reduction). Therefore, **MnO_4^- is the oxidizing agent.** C changes from +3 to +4 (oxidation), so **$\text{H}_2\text{C}_2\text{O}_4$ is the reducing agent.**
 b) $3 \text{Cu}(\text{s}) + 8 \text{H}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) \rightarrow 3 \text{Cu}^{2+}(\text{aq}) + 2 \text{NO}(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$
 Cu = 0 H = +1 N = +5 Cu = +2 N = +2 H = +1
 O = -2 O = -2 O = -2
 Cu changes from 0 to +2 (is oxidized) and **Cu is the reducing agent.** N changes from +5 (in NO_3^-) to +2 (in NO) and is reduced, so **NO_3^- is the oxidizing agent.**
- 4.54 Plan: Oxidizing agent: substance that accepts the electrons released by the substance that is oxidized; the oxidation number of the atom accepting electrons decreases. The oxidizing agent undergoes reduction.
 Reducing agent: substance that provides the electrons accepted by the substance that is reduced; the oxidation number of the atom providing the electrons increases. The reducing agent undergoes oxidation.
 First, assign oxidation numbers to all atoms. Second, recognize that the agent is the compound that contains the atom that is gaining or losing electrons, not just the atom itself.

Solution:



Oxidizing agent is NO_3^- because nitrogen changes from +5 O.N. in NO_3^- to +4 O.N. in NO_2 . **Reducing agent is Sn** because its O.N. changes from 0 as the element to +4 in SnCl_6^{2-} .



Oxidizing agent is MnO_4^- because manganese changes from +7 O.N. in MnO_4^- to +2 O.N. in Mn^{2+} . **Reducing agent is Cl^-** because its O.N. changes from -1 in Cl^- to 0 as the element to Cl_2 .

- 4.56 Plan: S is in Group 6A (16), so its highest possible O.N. is +6 and its lowest possible O.N. is $6 - 8 = -2$. Remember that a reducing agent has an atom whose O.N. increases while an oxidizing agent has an atom whose O.N. decreases.

Solution:

- a) The lowest O.N. for S [(Group 6A(16))] is $6 - 8 = -2$, which occurs in S^{2-} . Therefore, when S^{2-} reacts in an oxidation-reduction reaction, S can only increase its O.N. (oxidize), so S^{2-} can only function as a reducing agent.
b) The highest O.N. for S [(Group 6A(16))] is +6, which occurs in SO_4^{2-} . Therefore, when SO_4^{2-} reacts in an oxidation-reduction reaction, the S can only decrease its O.N. (reduce), so SO_4^{2-} can only function as an oxidizing agent.
c) The O.N. of S in SO_2 is +4, so it can increase or decrease its O.N. Therefore, SO_2 can function as either an oxidizing or reducing agent.

- 4.62 Plan: Recall the definitions of each type of reaction:

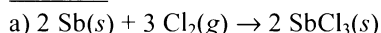
Combination: $\text{X} + \text{Y} \rightarrow \text{Z}$;

decomposition: $\text{Z} \rightarrow \text{X} + \text{Y}$

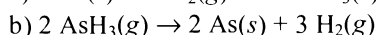
Single displacement: $\text{X} + \text{YZ} \rightarrow \text{XZ} + \text{Y}$

double displacement: $\text{WX} + \text{YZ} \rightarrow \text{WZ} + \text{YX}$

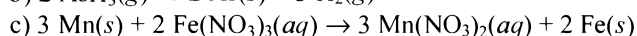
Solution:



combination



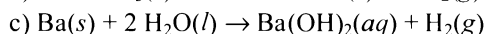
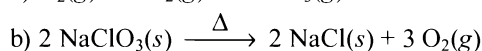
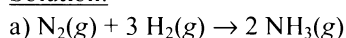
decomposition



displacement

- 4.64 Plan: Two elements as reactants often results in a combination reaction while one reactant only often indicates a decomposition reaction. Review the types of reactions in Section 4.6

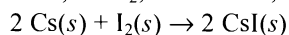
Solution:



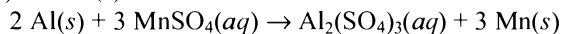
- 4.66 Plan: Review the types of reactions in Section 4.6

Solution:

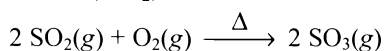
a) Cs, a metal, and I_2 , a nonmetal, react to form the binary ionic compound, CsI.



b) Al is a stronger reducing agent than Mn and is able to displace Mn from solution, i.e., cause the reduction from $\text{Mn}^{2+}(\text{aq})$ to $\text{Mn}^0(\text{s})$.

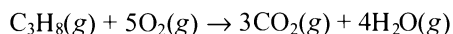


c) Sulfur dioxide, SO_2 , is a nonmetal oxide that reacts with oxygen, O_2 , to form the higher oxide, SO_3 .

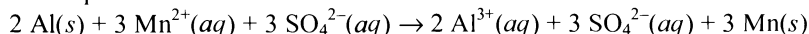


It is not clear from the problem, but energy must be added to force this reaction to proceed.

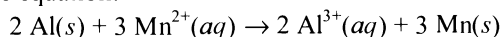
d) Propane is a three-carbon hydrocarbon with the formula C_3H_8 . It burns in the presence of oxygen, O_2 , to form carbon dioxide gas and water vapor. Although this is a redox reaction that could be balanced using the oxidation number method, it is easier to balance by considering only atoms on either side of the equation. First balance carbon and hydrogen (because they only appear in one species on each side of the equation), and then balance oxygen.



e) Total ionic equation:



Net ionic equation:



Note that the molar coefficients are not simplified because the number of electrons lost ($6e^-$) must equal the electrons gained ($6e^-$).

- 4.68 **Plan:** Write a balanced equation; convert the mass of HgO to moles and use the molar ratio from the balanced equation to find the moles and then the mass of O_2 . Perform the same calculation to find the mass of the other product.

Solution:

The balanced chemical equation is $2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$

$$\text{Mass } O_2 = (4.27 \text{ kg } HgO) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol } HgO}{216.6 \text{ g } HgO} \right) \left(\frac{1 \text{ mol } O_2}{2 \text{ mol } HgO} \right) \left(\frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} \right) = 315.420 = \mathbf{315 \text{ g } O_2}$$

The other product is **mercury**.

$$\begin{aligned} \text{Mass Hg} &= (4.27 \text{ kg } HgO) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol } HgO}{216.6 \text{ g } HgO} \right) \left(\frac{2 \text{ mol } Hg}{2 \text{ mol } HgO} \right) \left(\frac{200.6 \text{ g } Hg}{1 \text{ mol } Hg} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \\ &= 3.95458 = \mathbf{3.95 \text{ kg Hg}} \end{aligned}$$

- 4.70 **Plan:** To determine the reactant in excess, write the balanced equation (metal + $O_2 \rightarrow$ metal oxide), convert reactant masses to moles, and use molar ratios to see which reactant makes the smaller ("limiting") amount of product. Use the limiting reactant to calculate the amount of product formed.

Solution:

The balanced equation is $4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$

$$\text{a) Moles } Li_2O \text{ if Li limiting} = (1.62 \text{ g Li}) \left(\frac{1 \text{ mol Li}}{6.941 \text{ g Li}} \right) \left(\frac{2 \text{ mol } Li_2O}{4 \text{ mol Li}} \right) = 0.1166979 \text{ mol } Li_2O \text{ (unrounded)}$$

$$\text{Moles } Li_2O \text{ if } O_2 \text{ limiting} = (6.00 \text{ g } O_2) \left(\frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \right) \left(\frac{2 \text{ mol } Li_2O}{1 \text{ mol } O_2} \right) = 0.375 \text{ mol } Li_2O \text{ (unrounded)}$$

Li is the limiting reactant; **O_2 is in excess.**

$$\text{b) } 0.1166979 = \mathbf{0.117 \text{ mol } Li_2O}$$

c) Li is limiting, thus there will be none remaining (**0 g Li**).

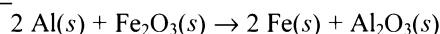
$$\text{Grams } Li_2O = (1.62 \text{ g Li}) \left(\frac{1 \text{ mol Li}}{6.941 \text{ g Li}} \right) \left(\frac{2 \text{ mol } Li_2O}{4 \text{ mol Li}} \right) \left(\frac{29.88 \text{ g } Li_2O}{1 \text{ mol } Li_2O} \right) = 3.4869 = \mathbf{3.49 \text{ g } Li_2O}$$

$$\text{Grams } O_2 \text{ used} = (1.62 \text{ g Li}) \left(\frac{1 \text{ mol Li}}{6.941 \text{ g Li}} \right) \left(\frac{1 \text{ mol } O_2}{4 \text{ mol Li}} \right) \left(\frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} \right) = 1.867166 \text{ g } O_2 \text{ (unrounded)}$$

$$\text{Remaining } O_2 = 6.00 \text{ g } O_2 - 1.867166 \text{ g } O_2 = 4.13283 = \mathbf{4.13 \text{ g } O_2}$$

- 4.73 Plan: To find the mass of Fe, write a balanced equation for the reaction, determine whether Al or Fe₂O₃ is the limiting reactant, and convert to mass.

Solution:



When the masses of both reactants are given, you must determine which reactant is limiting.

$$\text{Mole Fe (from Al)} = (1.00 \text{ kg Al}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{2 \text{ mol Fe}}{2 \text{ mol Al}} \right) = 37.064 \text{ mol Fe (unrounded)}$$

$$\text{Mole Fe (from Fe}_2\text{O}_3) = (2.00 \text{ mol Fe}_2\text{O}_3) \left(\frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} \right) = 4.00 \text{ mol Fe}$$

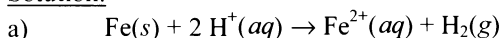
Fe₂O₃ is limiting, so 4.00 moles of Fe forms.

$$\text{Mass} = (4.00 \text{ mol Fe}) \left(\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \right) = 223.4 = 223 \text{ g Fe}$$

Though not required by the problem, this could be converted to **0.223 kg**.

- 4.74 Plan: Convert the mass of Fe in a 125-g serving to the mass of Fe in a 737-g sample. Use molar mass to convert mass to moles and use Avogadro's number to convert moles of Fe to moles of ions.

Solution:



O.N.: 0 +1 +2 0

$$\begin{aligned} \text{b) Fe}^{2+} \text{ ions} &= (737 \text{ g Sauce}) \left(\frac{49 \text{ mg Fe}}{125 \text{ g Sauce}} \right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \right) \left(\frac{1 \text{ mol Fe}^{2+}}{1 \text{ mol Fe}} \right) \left(\frac{6.022 \times 10^{23} \text{ Fe}^{2+} \text{ ions}}{1 \text{ mol Fe}^{2+}} \right) \\ &= 3.11509 \times 10^{21} = \mathbf{3.1 \times 10^{21} \text{ Fe}^{2+} \text{ ions}} \text{ per jar of sauce} \end{aligned}$$

- 4.75 Plan: Convert the mass of glucose to moles and use the molar ratios from the balanced equation to find the moles of ethanol and CO₂. The amount of ethanol is converted from moles to grams using its molar mass.

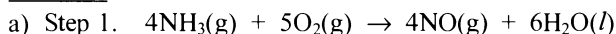
Solution:

$$\begin{aligned} \text{Mass of C}_2\text{H}_5\text{OH} &= (10.0 \text{ g C}_6\text{H}_{12}\text{O}_6) \left(\frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.16 \text{ g C}_6\text{H}_{12}\text{O}_6} \right) \left(\frac{2 \text{ mol C}_2\text{H}_5\text{OH}}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \right) \left(\frac{46.07 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ mol C}_2\text{H}_5\text{OH}} \right) \\ &= 5.1143 = \mathbf{5.11 \text{ g C}_2\text{H}_5\text{OH}} \end{aligned}$$

$$\begin{aligned} \text{Volume CO}_2 &= (10.0 \text{ g C}_6\text{H}_{12}\text{O}_6) \left(\frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.16 \text{ g C}_6\text{H}_{12}\text{O}_6} \right) \left(\frac{2 \text{ mol CO}_2}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \right) \left(\frac{22.4 \text{ L CO}_2}{1 \text{ mol CO}_2} \right) \\ &= 2.4866785 = \mathbf{2.49 \text{ L CO}_2} \end{aligned}$$

- 4.80 Plan: For part (a), assign oxidation numbers to each element; the oxidizing agent has an atom whose oxidation number decreases while the reducing agent has an atom whose oxidation number increases. For part (b), use the molar ratios, beginning with Step 3, to find the moles of NO₂, then moles of NO, then moles of NH₃ required to produce the given mass of HNO₃.

Solution:

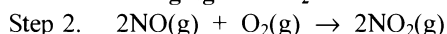


O.N.: N = -3 O = 0 N = +2 H = +1

 H = +1 O = -2 O = -2

N oxidized from -3 to +2 by O₂, and O is reduced from 0 to -2.

Oxidizing agent = O₂ Reducing agent = NH₃



O.N.: N = +2 O = 0 N = +4

 O = -2 O = -2

N oxidized from +2 to +4 by O₂, and O is reduced from 0 to -2.

Oxidizing agent = O₂ Reducing agent = NO

$$\text{Moles H} = (0.02750 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) \left(\frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right) = 3.052164 \times 10^{-3} \text{ mol H (unrounded)}$$

$$\text{Moles Bi} = (0.1422 \text{ g Bi}_2\text{O}_3) \left(\frac{1 \text{ mol Bi}_2\text{O}_3}{466.0 \text{ g Bi}_2\text{O}_3} \right) \left(\frac{2 \text{ mol Bi}}{1 \text{ mol Bi}_2\text{O}_3} \right) = 6.103004 \times 10^{-4} \text{ mol Bi (unrounded)}$$

Subtracting the mass of each element present from the mass of the sample will give the mass of oxygen originally present in the sample. This mass is used to find the moles of oxygen.

$$\text{Mass C} = (4.271756 \times 10^{-3} \text{ mol C}) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 0.0513038 \text{ g C}$$

$$\text{Mass H} = (3.052164 \times 10^{-3} \text{ mol H}) \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 0.0030766 \text{ g H}$$

$$\text{Mass Bi} = (6.103004 \times 10^{-4} \text{ mol Bi}) \left(\frac{209.0 \text{ g Bi}}{1 \text{ mol Bi}} \right) = 0.127553 \text{ g Bi}$$

$$\text{Mass O} = 0.22105 \text{ g sample} - (0.0513038 \text{ g C} + 0.0030766 \text{ g H} + 0.127553 \text{ g Bi}) = 0.0391166 \text{ g O}$$

$$\text{Moles O} = (0.0391166 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 0.0024448 \text{ mol O}$$

Divide each of the moles by the smallest value (moles Bi).

$$\text{C} = (4.271756 \times 10^{-3} \text{ mol}) / (6.103004 \times 10^{-4} \text{ mol}) = 7$$

$$\text{H} = (3.052164 \times 10^{-3} \text{ mol}) / (6.103004 \times 10^{-4} \text{ mol}) = 5$$

$$\text{O} = (2.4448 \times 10^{-3} \text{ mol}) / (6.103004 \times 10^{-4} \text{ mol}) = 4$$

$$\text{Bi} = (6.103004 \times 10^{-4} \text{ mol}) / (6.103004 \times 10^{-4} \text{ mol}) = 1$$

Empirical formula = **C₇H₅O₄Bi**

b) The empirical formula mass is 362 g/mol. Therefore, there are $1086 / 362 = 3$ empirical formula units per molecular formula making the molecular formula = $3 \times \text{C}_7\text{H}_5\text{O}_4\text{Bi} = \text{C}_{21}\text{H}_{15}\text{O}_{12}\text{Bi}_3$.

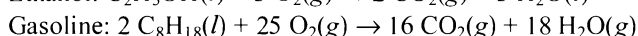
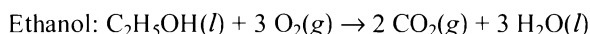
c) $\text{Bi}(\text{OH})_3(s) + 3 \text{HC}_7\text{H}_5\text{O}_3(aq) \rightarrow \text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3(s) + 3 \text{H}_2\text{O}(l)$

$$\begin{aligned} \text{d) } (0.600 \text{ mg}) & \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mol Active}}{1086 \text{ g}} \right) \left(\frac{3 \text{ mol Bi}}{1 \text{ mol Active}} \right) \left(\frac{1 \text{ mol Bi}(\text{OH})_3}{1 \text{ mol Bi}} \right) \left(\frac{260.0 \text{ g Bi}(\text{OH})_3}{1 \text{ mol Bi}(\text{OH})_3} \right) \left(\frac{1 \text{ mg}}{10^{-3} \text{ g}} \right) \left(\frac{100\%}{88.0\%} \right) \\ & = 0.48970 = \mathbf{0.490 \text{ mg Bi}(\text{OH})_3} \end{aligned}$$

4.90 Plan: Write balanced equations and use the molar ratios to convert mass of each fuel to the mass of oxygen required for the reaction.

Solution:

a) Complete combustion of hydrocarbons involves heating the hydrocarbon in the presence of oxygen to produce carbon dioxide and water.



b) The amounts of each fuel must be found:

$$\text{Gasoline} = (1.00 \text{ L}) \left(\frac{90\%}{100\%} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{0.742 \text{ g}}{1 \text{ mL}} \right) = 667.8 \text{ g gasoline (unrounded)}$$

$$\text{Ethanol} = (1.00 \text{ L}) \left(\frac{10\%}{100\%} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{0.789 \text{ g}}{1 \text{ mL}} \right) = 78.9 \text{ g ethanol}$$

$$\begin{aligned} \text{Mass O}_2 (\text{gasoline}) &= (667.8 \text{ g C}_8\text{H}_{18}) \left(\frac{1 \text{ mol C}_8\text{H}_{18}}{114.22 \text{ g C}_8\text{H}_{18}} \right) \left(\frac{25 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} \right) \left(\frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \right) \\ &= 2338.64 \text{ g O}_2 (\text{unrounded}) \end{aligned}$$

$$\begin{aligned} \text{Mass O}_2 (\text{ethanol}) &= (78.9 \text{ g C}_2\text{H}_5\text{OH}) \left(\frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} \right) \left(\frac{3 \text{ mol O}_2}{1 \text{ mol C}_2\text{H}_5\text{OH}} \right) \left(\frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \right) \\ &= 164.41 \text{ g O}_2 (\text{unrounded}) \end{aligned}$$

$$\text{Total O}_2 = 2338.64 \text{ g O}_2 + 164.41 \text{ g O}_2 = 2503.05 = \mathbf{2.50 \times 10^3 \text{ g O}_2}$$

$$\text{c) } (2503.05 \text{ g O}_2) \left(\frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left(\frac{22.4 \text{ L}}{1 \text{ mol O}_2} \right) = 1752.135 = \mathbf{1.75 \times 10^3 \text{ L O}_2}$$

$$\text{d) } (1752.135 \text{ L O}_2) \left(\frac{100\%}{20.9\%} \right) = 8383.42 = \mathbf{8.38 \times 10^3 \text{ L air}}$$

- 4.92 Plan: From the molarity and volume of the base NaOH, find the moles of NaOH and use the molar ratios from the two balanced equations to convert the moles of NaOH to moles of HBr to moles of vitamin C. Use the molar mass of vitamin C to convert moles to grams.

Solution:

Mass vitamin C:

$$(43.20 \text{ mL NaOH}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.1350 \text{ mol NaOH}}{1 \text{ L}} \right) \left(\frac{1 \text{ mol HBr}}{1 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mol C}_6\text{H}_8\text{O}_6}{2 \text{ mol HBr}} \right) \left(\frac{176.12 \text{ g C}_6\text{H}_8\text{O}_6}{1 \text{ mol C}_6\text{H}_8\text{O}_6} \right) \left(\frac{1 \text{ mg}}{10^{-3} \text{ g}} \right)$$

$$= 513.5659 = 513.6 \text{ mg C}_6\text{H}_8\text{O}_6$$

Yes, the tablets have the quantity advertised.

- 4.93 Plan: Remember that oxidation numbers change in a redox reaction. For the calculations, use the molarity and volume of HCl to find the moles of HCl and use the molar ratios from the balanced equation to convert moles of HCl to moles and then grams of the desired substance.

Solution:

a) The **second reaction is a redox process** because the O.N. of iron changes from 0 to +2 (it oxidizes) while the O.N. of hydrogen changes from +1 to 0 (it reduces).

b) Determine the moles of HCl present and use the balanced chemical equation to determine the appropriate quantities.

$$\text{Mass Fe}_2\text{O}_3 = (2.50 \times 10^3 \text{ L}) \left(\frac{3.00 \text{ mol HCl}}{\text{L}} \right) \left(\frac{1 \text{ mol Fe}_2\text{O}_3}{6 \text{ mol HCl}} \right) \left(\frac{159.70 \text{ g Fe}_2\text{O}_3}{1 \text{ mol Fe}_2\text{O}_3} \right)$$

$$= 199625 = \mathbf{2.00 \times 10^5 \text{ g Fe}_2\text{O}_3}$$

$$\text{Mass FeCl}_3 = (2.50 \times 10^3 \text{ L}) \left(\frac{3.00 \text{ mol HCl}}{\text{L}} \right) \left(\frac{2 \text{ mol FeCl}_3}{6 \text{ mol HCl}} \right) \left(\frac{162.20 \text{ g FeCl}_3}{1 \text{ mol FeCl}_3} \right)$$

$$= 405500 = \mathbf{4.06 \times 10^5 \text{ g FeCl}_3}$$

c) Use reaction 2 like reaction 1 was used in part b.

$$\text{Mass Fe} = (2.50 \times 10^3 \text{ L}) \left(\frac{3.00 \text{ mol HCl}}{\text{L}} \right) \left(\frac{1 \text{ mol Fe}}{2 \text{ mol HCl}} \right) \left(\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \right)$$

$$= 209437.5 = \mathbf{2.09 \times 10^5 \text{ g Fe}}$$

$$\text{Mass FeCl}_2 = (2.50 \times 10^3 \text{ L}) \left(\frac{3.00 \text{ mol HCl}}{\text{L}} \right) \left(\frac{1 \text{ mol FeCl}_2}{2 \text{ mol HCl}} \right) \left(\frac{126.75 \text{ g FeCl}_2}{1 \text{ mol FeCl}_2} \right)$$

$$= 475312.5 = \mathbf{4.75 \times 10^5 \text{ g FeCl}_2}$$

d) Use 1.00 g Fe₂O₃ to determine the mass of FeCl₃ formed (reaction 1), and 0.280 g Fe to determine the mass of FeCl₂ formed (reaction 2).

$$\text{Mass FeCl}_3 = (1.00 \text{ g Fe}_2\text{O}_3) \left(\frac{1 \text{ mol Fe}_2\text{O}_3}{159.70 \text{ g Fe}_2\text{O}_3} \right) \left(\frac{2 \text{ mol FeCl}_3}{1 \text{ mol Fe}_2\text{O}_3} \right) \left(\frac{162.20 \text{ g FeCl}_3}{1 \text{ mol FeCl}_3} \right)$$

$$= 2.0313 \text{ g FeCl}_3 \text{ (unrounded)}$$

$$\text{Mass FeCl}_2 = (0.280 \text{ g Fe}) \left(\frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \right) \left(\frac{1 \text{ mol FeCl}_2}{1 \text{ mol Fe}} \right) \left(\frac{126.75 \text{ g FeCl}_2}{1 \text{ mol FeCl}_2} \right)$$

$$= 0.635452 \text{ g FeCl}_2 \text{ (unrounded)}$$

$$\text{Ratio} = (0.635452 \text{ g FeCl}_2) / (2.0313 \text{ g FeCl}_3) = 0.312830 = \mathbf{0.313}$$

Chapter 5 Gases and the Kinetic-Molecular Theory

FOLLOW-UP PROBLEMS

- 5.1 Plan: Use conversion factors in Table 5.1 to convert pressure in torr to units of mmHg, pascals and lb/in².

Solution:

$$P_{\text{CO}_2} = 579.6 \text{ torr}$$

$$\text{Converting from torr to mmHg: } P = (579.6 \text{ torr}) \left(\frac{1 \text{ mmHg}}{1 \text{ torr}} \right) = \mathbf{579.6 \text{ torr}}$$

$$\begin{aligned} \text{Converting from torr to pascals: } P &= (579.6 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) \\ &= 7.727364 \times 10^4 = \mathbf{7.727 \times 10^4 \text{ Pa}} \end{aligned}$$

$$\text{Converting from torr to lb/in}^2: P = (579.6 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{14.7 \text{ lb/in}^2}{1 \text{ atm}} \right) = 11.21068 = \mathbf{11.2 \text{ lb/in}^2}$$

Check: For conversion to mmHg, the value of the pressure should stay the same. The order of magnitude for each conversion corresponds to the calculated answer. For conversion to pascals the order of magnitude calculation is $10^2 \times 10^5 / 10^2 = 10^5$. For conversion to lb/in² the order of magnitude calculation is $10^2 \times 10^1 / 10^2 = 10^1$.

- 5.2 Plan: Given in the problem is an initial volume, initial pressure, and final pressure for the argon gas. The final volume can be calculated from the relationship $P_1 V_1 = P_2 V_2$. Unit conversions for mL to L and atm to kPa must be included.

Solution:

$$\begin{aligned} P_1 = 0.871 \text{ atm; } V_1 &= (105 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.105 \text{ L; } P_2 = (26.3 \text{ kPa}) \left(\frac{10^3 \text{ Pa}}{1 \text{ kPa}} \right) \left(\frac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} \right) \\ &= 0.25956 \text{ atm} \end{aligned}$$

$$V_2 = (V_1) \left(\frac{P_1}{P_2} \right) = \frac{(0.871 \text{ atm})(0.105 \text{ L})}{(0.25956 \text{ atm})} = 0.352346 = \mathbf{0.352 \text{ L}}$$

Check: As the pressure goes from 0.871 atm to 0.25956 atm, it is decreasing by a factor of about 3 and the volume should increase by the same factor. The calculated volume of 0.352 L is approximately 3 times greater than the initial volume of 0.105 L.

- 5.3 Plan: The problem asked for a temperature with given initial temperature, initial volume, and final volume. The relationship to use is $V_1/T_1 = V_2/T_2$. The units of volume in both cases are the same, but the initial temperature must be converted to Kelvin.

Solution:

$$V_1 = 6.83 \text{ cm}^3; T_1 = 0^\circ\text{C} + 273 = 273 \text{ K; } V_2 = 9.75 \text{ cm}^3; T_2 = ?$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = T_1 \left(\frac{V_2}{V_1} \right) = (273 \text{ K}) \left(\frac{9.75 \text{ cm}^3}{6.83 \text{ cm}^3} \right) = 389.714 = \mathbf{390. \text{ K}}$$

Check: The volume increases by a factor of about 1.4 so the temperature must have increased by the same factor. The initial temperature of 273 K times 1.4 is 380 K, so the answer 390 K appears to be correct.

- 5.4 Plan: In this problem, the amount of gas is decreasing. Since the container is rigid, the volume of the gas will not change with the decrease in moles of gas. The temperature is also constant. So, the only change will be that the pressure of the gas will decrease since fewer moles of gas will be present after removal of the 5.0 g of ethylene. To calculate the final pressure, use the relationship $n_1/P_1 = n_2/P_2$. Since the ratio of moles of ethylene is equal to the ratio of grams of ethylene, there is no need to convert the grams to moles. (This is illustrated in the solution by listing the molar mass conversion twice.)

Solution:

$$\frac{n_1}{P_1} = \frac{n_2}{P_2}$$

$$P_2 = (P_1) \left(\frac{n_2}{n_1} \right) = (793 \text{ torr}) \frac{((35.0 - 5.0) \text{ g C}_2\text{H}_4) \left(\frac{1 \text{ mol C}_2\text{H}_4}{28.05 \text{ g C}_2\text{H}_4} \right)}{(35.0 \text{ g C}_2\text{H}_4) \left(\frac{1 \text{ mol C}_2\text{H}_4}{28.05 \text{ g C}_2\text{H}_4} \right)} = 679.714 = \mathbf{680. \text{ torr}}$$

Check: The amount of gas decreases by a factor of 6/7. Since pressure is proportional to the amount of gas, the pressure should decrease by the same factor, $6/7 \times 793 = 680$.

- 5.5 Plan: From Sample Problem 5.5 the temperature of 21°C and volume of 438 L are given. The pressure is 1.37 atm and the unknown is the moles of oxygen gas. Use the ideal gas equation to calculate the number of moles of gas.

Solution:

$$n = PV / RT = \frac{(1.37 \text{ atm})(438 \text{ L})}{\left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) ((273.15 + 21) \text{ K})} = 24.847 \text{ mol O}_2$$

$$\text{Mass of O}_2 = (24.847 \text{ mol O}_2) \times (32.00 \text{ g/mol}) = 795.104 = \mathbf{795 \text{ g O}_2}$$

- 5.6 Plan: The pressure is constant and, according to the picture, the volume approximately doubles. The volume change may be due to the temperature and/or a change in moles.

Solution:

The balanced chemical equation must be $2 \text{ CD} \rightarrow \text{C}_2 + \text{D}_2$.

Thus, the number of mole of gas does not change (2 moles both before and after the reaction). Only the temperature remains as a variable to cause the volume change. Using $V_1 / T_1 = V_2 / T_2$ with $V_2 = 2 V_1$, and $T_1 = (-73 + 273.15) \text{ K}$ gives:

$$T_2 = T_1 \left(\frac{V_2}{V_1} \right) = \frac{(2V_1)(-73 + 273.15) \text{ K}}{(V_1)} = 400.30 \text{ K} - 273.15 = 127.15 = \mathbf{127^\circ \text{C}}$$

- 5.7 Plan: Density of a gas can be calculated using a version of the ideal gas equation, $d = \frac{\mathcal{M}P}{RT}$

Two calculations are required, one with $T = 0^\circ \text{C} = 273 \text{ K}$ and $P = 380 \text{ torr}$ and the other at STP which is defined as $T = 273 \text{ K}$ and $P = 1 \text{ atm}$.

Solution: Density at $T = 273 \text{ K}$ and $P = 380 \text{ torr}$

$$d = \frac{(44.01 \text{ g/mol})(380 \text{ torr})}{\left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) (273 \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.981783 = \mathbf{0.982 \text{ g/L}}$$

Density at $T = 273 \text{ K}$ and $P = 1 \text{ atm}$. (Note: The 1 atm is an exact number and does not affect the significant figures in the answer.)

$$d = \frac{(44.01 \text{ g/mol})(1 \text{ atm})}{\left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) (273 \text{ K})} = 1.9638566 = \mathbf{1.96 \text{ g/L}}$$

The density of a gas increases proportionally to the increase in pressure.

Check: In the two density calculations, the temperature of the gas is the same, but the pressure differs by a factor of two. The calculation of density shows that it is proportional to pressure. The pressure in the first case is half the pressure at STP, so the density at 380 torr should be half the density at STP and it is.

- 5.8 Plan: Use the ideal gas equation for density, $d = \frac{MP}{RT}$, and solve for molar mass.

Solution:

$$\text{Molar mass} = \frac{dRT}{P} = \frac{(1.26 \text{ g/L}) \left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) ((10.0 + 273.15) \text{ K})}{(102.5 \text{ kPa})} \left(\frac{101.325 \text{ kPa}}{1 \text{ atm}} \right)$$

$$= 28.95496 = \mathbf{29.0 \text{ g/mol}}$$

Check: Dry air would consist of about 80% N₂ and 20% O₂. Estimating a molar mass for this mixture gives (0.80 x 28) + (0.20 x 32) = 28.8 g/mol, which is close to the calculated value.

- 5.9 Plan: Calculate the number of moles of each gas present and then the mole fraction of each gas. The partial pressure of each gas equals the mole fraction times the total pressure. Total pressure equals 1 atm since the problem specifies STP. This pressure is an exact number, and will not affect the significant figures in the answer. No intermediate values, such as the moles of each gas, will be rounded. This will avoid intermediate rounding.

Solution:

$$n_{\text{He}} = (5.50 \text{ g He}) \left(\frac{1 \text{ mol He}}{4.003 \text{ g He}} \right) = 1.37397 \text{ mol He}$$

$$n_{\text{Ne}} = (15.0 \text{ g Ne}) \left(\frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} \right) = 0.74331 \text{ mol Ne}$$

$$n_{\text{Kr}} = (35.0 \text{ g Kr}) \left(\frac{1 \text{ mol Kr}}{83.80 \text{ g Kr}} \right) = 0.41766 \text{ mol He}$$

Total number of moles of gas = 1.37397 + 0.74331 + 0.41766 = 2.53494 mol

$$P_A = X_A \times P_{\text{total}}$$

$$P_{\text{He}} = \left(\frac{1.37397 \text{ mol He}}{2.53494 \text{ mol}} \right) (1 \text{ atm}) = 0.54201 = \mathbf{0.542 \text{ atm He}}$$

$$P_{\text{Ne}} = \left(\frac{0.74331 \text{ mol Ne}}{2.53494 \text{ mol}} \right) (1 \text{ atm}) = 0.29322 = \mathbf{0.293 \text{ atm Ne}}$$

$$P_{\text{Kr}} = \left(\frac{0.41766 \text{ mol Kr}}{2.53494 \text{ mol}} \right) (1 \text{ atm}) = 0.16476 = \mathbf{0.165 \text{ atm Kr}}$$

Check: One way to check is that the partial pressures add to the total pressure, 0.542 + 0.293 + 0.165 = 1.000 atm, which agrees with the total pressure of 1 atm at STP.

- 5.10 Plan: The gas collected over the water will consist of H₂ and H₂O gas molecules. The partial pressure of the water can be found from the vapor pressure of water at the given temperature (Table 5.2). Subtracting this partial pressure of water from total pressure gives the partial pressure of hydrogen gas collected over the water. Calculate the moles of hydrogen gas using the ideal gas equation. The mass of hydrogen can then be calculated by converting the moles of hydrogen from the ideal gas equation to grams.

Solution: From Table 5.3, the partial pressure of water is 13.6 torr at 16°C.

$$P = 752 \text{ torr} - 13.6 \text{ torr} = 738.4 = \mathbf{738 \text{ torr H}_2}$$

The unrounded partial pressure (738.4 torr) will be used to avoid rounding error.

$$\text{Moles of hydrogen} = n = PV/RT = \frac{(738.4 \text{ torr})(1495 \text{ mL})}{\left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) ((273.15 + 16) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right)$$

$$= 0.061186 \text{ mol H}_2 \text{ (unrounded)}$$

$$\text{Mass of hydrogen} = (0.061186 \text{ mol H}_2) \left(\frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} \right) = 0.123351 = \mathbf{0.123 \text{ g H}_2}$$

Check: Since the pressure and temperature are close to STP, and the volume is near 1.5 L, the molar volume at STP (22.4 L/mol) may be used to estimate the mass of hydrogen.

$(1 \text{ mol}/22.4 \text{ L}) (1.5 \text{ L}) (2 \text{ g/mol}) = 0.13 \text{ g}$, which is close to the calculated value.

- 5.11 Plan: Write a balanced equation for the reaction. Calculate the moles of $\text{HCl}(g)$ from the starting amount of sodium chloride using the stoichiometric ratio from the balanced equation. Find the volume of the $\text{HCl}(g)$ from the molar volume at STP.

Solution:

The balanced equation is $\text{H}_2\text{SO}_4(aq) + 2 \text{ NaCl}(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + 2 \text{ HCl}(g)$.

$$(0.117 \text{ kg NaCl}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) \left(\frac{2 \text{ mol HCl}}{2 \text{ mol NaCl}} \right) = 2.00205 \text{ mol HCl}$$

$$\text{At STP: } (2.00205 \text{ mol HCl}) \left(\frac{22.4 \text{ L}}{1 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 4.4846 \times 10^4 = \mathbf{4.48 \times 10^4 \text{ mL HCl}}$$

Check: 117 g NaCl is about 2 moles, which would form 2 moles of $\text{HCl}(g)$. Twice the molar volume is 44.8 L, which is the answer as calculated.

- 5.12 Plan: Balance the equation for the reaction. Determine the limiting reactant by finding the moles of each reactant from the ideal gas equation, and comparing the values. Calculate the moles of remaining excess reactant. This is the only gas left in the flask, so it is used to calculate the pressure inside the flask. There will be no intermediate rounding.

Solution:

The balanced equation is $\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$.

The stoichiometric ratio of NH_3 to HCl is 1:1, so the reactant present in the lower quantity of moles is the limiting reactant.

$$\text{Moles ammonia} = \frac{PV}{RT} = \frac{(0.452 \text{ atm})(10.0 \text{ L})}{\left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) ((273.15 + 22) \text{ K})} = 0.18653 \text{ mol NH}_3$$

$$\text{Moles hydrogen chloride} = \frac{(7.50 \text{ atm})(155 \text{ mL})}{\left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) (271 \text{ K})} \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.052249 \text{ mol HCl}$$

The HCl is limiting so the moles of ammonia gas left after the reaction would be $0.18653 - 0.052249 = 0.134281 \text{ mol NH}_3$

$$\text{Pressure ammonia} = \frac{nRT}{V} = \frac{(0.134281 \text{ mol}) \left(\frac{0.0821 \text{ atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \right) ((273.15 + 22) \text{ K})}{(10.0 \text{ L})}$$

$$= 0.325387 = \mathbf{0.325 \text{ atm NH}_3}$$

Check: Doing a rough calculation of moles gives for NH_3

$(0.5 \times 10) / (0.1 \times 300) = 0.17 \text{ mol}$ and for HCl $(8 \times 0.1) / (0.1 \times 300) = 0.027 \text{ mol}$ which means 0.14 mol NH_3 is left. Plugging this value into a rough calculation of the pressure gives $(0.14 \times 0.1 \times 300) / 10 = 0.4 \text{ atmospheres}$. This is close to the calculated answer.

- 5.13 Plan: Graham's Law can be used to solve for the effusion rate of the ethane since the rate and molar mass of helium is known, along with the molar mass of ethane. In the same way that running slower increases the time to go from one point to another, so the rate of effusion decreases as the time increases. The rate can be expressed as 1/time.

Solution:

$$\frac{\text{Rate He}}{\text{Rate C}_2\text{H}_6} = \sqrt{\frac{M_{\text{C}_2\text{H}_6}}{M_{\text{He}}}}$$

$$\frac{\left(\frac{0.010 \text{ mol He}}{1.25 \text{ min}}\right)}{\left(\frac{0.010 \text{ mol C}_2\text{H}_6}{t_{\text{C}_2\text{H}_6}}\right)} = \sqrt{\frac{(30.07 \text{ g/mol})}{(4.003 \text{ g/mol})}}$$

Time for C₂H₆ = 3.42597 = **3.43 min**

Check: The ethane should move slower than the helium since ethane has a larger molar mass. This is consistent with the calculation that the ethane molecule takes longer to effuse. The second check is an estimate. The square root of 30 is estimated as 5 and the square root of 4 is 2. The time 1.25 min x 5/2 = 3.1 min, which validates the calculated answer of 3.42 min.

END-OF-CHAPTER PROBLEMS

- 5.1 a) The volume of the liquid remains constant, but the volume of the gas increases to the volume of the larger container.
b) The volume of the container holding the gas sample increases when heated, but the volume of the container holding the liquid sample remains essentially constant when heated.
c) The volume of the liquid remains essentially constant, but the volume of the gas is reduced.
- 5.6 The ratio of the heights of columns of mercury and water are inversely proportional to the ratio of the densities of the two liquids.

$$\frac{h_{\text{H}_2\text{O}}}{h_{\text{Hg}}} = \frac{d_{\text{Hg}}}{d_{\text{H}_2\text{O}}}$$

$$h_{\text{H}_2\text{O}} = \frac{d_{\text{Hg}}}{d_{\text{H}_2\text{O}}} \times h_{\text{Hg}} = \left(\frac{13.5 \text{ g/mL}}{1.00 \text{ g/mL}}\right)(725 \text{ mmHg})\left(\frac{10^{-3} \text{ m}}{1 \text{ mm}}\right)\left(\frac{1 \text{ cm}}{10^{-2} \text{ m}}\right) = 978.75 = \mathbf{979 \text{ cm H}_2\text{O}}$$

- 5.8 Plan: Use the conversion factors between pressure units:
1 atm = 760 mmHg = 760 torr = 101.325 kPa = 1.01325 bar

Solution:

- a) $(0.745 \text{ atm})\left(\frac{760 \text{ mmHg}}{1 \text{ atm}}\right) = 566.2 = \mathbf{566 \text{ mmHg}}$
- b) $(992 \text{ torr})\left(\frac{1.01325 \text{ bar}}{760 \text{ torr}}\right) = 1.32256 = \mathbf{1.32 \text{ bar}}$
- c) $(365 \text{ kPa})\left(\frac{1 \text{ atm}}{101.325 \text{ kPa}}\right) = 3.60227 = \mathbf{3.60 \text{ atm}}$
- d) $(804 \text{ mmHg})\left(\frac{101.325 \text{ kPa}}{760 \text{ mmHg}}\right) = 107.191 = \mathbf{107 \text{ kPa}}$

- 5.14 At constant temperature and volume, the pressure of the gas is directly proportional to the number of moles of the gas. Verify this by examining the ideal gas equation. At constant T and V, the ideal gas equation becomes $P = n(RT/V)$ or $P = n \times \text{constant}$.

- 5.16 a) As the pressure on a gas increases, the molecules move closer together, decreasing the volume. When the pressure is tripled, the **volume decreases to one third of the original volume** at constant temperature (Boyle's Law).
 b) As the temperature of a gas increases, the gas molecules gain kinetic energy. With higher energy, the gas molecules collide with the walls of the container with greater force, which increases the size (volume) of the container. If the temperature is increased by a factor of 2.5 (at constant pressure) then the **volume will increase by a factor of 2.5** (Charles's Law).
 c) As the number of molecules of gas increase, the force they exert on the container increases. This results in an increase in the volume of the container. Adding two moles of gas to one mole increases the number of moles by a factor of three, thus the **volume increases by a factor of three** (Avogadro's Law).

- 5.18 Plan: This is Charles's Law. Charles's Law states that at constant pressure and with a fixed amount of gas, the volume of a gas is directly proportional to the absolute temperature of the gas. The temperature must be lowered to reduce the volume of a gas.

Solution:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{at constant } n \text{ and } P \quad T_2 = T_1 \frac{V_2}{V_1}$$

$$V_1 = 5.10 \text{ L}; \quad T_1 = 198^\circ\text{C} + 273 = 471 \text{ K}; \quad V_2 = 2.50 \text{ L} \quad T_2 = ?$$

$$T_2 = 471 \text{ K} \left(\frac{2.50 \text{ L}}{5.10 \text{ L}} \right) = 230.88 \text{ K} - 273 = -42.12 = -42^\circ\text{C}$$

- 5.20 Plan: Since the volume, temperature, and pressure of the gas are changing, use the combined gas law.

Solution:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad P_1 = 153.3 \text{ kPa}; \quad V_1 = 25.5 \text{ L}; \quad T_1 = 298 \text{ K}; \quad P_2 = 101.325 \text{ kPa}; \quad T_2 = 273 \text{ K}; \quad V_2 = ?$$

$$V_2 = V_1 \left(\frac{T_2}{T_1} \right) \left(\frac{P_1}{P_2} \right) = (25.5 \text{ L}) \left(\frac{273 \text{ K}}{298 \text{ K}} \right) \left(\frac{153.3 \text{ kPa}}{101.325 \text{ kPa}} \right) = 35.3437 = \mathbf{35.3 \text{ L}}$$

- 5.22 Plan: Given the volume, pressure, and temperature of a gas, the number of moles of the gas can be calculated using the ideal gas equation, $n = PV/RT$. The gas constant, $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$, gives pressure in atmospheres and temperature in Kelvin. The given pressure in torr must be converted to atmospheres and the temperature converted to Kelvin.

Solution:

$$PV = nRT \quad \text{or} \quad n = PV/RT \quad P = (228 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.300 \text{ atm}; \quad V = 5.0 \text{ L}; \quad T = 27^\circ\text{C} + 273 = 300 \text{ K}$$

$$n = \frac{PV}{RT} = \frac{(0.300 \text{ atm})(5.0 \text{ L})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(300 \text{ K})} = 0.060901 = \mathbf{0.061 \text{ mol chlorine}}$$

- 5.24 Plan: Solve the ideal gas equation for moles and convert to mass using the molar mass of ClF_3 . Volume must be converted to L, pressure to atm and temperature to K.

Solution:

$$PV = nRT \quad \text{or} \quad n = PV/RT \quad P = (699 \text{ mmHg}) \left(\frac{1 \text{ atm}}{760 \text{ mmHg}} \right) = 0.91974 \text{ atm}; \quad V = 0.207 \text{ L}$$

$$T = 45^\circ\text{C} + 273 = 318 \text{ K}$$

$$n = \frac{PV}{RT} = \frac{(0.91974 \text{ atm})(0.207 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(318 \text{ K})} = 0.0072923 \text{ mol ClF}_3$$

$$\text{mass ClF}_3 = (0.0072923 \text{ mol ClF}_3) \left(\frac{92.45 \text{ g ClF}_3}{1 \text{ mol ClF}_3} \right) = 0.67417 = \mathbf{0.674 \text{ g ClF}_3}$$

- 5.28 The molar mass of H_2 is less than the average molar mass of air (mostly N_2 , O_2 , and Ar), so air is denser. To collect a beaker of $\text{H}_2(\text{g})$, **invert** the beaker so that the air will be replaced by the lighter H_2 . The molar mass of CO_2 is greater than the average molar mass of air, so $\text{CO}_2(\text{g})$ is more dense. Collect the CO_2 holding the beaker **upright**, so the lighter air will be displaced out the top of the beaker.

- 5.31 Plan: Using the ideal gas equation and the molar mass of xenon, 131.3 g/mol, we can find the density of xenon gas at STP. Standard temperature is 0°C and standard pressure is 1 atm. Do not forget that the pressure at STP is exact and will not affect the significant figures.

Solution:

$$d = \mathcal{M} P / RT = \frac{(131.3 \text{ g/mol})(1 \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(273 \text{ K})} = 5.8581 = \mathbf{5.86 \text{ g/L}}$$

- 5.33 Plan: Apply the ideal gas equation to determine the number of moles. Convert moles to mass and divide by the volume to obtain density in g/L. Do not forget that the pressure at STP is exact and will not affect the significant figures.

Solution:

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(0.0400 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(273 \text{ K})} = 1.78465 \times 10^{-3} = \mathbf{1.78 \times 10^{-3} \text{ mol AsH}_3}$$

$$d = \frac{\text{mass}}{\text{volume}} = \frac{(1.78465 \times 10^{-3} \text{ mol})(77.94 \text{ g/mol})}{(0.0400 \text{ L})} = 3.47740 = \mathbf{3.48 \text{ g/L}}$$

- 5.35 Plan: Rearrange the formula $PV = (m / \mathcal{M})RT$ to solve for molar mass: $\mathcal{M} = mRT / PV$. Convert the mass in ng to grams and volume in μL to L. Temperature must be in Kelvin and pressure in torr.

Solution:

$$P = (388 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.510526 \text{ atm} \quad T = 45^\circ\text{C} + 273 = 318 \text{ K}$$

$$V = (0.206 \mu\text{L}) \left(\frac{10^{-6} \text{ L}}{1 \mu\text{L}} \right) = 2.06 \times 10^{-7} \text{ L} \quad \text{mass} = (206 \text{ ng}) \left(\frac{10^{-9} \text{ g}}{1 \text{ ng}} \right) = 2.06 \times 10^{-7} \text{ g}$$

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(2.06 \times 10^{-7} \text{ g})(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(318 \text{ K})}{(0.510526 \text{ atm})(2.06 \times 10^{-7} \text{ L})} = 51.1390 = \mathbf{51.1 \text{ g/mol}}$$

- 5.37 Plan: Use the ideal gas equation to determine the number of moles of Ar and O₂. The gases are combined ($n_{\text{TOT}} = n_{\text{Ar}} + n_{\text{O}}$) into a 400 mL flask (V) at 27°C (T). Determine the total pressure from n_{TOT} , V, and T. Pressure must be in units of atm, volume in units of L and temperature in K.

Solution:

$$PV = nRT \quad n = \frac{PV}{RT}$$

$$\text{Moles Ar} = \frac{PV}{RT} = \frac{(1.20 \text{ atm})(0.600 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 227) \text{ K})} = 0.017539585 \text{ mol Ar (unrounded)}$$

$$\text{Moles O}_2 = \frac{PV}{RT} = \frac{(501 \text{ torr})(0.200 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 127) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.004014680 \text{ mol O}_2 \text{ (unrounded)}$$

$$n_{\text{TOT}} = n_{\text{Ar}} + n_{\text{O}} = 0.017539585 \text{ mol} + 0.004014680 \text{ mol} = 0.021554265 \text{ mol}$$

$$P_{\text{mixture}} = \frac{nRT}{V} = \frac{(0.021554265 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 27) \text{ K})}{400 \text{ mL}} \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$$= 1.32720 = \mathbf{1.33 \text{ atm}}$$

- 5.41 Plan: The problem gives the mass, volume, temperature, and pressure of a gas, so we can solve for molar mass using $\mathcal{M} = mRT/PV$. The problem also states that the gas is a hydrocarbon, which by, definition, contains only carbon and hydrogen atoms. We are also told that each molecule of the gas contains five carbon atoms so we can use this information and the calculated molar mass to find out how many hydrogen atoms are present and the formula of the compound. Convert pressure to atm and temperature to K.

Solution:

$$\mathcal{M} = mRT/PV = \frac{(0.482 \text{ g}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 101) \text{ K})}{(767 \text{ torr})(0.204 \text{ L})} \left(\frac{760 \text{ torr}}{1 \text{ atm}}\right) = 71.8869 \text{ g/mol (unrounded)}$$

The carbon accounts for $[5 (12 \text{ g/mol})] = 60 \text{ g/mol}$, thus, the hydrogen must make up the difference $(72 - 60) = 12 \text{ g/mol}$. A value of 12 g/mol corresponds to 12 H atoms. (Since fractional atoms are not possible, rounding is acceptable.)

Therefore, the molecular formula is **C₅H₁₂**.

- 5.43 Plan: Since you have the pressure, volume and temperature, use the ideal gas equation to solve for the total moles of gas.

Solution:

a) $PV = nRT$

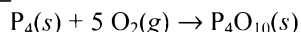
$$n = PV / RT = \frac{(850. \text{ torr})(21 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 45) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.89961 = \mathbf{0.90 \text{ mol gas}}$$

b) The information given in ppm is a way of expressing the proportion, or fraction, of SO₂ present in the mixture. Since n is directly proportional to V, the *volume* fraction can be used in place of the *mole* fraction used in equation 5.12. There are 7.95×10^3 parts SO₂ in a million parts of mixture, so volume fraction = $(7.95 \times 10^3 / 1 \times 10^6) = 7.95 \times 10^{-3}$.

Therefore, $P_{\text{SO}_2} = \text{volume fraction} \times P_{\text{TOT}} = (7.95 \times 10^{-3}) (850. \text{ torr}) = 6.7575 = \mathbf{6.76 \text{ torr}}$.

- 5.44 Plan: We can find the moles of oxygen from the standard molar volume of gases (1 L of gas occupies 22.4 L at STP) and use the stoichiometric ratio from the balanced equation to determine the moles of phosphorus that will react with the oxygen.

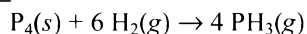
Solution:



$$\text{Mass P}_4 = (35.5 \text{ L O}_2) \left(\frac{1 \text{ mol O}_2}{22.4 \text{ L O}_2} \right) \left(\frac{1 \text{ mol P}_4}{5 \text{ mol O}_2} \right) \left(\frac{123.88 \text{ g P}_4}{1 \text{ mol P}_4} \right) = 39.2655 = \mathbf{39.3 \text{ g P}_4}$$

- 5.46 Plan: To find the mass of PH₃, write the balanced equation and find the number of moles of PH₃ produced by each reactant. The smaller number of moles of product indicates the limiting reagent. Solve for moles of H₂ using the standard molar volume (or use ideal gas equation).

Solution:



$$\text{Moles hydrogen} = (83.0 \text{ L}) \left(\frac{1 \text{ mol}}{22.4 \text{ L}} \right) = 3.705357 \text{ mol H}_2 \text{ (unrounded)}$$

$$\text{PH}_3 \text{ from P}_4 = (37.5 \text{ g P}_4) \left(\frac{1 \text{ mol P}_4}{123.88 \text{ g P}_4} \right) \left(\frac{4 \text{ mol PH}_3}{1 \text{ mol P}_4} \right) = 1.21085 \text{ mol PH}_3$$

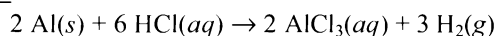
$$\text{PH}_3 \text{ from H}_2 = (3.705357 \text{ mol H}_2) \left(\frac{4 \text{ mol PH}_3}{6 \text{ mol H}_2} \right) = 2.470238 \text{ mol PH}_3$$

P₄ is the limiting reactant.

$$\text{Mass PH}_3 = (37.5 \text{ g P}_4) \left(\frac{1 \text{ mol P}_4}{123.88 \text{ g P}_4} \right) \left(\frac{4 \text{ mol PH}_3}{1 \text{ mol P}_4} \right) \left(\frac{33.99 \text{ g PH}_3}{1 \text{ mol PH}_3} \right) = 41.15676 = \mathbf{41.2 \text{ g PH}_3}$$

- 5.48 Plan: First, write the balanced equation. The moles of hydrogen produced can be calculated from the ideal gas equation and then the stoichiometric ratio from the balanced equation is used to determine the moles of aluminum that reacted. The problem specifies “hydrogen gas collected over water,” so the partial pressure of water must first be subtracted. Table 5.2 reports pressure at 26°C (25.2 torr) and 28°C (28.3 torr), so take the average of the two values to obtain the partial pressure of water at 27°C.

Solution:



Hydrogen pressure = total pressure – pressure of water vapor =

$$(751 \text{ mmHg}) - [(28.3 + 25.2) \text{ torr} / 2] = 724.25 \text{ torr (unrounded)}$$

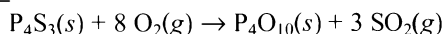
Moles of hydrogen:

$$\text{PV} = nRT \quad n = \frac{\text{PV}}{\text{RT}} = \left[\frac{(724.25 \text{ torr})(35.8 \text{ mL})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273 + 27) \text{ K}} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \right] = 0.00138514 \text{ mol H}_2$$

$$\text{Mass of Al} = (0.00138514 \text{ mol H}_2) \left(\frac{2 \text{ mol Al}}{3 \text{ mol H}_2} \right) \left(\frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \right) = 0.024914 = \mathbf{0.0249 \text{ g Al}}$$

- 5.50 Plan: To find mL of SO₂, write the balanced equation, convert the given mass of P₄S₃ to moles, use the molar ratio to find moles of SO₂, and use the ideal gas equation to find volume.

Solution:



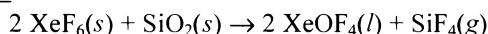
$$\text{Moles SO}_2 = (0.800 \text{ g P}_4\text{S}_3) \left(\frac{1 \text{ mol P}_4\text{S}_3}{220.09 \text{ g P}_4\text{S}_3} \right) \left(\frac{3 \text{ mol SO}_2}{1 \text{ mol P}_4\text{S}_3} \right) = 0.010905 \text{ mol SO}_2$$

$$\text{Volume SO}_2 = \frac{nRT}{P} = \frac{(0.010905 \text{ mol SO}_2) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 32) \text{ K})}{725 \text{ torr}} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 286.249 = \mathbf{286 \text{ mL SO}_2}$$

- 5.51 Plan: First, write the balanced equation. Given the amount of xenon hexafluoride that reacts, we can find the number of moles of silicon tetrafluoride gas formed. Then, using the ideal gas equation with the moles of gas, the temperature and the volume, we can calculate the pressure of the silicon tetrafluoride gas.

Solution:



$$\text{Mole SiF}_4 = n = (2.00 \text{ g XeF}_6) \left(\frac{1 \text{ mol XeF}_6}{245.3 \text{ g XeF}_6} \right) \left(\frac{1 \text{ mol SiF}_4}{2 \text{ mol XeF}_6} \right) = 0.0040766 \text{ mol SiF}_4$$

$$\text{Pressure SiF}_4 = P = \frac{nRT}{V} = \frac{(0.0040766 \text{ mol SiF}_4) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 25) \text{ K})}{1.00 \text{ L}}$$

$$= 0.099737 = \mathbf{0.0997 \text{ atm SiF}_4}$$

- 5.54 At STP (or any identical temperature and pressure), the volume occupied by a mole of any gas will be identical. This is because at the same temperature, all gases have the same average kinetic energy, resulting in the same pressure.

- 5.57 Plan: The molar masses of the three gases are 2.016 for H₂ (Flask A), 4.003 for He (Flask B), and 16.04 for CH₄ (Flask C). Since hydrogen has the smallest molar mass of the three gases, 4 g of H₂ will contain more gas molecules (about 2 mole's worth) than 4 g of He or 4 g of CH₄. Since helium has a smaller molar mass than methane, 4 g of He will contain more gas molecules (about 1 mole's worth) than 4 g of CH₄ (about 0.25 mole's worth).

Solution:

a) **P_A > P_B > P_C** The pressure of a gas is proportional to the number of gas molecules. So, the gas sample with more gas molecules will have a greater pressure.

b) **E_A = E_B = E_C** Average kinetic energy depends only on temperature. The temperature of each gas sample is 273 K, so they all have the same average kinetic energy.

c) **rate_A > rate_B > rate_C** When comparing the speed of two gas molecules, the one with the lower mass travels faster.

d) **total E_A > total E_B > total E_C** Since the average kinetic energy for each gas is the same (part b of this problem) then the total kinetic energy would equal the average times the number of molecules. Since the hydrogen flask contains the most molecules, its total kinetic energy will be the greatest.

e) **d_A = d_B = d_C** Under the conditions stated in this problem, each sample has the same volume, 5 L, and the same mass, 4 g. Thus, the density of each is 4 g/5 L = 0.8 g/L.

- 5.58 To find the ratio of effusion rates, calculate the inverse of the ratio of the square roots of the molar masses (equation 5.14, Graham's Law).

$$\frac{\text{Rate H}_2}{\text{Rate UF}_6} = \sqrt{\frac{\text{Molar Mass UF}_6}{\text{Molar Mass H}_2}} = \sqrt{\frac{352.0 \text{ g/mol}}{2.016 \text{ g/mol}}} = 13.2137 = \mathbf{13.21}$$

- 5.60 a) The gases have the same average kinetic energy because they are at the same temperature. The heavier Ar atoms are moving slower than the lighter He atoms to maintain the same average kinetic energy. Therefore, **Curve 1** better represents the behavior of Ar.
- b) A gas that has a slower molecular speed would effuse more slowly, so **Curve 1** is the better choice.
- c) Fluorine gas exists as a diatomic molecule, F₂, with **M** = 38.00 g/mol. Therefore, F₂ is much closer in size to Ar (39.95 g/mol) than He (4.003 g/mol), so **Curve 1** more closely represents F₂'s behavior.

- 5.62 Plan: To find the ratio of effusion rates, calculate the inverse of the ratio of the square roots of the molar masses (equation 5.14). Then use the ratio of effusion rates to find the time for the F₂ effusion.

Solution:

$$\frac{\text{Rate He}}{\text{Rate F}_2} = \sqrt{\frac{\text{Molar Mass F}_2}{\text{Molar Mass He}}} = \sqrt{\frac{38.00 \text{ g/mol}}{4.003 \text{ g/mol}}} = 3.08105 \text{ (unrounded)}$$

$$\frac{\text{Rate He}}{\text{Rate F}_2} = \frac{\text{Time F}_2}{\text{Time He}} \quad \frac{3.08105}{1.00} = \frac{\text{Time F}_2}{4.55 \text{ min He}} \quad \text{Time F}_2 = 14.01878 = \mathbf{14.0 \text{ min}}$$

- 5.64 Plan: White phosphorus is a molecular form of the element phosphorus consisting of some number, *x*, of phosphorus atoms. Use the relative rates of effusion of white phosphorus and neon to determine the molar mass of white phosphorus. From the molar mass of white phosphorus, determine the number of phosphorus atoms, *x*, in one molecule of white phosphorus.

Solution:

$$\frac{\text{Rate P}_x}{\text{Rate Ne}} = 0.404 = \sqrt{\frac{\text{Molar Mass Ne}}{\text{Molar Mass P}_x}}$$

$$(0.404)^2 = \frac{\text{Molar Mass Ne}}{\text{Molar Mass P}_x} = \frac{20.18 \text{ g/mol}}{\text{Molar Mass P}_x}$$

$$0.163216 = \frac{20.18 \text{ g/mol}}{\text{Molar Mass P}_x}$$

$$\text{Molar Mass P}_x = 123.6398 \text{ g/mol}$$

$$\left(\frac{123.6398 \text{ g}}{\text{mol P}_x} \right) \left(\frac{1 \text{ mol P}}{30.97 \text{ g P}} \right) = 3.992244 = 4 \text{ mol P/mol P}_x \text{ or } 4 \text{ atoms P/molecule P}_x$$

Thus, **4 atoms per molecule**, so P_x = P₄.

- 5.66 Intermolecular attractions cause the real pressure to be *less than* ideal pressure, so it causes a *negative* deviation. The size of the intermolecular attraction is related to the constant *a*. According to Table 5.4, *a*_{N₂} = 1.39, *a*_{Kr} = 2.32 and *a*_{CO₂} = 3.59. Therefore, CO₂ experiences a greater negative deviation in pressure than the other two gases: N₂ < Kr < CO₂.

- 5.68 Nitrogen gas behaves more ideally at 1 atm than at 500 atm because at lower pressures the gas molecules are farther apart. An ideal gas is defined as consisting of gas molecules that act independently of the other gas molecules. When gas molecules are far apart, they act ideally, because intermolecular attractions are less important and the volume of the molecules is a smaller fraction of the container volume.

- 5.71 Plan: Use the Ideal Gas Equation to find the number of moles of O₂. Moles of O₂ combine with Hb in a 4:1 ratio. Divide the mass of Hb by the number of moles to obtain molar mass, g/mol.

Solution:

$$PV = nRT$$

$$\text{Moles O}_2 = \frac{PV}{RT} = \frac{(743 \text{ torr})(1.53 \text{ mL})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 37) \text{ K}) \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)}$$

$$= 5.87708 \times 10^{-5} \text{ mol O}_2 \text{ (unrounded)}$$

$$\text{Moles Hb} = (5.87708 \times 10^{-5} \text{ mol O}_2) \left(\frac{1 \text{ mol Hb}}{4 \text{ mol O}_2} \right) = 1.46927 \times 10^{-5} \text{ mol Hb (unrounded)}$$

$$\text{Molar mass hemoglobin} = (1.00 \text{ g Hb}) / (1.46927 \times 10^{-5} \text{ mol Hb}) = 6.806098 \times 10^4 = \mathbf{6.81 \times 10^4 \text{ g/mol}}$$

- 5.73 Plan: Convert the mass of Cl_2 to moles and use the ideal gas law and van der Waals equation to find the pressure of the gas.

Solution:

$$\text{a) Moles Cl}_2: (0.5850 \text{ kg Cl}_2) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} \right) = 8.2510578 \text{ mol}$$

Ideal gas equation: $PV = nRT$

$$P_{\text{IGL}} = nRT/V = \frac{8.2510578 \text{ mol} \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 225) \text{ K})}{15.00 \text{ L}}$$

$$= 22.4901 = \mathbf{22.5 \text{ atm}}$$

$$\text{b) } \left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$P_{\text{VDW}} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad \text{From Table 5.4: } a = 6.49 \frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}; \quad b = 0.0562 \frac{\text{L}}{\text{mol}}$$

$n = 8.2510578 \text{ mol}$ from Part (a)

$$P_{\text{VDW}} = \frac{(8.2510578 \text{ mol Cl}_2) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 225) \text{ K}) - (8.2510578 \text{ mol Cl}_2)^2 \left(6.49 \frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)}{15.00 \text{ L} - (8.2510578 \text{ mol Cl}_2) \left(0.0562 \frac{\text{L}}{\text{mol}} \right) - (15.00 \text{ L})^2}$$

$$= 21.24378 = \mathbf{21.2 \text{ atm}}$$

- 5.75 Plan: Partial pressures and mole fractions are calculated from Dalton's Law of Partial Pressures: $P_A = X_A(P_{\text{total}})$

Solution:

a) Convert each mole percent to a mole fraction by dividing by 100%.

$$P_{\text{Nitrogen}} = X_{\text{Nitrogen}} P_{\text{Total}} = (0.786) (1.00 \text{ atm}) (760 \text{ torr} / 1 \text{ atm}) = 597.36 = \mathbf{597 \text{ torr N}_2}$$

$$P_{\text{Oxygen}} = X_{\text{Oxygen}} P_{\text{Total}} = (0.209) (1.00 \text{ atm}) (760 \text{ torr} / 1 \text{ atm}) = 158.84 = \mathbf{159 \text{ torr O}_2}$$

$$P_{\text{Carbon Dioxide}} = X_{\text{Carbon Dioxide}} P_{\text{Total}} = (0.0004) (1.00 \text{ atm}) (760 \text{ torr} / 1 \text{ atm}) = 0.304 = \mathbf{0.3 \text{ torr CO}_2}$$

$$P_{\text{Water}} = X_{\text{Water}} P_{\text{Total}} = (0.0046) (1.00 \text{ atm}) (760 \text{ torr} / 1 \text{ atm}) = 3.496 = \mathbf{3.5 \text{ torr O}_2}$$

b) Mole fractions can be calculated by rearranging Dalton's Law of Partial Pressures:

$X_A = P_A/P_{\text{total}}$ and multiply by 100 to express mole fraction as percent.

$$P_{\text{Total}} = (569 + 104 + 40 + 47) \text{ torr} = 760 \text{ torr}$$

$$\text{N}_2: [(569 \text{ torr}) / (760 \text{ torr})] \times 100\% = 74.8684 = \mathbf{74.9 \text{ mol\% N}_2}$$

$$\text{O}_2: [(104 \text{ torr}) / (760 \text{ torr})] \times 100\% = 13.6842 = \mathbf{13.7 \text{ mol\% O}_2}$$

$$\text{CO}_2: [(40 \text{ torr}) / (760 \text{ torr})] \times 100\% = 5.263 = \mathbf{5.3 \text{ mol\% CO}_2}$$

$$\text{H}_2\text{O}: [(47 \text{ torr}) / (760 \text{ torr})] \times 100\% = 6.1842 = \mathbf{6.2 \text{ mol\% CO}_2}$$

c) Number of molecules of O_2 can be calculated using the Ideal Gas Equation and Avogadro's number.

$$PV = nRT$$

$$\text{Moles O}_2 = \frac{PV}{RT} = \frac{(104 \text{ torr})(0.50 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 37) \text{ K})} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.0026883 \text{ mol O}_2$$

$$\text{Molecules O}_2 = (0.0026883 \text{ mol O}_2) \left(\frac{6.022 \times 10^{23} \text{ molecules O}_2}{1 \text{ mol O}_2} \right)$$

$$= 1.6189 \times 10^{21} = \mathbf{1.6 \times 10^{21} \text{ molecules O}_2}$$

- 5.77 **Plan:** For part a, since the volume, temperature, and pressure of the gas are changing, use the combined gas law. For part b, use the ideal gas equation to solve for moles of air and then moles of N₂.

Solution:

$$\text{a) } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad P_1 = (1400. \text{ mmHg}) \left(\frac{1 \text{ atm}}{760 \text{ mmHg}} \right) = 1.8421 \text{ atm}; \quad V_1 = 208 \text{ mL};$$

$$T_1 = 286 \text{ K}; \quad P_2 = 1 \text{ atm}; \quad T_2 = 273 \text{ K}; \quad V_2 = ?$$

$$V_2 = V_1 \left(\frac{T_2}{T_1} \right) \left(\frac{P_1}{P_2} \right) = (208 \text{ mL}) \left(\frac{298 \text{ K}}{286 \text{ K}} \right) \left(\frac{1.8421 \text{ atm}}{1 \text{ atm}} \right) = 399.23 \text{ mL} = \mathbf{4 \times 10^2 \text{ mL}}$$

$$\text{b) Mole air} = n = \frac{PV}{RT} = \frac{(1.8421 \text{ atm})(0.208 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (286 \text{ K})} = 0.016318 \text{ mol air}$$

$$\text{Mole N}_2 = (0.016318 \text{ mol}) \left(\frac{77\% \text{ N}_2}{100\%} \right) = 0.0125649 = \mathbf{0.013 \text{ mol N}_2}$$

- 5.78 The balanced equation and reactant amounts are given, so the first step is to identify the limiting reactant.

$$\text{Moles NO}_2 \text{ from Cu} = (4.95 \text{ cm}^3) \left(\frac{8.95 \text{ g Cu}}{\text{cm}^3} \right) \left(\frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \right) \left(\frac{2 \text{ mol NO}_2}{1 \text{ mol Cu}} \right) = 1.394256 \text{ mol NO}_2 \text{ (unrounded)}$$

$$\begin{aligned} \text{Moles NO}_2 \text{ from HNO}_3 &= (230.0 \text{ mL}) \left(\frac{68.0\% \text{ HNO}_3}{100\%} \right) \left(\frac{1 \text{ cm}^3}{1 \text{ mL}} \right) \left(\frac{1.42 \text{ g}}{\text{mL}} \right) \left(\frac{1 \text{ mol HNO}_3}{63.02 \text{ g}} \right) \left(\frac{2 \text{ mol NO}_2}{4 \text{ mol HNO}_3} \right) \\ &= 1.7620 \text{ mol NO}_2 \text{ (unrounded)} \end{aligned}$$

Since less product can be made from the copper, it is the limiting reactant and excess nitric acid will be left after the reaction goes to completion. Use the calculated number of moles of NO₂ and the given temperature and pressure in the ideal gas equation to find the volume of nitrogen dioxide produced. Note that nitrogen dioxide is the only gas involved in the reaction.

$$\begin{aligned} V = nRT / P &= \frac{(1.394256 \text{ mol NO}_2) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273.2 + 28.2) \text{ K})}{(735 \text{ torr})} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) \\ &= 35.67427 = \mathbf{35.7 \text{ L NO}_2} \end{aligned}$$

- 5.82 **Plan:** The empirical formula for aluminum chloride is AlCl₃ (Al³⁺ and Cl⁻). The empirical formula mass is 133.33 g/mol. Calculate the molar mass of the gaseous species from the ratio of effusion rates. This molar mass, divided by the empirical weight, should give a whole number multiple that will yield the molecular formula.

Solution:

$$\frac{\text{Rate Unk}}{\text{Rate He}} = 0.122 = \sqrt{\frac{\text{Molar Mass He}}{\text{Molar Mass Unk}}}$$

$$0.122 = \sqrt{\frac{4.003 \text{ g/mol}}{\text{Molar Mass Unk}}}$$

$$\text{Molar mass Unknown} = 268.9465 \text{ g/mol}$$

The whole number multiple is 268.9465/133.33, which is about 2. Therefore, the molecular formula of the gaseous species is 2 x (AlCl₃) = **Al₂Cl₆**.

- 5.84 **Plan:** First, write the balanced equation for the reaction: 2 SO₂ + O₂ → 2 SO₃. The total number of moles of gas will change as the reaction occurs since 3 moles of reactant gas forms 2 moles of product gas. From the volume, temperature and pressures given, we can calculate the number of moles of gas before and after the reaction using ideal gas equation. For each mole of SO₃ formed, the total number of moles of gas decreases by 1/2 mole. Thus, twice the decrease in moles of gas equals the moles of SO₃ formed.

Solution:

Moles of gas before and after reaction

$$\text{Initial moles} = \frac{PV}{RT} = \frac{(1.95 \text{ atm})(2.00 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(900. \text{ K})} = 0.05278116 \text{ mol (unrounded)}$$

$$\text{Final moles} = \frac{PV}{RT} = \frac{(1.65 \text{ atm})(2.00 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(900. \text{ K})} = 0.04466098 \text{ mol (unrounded)}$$

$$\begin{aligned}\text{Moles of SO}_3 \text{ produced} &= 2 \times \text{decrease in the total number of moles} \\ &= 2 \times (0.05278116 \text{ mol} - 0.04466098 \text{ mol}) \\ &= 0.01624036 = \mathbf{1.62 \times 10^{-2} \text{ mol}}\end{aligned}$$

Check: If the starting amount is 0.0528 total moles of SO₂ and O₂, then $x + y = 0.0528 \text{ mol}$, where $x = \text{mol of SO}_2$ and $y = \text{mol of O}_2$. After the reaction:

$$(x - z) + (y - 0.5z) + z = 0.0447 \text{ mol}$$

Where $z = \text{mol of SO}_3 \text{ formed} = \text{mol of SO}_2 \text{ reacted} = 2(\text{mol of O}_2 \text{ reacted})$.

Subtracting the two equations gives:

$$\begin{aligned}x - (x - z) + y - (y - 0.5z) - z &= 0.0528 - 0.0447 \\ z &= 0.0163 \text{ mol SO}_3\end{aligned}$$

The approach of setting up two equations and solving them gives the same result as above.

- 5.88 a) A preliminary equation for this reaction is $\text{C}_x\text{H}_y\text{N}_z + n \text{ O}_2 \rightarrow 4 \text{ CO}_2 + 2 \text{ N}_2 + 10 \text{ H}_2\text{O}$. Since the organic compound does not contain oxygen, the only source of oxygen as a reactant is oxygen gas. To form 4 volumes of CO₂ would require 4 volumes of O₂ and to form 10 volumes of H₂O would require 5 volumes of O₂. Thus, **9 volumes of O₂** was required.
- b) Since the volume of a gas is proportional to the number of moles of the gas, we can equate volume and moles. From a volume ratio of 4 CO₂:2 N₂:10 H₂O we deduce a mole ratio of 4 C:4 N:20 H or 1 C:1 N:5 H for an empirical formula of **CH₅N**.

- 5.90 Plan: To find the factor by which a diver's lungs would expand, find the factor by which P changes from 125 ft to the surface, and apply Boyle's Law. To find that factor, calculate P_{seawater} at 125 ft by converting the given depth from ft-seawater to mmHg to atm and adding the surface pressure (1.00 atm).

Solution:

$$P(\text{H}_2\text{O}) = (125 \text{ ft}) \left(\frac{12 \text{ in}}{1 \text{ ft}} \right) \left(\frac{2.54 \text{ cm}}{1 \text{ in}} \right) \left(\frac{10^{-2} \text{ m}}{1 \text{ cm}} \right) \left(\frac{1 \text{ mm}}{10^{-3} \text{ m}} \right) = 3.81 \times 10^4 \text{ mmHg}$$

$$P(\text{Hg}): \frac{h_{\text{H}_2\text{O}}}{h_{\text{Hg}}} = \frac{d_{\text{Hg}}}{d_{\text{H}_2\text{O}}} \quad \frac{3.81 \times 10^4 \text{ mmHg}}{h_{\text{Hg}}} = \frac{13.5 \text{ g/mL}}{1.04 \text{ g/mL}} \quad h_{\text{Hg}} = 2935.1111 \text{ mmHg}$$

$$P(\text{Hg}) = (2935.1111 \text{ mmHg}) \left(\frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) = 3.861988 \text{ atm (unrounded)}$$

$$P_{\text{total}} = (1.00 \text{ atm}) + (3.861988 \text{ atm}) = 4.861988 \text{ atm (unrounded)}$$

Use Boyle's Law to find the volume change of the diver's lungs:

$$P_1 V_1 = P_2 V$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \frac{V_2}{V_1} = \frac{4.861988 \text{ atm}}{1 \text{ atm}} = \mathbf{4.86}$$

To find the depth to which the diver could ascend safely, use the given safe expansion factor (1.5) and the pressure at 125 ft, P_{125} , to find the safest ascended pressure, P_{safe} .

$$P_{125} / P_{\text{safe}} = 1.5$$

$$P_{\text{safe}} = P_{125} / 1.5 = (4.861988 \text{ atm}) / 1.5 = 3.241325 \text{ atm (unrounded)}$$

Convert the pressure in atm to pressure in ft of seawater using the conversion factors above. Subtract this distance from the initial depth to find how far the diver could ascend.

$$h(\text{Hg}): (4.861988 - 3.241325 \text{ atm}) \left(\frac{760 \text{ mmHg}}{1 \text{ atm}} \right) = 1231.7039 \text{ mmHg}$$

$$\frac{h_{\text{H}_2\text{O}}}{h_{\text{Hg}}} = \frac{d_{\text{Hg}}}{d_{\text{H}_2\text{O}}} \quad \frac{h_{\text{H}_2\text{O}}}{1231.7039 \text{ mmHg}} = \frac{13.5 \text{ g/mL}}{1.04 \text{ g/mL}} \quad h_{\text{H}_2\text{O}} = 15988.464 \text{ mm}$$

$$(15988.464 \text{ mmH}_2\text{O}) \left(\frac{10^{-3} \text{ m}}{1 \text{ mm}} \right) \left(\frac{1.094 \text{ yd}}{1 \text{ m}} \right) \left(\frac{3 \text{ ft}}{1 \text{ yd}} \right) = 52.4741 \text{ ft}$$

Therefore, the diver can safely ascend 52.5 ft to a depth of $(125 - 52.4741) = 72.5259 = \mathbf{73 \text{ ft}}$.

- 5.97 Plan: Deviations from ideal gas behavior are due to attractive forces between particles which reduce the pressure of the real gas and due to the size of the particle which affects the volume. Compare the size and/or attractive forces between the substances.

Solution:

- a) **Xenon** would show greater deviation from ideal behavior than argon since xenon is a larger atom than argon. The electron cloud of Xe is more easily distorted so intermolecular attractions are greater. Xe's larger size also means that the volume the gas occupies becomes a greater proportion of the container's volume at high pressures.
- b) **Water** vapor would show greater deviation from ideal behavior than neon gas since the attractive forces between water molecules are greater than the attractive forces between neon atoms. We know the attractive forces are greater for water molecules because it remains a liquid at a higher temperature than neon (water is a liquid at room temperature while neon is a gas at room temperature).
- c) **Mercury** vapor would show greater deviation from ideal behavior than radon gas since the attractive forces between mercury atoms is greater than that between radon atoms. We know that the attractive forces for mercury are greater because it is a liquid at room temperature while radon is a gas.
- d) **Water** is a liquid at room temperature; methane is a gas at room temperature (think about where you have heard of methane gas before – Bunsen burners in lab, cows' digestive system). Therefore, water molecules have stronger attractive forces than methane molecules and should deviate from ideal behavior to a greater extent than methane molecules.

- 5.100 Plan: V and T are not given, so the ideal gas equation cannot be used. The total pressure of the mixture is given. Use $P_A = X_A \times P_{\text{total}}$ to find the mole fraction of each gas and then the mass fraction. The total mass of the two gases is 35.0 g.

Solution:

$$P_{\text{total}} = P_{\text{krypton}} + P_{\text{carbon dioxide}} = 0.708 \text{ atm}$$

The NaOH absorbed the CO_2 leaving the Kr, thus $P_{\text{krypton}} = 0.250 \text{ atm}$

$$P_{\text{carbon dioxide}} = P_{\text{total}} - P_{\text{krypton}} = 0.708 \text{ atm} - 0.250 \text{ atm} = 0.458 \text{ atm}$$

Determining mole fractions: $P_A = X_A \times P_{\text{total}}$

$$\text{Carbon dioxide: } X = \frac{P_{\text{CO}_2}}{P_{\text{total}}} = \frac{0.458 \text{ atm}}{0.708 \text{ atm}} = 0.64689 \text{ (unrounded)}$$

$$\text{Krypton: } X = \frac{P_{\text{Kr}}}{P_{\text{total}}} = \frac{0.250 \text{ atm}}{0.708 \text{ atm}} = 0.353107 \text{ (unrounded)}$$

$$\text{Relative mass fraction} = \frac{\left((0.353107) \left(\frac{83.80 \text{ g Kr}}{\text{mol}} \right) \right)}{\left((0.64689) \left(\frac{44.01 \text{ g CO}_2}{\text{mol}} \right) \right)} = 1.039366 \text{ (unrounded)}$$

$$35.0 \text{ g} = x \text{ g CO}_2 + (1.039366 x) \text{ g Kr}$$

$$35.0 \text{ g} = 2.039366 x$$

$$\text{Grams CO}_2 = x = (35.0 \text{ g}) / (2.039366) = 17.16219581 = \mathbf{17.2 \text{ g CO}_2}$$

$$\text{Grams Kr} = 35.0 \text{ g} - 17.162 \text{ g CO}_2 = 17.83780419 = \mathbf{17.8 \text{ g Kr}}$$

5.103 a) Derive $u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$

Set the given relationships equal to each other.

$$\frac{1}{2} m \overline{u^2} = \frac{3}{2} \left(\frac{R}{N_A} \right) T \quad \text{Multiply each side by 2 and divide by } m.$$

$$\overline{u^2} = \frac{3}{m} \left(\frac{R}{N_A} \right) T$$

$$\overline{u^2} = \frac{3RT}{mN_A}$$

Solve for u by taking the square root of each side; substitute molar mass, \mathcal{M} , for mN_A (mass of one molecule x Avogadro's number of molecules).

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

b) Derive Graham's Law $\frac{\sqrt{\mathcal{M}_1}}{\sqrt{\mathcal{M}_2}} = \frac{rate_2}{rate_1}$

At a given T, the average kinetic energy is equal for two substances, with molecular masses m_1 and m_2 :

$$\overline{E_k} = \frac{1}{2} m_1 \overline{u_1^2} = \frac{1}{2} m_2 \overline{u_2^2}$$

$$m_1 \overline{u_1^2} = m_2 \overline{u_2^2}$$

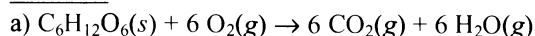
$$\frac{m_1}{m_2} = \frac{\overline{u_2^2}}{\overline{u_1^2}} \rightarrow \frac{\sqrt{m_1}}{\sqrt{m_2}} = \frac{\overline{u_2}}{\overline{u_1}}$$

The average molecular speed, u , is directly proportional to the rate of effusion. Therefore, substitute "rate" for each " u ." In addition, the molecular mass is directly proportional to the molar mass, so substitute \mathcal{M} for each m :

$$\frac{\sqrt{\mathcal{M}_1}}{\sqrt{\mathcal{M}_2}} = \frac{rate_2}{rate_1}$$

5.107 Plan: Find the number of moles of carbon dioxide produced by converting the mass of glucose in grams to moles and using the stoichiometric ratio from the balanced equation. Then use the T and P given to calculate volume from the ideal gas equation.

Solution:



$$\text{Moles } CO_2: (18.0 \text{ g } C_6H_{12}O_6) \left(\frac{1 \text{ mol } C_6H_{12}O_6}{180.16 \text{ g } C_6H_{12}O_6} \right) \left(\frac{6 \text{ mol } CO_2}{1 \text{ mol } C_6H_{12}O_6} \right) = 0.599467 \text{ mol } CO_2$$

$$V = \frac{nRT}{P} = \frac{(0.599467 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 35) \text{ K})}{(780. \text{ torr})} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right)$$

$$= 14.76992 = \mathbf{14.8 \text{ Liters } CO_2}$$

This solution assumes that partial pressure of O_2 does not interfere with the reaction conditions.

b) Plan: From the stoichiometric ratios in the balanced equation, calculate the moles of each gas and then use Dalton's law of partial pressures to determine the pressure of each gas.

Solution:

$$\begin{aligned}\text{Moles CO}_2 = \text{Moles O}_2 &= (9.0 \text{ g C}_6\text{H}_{12}\text{O}_6) \left(\frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.16 \text{ g C}_6\text{H}_{12}\text{O}_6} \right) \left(\frac{6 \text{ mol}}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \right) \\ &= 0.299734 \text{ mol CO}_2 = \text{mol O}_2\end{aligned}$$

At 35°C, the vapor pressure of water is 42.2 torr. No matter how much water is produced, the partial pressure of H₂O will still be 42.2 torr. The remaining pressure, 780 torr – 42.2 torr = 737.8 torr (unrounded) is the sum of partial pressures for O₂ and CO₂. Since the mole fractions of O₂ and CO₂ are equal, their pressures must be equal, and be one-half of sum of the partial pressures just found.

P_{water} = 42.2 torr

$$(737.8 \text{ torr}) / 2 = 368.9 = \mathbf{3.7 \times 10^2 \text{ torr}} \quad \mathbf{P_{oxygen} = P_{carbon dioxide}}$$

- 5.111 Plan: To find the number of steps through the membrane, calculate the molar masses to find the ratio of effusion rates. This ratio is the enrichment factor for each step.

Solution:

$$\begin{aligned}\frac{\text{Rate}_{^{235}\text{UF}_6}}{\text{Rate}_{^{238}\text{UF}_6}} &= \sqrt{\frac{\text{Molar Mass } ^{238}\text{UF}_6}{\text{Molar Mass } ^{235}\text{UF}_6}} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} \\ &= 1.004302694 \text{ enrichment factor (unrounded)}\end{aligned}$$

Therefore, the abundance of ²³⁵UF₆ after one membrane is 0.72% x 1.004302694;

Abundance of ²³⁵UF₆ after "N" membranes = 0.72% * (1.004302694)^N

Desired abundance of ²³⁵UF₆ = 3.0% = 0.72% * (1.004302694)^N

Solving for N:

$$4.16667 = (1.004302694)^N$$

$$\ln 4.16667 = \ln (1.004302694)^N$$

$$\ln 4.16667 = N * \ln (1.004302694)$$

$$N = (\ln 4.16667) / (\ln 1.004302694) = 332.392957 = \mathbf{332 \text{ steps}}$$

- 5.112 Plan: The amount of each gas that leaks from the balloon is proportional to its effusion rate. Using 45% as the rate for H₂, the rate for O₂ can be determined from Graham's Law.

Solution:

$$\frac{\text{Rate O}_2}{\text{Rate H}_2} = \sqrt{\frac{\text{Molar Mass H}_2}{\text{Molar Mass O}_2}} = \sqrt{\frac{2.016 \text{ g/mol}}{32.00 \text{ g/mol}}} = \frac{\text{Rate O}_2}{45}$$

$$\text{Rate O}_2 = 0.250998(45) = 11.2949 \text{ (unrounded)}$$

Amount of H₂ that leaks = 45%; 100–45 = 55% H₂ remains

Amount of O₂ that leaks = 11.2949%; 100–11.2949 = 88.705% O₂ remains

$$\frac{\text{O}_2}{\text{H}_2} = \frac{88.705}{55} = 1.6128 = \mathbf{1.6}$$

Chapter 6 Thermochemistry: Energy Flow and Chemical Change

FOLLOW-UP PROBLEMS

- 6.1 Plan: The system is the reactant and products of the reaction. Since heat is absorbed by the surroundings, the system releases heat and q is negative. Because work is done on the system, w is positive. Use equation 6.2 to calculate ΔE .

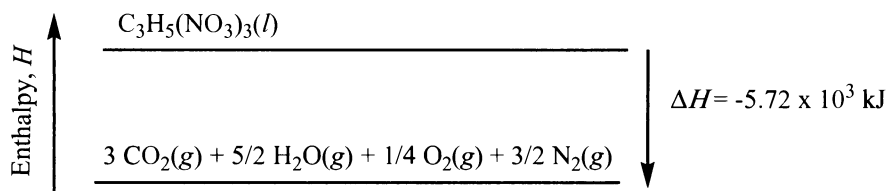
Solution:

$$\Delta E = q + w = (-26.0 \text{ kcal}) \left(\frac{4.184 \text{ kJ}}{1 \text{ kcal}} \right) + (+15.0 \text{ Btu}) \left(\frac{1.055 \text{ kJ}}{1 \text{ Btu}} \right) = -92.959 = -\mathbf{93 \text{ kJ}}$$

Check: A negative ΔE seems reasonable since energy must be removed from the system to condense gaseous reactants into a liquid product.

- 6.2 Plan: Since heat is a “product” in this reaction, the reaction is **exothermic** ($\Delta H < 0$) and the reactants are above the products in an enthalpy diagram.

Solution:



- 6.3 Plan: Heat is transferred away from the ethylene glycol as it cools. Table 6.2 lists the specific heat of ethylene glycol as 2.42 J/gK. This value becomes negative because heat is lost. The heat released is calculated using equation 6.7.

Solution:

$$\Delta T = 37.0^\circ\text{C} - 25.0^\circ\text{C} = 12^\circ\text{C} = 12.0 \text{ K}$$

$$q = c \times \text{mass} \times \Delta T = (2.42 \text{ J/gK}) \left[(5.50 \text{ L}) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1.11 \text{ g}}{\text{mL}} \right) \right] (12.0 \text{ K}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right)$$

$$= -177.289 = -\mathbf{177 \text{ kJ}}$$

- 6.4 Plan: To find ΔT , find the T_{final} by applying equation 6.7. The diamond loses heat ($-q_{\text{diamond}}$) whereas the water gains heat (q_{water}). Although the Celsius degree and Kelvin degree are the same size, be careful when interchanging the units. To be safe, always convert the Celsius temperature to Kelvin temperatures. Use the initial temperatures, masses, and specific heat capacities to solve the expression below.

Solution:

$$-q_{\text{diamond}} = q_{\text{water}}$$

$$-(m c_{\text{diamond}} \Delta T) = m c_{\text{water}} \Delta T$$

$$\text{mass of diamond} = (10.25 \text{ carat}) \left(\frac{0.2000 \text{ g}}{1 \text{ carat}} \right) = 2.050 \text{ g}$$

$$T_{\text{init}} (\text{diamond}) = 74.21 + 273.15 = 347.36 \text{ K}$$

$$T_{\text{init}} (\text{water}) = 27.20 + 273.15 = 300.35 \text{ K}$$

$$-(2.050 \text{ g}) (0.519 \text{ J/g-K}) (T_{\text{final}} - 347.36) = (26.05 \text{ g}) (4.184 \text{ J/g-K}) (T_{\text{final}} - 300.35)$$

$$(-1.06395 \text{ J/K}) (T_{\text{final}} - 347.36) = (108.9932 \text{ J/K}) (T_{\text{final}} - 300.35)$$

$$-1.06395 T_{\text{final}} + 369.5737 = 108.9932 T_{\text{final}} - 32736.108$$

$$33105.6817 = 110.05715 T_{\text{final}}$$

$$T_{\text{final}} = 300.80446 \text{ K}$$

$$\Delta T_{\text{diamond}} = 300.80446 - 347.36 = -46.55554 = \mathbf{-46.56 \text{ K}}$$

$$\Delta T_{\text{water}} = 300.80446 - 300.35 = 0.45446 \text{ K} = \mathbf{0.45 \text{ K}}$$

Check: Rounding errors account for the slight differences in the final answer when compared to the identical calculation using Celsius temperatures. The temperature of the diamond decreases as the temperature of the water increases. The temperature of the water does not increase significantly because its specific heat capacity is large in comparison to the diamond, so it takes more heat to raise 1 g of the substance by 1°C.

- 6.5 Plan: The bomb calorimeter gains heat from the combustion of graphite, so $-q_{\text{graphite}} = q_{\text{calorimeter}}$. Convert the mass of graphite from grams to moles and use the given kJ/mol to find q_{graphite} . The heat lost by graphite equals the heat gained from the calorimeter, or ΔT multiplied by $C_{\text{calorimeter}}$.

Solution:

$$\begin{aligned} -(\text{mol graphite} \times \text{kJ/mol graphite}) &= C_{\text{calorimeter}} \Delta T_{\text{calorimeter}} \\ -(0.8650 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) \left(\frac{-393.5 \text{ kJ}}{1 \text{ mol C}} \right) &= C_{\text{calorimeter}} (2.613 \text{ K}) \\ -28.34117 &= C_{\text{calorimeter}} (2.613 \text{ K}) \\ C_{\text{calorimeter}} &= 10.84622 = \mathbf{10.85 \text{ kJ/K}} \end{aligned}$$

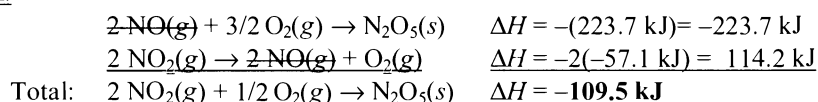
- 6.6 Plan: To find the heat required, write a balanced thermochemical equation and use appropriate molar ratios to solve for required heat.

Solution:

$$\begin{aligned} \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) &\rightarrow \text{C}_2\text{H}_6(\text{g}) \quad \Delta H = -137 \text{ kJ} \\ \text{Heat} &= (15.0 \text{ kg C}_2\text{H}_6) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol C}_2\text{H}_6}{30.07 \text{ g C}_2\text{H}_6} \right) \left(\frac{-137 \text{ kJ}}{1 \text{ mol C}_2\text{H}_6} \right) = -6.83405 \times 10^4 = \mathbf{-6.83 \times 10^4 \text{ kJ}} \end{aligned}$$

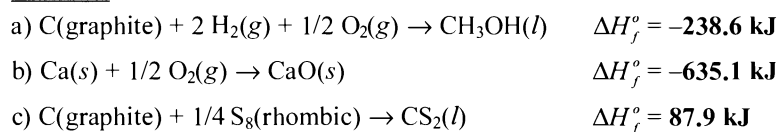
- 6.7 Plan: Manipulate the two equations so that their sum will result in the overall equation. Reverse the first equation (and change the sign of ΔH); reverse the second equation and multiply the coefficients (and ΔH) by two.

Solution:



- 6.8 Plan: Write the elements as reactants (each in its standard state), and place one mole of the substance formed on the product side. Balance the equation with the following differences from “normal” balancing — only one mole of the desired product can be on the right hand side of the arrow (and nothing else), and fractional coefficients are allowed on the reactant side. The values for the standard heats of formation (ΔH_f°) may be found in the appendix.

Solution:



- 6.9 Plan: Apply equation 6.8 to this reaction, substitute given values, and solve for the ΔH_f° (CH_3OH).

Solution:

$$\begin{aligned} \Delta H_{\text{comb}}^\circ &= \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \\ \Delta H_{\text{comb}}^\circ &= [\Delta H_f^\circ (\text{CO}_2(\text{g})) + 2 \Delta H_f^\circ (\text{H}_2\text{O}(\text{g}))] - [\Delta H_f^\circ (\text{CH}_3\text{OH}(\text{l})) + 3/2 \Delta H_f^\circ (\text{O}_2(\text{g}))] \\ -638.5 \text{ kJ} &= [1 \text{ mol}(-393.5 \text{ kJ/mol}) + 2 \text{ mol}(-241.826 \text{ kJ/mol})] - [\Delta H_f^\circ (\text{CH}_3\text{OH}(\text{l})) + 3/2(0)] \\ -638.5 \text{ kJ} &= (-877.152 \text{ kJ}) - \Delta H_f^\circ (\text{CH}_3\text{OH}(\text{l})) \\ \Delta H_f^\circ (\text{CH}_3\text{OH}(\text{l})) &= -238.652 = \mathbf{-238.6 \text{ kJ}} \end{aligned}$$

Check: You solved for this value in Follow-Up 6.8. Are they the same?

END-OF-CHAPTER PROBLEMS

6.5 The change in a system's energy is $\Delta E = q + w$. If the system receives heat, then its q_{final} is greater than q_{initial} so q is positive. Since the system performs work, its $w_{\text{final}} < w_{\text{initial}}$ so w is negative. The change in energy is $(+425 \text{ J}) + (-425 \text{ J}) = \mathbf{0 \text{ J}}$.

6.7 $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 3.3 \times 10^{10} \text{ J}$
(1.0 ton)

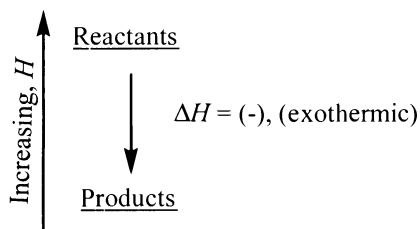
$$\text{a) } \Delta E(\text{kJ}) = (3.3 \times 10^{10} \text{ J}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = \mathbf{3.3 \times 10^7 \text{ kJ}}$$

$$\text{b) } \Delta E(\text{kcal}) = (3.3 \times 10^{10} \text{ J}) \left(\frac{1 \text{ cal}}{4.184 \text{ J}} \right) \left(\frac{1 \text{ kcal}}{10^3 \text{ cal}} \right) = 7.887 \times 10^6 = \mathbf{7.9 \times 10^6 \text{ kcal}}$$

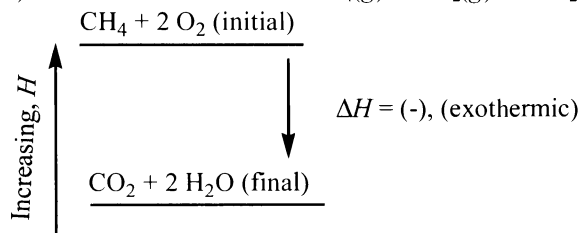
$$\text{c) } \Delta E(\text{Btu}) = (3.3 \times 10^{10} \text{ J}) \left(\frac{1 \text{ Btu}}{1055 \text{ J}} \right) = 3.12796 \times 10^7 = \mathbf{3.1 \times 10^7 \text{ Btu}}$$

- 6.10 a) **Exothermic**, the system (water) is releasing heat in changing from liquid to solid.
 b) **Endothermic**, the system (water) is absorbing heat in changing from liquid to gas.
 c) **Exothermic**, the process of digestion breaks down food and releases energy.
 d) **Exothermic**, heat is released as a person runs and muscles perform work.
 e) **Endothermic**, heat is absorbed as food calories are converted to body tissue.
 f) **Endothermic**, the wood being chopped absorbs heat (and work).
 g) **Exothermic**, the furnace releases heat from fuel combustion. Alternatively, if the system is defined as the air in the house, the change is endothermic since the air's temperature is increasing by the input of heat energy from the furnace.

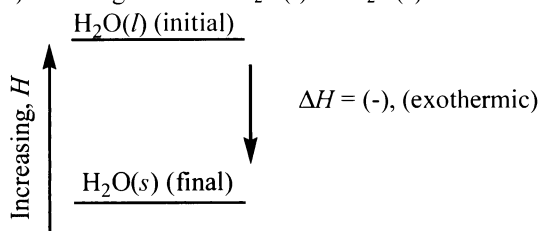
6.11 An exothermic reaction releases heat, so the reactants have greater H (H_{initial}) than the products (H_{final}).
 $\Delta H = H_{\text{final}} - H_{\text{initial}} < 0$.



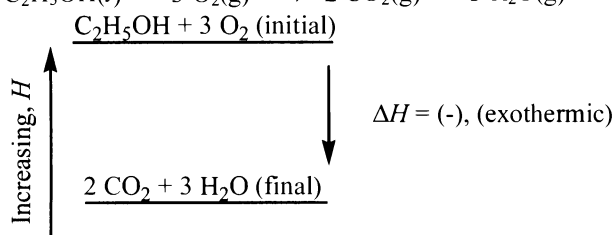
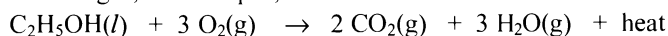
6.13 a) Combustion of methane: $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) + \text{heat}$



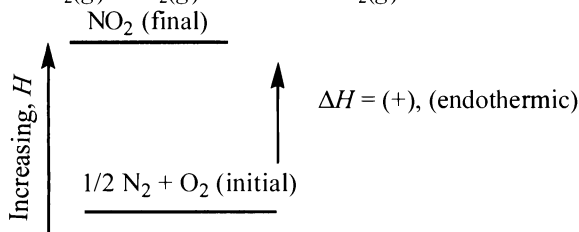
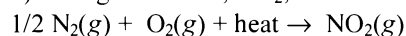
b) Freezing of water: $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) + \text{heat}$



6.15 a) Combustion of hydrocarbons and related compounds require oxygen (and a heat catalyst) to yield carbon dioxide gas, water vapor, and heat.



b) Nitrogen dioxide, NO_2 , forms from N_2 and O_2 .



6.18 To determine the specific heat capacity of a substance, you need its mass, the heat added (or lost), and the change in temperature.

6.20 **Plan:** The heat required to raise the temperature of water is found by using the equation $q = c \times \text{mass} \times \Delta T$. The specific heat capacity, c_{water} , is found in Table 6.2. Because the Celsius degree is the same size as the kelvin degree, $\Delta T = 100.^{\circ}\text{C} - 20.^{\circ}\text{C} = 80.^{\circ}\text{C} = 80. \text{ K}$.

$$q(\text{J}) = c \times \text{mass} \times \Delta T = \left(4.184 \frac{\text{J}}{\text{g}^{\circ}\text{C}} \right) (12.0 \text{ g}) ((100. - 20.)^{\circ}\text{C}) = 4016.64 = \mathbf{4.0 \times 10^3 \text{ J}}$$

6.22 $q(\text{J}) = c \times \text{mass} \times \Delta T$ $T_i = 3.00^{\circ}\text{C}$ $T_f = ?$ $\text{mass} = 295 \text{ g}$ $c = 0.900 \text{ J/g}^{\circ}\text{C}$

$$q = (85.0 \text{ kJ}) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 8.50 \times 10^4 \text{ J}$$

$$8.50 \times 10^4 \text{ J} = (0.900 \text{ J/g}^{\circ}\text{C}) (295 \text{ g}) (T_f - 3.00)^{\circ}\text{C}$$

$$(T_f - 3.00)^{\circ}\text{C} = \frac{(8.50 \times 10^4 \text{ J})}{(295 \text{ g}) \left(\frac{0.900 \text{ J}}{\text{g}^{\circ}\text{C}} \right)}$$

$$(T_f - 3.00)^{\circ}\text{C} = 320.15^{\circ}\text{C} \text{ (unrounded)}$$

$$T_f = \mathbf{323^{\circ}\text{C}}$$

- 6.24 Since the bolts have the same mass, and one must cool as the other heats, the intuitive answer is

$$\left[\frac{(T_1 + T_2)}{2} \right] = \left[\frac{(100.^{\circ}\text{C} + 55.^{\circ}\text{C})}{2} \right] = 77.5^{\circ}\text{C}.$$

- 6.26 The heat lost by the water originally at 82°C is gained by the water that is originally at 22°C . Therefore $-q_{\text{lost}} = q_{\text{gained}}$. Both volumes are converted to mass using the density.

$$\text{Mass of } 85 \text{ mL} = (85 \text{ mL}) \left(\frac{1.00 \text{ g}}{1 \text{ mL}} \right) = 85 \text{ g}$$

$$\text{Mass of } 165 \text{ mL} = (165 \text{ mL}) \left(\frac{1.00 \text{ g}}{1 \text{ mL}} \right) = 165 \text{ g}$$

$$-q_{\text{lost}} = q_{\text{gained}}$$

$$c \times \text{mass} \times \Delta T (82^{\circ}\text{C water}) = c \times \text{mass} \times \Delta T (22^{\circ}\text{C water})$$

$$- (4.184 \text{ J/g}^{\circ}\text{C}) (85 \text{ g}) (T_f - 82)^{\circ}\text{C} = (4.184 \text{ J/g}^{\circ}\text{C}) (165 \text{ g}) (T_f - 22)^{\circ}\text{C}$$

$$- [85](T_f - 82) = [165] (T_f - 22)$$

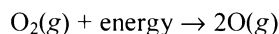
$$6970 - 85 T_f = 165 T_f - 3630$$

$$6970 + 3630 = 165 T_f + 85 T_f$$

$$10600. = 250. T_f$$

$$T_f = (10600. / 250.) = 42.4 = 42^{\circ}\text{C}$$

- 6.31 The reaction has a positive ΔH_{rxn} , because this reaction requires the input of energy to break the oxygen–oxygen bond:



- 6.32 As a substance changes from the gaseous state to the liquid state, energy is released so ΔH would be negative for the condensation of 1 mol of water. The value of ΔH for the vaporization of 2 mol of water would be twice the value of ΔH for the condensation of 1 mol of water vapor but would have an opposite sign ($+\Delta H$).



$$\Delta H_{\text{cond}} = (-)$$

$$\Delta H_{\text{vap}} = (+)2[\Delta H_{\text{cond}}]$$

The enthalpy for 1 mole of water condensing would be opposite in sign to and one-half the value for the conversion of 2 moles of liquid H_2O to H_2O vapor.

- 6.33 a) This reaction is **exothermic** because ΔH is negative.
 b) Because ΔH is a state function, the total energy required for the reverse reaction, regardless of how the change occurs, is the same magnitude but different sign of the forward reaction. Therefore, $\Delta H = +20.2 \text{ kJ}$.
 c) The ΔH_{rxn} is specific for the reaction as written, meaning that 20.2 kJ is released when 1/8 of a mole of sulfur reacts. In this case, 3.2 moles of sulfur react and we therefore expect that much more energy will be released.

$$\Delta H_{\text{rxn}} = (3.2 \text{ mol S}_8) \left(\frac{-20.2 \text{ kJ}}{(1/8) \text{ mol S}_8} \right) = -517.12 = -5.2 \times 10^2 \text{ kJ}$$

- d) The mass of S_8 requires conversion to moles and then a calculation identical to c) can be performed.

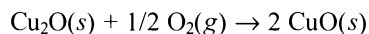
$$\Delta H_{\text{rxn}} = (20.0 \text{ g S}_8) \left(\frac{1 \text{ mol S}_8}{256.56 \text{ g S}_8} \right) \left(\frac{-20.2 \text{ kJ}}{(1/8) \text{ mol S}_8} \right) = -12.5974 = -12.6 \text{ kJ}$$

- 6.35 a) $1/2 \text{ N}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}) \rightarrow \text{NO}(\text{g}) \qquad \Delta H = 90.29 \text{ kJ}$

$$\text{b) } \Delta H_{\text{rxn}} = (1.50 \text{ g NO}) \left(\frac{1 \text{ mol NO}}{30.01 \text{ g NO}} \right) \left(\frac{-90.29 \text{ kJ}}{1 \text{ mol NO}} \right) = -4.5129957 = -4.51 \text{ kJ}$$

- 6.37 For the reaction written, 2 moles of H_2O_2 release 196.1 kJ of energy upon decomposition.
- $$2 \text{H}_2\text{O}_2(l) \rightarrow 2 \text{H}_2\text{O}(l) + \text{O}_2(g) \quad \Delta H_{\text{rxn}} = -196.1 \text{ kJ}$$
- $$\text{Heat} = q = (732 \text{ kg H}_2\text{O}_2) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \right) \left(\frac{-196.1 \text{ kJ}}{2 \text{ mol H}_2\text{O}_2} \right) = -2.1097 \times 10^6 = \mathbf{-2.11 \times 10^6 \text{ kJ}}$$
- 6.39 a) $\text{C}_2\text{H}_4(g) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l) \quad \Delta H_{\text{rxn}} = -1411 \text{ kJ}$
 b) $\text{Mass C}_2\text{H}_4 = (-70.0 \text{ kJ}) \left(\frac{1 \text{ mol C}_2\text{H}_4}{-1411 \text{ kJ}} \right) \left(\frac{28.05 \text{ g C}_2\text{H}_4}{1 \text{ mol C}_2\text{H}_4} \right) = 1.39157 = \mathbf{1.39 \text{ g C}_2\text{H}_4}$
- 6.42 To obtain the overall reaction, add the first reaction to the reverse of the second. When the second reaction is reversed, the sign of its enthalpy change is reversed from positive to negative.
- $$\begin{array}{rcl} \text{Ca}(s) + 1/2 \text{O}_2(g) & \rightarrow & \text{CaO}(s) & \Delta H = -635.1 \text{ kJ} \\ \text{CaO}(s) + \text{CO}_2(g) & \rightarrow & \text{CaCO}_3(s) & \Delta H = -178.3 \text{ kJ} \\ \hline \text{Ca}(s) + 1/2 \text{O}_2(g) + \text{CO}_2(g) & \rightarrow & \text{CaCO}_3(s) & \Delta H = \mathbf{-813.4 \text{ kJ}} \end{array}$$
- 6.44 $\text{N}_2(g) + \text{O}_2(g) \rightarrow \mathbf{2\text{NO}(g)}$ $\Delta H = 180.6 \text{ kJ}$
 $\mathbf{2\text{NO}(g)} + \text{O}_2(g) \rightarrow \mathbf{2\text{NO}_2(g)}$ $\Delta H = -114.2 \text{ kJ}$
 $\text{N}_2(g) + 2 \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \quad \Delta H_{\text{rxn}} = +66.4 \text{ kJ}$
 In Figure P6.44, A represents reaction 1 with a larger amount of energy absorbed, B represents reaction 2 with a smaller amount of energy released, and C represents reaction 3 as the sum of A and B.
- 6.47 The standard heat of reaction, $\Delta H_{\text{rxn}}^\circ$, is the enthalpy change for any reaction where all substances are in their standard states. The standard heat of formation, ΔH_f° , is the enthalpy change that accompanies the formation of one mole of a compound in its standard state from elements in their standard states. Standard state is 1 atm for gases, 1 M for solutes, and pure state for liquids and solids. Standard state does not include a specific temperature, but a temperature must be specified in a table of standard values.
- 6.48 a) $1/2 \text{Cl}_2(g) + \text{Na}(s) \rightarrow \text{NaCl}(s)$ The element chlorine occurs as Cl_2 , not Cl.
 b) $\text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$ The element hydrogen exists as H_2 , not H, and the formation of water is written with water as the product in the liquid state.
 c) No changes
- 6.49 Formation equations show the formation of one mole of compound from its elements. The elements must be in their most stable states ($\Delta H_f^\circ = 0$)
- $\text{Ca}(s) + \text{Cl}_2(g) \rightarrow \text{CaCl}_2(s)$
 - $\text{Na}(s) + 1/2 \text{H}_2(g) + \text{C}(\text{graphite}) + 3/2 \text{O}_2(g) \rightarrow \text{NaHCO}_3(s)$
 - $\text{C}(\text{graphite}) + 2 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l)$
 - $1/2 \text{H}_2(g) + 1/2 \text{N}_2(g) + 3/2 \text{O}_2(g) \rightarrow \text{HNO}_3(l)$
- 6.51 The enthalpy change of a reaction is the sum of the ΔH_f° of the products minus the sum of the ΔH_f° of the reactants. Since the ΔH_f° values (Appendix B) are reported as energy per one mole, use the appropriate coefficient to reflect the higher number of moles.
- $$\Delta H_{\text{rxn}}^\circ = \sum m[\Delta H_f^\circ (\text{products})] - \sum n[\Delta H_f^\circ (\text{reactants})]$$
- $$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \{2 \Delta H_f^\circ [\text{SO}_2(g)] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(g)]\} - \{2 \Delta H_f^\circ [\text{H}_2\text{S}(g)] + 3 \Delta H_f^\circ [\text{O}_2(g)]\} \\ &= 2 \text{ mol}(-296.8 \text{ kJ/mol}) + 2 \text{ mol}(-241.826 \text{ kJ/mol}) - [2 \text{ mol}(-20.2 \text{ kJ/mol}) + 3(0.0)] \\ &= \mathbf{-1036.8 \text{ kJ}} \end{aligned}$$
 - $$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \{1 \Delta H_f^\circ [\text{CCl}_4(l)] + 4 \Delta H_f^\circ [\text{HCl}(g)]\} - \{1 \Delta H_f^\circ [\text{CH}_4(g)] + 4 \Delta H_f^\circ [\text{Cl}_2(g)]\} \\ \Delta H_{\text{rxn}}^\circ &= 1 \text{ mol}(-139 \text{ kJ/mol}) + 4 \text{ mol}(-92.31 \text{ kJ/mol}) - [1 \text{ mol}(-74.87 \text{ kJ/mol}) + 4 \text{ mol}(0)] \\ &= \mathbf{-433 \text{ kJ}} \end{aligned}$$

$$6.53 \quad \Delta H_{rxn}^{\circ} = \sum m[\Delta H_f^{\circ} (\text{products})] - \sum n[\Delta H_f^{\circ} (\text{reactants})]$$



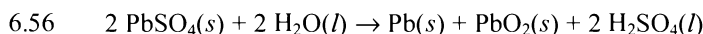
$$\Delta H_{rxn}^{\circ} = -146.0 \text{ kJ}$$

$$\Delta H_{rxn}^{\circ} = \{ 2 \text{ mol } (\Delta H_f^{\circ}, \text{CuO}(s)) \} - \{ 1 \text{ mol } (\Delta H_f^{\circ}, \text{Cu}_2\text{O}(s)) + 1/2 \text{ mol } (\Delta H_f^{\circ}, \text{O}_2(g)) \}$$

$$-146.0 \text{ kJ} = 2 \text{ mol } (\Delta H_f^{\circ}, \text{CuO}(s)) - [1 \text{ mol } (-168.6 \frac{\text{kJ}}{\text{mol}}) + 1/2 \text{ mol } (0)]$$

$$-146.0 \text{ kJ} = 2 \text{ mol } (\Delta H_f^{\circ}, \text{CuO}(s)) + 168.6 \text{ kJ}$$

$$\Delta H_f^{\circ}, \text{CuO}(s) = -\frac{314.6 \text{ kJ}}{2 \text{ mol}} = \mathbf{-157.3 \text{ kJ/mol}}$$

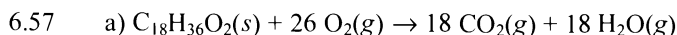
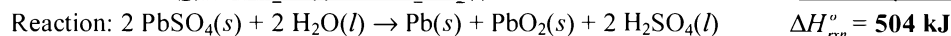
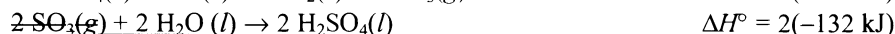
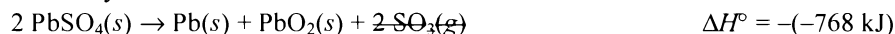


$$\text{a) } \Delta H_{rxn}^{\circ} = \{ 1 \text{ mol } (\Delta H_f^{\circ}, \text{Pb}(s)) + 1 \text{ mol } (\Delta H_f^{\circ}, \text{PbO}_2(s)) + 2 \text{ mol } (\Delta H_f^{\circ}, \text{H}_2\text{SO}_4(l)) \} - \{ 2 \text{ mol } (\Delta H_f^{\circ}, \text{PbSO}_4(s)) + 2 \text{ mol } (\Delta H_f^{\circ}, \text{H}_2\text{O}(l)) \}$$

$$= [1 \text{ mol } (0 \frac{\text{kJ}}{\text{mol}}) + 1 \text{ mol } (-276.6 \frac{\text{kJ}}{\text{mol}}) + 2 \text{ mol } (-813.989 \frac{\text{kJ}}{\text{mol}})] - [2 \text{ mol } (-918.39 \frac{\text{kJ}}{\text{mol}}) + 2 \text{ mol } (-285.840 \frac{\text{kJ}}{\text{mol}})] = \mathbf{503.9 \text{ kJ}}$$

b) Use Hess's Law to rearrange equations (1) and (2) to give the equation wanted.

Reverse the first equation (changing the sign of ΔH_{rxn}°) and multiply the coefficients (and ΔH_{rxn}°) of the second reaction by 2.



$$\text{b) } \Delta H_{\text{comb}}^{\circ} = \{ 18 \text{ mol } (\Delta H_f^{\circ}, \text{CO}_2(g)) + 18 \text{ mol } (\Delta H_f^{\circ}, \text{H}_2\text{O}(g)) \} - \{ 1 \text{ mol } (\Delta H_f^{\circ}, \text{C}_{18}\text{H}_{36}\text{O}_2(s)) + 26 \text{ mol } (\Delta H_f^{\circ}, \text{O}_2(g)) \}$$

$$= 18 \text{ mol } (-393.5 \text{ kJ/mol}) + 18 \text{ mol } (-241.826 \text{ kJ/mol}) - [1 \text{ mol } (-948 \text{ kJ/mol}) + 26 \text{ mol } (0 \text{ kJ/mol})] = \mathbf{-10,488 \text{ kJ}}$$

$$\text{c) } q(\text{kJ}) = (1.00 \text{ g C}_{18}\text{H}_{36}\text{O}_2) \left(\frac{1 \text{ mol C}_{18}\text{H}_{36}\text{O}_2}{284.47 \text{ g C}_{18}\text{H}_{36}\text{O}_2} \right) \left(\frac{-10,488 \text{ kJ}}{1 \text{ mol C}_{18}\text{H}_{36}\text{O}_2} \right) = \mathbf{-36.9 \text{ kJ}}$$

$$q(\text{kcal}) = (-36.9 \text{ kJ}) \left(\frac{1 \text{ kcal}}{4.184 \text{ kJ}} \right) = \mathbf{-8.81 \text{ kcal}}$$

$$\text{d) } q(\text{kcal}) = (11.0 \text{ g fat}) \left[\frac{-8.81 \text{ kcal}}{1.0 \text{ g fat}} \right] = \mathbf{96.9 \text{ kcal}}$$

The calculated calorie content is consistent with the package information.

6.58 a) A first read of this problem suggests there is insufficient information to solve the problem. Upon more careful reading, you find that the question asks volumes for each mole of helium.

$$T = 273 + 15 = 288 \text{ K} \quad \text{or} \quad T = 273 + 30 = 303 \text{ K}$$

$$\frac{V_{15}}{n} = \frac{RT}{P} = \frac{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (288 \text{ K})}{(1.00 \text{ atm})} = 23.6448 = \mathbf{23.6 \text{ L/mol}}$$

$$\frac{V_{30}}{n} = \frac{RT}{P} = \frac{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (303 \text{ K})}{(1.00 \text{ atm})} = 24.8763 = \mathbf{24.9 \text{ L/mol}}$$

b) Internal energy is the sum of the potential and kinetic energies of each He atom in the system (the balloon). The energy of one mole of helium atoms can be described as a function of temperature, $E = 3/2 nRT$, where $n = 1$ mole. Therefore, the internal energy at 15°C and 30°C can be calculated. The inside back cover lists values of R with different units.

$$E = 3/2 nRT = (3/2) (1.00 \text{ mol}) (8.314 \text{ J/mol}\cdot\text{K}) (303 - 288)\text{K} = 187.065 = \mathbf{187 \text{ J}}$$

c) When the balloon expands as temperature rises, the balloon performs PV work. However, the problem specifies that pressure remains constant, so work done on the surroundings by the balloon is defined by the equation :

$w = -P\Delta V$. When pressure and volume are multiplied together, the unit is L•atm. Since we would like to express work in Joules, we can create a conversion factor between L•atm and J.

$$w = -P\Delta V = -(1.00 \text{ atm})((24.8763 - 23.6448) \text{ L}) \left[\left(\frac{101325 \text{ Pa}}{1 \text{ atm}} \right) \left(\frac{\text{kg}/\text{ms}^2}{\text{Pa}} \right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right) \right] \left(\frac{1 \text{ J}}{\text{kg} \cdot \text{m}^2/\text{s}^2} \right)$$

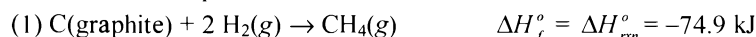
$$= -124.78 = \mathbf{-1.2 \times 10^2 \text{ J}}$$

$$\text{d) } q_p = \Delta E + P\Delta V = (187.065 \text{ J}) + (124.78 \text{ J}) = 311.845 = \mathbf{3.1 \times 10^2 \text{ J}}$$

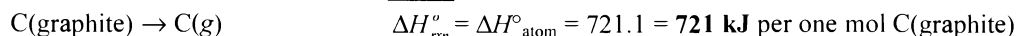
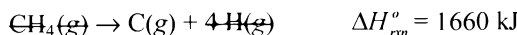
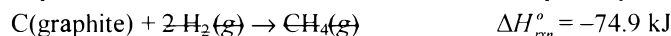
$$\text{e) } \Delta H = q_p = \mathbf{310 \text{ J.}}$$

f) When a process occurs at constant pressure, the change in heat energy of the system can be described by a state function called enthalpy. The change in enthalpy equals the heat (q) lost at constant pressure: $\Delta H = \Delta E + P\Delta V = \Delta E - w = (q + w) - w = q_p$

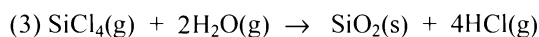
- 6.66 Chemical equations can be written that describe the three processes. Assume one mole of each substance of interest so that units are expressed as kJ.



The third equation is reversed and its coefficients are multiplied by 2 to add the three equations.



- 6.73 a) The heat of reaction is calculated from the heats of formation found in Appendix B. The ΔH_f° 's for all of the species, except SiCl_4 , are found in Appendix B. Use reaction 3, with its given ΔH_{rxn}° , to find $\Delta H_f^\circ [\text{SiCl}_4(\text{g})]$.



$$\Delta H_{rxn}^\circ = \{ \Delta H_f^\circ [\text{SiO}_2(\text{s})] + 4 \Delta H_f^\circ [\text{HCl}(\text{g})] \} - \{ \Delta H_f^\circ [\text{SiCl}_4(\text{g})] + 2 \Delta H_f^\circ [\text{H}_2\text{O}(\text{g})] \}$$

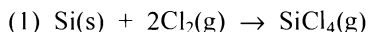
$$-139.5 \text{ kJ} = (-910.9 \text{ kJ}) + 4(-92.31 \text{ kJ}) - \{ \Delta H_f^\circ [\text{SiCl}_4(\text{g})] + 2(-241.826 \text{ kJ}) \}$$

$$-139.5 \text{ kJ} = -1280.14 - \{ \Delta H_f^\circ [\text{SiCl}_4(\text{g})] + (-483.652 \text{ kJ}) \}$$

$$1140.64 \text{ kJ} = - \{ \Delta H_f^\circ [\text{SiCl}_4(\text{g})] + (-483.652 \text{ kJ}) \}$$

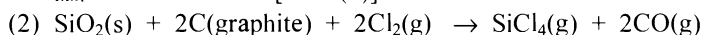
$$\Delta H_f^\circ [\text{SiCl}_4(\text{g})] = -656.988 \text{ kJ/mol (unrounded)}$$

The heats of reaction for the first two steps can now be calculated.



$$\Delta H_{rxn1}^\circ = \Delta H_f^\circ [\text{SiCl}_4(\text{g})] - \{ \Delta H_f^\circ [\text{Si}(\text{s})] + 2 \Delta H_f^\circ [\text{Cl}_2(\text{g})] \}$$

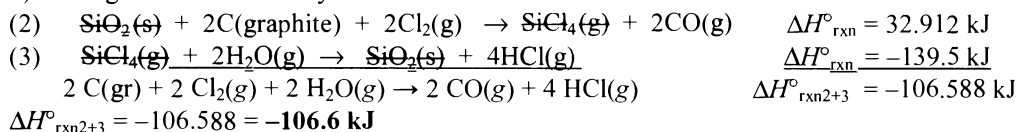
$$\Delta H_{rxn1}^\circ = -656.988 \text{ kJ} - [0 + 2(0)] = -656.988 = \mathbf{-657.0 \text{ kJ}}$$



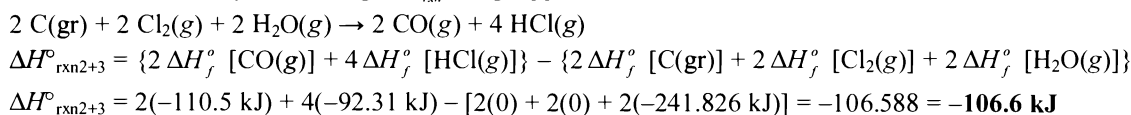
$$\Delta H_{rxn2}^\circ = \{ \Delta H_f^\circ [\text{SiCl}_4(\text{g})] + 2 \Delta H_f^\circ [\text{CO}(\text{g})] \} - \{ \Delta H_f^\circ [\text{SiO}_2(\text{s})] + 2 \Delta H_f^\circ [\text{C}(\text{gr})] + 2 \Delta H_f^\circ [\text{Cl}_2(\text{g})] \}$$

$$\Delta H_{rxn2}^\circ = -656.988 \text{ kJ} + 2(-110.5 \text{ kJ}) - \{ (-910.9 \text{ kJ}) + 2(0) + 2(0) \} = 32.912 = \mathbf{32.9 \text{ kJ}}$$

b) Adding reactions 2 and 3 yields:



Confirm this result by calculating $\Delta H^\circ_{\text{rxn}}$ using Appendix B values.



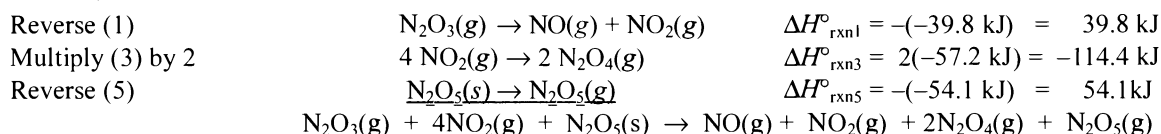
6.76 a) $\Delta T = 819^\circ\text{C} - 0^\circ\text{C} = 819^\circ\text{C} = 819 \text{ K}$

$$w = P\Delta V = nR\Delta T = (1 \text{ mol}) \times (8.314 \text{ J/mol}\cdot\text{K}) \times (819 \text{ K}) = -6809.166 = \mathbf{-6.81 \times 10^3 \text{ J}}$$

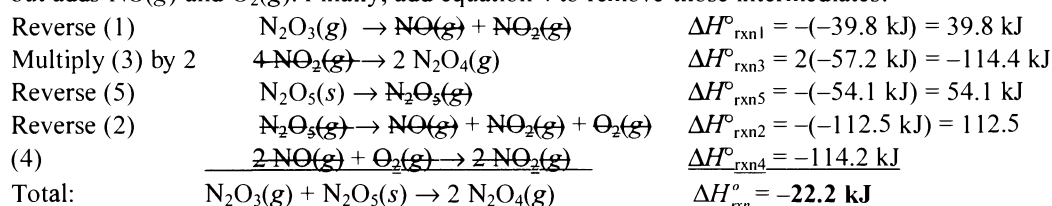
b) $q = (\text{mass})(c)(\Delta T)$

$$\Delta T = \frac{q}{(\text{mass})(c)} = \frac{6.809166 \times 10^3 \text{ J}}{\left[1 \text{ mol N}_2 \left(\frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2}\right)\right](1.00 \text{ J/g}\cdot\text{K})}$$

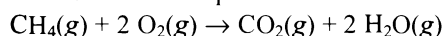
6.77 Only reaction 3 contains $\text{N}_2\text{O}_4(\text{g})$, and only reaction 1 contains $\text{N}_2\text{O}_3(\text{g})$, so we can use those reactions as a starting point. N_2O_5 appears in both reactions 2 and 5, but note the physical states present: solid and gas. As a rough start, adding reactions 1, 3, and 5 yield the desired reactants and products, with some undesired intermediates:



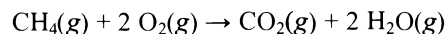
To cancel out the $\text{N}_2\text{O}_5(\text{g})$ intermediate, reverse equation 2. This also cancels out some of the undesired $\text{NO}_2(\text{g})$ but adds $\text{NO}(\text{g})$ and $\text{O}_2(\text{g})$. Finally, add equation 4 to remove those intermediates:



6.79 a) The balanced chemical equation for this reaction is



Instead of burning one mole of methane, $(25.0 \text{ g CH}_4) \left(\frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \right) = 1.5586 \text{ mol CH}_4$ (unrounded) of methane are burned.



$$\Delta H^\circ_{\text{comb}} = [1 \text{ mol } (\Delta H^\circ_f \text{CO}_2(\text{g})) + 2 \text{ mol } (\Delta H^\circ_f \text{H}_2\text{O}(\text{g}))] - [1 \text{ mol } (\Delta H^\circ_f \text{CH}_4(\text{g})) + 2 \text{ mol } (\Delta H^\circ_f \text{O}_2(\text{g}))]$$

$$\begin{aligned}
 \Delta H^\circ_{\text{comb}} &= 1 \text{ mol } (-393.5 \text{ kJ/mol}) + 2 \text{ mol } (-241.826 \text{ kJ/mol}) - [1 \text{ mol } (-74.87 \text{ kJ/mol}) + 2 \text{ mol } (0.0 \text{ kJ/mol})] \\
 &= -802.282 \text{ kJ/mol CH}_4 \text{ (unrounded)}
 \end{aligned}$$

$$(1.5586 \text{ mol CH}_4) \left(\frac{-802.282 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -1250.4 = \mathbf{-1.25 \times 10^3 \text{ kJ}}$$

b) The heat released by the reaction is “stored” in the gaseous molecules by virtue of their specific heat capacities, c , using the equation $\Delta H = mc\Delta T$. The problem specifies heat capacities on a molar basis, so we modify the equation to use moles, instead of mass. The gases that remain at the end of the reaction are CO_2 and H_2O . All of the methane and oxygen molecules were consumed. However, the oxygen was added as a component of air, which is 78% N_2 and 21% O_2 , and there is leftover N_2 .

$$\text{Moles of CO}_2(g) = (1.5586 \text{ mol CH}_4) \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} \right) = 1.5586 \text{ mol}$$

$$\text{Moles of H}_2\text{O}(g) = (1.5586 \text{ mol CH}_4) \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol CH}_4} \right) = 3.1172 \text{ mol}$$

$$\text{Mole fraction N}_2 = (79\% / 100\%) = 0.79$$

$$\text{Mole fraction O}_2 = (21\% / 100\%) = 0.21$$

$$\text{Moles of N}_2(g) = (3.1172 \text{ mol O}_2 \text{ used}) (0.79 \text{ mol N}_2 / 0.21 \text{ mol O}_2) = 11.7266 \text{ mol N}_2 \text{ (unrounded)}$$

$$Q = (\text{mol})(c)(\Delta T)$$

$$1250.4 \text{ kJ } (10^3 \text{ J / kJ}) = 1.5586 \text{ mol CO}_2 (57.2 \text{ J / mol}^\circ\text{C}) (T_f - 0.0)^\circ\text{C}$$

$$+ 3.1172 \text{ mol H}_2\text{O} (36.0 \text{ J / mol}^\circ\text{C}) (T_f - 0.0)^\circ\text{C}$$

$$+ 11.7266 \text{ mol N}_2 (30.5 \text{ J / mol}^\circ\text{C}) (T_f - 0.0)^\circ\text{C}$$

$$1.2504 \times 10^6 \text{ J} = ((89.1519 + 112.2192 + 357.6613) \text{ J /}^\circ\text{C}) T_f = (559.0324 \text{ J /}^\circ\text{C}) T_f$$

$$T_f = (1.2504 \times 10^6 \text{ J}) / (559.0324 \text{ J /}^\circ\text{C}) = 2236.72 = \mathbf{2.24 \times 10^3}^\circ\text{C}$$

Chapter 7 Quantum Theory and Atomic Structure

The value for the speed of light will be 3.00×10^8 m/s except when more significant figures are necessary, in which cases, 2.9979×10^8 m/s will be used.

FOLLOW-UP PROBLEMS

7.1 Plan: Given the frequency of the light, use the equation $c = \lambda\nu$ to solve for wavelength.

Solution:

$$\lambda = c / \nu = \frac{3.00 \times 10^8 \text{ m/s}}{7.23 \times 10^{14} \text{ s}^{-1}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 414.938 = \mathbf{415 \text{ nm}}$$

$$\lambda = c / \nu = \frac{3.00 \times 10^8 \text{ m/s}}{7.23 \times 10^{14} \text{ s}^{-1}} \left(\frac{1 \text{ \AA}}{10^{-10} \text{ m}} \right) = 4149.38 = \mathbf{4150 \text{ \AA}}$$

Check: The purple region of the visible light spectrum occurs between approximately 400 to 450 nm, so 415 nm is in the correct range for wavelength of purple light.

7.2 Plan: To calculate the energy for each wavelength we use the formula $E = hc / \lambda$

Solution:

$$E = hc / \lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{1 \times 10^{-8} \text{ m}} = 1.9878 \times 10^{-17} = \mathbf{2 \times 10^{-17} \text{ J}}$$

$$E = hc / \lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{5 \times 10^{-7} \text{ m}} = 3.9756 \times 10^{-19} = \mathbf{4 \times 10^{-19} \text{ J}}$$

$$E = hc / \lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{1 \times 10^{-4} \text{ m}} = 1.9878 \times 10^{-21} = \mathbf{2 \times 10^{-21} \text{ J}}$$

As the wavelength of light increases from ultraviolet (uv) to visible (vis) to infrared (ir) the energy of the light decreases.

Check: The decrease in energy with increase in wavelength follows the inverse relationship between energy and wavelength in the equation $E = hc / \lambda$.

7.3 Plan: With the equation for the de Broglie wavelength, $\lambda = h/mu$ and the given de Broglie wavelength, calculate the electron speed.

Solution:

$$u = h / m \lambda = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.11 \times 10^{-31} \text{ kg}) \left[(100. \text{ nm}) \left(\frac{10^{-9} \text{ m}}{1 \text{ nm}} \right) \right]} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}} \right) = 7273.3 = \mathbf{7.27 \times 10^3 \text{ m/s}}$$

Check: Perform a rough calculation to check order of magnitude:

$$\frac{10^{-34}}{(10^{-31}) \left[(100.) \left(\frac{10^{-9}}{1} \right) \right]} = 1 \times 10^4$$

- 7.4 **Plan:** Following the rules for l (integer from 0 to $n - 1$) and m_l (integer from $-l$ to $+l$) write quantum numbers for $n = 4$.

Solution:

For $n = 4$ $l = 0, 1, 2, 3$

For $l = 0$, $m_l = 0$

For $l = 1$, $m_l = -1, 0, 1$

For $l = 2$, $m_l = -2, -1, 0, 1, 2$

For $l = 3$, $m_l = -3, -2, -1, 0, 1, 2, 3$

Check: The total number of orbitals with a given n is n^2 . For $n = 4$, the total number of orbitals would be 16.

Adding the number of orbitals identified in the solution, gives

1 (for $l = 0$) + 3 (for $l = 1$) + 5 (for $l = 2$) + 7 (for $l = 3$) = 16 orbitals.

- 7.5 **Plan:** Identify n and l from the subshell designation and knowing the value for l , find the m_l values.

The subshells are given a letter designation, in which s represents $l = 0$, p represents $l = 1$, d represents $l = 2$, f represents $l = 3$.

Solution:

Sublevel name	n value	l value	m_l values
$2p$	2	1	-1, 0, 1
$5f$	5	3	-3, -2, -1, 0, 1, 2, 3

Check: The number of orbitals for each sublevel equals $2l + 1$. Sublevel $2p$ should have 3 orbitals and sublevel $5f$ should have 7 orbitals. Both of these agree with the number of m_l values for the sublevel.

- 7.6 **Plan:** Use the rules for designating quantum numbers to fill in the blanks.

For a given n , l can be any integer from 0 to $n - 1$.

For a given l , m_l can be any integer from $-l$ to $+l$.

The subshells are given a letter designation, in which s represents $l = 0$, p represents $l = 1$, d represents $l = 2$, f represents $l = 3$.

Solution:

The completed table is:

	n	l	m_l	Name
a)	4	1	0	$4p$
b)	2	1	0	$2p$
c)	3	2	-2	$3d$
d)	2	0	0	$2s$

Check: All the given values are correct designations.

END-OF-CHAPTER PROBLEMS

- 7.2 a) Figure 7.3 describes the electromagnetic spectrum by wavelength and frequency. Wavelength increases from left (10^{-2} nm) to right (10^{12} nm). The trend in increasing wavelength is: **x-ray < ultraviolet < visible < infrared < microwave < radio waves**.
- b) Frequency is inversely proportional to wavelength according to equation 7.1, so frequency has the opposite trend: **radio < microwave < infrared < visible < ultraviolet < x-ray**.
- c) Energy is directly proportional to frequency according to equation 7.2. Therefore, the trend in increasing energy matches the trend in increasing frequency: **radio < microwave < infrared < visible < ultraviolet < x-ray**. High-energy electromagnetic radiation disrupts cell function. It makes sense that you want to limit exposure to ultraviolet and x-ray radiation.
- 7.4 In order to explain the formula he developed for the energy vs. wavelength data of blackbody radiation, Max Planck assumed that only certain quantities of energy, called quanta, could be emitted or absorbed. The magnitude of these gains and losses were whole number multiples of the frequency: $\Delta E = nh\nu$.

- 7.6 Plan: Wavelength is related to frequency through the equation $c = \lambda\nu$. Recall that a Hz is a reciprocal second, or $1/\text{s} = \text{s}^{-1}$. Assume that the number “960” has three significant figures.

Solution:

$$c = \lambda\nu$$

$$\lambda(\text{m}) = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{(960. \text{ kHz}) \left(\frac{10^3 \text{ Hz}}{1 \text{ kHz}} \right) \left(\frac{\text{s}^{-1}}{\text{Hz}} \right)} = 312.5 = \mathbf{312 \text{ m}}$$

$$\lambda(\text{nm}) = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{(960. \text{ kHz}) \left(\frac{10^3 \text{ Hz}}{1 \text{ kHz}} \right) \left(\frac{\text{s}^{-1}}{\text{Hz}} \right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right)} = 3.125 \times 10^{11} = \mathbf{3.12 \times 10^{11} \text{ nm}}$$

$$\lambda(\text{\AA}) = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{(960. \text{ kHz}) \left(\frac{10^3 \text{ Hz}}{1 \text{ kHz}} \right) \left(\frac{\text{s}^{-1}}{\text{Hz}} \right) \left(\frac{1 \text{\AA}}{10^{-10} \text{ m}} \right)} = 3.125 \times 10^{12} = \mathbf{3.12 \times 10^{12} \text{\AA}}$$

- 7.8 Plan: Frequency is related to energy through the equation $E = h\nu$. Note that $1 \text{ Hz} = 1 \text{ s}^{-1}$.

Solution:

$$E = h\nu$$

$$E = (6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (3.6 \times 10^{10} \text{ s}^{-1}) = 2.385 \times 10^{-23} = \mathbf{2.4 \times 10^{-23} \text{ J}}$$

- 7.10 Since energy is directly proportional to frequency ($E = h\nu$) and frequency and wavelength are inversely related ($\nu = c/\lambda$), it follows that energy is inversely related to wavelength ($E = \frac{hc}{\lambda}$). As wavelength decreases, energy increases. In terms of increasing energy the order is **red < yellow < blue**.

- 7.13 Plan: a) The least energetic photon has the longest wavelength (242 nm). b) The most energetic photon has the shortest wavelength (2200 \AA).

$$\text{a) } \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{242 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 1.239669 \times 10^{15} = \mathbf{1.24 \times 10^{15} \text{ s}^{-1}}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (3.00 \times 10^8 \text{ m/s})}{242 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 8.2140 \times 10^{-19} = \mathbf{8.21 \times 10^{-19} \text{ J}}$$

$$\text{b) } \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{2200 \text{ \AA}} \left(\frac{1 \text{ \AA}}{10^{-10} \text{ m}} \right) = 1.3636 \times 10^{15} = \mathbf{1.4 \times 10^{15} \text{ s}^{-1}}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (3.00 \times 10^8 \text{ m/s})}{2200 \text{ \AA}} \left(\frac{1 \text{ \AA}}{10^{-10} \text{ m}} \right) = 9.03545 \times 10^{-19} = \mathbf{9.0 \times 10^{-19} \text{ J}}$$

- 7.16 The quantum number n is related to the energy level of the electron. An electron *absorbs* energy to change from lower energy (low n) to higher energy (high n) giving an absorption spectrum. An electron *emits* energy as it drops from a higher energy level to a lower one giving an emission spectrum.

a) **absorption** b) **emission** c) **emission** d) **absorption**

- 7.18 Plan: Calculate wavelength by substituting the given values into equation 7.3, where $n_1 = 2$ and $n_2 = 5$ because $n_2 > n_1$. Although more significant figures could be used, five significant figures are adequate for this calculation.
Solution:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad R = 1.096776 \times 10^7 \text{ m}^{-1}$$

$$n_1 = 2 \quad n_2 = 5$$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = (1.096776 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = 2303229.6 \text{ m}^{-1} \text{ (unrounded)}$$

$$\lambda \text{ (nm)} = \left(\frac{1}{2303229.6 \text{ m}^{-1}} \right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 434.1729544 = \mathbf{434.17 \text{ nm}}$$

- 7.20 Plan: To find the transition energy, apply equation 7.4 and multiply by Avogadro's number.
Solution:

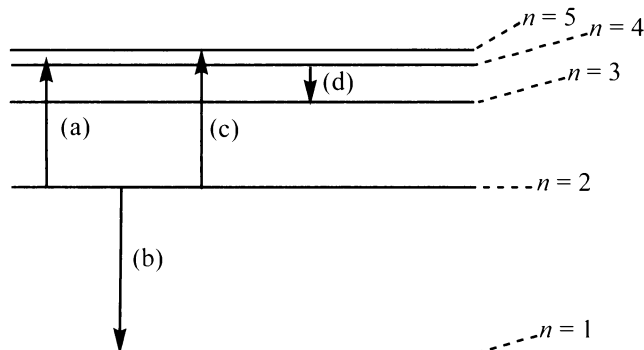
$$\Delta E = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right)$$

$$\Delta E = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{2^2} - \frac{1}{5^2} \right) = -4.578 \times 10^{-19} \text{ J/photon}$$

$$\Delta E = \left(\frac{-4.578 \times 10^{-19} \text{ J}}{\text{photon}} \right) \left(\frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \right) = -2.75687 \times 10^5 = \mathbf{-2.76 \times 10^5 \text{ J/mol}}$$

Check: The value is negative and so light is emitted.

- 7.22 Looking at an energy chart will help answer this question.



Frequency is proportional to energy so the smallest frequency will be d) $n = 4$ to $n = 3$; levels 4 and 5 have a smaller ΔE than the levels in the other transitions. The largest frequency is b) $n = 2$ to $n = 1$ since levels 1 and 2 have a larger ΔE than the levels in the other transitions. Transition a) $n = 2$ to $n = 4$ will be smaller than transition c) $n = 2$ to $n = 5$ since level 5 is a higher energy than level 4. In order of increasing frequency the transitions are $\mathbf{d < a < c < b}$.

- 7.24 Plan: Use the Rydberg equation. A combination of $E = hc/\lambda$, and equation 7.4, would also work.

Solution:

$$\lambda = (97.20 \text{ nm}) \left(\frac{10^{-9} \text{ m}}{1 \text{ nm}} \right) = 9.720 \times 10^{-8} \text{ m} \quad \text{ground state: } n_1 = 1; \quad n_2 = ?$$

$$\frac{1}{\lambda} = (1.096776 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{9.72 \times 10^{-8} \text{ m}} = (1.096776 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right)$$

$$0.9380 = \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right)$$

$$\frac{1}{n_2^2} = 1 - 0.9380 = 0.0620$$

$$n_2^2 = 16.1$$

$$n_2 = 4$$

- 7.27 Macroscopic objects have significant mass. A large m in the denominator of $\lambda = h/mu$ will result in a very small wavelength. Macroscopic objects do exhibit a wavelike motion, but the wavelength is too small for humans to see.

- 7.29 Plan: Use the de Broglie equation. Mass in pounds must be converted to kg and velocity in mi/h must be converted to m/s because a joule is equivalent to $\text{kg} \cdot \text{m}^2/\text{s}^2$.

Solution:

$$\begin{aligned} \text{a) } \lambda &= \frac{h}{mu} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{(220 \text{ lb}) \left(19.6 \frac{\text{mi}}{\text{h}} \right)} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}} \right) \left(\frac{2.205 \text{ lb}}{1 \text{ kg}} \right) \left(\frac{0.62 \text{ mi}}{1 \text{ km}} \right) \left(\frac{1 \text{ km}}{10^3 \text{ m}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \\ &= 7.562675 \times 10^{-37} = \mathbf{7.6 \times 10^{-37} \text{ m}} \end{aligned}$$

$$7.31 \quad \lambda = \frac{h}{mu}$$

$$u = \frac{h}{m\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{(56.5 \text{ g})(5400 \text{ Å})} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ Å}}{10^{-10} \text{ m}} \right) = 2.1717 \times 10^{-26} = \mathbf{2.2 \times 10^{-26} \text{ m/s}}$$

- 7.33 Plan: The de Broglie wavelength equation will give the mass equivalent of a photon with known wavelength and velocity. The term “mass-equivalent” is used instead of “mass of photon” because photons are quanta of electromagnetic energy that have no mass. A light photon’s velocity is the speed of light, $3.00 \times 10^8 \text{ m/s}$.

Solution:

$$\lambda = \frac{h}{mu}$$

$$m = \frac{h}{\lambda u} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{(589 \text{ nm})(3.00 \times 10^8 \text{ m/s})} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}} \right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 3.7498 \times 10^{-36} = \mathbf{3.75 \times 10^{-36} \text{ kg/photon}}$$

- 7.37 a) Principal quantum number, n , relates to the size of the orbital. More specifically, it relates to the distance from the nucleus at which the probability of finding an electron is greatest. This distance is determined by the energy of the electron.
 b) Angular momentum quantum number, l , relates to the shape of the orbital. It is also called the azimuthal quantum number.
 c) Magnetic quantum number, m_l , relates to the orientation of the orbital in space in three-dimensional space.

- 7.38 a) **one** b) **five** c) **three** d) **nine**
 a) There is only a single s orbital in any shell.
 b) All d -orbitals consists of sets of five ($m_l = -2, -1, 0, +1, +2$).
 c) All p -orbitals consists of sets of three ($m_l = -1, 0, +1$).
 d) If $n = 3$, then there is a $3s$ (1 orbital), a $3p$ set (3 orbitals), and a $3d$ set (5 orbitals) giving $1 + 3 + 5 = 9$.

7.40 Magnetic quantum numbers (m_l) can have integer values from $-l$ to $+l$.

- a) m_l : $-2, -1, 0, +1, +2$
 b) m_l : 0 (if $n = 1$, then $l = 0$)
 c) m_l : $-3, -2, -1, 0, +1, +2, +3$

7.42 Plan: The following letter designations correlate with the following l quantum numbers:
 $l = 0 = s$ orbital; $l = 1 = p$ orbital; $l = 2 = d$ orbital; $l = 3 = f$ orbital. Remember that allowed m_l values are $-l$ to $+l$.

Solution:

sublevel	allowable m_l	no of possible orbitals
a) $d (l = 2)$	$-2, -1, 0, +1, +2$	5
b) $p (l = 1)$	$-1, 0, +1$	3
c) $f (l = 3)$	$-3, -2, -1, 0, +1, +2, +3$	7

7.44 Plan: The integer in front of the letter represents the n value. The letter designates the l value:
 $l = 0 = s$ orbital; $l = 1 = p$ orbital; $l = 2 = d$ orbital; $l = 3 = f$ orbital.

Solution:

- a) For the $5s$ subshell, $n = 5$ and $l = 0$. Since $m_l = 0$, there is one orbital.
 b) For the $3p$ subshell, $n = 3$ and $l = 1$. Since $m_l = -1, 0, +1$, there are three orbitals.
 c) For the $4f$ subshell, $n = 4$ and $l = 3$. Since $m_l = -3, -2, -1, 0, +1, +2, +3$, there are seven orbitals.

7.46 Plan: Allowed values of quantum numbers: $n =$ positive integers; $l =$ integers from 0 to $n - 1$;
 $m_l =$ integers from $-l$ through 0 to $+l$.

Solution:

- a) With $l = 0$, the only allowable m_l value is 0. To correct, either change l or m_l value.
 Correct $n = 2, l = 1, m_l = -1$; $n = 2, l = 0, m_l = 0$.
 b) Combination is allowed.
 c) Combination is allowed.
 d) With $l = 2, m_l = -2, -1, 0, +1, +2, +3$ is not an allowable m_l value. To correct, either change l or m_l value.
 Correct: $n = 5, l = 3, m_l = +3$; $n = 5, l = 2, m_l = 0$.

7.48 a) The mass of the electron is 9.1094×10^{-31} kg.

$$\begin{aligned}
 E &= -\frac{h^2}{8\pi^2 m_e a_0^2 n^2} = -\frac{h^2}{8\pi^2 m_e a_0^2} \left(\frac{1}{n^2} \right) \\
 &= -\frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8\pi^2 (9.1094 \times 10^{-31} \text{ kg}) (52.92 \times 10^{-12} \text{ m})^2} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}} \right) \left(\frac{1}{n^2} \right) \\
 &= -(2.17963 \times 10^{-18} \text{ J}) \left(\frac{1}{n^2} \right) = -(2.180 \times 10^{-18} \text{ J}) \left(\frac{1}{n^2} \right)
 \end{aligned}$$

This is identical with the result from Bohr's theory. For the H atom, $Z = 1$ and Bohr's constant $= -2.18 \times 10^{-18}$ J. For the hydrogen atom, derivation using classical principles or quantum-mechanical principles yields the same constant.

b) The $n = 3$ energy level is higher in energy than the $n = 2$ level. Because the zero point of the atom's energy is defined as an electron's infinite distance from the nucleus, a larger negative number describes a lower energy level. Although this may be confusing, it makes sense that an energy *change* would be a positive number.

$$\Delta E = -(2.180 \times 10^{-18} \text{ J}) \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = -3.027778 \times 10^{-19} = \mathbf{3.028 \times 10^{-19} \text{ J}}$$

$$c) E = \frac{hc}{\lambda} \quad \lambda \text{ (m)} = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{(3.027778 \times 10^{-19} \text{ J})} = 6.56061 \times 10^{-7} = \mathbf{6.561 \times 10^{-7} \text{ m}}$$

$$(6.56061 \times 10^{-7} \text{ m}) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 656.061 = \mathbf{656.1 \text{ nm}}$$

This is the wavelength for the observed red line in the hydrogen spectrum.

- 7.49 a) The lines do not begin at the origin because an electron must absorb a minimum amount of energy before it has enough energy to overcome the attraction of the nucleus and leave the atom. This minimum energy is the energy of photons of light at the threshold frequency.
 b) The lines for K and Ag do not begin at the same point, because the amount of energy that an electron must absorb to leave the K atom is less than the amount of energy that an electron must absorb to leave the Ag atom, where the attraction between the nucleus and outer electron is stronger than in a K atom.
 c) Wavelength is inversely proportional to energy. Thus, the metal that requires a larger amount of energy to be absorbed before electrons are emitted will require a shorter wavelength of light. Electrons in Ag atoms require more energy to leave, so Ag requires a shorter wavelength of light than K to eject an electron.
 d) The slopes of the line show an increase in kinetic energy as the frequency (or energy) of light is increased. Since the slopes are the same, this means that for an increase of one unit of frequency (or energy) of light, the increase in kinetic energy of an electron ejected from K is the same as the increase in the kinetic energy of an electron ejected from Ag. After an electron is ejected, the energy that it absorbs above the threshold energy becomes kinetic energy of the electron. For the same increase in energy above the threshold energy, for either K or Ag, the kinetic energy of the ejected electron will be the same.

- 7.52 The Bohr model has been successfully applied to predict the spectral lines for one-electron species other than H. Common one-electron species are small cations with all but one electron removed. Since the problem specifies a metal ion, assume that the possible choices are Li^{+2} or Be^{+3} , and solve Bohr's equation to verify if a whole number for Z can be calculated. Recall that the negative sign is a convention based on the zero point of the atom's energy; it is deleted in this calculation to avoid taking the square root of a negative number.

The highest-energy line corresponds to the transition from $n = 1$ to $n = \infty$.

$$E = h\nu = (6.626 \times 10^{-34} \text{ Js})(2.961 \times 10^{16} \text{ Hz})(\text{s}^{-1}/\text{Hz}) = -1.9619586 \times 10^{-17} \text{ J (unrounded)}$$

$$E = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{Z^2}{n^2} \right) \quad Z = \text{charge of the nucleus}$$

$$Z^2 = -\frac{En^2}{2.18 \times 10^{-18} \text{ J}} = \frac{-1.9619586 \times 10^{-17} (1^2)}{-2.18 \times 10^{-18} \text{ J}} = 8.99998$$

Then $Z^2 = 9$ and $Z = 3$.

Therefore, the ion is Li^{2+} .

- 7.55 $E = hc/\lambda$ thus $\lambda = hc/E$

a) The energy of visible light is lower than that of UV light. Thus, metal A must be **barium** since, of the three metals listed, barium has the smallest work function indicating the attraction between barium's nucleus and outer electron is less than the attraction in tantalum or tungsten. The longest wavelength corresponds to the lowest energy (work function).

$$\text{Ta: } \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{6.81 \times 10^{-19} \text{ J}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 291.894 = \mathbf{292 \text{ nm}}$$

$$\text{Ba: } \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{4.30 \times 10^{-19} \text{ J}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 462.279 = \mathbf{462 \text{ nm}}$$

$$\text{W: } \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{7.16 \times 10^{-19} \text{ J}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 277.6257 = \mathbf{278 \text{ nm}}$$

Metal A must be barium, because barium is the only metal that emits in the visible range (462 nm).

b) A UV range of 278 nm to 292 nm is necessary to distinguish between tantalum and tungsten.

7.57 The speed of light is necessary; however, the frequency is irrelevant.

$$\text{a) Time} = (8.1 \times 10^7 \text{ km}) \left(\frac{10^3 \text{ m}}{1 \text{ km}} \right) \left(\frac{1 \text{ s}}{3.00 \times 10^8 \text{ m}} \right) = 270 = \mathbf{2.7 \times 10^2 \text{ s}}$$

$$\text{b) Distance} = (1.2 \text{ s}) \left(\frac{3.00 \times 10^8 \text{ m}}{\text{s}} \right) = \mathbf{3.6 \times 10^8 \text{ m}}$$

7.60 Plan: Refer to Chapter 6 for the calculation of the amount of heat energy absorbed by a substance from its heat capacity and temperature change ($q = C \times \text{mass} \times \Delta T$). Using this equation, calculate the energy absorbed by the water. This energy equals the energy from the microwave photons. The energy of each photon can be calculated from its wavelength: $E = hc/\lambda$. Dividing the total energy by the energy of each photon gives the number of photons absorbed by the water.

Solution:

$$q = C \times \text{mass} \times \Delta T$$

$$q = (4.184 \text{ J/g}^\circ\text{C}) (252 \text{ g}) (98 - 20.)^\circ\text{C} = 8.22407 \times 10^4 \text{ J (unrounded)}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{1.55 \times 10^{-2} \text{ m}} = 1.28245 \times 10^{-23} \text{ J/photon (unrounded)}$$

$$\text{Number of photons} = (8.22407 \times 10^4 \text{ J}) \left(\frac{1 \text{ photon}}{1.28245 \times 10^{-23} \text{ J}} \right) = 6.41278 \times 10^{27} = \mathbf{6.4 \times 10^{27} \text{ photons}}$$

Check: The order of magnitude appears to be correct for the calculation of total energy absorbed: $10^1 \times 10^2 \times 10^1 = 10^4$. The order of magnitude of the energy for one photon also appears correct: $10^{-34} \times 10^8 / 10^{-2} = 10^{-24}$. In addition, the order of magnitude of the number of photons is estimated as $10^4 / 10^{-24} = 10^{28}$, which agrees with the calculated 6×10^{27} .

7.63 Plan: The energy differences sought may be determined by looking at the energy changes in steps.

Solution:

a) The difference between levels 3 and 2 (E_{32}) may be found by taking the difference in the energies for the $3 \rightarrow 1$ transition (E_{31}) and the $2 \rightarrow 1$ transition (E_{21}).

$$E_{32} = E_{31} - E_{21} = (4.844 \times 10^{-17} \text{ J}) - (4.088 \times 10^{-17} \text{ J}) = \mathbf{7.56 \times 10^{-18} \text{ J}}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{(7.56 \times 10^{-18} \text{ J})} = 2.629365 \times 10^{-8} = \mathbf{2.63 \times 10^{-8} \text{ m}}$$

b) The difference between levels 4 and 1 (E_{41}) may be found by adding the energies for the $4 \rightarrow 2$ transition (E_{42}) and the $2 \rightarrow 1$ transition (E_{21}).

$$E_{41} = E_{42} + E_{21} = (1.022 \times 10^{-17} \text{ J}) + (4.088 \times 10^{-17} \text{ J}) = \mathbf{5.110 \times 10^{-17} \text{ J}}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{(5.110 \times 10^{-17} \text{ J})} = 3.8900 \times 10^{-9} = \mathbf{3.890 \times 10^{-9} \text{ m}}$$

c) The difference between levels 5 and 4 (E_{54}) may be found by taking the difference in the energies for the $5 \rightarrow 1$ transition (E_{51}) and the $4 \rightarrow 1$ transition (see part b).

$$E_{54} = E_{51} - E_{41} = (5.232 \times 10^{-17} \text{ J}) - (5.110 \times 10^{-17} \text{ J}) = \mathbf{1.22 \times 10^{-18} \text{ J}}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{(1.22 \times 10^{-18} \text{ J})} = 1.629344 \times 10^{-7} = \mathbf{1.63 \times 10^{-7} \text{ m}}$$

7.65 a) Figure 7.3 indicates that the 641 nm wavelength of Sr falls in the **red** region and the 493 nm wavelength of Ba falls in the **green** region.

b) Use the formula $E = hc/\lambda$ to calculate kJ/photon. Convert the 1.00 g amounts of BaCl_2 ($M = 208.2 \text{ g/mol}$) and SrCl_2 ($M = 158.52 \text{ g/mol}$) to moles, then to atoms, and assume each atom undergoes one electron transition (which produces the colored light) to find number of photons. Multiply kJ/photon by number of photons to find total energy.

SrCl_2

$$\begin{aligned}\text{Number of photons} &= (1.00 \text{ g SrCl}_2) \left(\frac{1 \text{ mol SrCl}_2}{158.52 \text{ g SrCl}_2} \right) \left[\frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol SrCl}_2} \right] \\ &= 3.7988897 \times 10^{21} \text{ photons (unrounded)}\end{aligned}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{641 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right)$$

$$= 3.10109 \times 10^{-22} \text{ kJ/photon (unrounded)}$$

$$E_{\text{total}} = (3.7988897 \times 10^{21} \text{ photons})(3.10109 \times 10^{-22} \text{ kJ/photon}) = 1.17807 = \mathbf{1.18 \text{ kJ (Sr)}}$$

BaCl_2

$$\begin{aligned}\text{Number of photons} &= (1.00 \text{ g BaCl}_2) \left(\frac{1 \text{ mol BaCl}_2}{208.2 \text{ g BaCl}_2} \right) \left[\frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol BaCl}_2} \right] \\ &= 2.892411 \times 10^{21} \text{ photons (unrounded)}\end{aligned}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{493 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right)$$

$$= 4.0320487 \times 10^{-22} \text{ kJ/photon (unrounded)}$$

$$E_{\text{total}} = (2.892411 \times 10^{21} \text{ photons})(4.0320487 \times 10^{-22} \text{ kJ/photon}) = 1.16623 = \mathbf{1.17 \text{ kJ (Ba)}}$$

7.67 a) At this wavelength the sensitivity to absorbance of light by Vitamin A is maximized while minimizing interference due to the absorbance of light by other substances in the fish-liver oil.

b) The wavelength 329 nm lies in the **ultraviolet region** of the electromagnetic spectrum.

c) A known quantity of vitamin A ($1.67 \times 10^{-3} \text{ g}$) is dissolved in a known volume of solvent (250. mL) to give a standard concentration with a known response (1.018 units). This can be used to find the unknown quantity of Vitamin A that gives a response of 0.724 units. An equality can be made between the two concentration-to-absorbance ratios:

$$\frac{A_1}{C_1} = \frac{A_2}{C_2}$$

$$C_1 = \frac{A_1 C_2}{A_2} = \frac{(0.724) \left(\frac{1.67 \times 10^{-3} \text{ g}}{250. \text{ mL}} \right)}{(1.018)} = 4.7508 \times 10^{-6} \text{ g/mL (unrounded)}$$

$$\frac{(4.7508 \times 10^{-6} \text{ g Vitamin A/mL})(500. \text{ mL})}{(0.1232 \text{ g Oil})} = 1.92808 \times 10^{-2} = \mathbf{1.93 \times 10^{-2} \text{ g Vitamin A/g Oil}}$$

7.71 The amount of energy is calculated from the wavelength of light:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{550 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) = 3.61418 \times 10^{-19} \text{ J/photon (unrounded)}$$

$$\text{Amount of E from the bulb} = (75 \text{ W}) \left(\frac{1 \text{ J/s}}{\text{W}} \right) \left(\frac{10\%}{100\%} \right) \left(\frac{5\%}{100\%} \right) = 0.375 \text{ J/s}$$

$$\text{Number of photons: } \left(\frac{0.375 \text{ J}}{\text{s}} \right) \left(\frac{1 \text{ photon}}{3.61418 \times 10^{-19} \text{ J}} \right) = 1.0376 \times 10^{18} = \mathbf{1.0 \times 10^{18} \text{ photons/s}}$$

Chapter 8 Electron Configuration and Chemical Periodicity

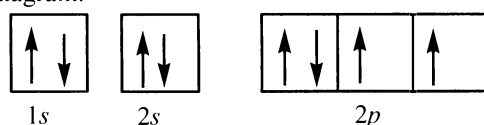
FOLLOW-UP PROBLEMS

- 8.1 Plan: The superscripts can be added to indicate the number of electrons in the element, and hence its identity. A horizontal orbital diagram is written for simplicity, although it does not indicate the sublevels have different energies. Based on the orbital diagram, we identify the electron of interest and determine its four quantum numbers.

Solution:

The number of electrons = $2 + 2 + 4 = 8$; element = oxygen.

Orbital diagram:



The electron in the middle $2p$ orbital is the sixth electron (this electron would have entered in this position due to Hund's rule). This electron has the following quantum numbers: $n = 2$, $l = 1$ (for p orbital), $m_l = 0$, $m_s = +1/2$. By convention, $+1/2$ is assigned to the first electron in an orbital. Also, the first p orbital is assigned a m_l value of -1 , the middle p orbital a m_l value of 0 and the last p orbital a m_l value of $+1$.

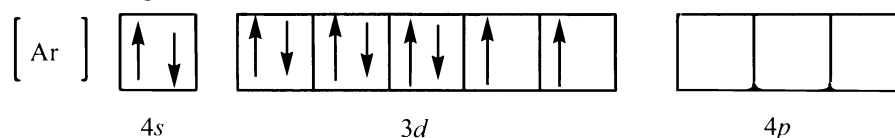
- 8.2 Plan: The atomic number gives the number of electrons. The order of filling may be inferred by the location of the element on the periodic table. The partial orbital diagrams shows only those electrons after the preceding noble gas except those used to fill inner d and f subshells. The number of inner electrons is simply the total electrons minus those electrons in the partial orbital diagram.

Solution:

a) For Ni ($Z = 28$), the full electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$.

The condensed configuration is $[\text{Ar}] 4s^2 3d^8$.

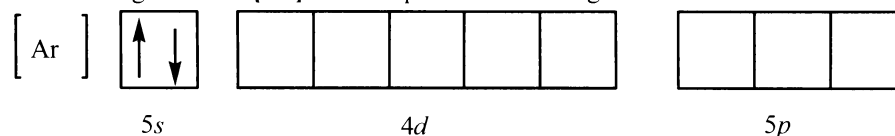
The partial orbital diagram for the valence electrons is



There are $28 - 10(\text{valence}) = 18$ inner electrons.

b) For Sr ($Z = 38$), the full electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$.

The condensed configuration is $[\text{Kr}] 5s^2$. The partial orbital diagram is

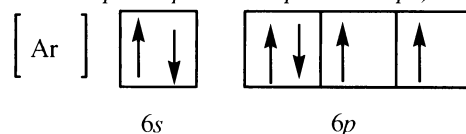


There are $38 - 2(\text{valence}) = 36$ inner electrons.

c) For Po (84 electrons), the full configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^4$.

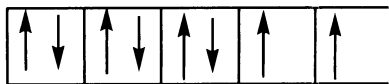
The condensed configuration is $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^4$.

The partial orbital diagram represents valence electrons only; the inner electrons are those in the previous noble gas (Xe or $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$) and filled transition ($5d^{10}$) and inner transition ($4f^{14}$) levels.



There are $84 - 6(\text{valence}) = 78$ inner electrons.

- 8.3 Plan: Locate each of the elements on the periodic table. All of these are main-group elements, so their sizes increase down and to the left in the periodic table.
Solution:
 a) $\text{Cl} < \text{Br} < \text{Se}$. Cl has a smaller n than Br and Se. Br experiences a higher Z_{eff} than Se and is smaller.
 b) $\text{Xe} < \text{I} < \text{Ba}$. Xe and I have the same n , but Xe experiences a higher Z_{eff} and is smaller. Ba has the highest n and is the largest.
- 8.4 Plan: These main-group elements must be located on the periodic table. The value of IE_1 increases toward the top (same column) and the right of the periodic table (same n).
Solution:
 a) $\text{Sn} < \text{Sb} < \text{I}$. These elements have the same n , so the values increase to the right on the periodic table. Iodine has the highest IE, because its outer electron is most tightly held and hardest to remove.
 b) $\text{Ba} < \text{Sr} < \text{Ca}$. These elements are in the same column, so the values decrease towards the bottom of the column. Barium's outer electron receives the most shielding; therefore, it is easiest to remove and has the lowest IE.
- 8.5 Plan: We must look for a large "jump" in the IE values. This jump occurs after the valence electrons have been removed. The next step is to determine the element in the designated period with the proper number of valence electrons.
Solution:
 The exceptionally large jump from IE_3 to IE_4 means that the fourth electron is an inner electron. Thus, Q has three valence electrons. Since Q is in period 3, it must be **aluminum**, Al: $1s^2 2s^2 2p^6 3s^2 3p^1$.
- 8.6 Plan: We need to locate each element on the periodic table. Elements in the first two columns on the left or the two columns to the left of the noble gases tend to adopt ions with a noble gas configuration. Elements in the remaining columns may use either their ns and np electrons, or just their np electrons.
Solution:
 a) Barium loses two electrons to be isoelectronic with Xe: $\text{Ba} ([\text{Xe}] 6s^2) \rightarrow \text{Ba}^{2+} ([\text{Xe}]) + 2e^-$
 b) Oxygen gains two e^- to be isoelectronic with Ne: $\text{O} ([\text{He}] 2s^2 2p^4 + 2e^- \rightarrow \text{O}^{2-} ([\text{Ne}])$
 c) Lead can lose two electrons to form an "inert pair" configuration:
 $\text{Pb} ([\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^2) \rightarrow \text{Pb}^{2+} ([\text{Xe}] 6s^2 4f^{14} 5d^{10}) + 2e^-$
 or lead can lose four electrons form a "pseudo-noble gas" configuration:
 $\text{Pb} ([\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^2) \rightarrow \text{Pb}^{4+} ([\text{Xe}] 4f^{14} 5d^{10}) + 4e^-$
- 8.7 Plan: Write the condensed electron configuration for each atom, being careful to note those elements, which are irregular. The charge on the cation tells how many electrons are to be removed. The electrons are removed beginning with the ns electrons. If any electrons in the final ion are unpaired, the ion is paramagnetic. If it is not obvious that there are unpaired electrons, a partial orbital diagram might help.
Solution:
 a) The V atom ($[\text{Ar}] 4s^2 3d^3$) loses the two $4s$ electrons and one $3d$ electron to form V^{3+} ($[\text{Ar}] 3d^2$). There are two unpaired d electrons, so V^{3+} is **paramagnetic**.
 b) The Ni atom ($[\text{Ar}] 4s^2 3d^8$) loses the two $4s$ electrons to form Ni^{2+} ($[\text{Ar}] 3d^8$). There are two unpaired d electrons, so Ni^{2+} is **paramagnetic**.



$3d$

- c) The La atom ($[\text{Xe}] 6s^2 5d^1$) loses all three valence electrons to form La^{3+} ($[\text{Xe}]$). There are no unpaired electrons, so La^{3+} is **diamagnetic**.

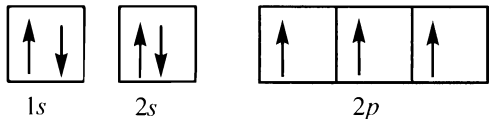
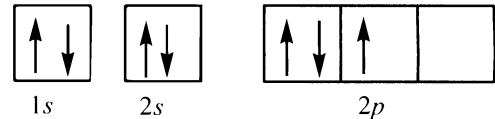
- 8.8 Plan: Locate each of the elements on the periodic table. Cations are smaller than the parent atoms, and anions are larger than the parent atoms. If the electrons are equal, anions are larger than cations. The more electrons added or removed; the greater the change in size.
Solution:
 a) Ionic size increases down a group, so $\text{F}^- < \text{Cl}^- < \text{Br}^-$.
 b) These species are isoelectronic (all have 10 electrons), so size increases with increasing negative charge:
 $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$.
 c) Ionic size increases as charge decreases for different cations of the same element, so $\text{Cr}^{3+} < \text{Cr}^{2+}$.

END-OF-CHAPTER PROBLEMS

- 8.1 Elements are listed in the periodic table in an ordered, systematic way that correlates with a periodicity of their chemical and physical properties. The theoretical basis for the table in terms of atomic number and electron configuration does not allow for an “unknown element” between Sn and Sb.
- 8.3 Plan: The value should be the average of the elements above and below the one of interest.
Solution:
 a) Predicted atomic mass (K) =

$$\frac{\text{Na} + \text{Rb}}{2} = \frac{22.99 + 85.47}{2} = \mathbf{54.23 \text{ amu}}$$
 (actual value = 39.10 amu)
 b) Predicted melting point (Br_2) =

$$\frac{\text{Cl}_2 + \text{I}_2}{2} = \frac{-101.0 + 113.6}{2} = \mathbf{6.3^\circ\text{C}}$$
 (actual value = -7.2°C)
 c) Predicted boiling point (HBr) =

$$\frac{\text{HCl} + \text{HI}}{2} = \frac{-84.9 + (-35.4)}{2} = -60.15 = \mathbf{-60.2^\circ\text{C}}$$
 (actual value = -67.0°C)
- 8.5 The quantum number m_l relates to just the electron; all the others describe the orbital.
- 8.8 Shielding occurs when inner electrons protect or shield outer electrons from the full nuclear attractive force. The effective nuclear charge is the nuclear charge an electron actually experiences. As the number of inner electrons increases, the effective nuclear charge decreases.
- 8.10 a) The $l = 1$ quantum number can only refer to a p orbital. These quantum numbers designate the $2p$ orbital set, which hold a maximum of **6** electrons, 2 electrons in each of the three $2p$ orbitals.
 b) There are five $3d$ orbitals, therefore a maximum of **10** electrons can have the $3d$ designation.
 c) There is one $4s$ orbital which holds a maximum of **2** electrons.
- 8.12 a) **6** electrons can be found in the three $4p$ orbitals, 2 in each orbital.
 b) The $l = 1$ quantum number can only refer to a p orbital, and the m_l value of +1 specifies one particular p orbital, which hold a maximum of **2** electrons with the difference between the two electrons being in the m_s quantum number.
 c) **14** electrons can be found in the $5f$ orbitals ($l = 3$ designates f orbitals; there are 7 f orbitals in a set).
- 8.15 Hund's rule states that electrons will fill empty orbitals in the same sublevel before filling half-filled orbitals. This lowest-energy arrangement has the maximum number of unpaired electrons with parallel spins. The correct electron configuration for nitrogen is shown in (a), which is contrasted to an incorrect configuration shown in (b). The arrows in the $2p$ orbitals of configuration (a) could alternatively all point down.
- (a) – correct
- 
- (b) – incorrect
- 
- In (a), there is one electron in each of the $2p$ orbitals; in (b) which is incorrect, 2 electrons were paired in one of the $2p$ orbitals while leaving one $2p$ orbital empty.

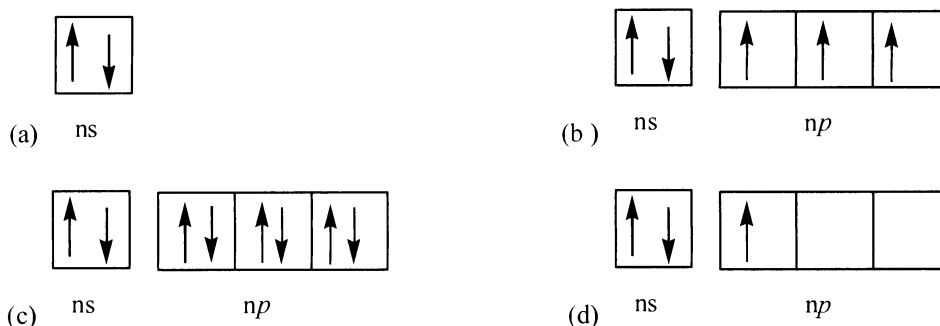
- 8.17 For elements in the same group (vertical column in periodic table), the electron configuration of the outer electrons are identical except for the n value. For elements in the same period (horizontal row in periodic table), their configurations vary because each succeeding element has one additional electron. The electron configurations are similar only in the fact that the same level (principal quantum number) is the outer level.
- 8.18 Plan: Assume that the electron is in the ground state configuration and that electrons fill in a p_x - p_y - p_z order. By convention, we assign the first electron to fill an orbital an $m_s = +1/2$. Also by convention, $m_l = -1$ for the p_x orbital, $m_l = 0$ for the p_y orbital, and $m_l = +1$ for the p_z orbital.
Solution:
 a) The outermost electron in a rubidium atom would be in a $5s$ orbital (rubidium is in Row 5, Group 1). The quantum numbers for this electron are $n = 5$, $l = 0$, $m_l = 0$, and $m_s = +1/2$.
 b) The S^- ion would have the configuration $[\text{Ne}]3s^23p^5$. The electron added would go into the $3p_z$ orbital and is the second electron in that orbital. Quantum numbers are $n = 3$, $l = 1$, $m_l = +1$, and $m_s = -1/2$.
 c) Ag atoms have the configuration $[\text{Kr}]5s^14d^{10}$. The electron lost would be from the $5s$ orbital with quantum numbers $n = 5$, $l = 0$, $m_l = 0$, and $m_s = +1/2$.
 d) The F atom has the configuration $[\text{He}]2s^22p^5$. The electron gained would go into the $2p_z$ orbital and is the second electron in that orbital. Quantum numbers are $n = 2$, $l = 1$, $m_l = +1$, and $m_s = -1/2$.
- 8.20 a) Rb: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1$
 b) Ge: $1s^22s^22p^63s^23p^64s^23d^{10}4p^2$
 c) Ar: $1s^22s^22p^63s^23p^6$
- 8.22 Valence electrons are those electrons beyond the previous noble gas configuration and unfilled d and f sublevels.
- a) Ti ($Z = 22$); $[\text{Ar}]4s^23d^2$
-
- $4s$
 $3d$
 $4p$
- b) Cl ($Z = 17$); $[\text{Ne}]3s^23p^5$
-
- $3s$
 $3p$
- c) V ($Z = 23$); $[\text{Ar}]4s^23d^3$
-
- $4s$
 $3d$
 $4p$
- 8.24 a) Element = O, Group 6A(16), period 2
-
- $2s$
 $2p$
- b) Element = P, Group 5A(15), period 3
-
- $3s$
 $3p$

- 8.26 a) The orbital diagram shows the element is in period 4 ($n = 4$ as outer level). The configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ or $[\text{Ar}]4s^2 3d^{10} 4p^1$. One electron in the p level indicates the element is in group **3A(13)**. The element is Ga.
 b) The orbital diagram shows the $2s$ and $2p$ orbitals filled which would represent the last element in period 2, Ne. The configuration is $1s^2 2s^2 2p^6$ or $[\text{He}]2s^2 2p^6$. Filled s and p orbitals indicate the group **8A(18)**.
- 8.28 Inner electrons are those seen in the previous noble gas and completed transition series (d orbitals). Outer electrons are those in the highest energy level (highest n value). Valence electrons are the outer electrons for main-group elements; for transition metals, valence electrons also include electrons in the unfilled d set of orbitals. It is easiest to determine the types of electrons by writing a condensed electron configuration.
 a) O ($Z = 8$); $[\text{He}]2s^2 2p^4$. There are **2** inner electrons (represented by $[\text{He}]$) and **6** outer electrons. The number of valence electrons (**6**) equals the outer electrons in this case.
 b) Sn ($Z = 50$); $[\text{Kr}]5s^2 4d^{10} 5p^2$. There are 36 (from $[\text{Kr}]$) + 10 (from the filled d level) = **46** inner electrons. There are **4** outer electrons (highest energy level is $n = 5$) and **4** valence electrons.
 c) Ca ($Z = 20$); $[\text{Ar}]4s^2$. There are **2** outer electrons, **2** valence electrons, and **18** inner electrons.
 d) Fe ($Z = 26$); $[\text{Ar}]4s^2 3d^6$. There are **2** outer electrons (from $n = 4$ level), **8** valence electrons (the d orbital electrons count in this case because the sublevel is not full), and **18** inner electrons.
 e) Se ($Z = 34$); $[\text{Ar}]4s^2 3d^{10} 4p^4$. There are **6** outer electrons (2 + 4 in the $n = 4$ level), **6** valence electrons (filled d sublevels count as inner electrons), and **28** ((18 + 10) or (34 – 6)) inner electrons.
- 8.30 a) The electron configuration $[\text{He}]2s^2 2p^1$ has a total of 5 electrons (3 + 2 from He configuration) which is element boron with symbol **B**. Boron is in group 3A(13). Other elements in this group are **Al, Ga, In, and Tl**.
 b) The electrons in this element total 16, 10 from the neon configuration plus 6 from the rest of the configuration. Element 16 is sulfur, S, in group 6A(16). Other elements in group 6A(16) are **O, Se, Te, and Po**.
 c) Electrons total 3 + 54 (from xenon) = 57. Element 57 is lanthanum, **La**, in group 3B(3). Other elements in this group are **Sc, Y, and Ac**.
- 8.33 Atomic size increases down a main group and decreases across a period. Ionization energy decreases down a main group and increases across a period. These opposite trends result because as the atom gets larger, the outer electron is further from the attraction of the positive charge of the nucleus, which is what holds the electron in the atom. It thus takes less energy (lower IE) to remove the outer electron in a larger atom than to remove the outer electron in a smaller atom. As the atomic size decreases across a period due to higher Z_{eff} , it takes more energy (higher IE) to remove the outer electron.
- 8.35 For a given element, successive ionization energies always increase. As each successive electron is removed, the positive charge on the ion increases, which results in a stronger attraction between the leaving electron and the ion. When a large jump between successive ionization energies is observed, the subsequent electron must come from a lower energy level. Thus, by looking at a series of successive ionization energies, we can determine the number of valence electrons. For instance, the electron configuration for potassium is $[\text{Ar}]4s^1$. The first electron lost is the one from the $4s$ level. The second electron lost must come from the $3p$ level, and hence breaks into the core electrons. Thus, we see a significant jump in the amount of energy for the second ionization when compared to the first ionization.
- 8.37 A high, endothermic IE_1 means it is very difficult to remove the first outer electron. This value would exclude any metal, because metals lose an outer electron easily. A very negative, exothermic EA_1 suggests that this element easily gains one electron. These values indicate that the element belongs to the halogens, Group **7A(17)**, which form -1 ions.
- 8.39 a) Increasing atomic size: **K < Rb < Cs**; these three elements are all part of the same group, the alkali metals. Atomic size increases down a main group (larger outer electron orbital), so potassium is the smallest and cesium is the largest.
 b) Increasing atomic size: **O < C < Be**; these three elements are in the same period and atomic size decreases across a period (increasing effective nuclear charge), so beryllium is the largest and oxygen the smallest.
 c) Increasing atomic size: **Cl < S < K**; chlorine and sulfur are in the same period so chlorine is smaller since it is further to the right in the period. Potassium is the first element in the next period so it is larger than either Cl or S.

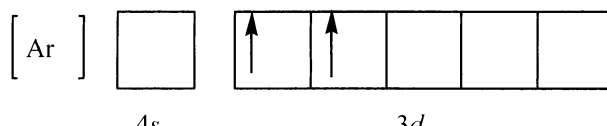
d) Increasing atomic size: **Mg < Ca < K**; calcium is larger than magnesium because Ca is further down the alkaline earth metal group on the periodic table than Mg. Potassium is larger than calcium because K is further to the left than Ca in period 4 of the periodic table.

- 8.41 a) **Ba < Sr < Ca** The “group” rule applies in this case. Ionization energy decreases down a main group. Barium’s outer electron receives the most shielding; therefore, it is easiest to remove and has the lowest IE.
 b) **B < N < Ne** These elements have the same n , so the “period” rule applies. Ionization energy increases across a period. B experiences the lowest Z_{eff} and has the lowest IE. Ne has the highest IE, because it’s very difficult to remove an electron from the stable noble gas configuration.
 c) **Rb < Se < Br** IE decreases with increasing atomic size, so Rb (largest atom) has the smallest IE. Se has a lower IE than Br because IE increases across a period.
 d) **Sn < Sb < As** IE decreases down a group, so Sn and Sb will have smaller IE’s than As. The “period” rule applies for ranking Sn and Sb.
- 8.43 The successive ionization energies show a significant jump between the first and second IE’s and between the third and fourth IE’s. This indicates that 1) the first electron removed occupies a different orbital than the second electron removed, 2) the second and third electrons occupy the same orbital, 3) the third and fourth electrons occupy different orbitals, and 4) the fourth and fifth electrons occupy the same orbital. The electron configurations for period 2 elements range from $1s^2 2s^1$ for lithium to $1s^2 2s^2 2p^6$ for neon. The three different orbitals are $1s$, $2s$, and $2p$. The first electron is removed from the $2p$ orbital and the second from the $2s$ orbital in order for there to be a significant jump in the ionization energy between the two. The third electron is removed from the $2s$ orbital while the fourth is removed from the $1s$ orbital since IE_4 is much greater than IE_3 . The configuration is $1s^2 2s^2 2p^1$ which represents the five electrons in boron, **B**.
- 8.45 a) **Na** would have the highest IE_2 because ionization of a second electron would require breaking the stable [Ne] configuration:
 First ionization: $\text{Na} ([\text{Ne}]3s^1) \rightarrow \text{Na}^+ ([\text{Ne}]) + e^-$ (low IE)
 Second ionization: $\text{Na}^+ ([\text{Ne}]) \rightarrow \text{Na}^{+2} ([\text{He}]2s^2 2p^5) + e^-$ (high IE)
 b) **Na** would have the highest IE_2 because it has one valence electron and is smaller than K.
 c) You might think that Sc would have the highest IE_2 , because removing a second electron would require breaking the stable, filled $4s$ shell. However, **Be** has the highest IE_2 because Be’s small size makes it difficult to remove a second electron.
- 8.47 Three of the ways that metals and nonmetals differ are: 1) metals conduct electricity, nonmetals do not; 2) when they form stable ions, metal ions tend to have a positive charge, nonmetal ions tend to have a negative charge; and 3) metal oxides are ionic and act as bases, nonmetal oxides are covalent and act as acids. How many other differences are there?
- 8.48 Metallic character increases down a group and decreases toward the right across a period. These trends are the same as those for atomic size and opposite those for ionization energy.
- 8.52 Metallic behavior increases down a group and decreases across a period.
 a) **Rb** is more metallic because it is to the left and below Ca.
 b) **Ra** is more metallic because it lies below Mg in Group 2A(2).
 c) **I** is more metallic because it lies below Br in Group 7A(17).
- 8.54 The reaction of a *nonmetal* oxide in water produces an *acidic* solution. An example of a Group 6A(16) nonmetal oxide is $\text{SO}_2(\text{g})$: $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$.
- 8.56 For main group elements, the most stable ions have electron configurations identical to noble gas atoms.
 a) Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$; Cl^- , $1s^2 2s^2 2p^6 3s^2 3p^6$, chlorine atoms are one electron short of the noble gas configuration, so a **-1** ion will form by adding an electron to have the same electron configuration as an argon atom.
 b) Na: $1s^2 2s^2 2p^6 3s^1$; Na^+ , $1s^2 2s^2 2p^6$, sodium atoms contain one more electron than the noble gas configuration of neon. Thus, a sodium atom loses one electron to form a **+1** ion.
 c) Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$; Ca^{2+} , $1s^2 2s^2 2p^6 3s^2 3p^6$, calcium atoms contain two more electrons than the noble gas configuration of argon. Thus, a calcium atom loses two electrons to form a **+2** ion.

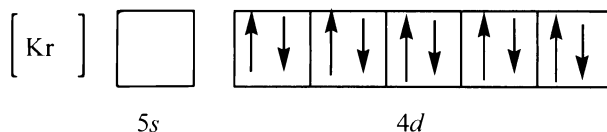
- 8.58 To find the number of unpaired electrons look at the electron configuration expanded to include the different orientations of the orbitals, such as p_x and p_y and p_z . Remember that one electron will occupy every orbital in a set (p , d , or f) before electrons will pair in an orbital in that set. In the noble gas configurations, all electrons are paired because all orbitals are filled.
- a) Configuration of 2A(2) group elements: [noble gas] ns^2 , **no unpaired electrons**.
- b) Configuration of 5A(15) group elements: [noble gas] $ns^2np_x^1np_y^1np_z^1$. **Three** unpaired electrons, one each in p_x , p_y , and p_z .
- c) Configuration of 8A(18) group elements: noble gas configuration with no half-filled orbitals, **no unpaired electrons**.
- d) Configuration of 3A(13) group elements: [noble gas] ns^2np^1 . There is **one** unpaired electron in one of the p orbitals.



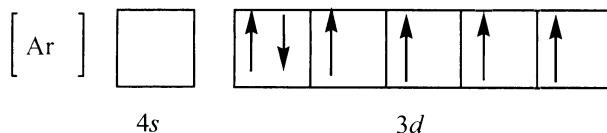
- 8.60 Substances are paramagnetic if they have unpaired electrons. This problem is more challenging if you have difficulty picturing the orbital diagram from the electron configuration. Obviously an odd number of electrons will necessitate that at least one electron is unpaired, so odd electron species are paramagnetic. However, a substance with an even number of electrons can also be paramagnetic, because even numbers of electrons do not guarantee all electrons are paired. Remember that all orbitals in a p , d , or f set will each have one electron before electrons pair in an orbital.
- a) V: [Ar] $4s^23d^3$; V^{3+} : [Ar] $3d^2$ Transition metals first lose the s electrons in forming ions, so to form the +3 ion a vanadium atom loses two $4s$ electrons and one $3d$ electron. **Paramagnetic**



- b) Cd: [Kr] $5s^24d^{10}$; Cd^{2+} : [Kr] $4d^{10}$ Cadmium atoms lose two electrons from the $4s$ orbital to form the +2 ion. **Diamagnetic**

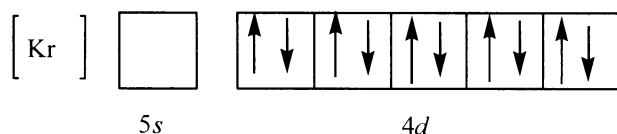


- c) Co: [Ar] $4s^23d^7$; Co^{3+} : [Ar] $3d^6$ Cobalt atoms lose two $4s$ electrons and one $3d$ electron to form the +3 ion. **Paramagnetic**

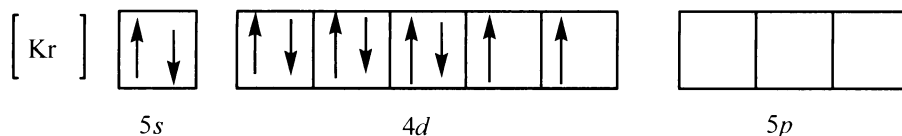


d) Ag: $[\text{Kr}]5s^14d^{10}$; Ag^+ : $[\text{Kr}]4d^{10}$ Silver atoms lose the one electron in the 5s orbital to form the +1 ion.

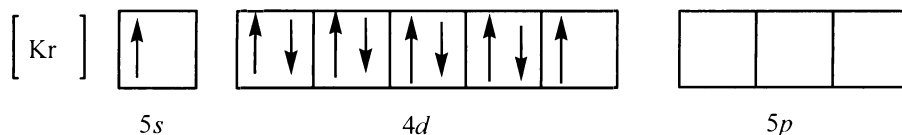
Diamagnetic



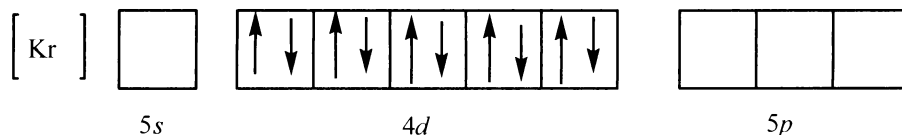
- 8.62 For palladium to be diamagnetic, all of its electrons must be paired. You might first write the condensed electron configuration for Pd as $[\text{Kr}]5s^24d^8$. However, the partial orbital diagram is not consistent with diamagnetism.



Promoting an s electron into the d sublevel (as in (c)) still leaves two electrons unpaired.



The only configuration that supports diamagnetism is (b) $[\text{Kr}]4d^{10}$.



- 8.64 The size of ions increases down a group. For ions that are isoelectronic (have the same electron configuration) size decreases with increasing atomic number.
- Increasing size: $\text{Li}^+ < \text{Na}^+ < \text{K}^+$, size increases down group 1A.
 - Increasing size: $\text{Rb}^+ < \text{Br}^- < \text{Se}^{2-}$, these three ions are isoelectronic with the same electron configuration as krypton. Size decreases with increasing atomic number in an isoelectronic series.
 - Increasing size: $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$, the three ions are isoelectronic with an electron configuration identical to neon. Size decreases with increasing atomic number in an isoelectronic series.
- 8.67 **Plan:** Write the formula of the oxoacid. Remember that in naming oxoacids (H + polyatomic ion), the suffix of the polyatomic changes: -ate becomes -ic acid and -ite becomes -ous acid. Determine the oxidation state of the nonmetal in the oxoacid – hydrogen has an O.N. of +1 and oxygen has an O.N. of -2. Based on the oxidation state of the nonmetal, and the oxidation state of the oxide ion (-2), the formula of the nonmetal oxide may be determined. The name of the nonmetal oxide comes from the formula; remember that nonmetal compounds use prefixes to indicate the number of each type of atom in the formula.
- Solution:**
- hypochlorous acid = HClO has Cl^+ so the oxide is Cl_2O = **dichlorine oxide** or **dichlorine monoxide**
 - chlorous acid = HClO_2 has Cl^{3+} so the oxide is Cl_2O_3 = **dichlorine trioxide**
 - chloric acid = HClO_3 has Cl^{5+} so the oxide is Cl_2O_5 = **dichlorine pentaoxide**
 - perchloric acid = HClO_4 has Cl^{7+} so the oxide is Cl_2O_7 = **dichlorine heptaoxide**
 - sulfuric acid = H_2SO_4 has S^{6+} so the oxide is SO_3 = **sulfur trioxide**
 - sulfurous acid = H_2SO_3 has S^{4+} so the oxide is SO_2 = **sulfur dioxide**
 - nitric acid = HNO_3 has N^{5+} so the oxide is N_2O_5 = **dinitrogen pentaoxide**
 - nitrous acid = HNO_2 has N^{3+} so the oxide is N_2O_3 = **dinitrogen trioxide**
 - carbonic acid = H_2CO_3 has C^{4+} so the oxide is CO_2 = **carbon dioxide**
 - phosphoric acid = H_3PO_4 has P^{5+} so the oxide is P_2O_5 = **diphosphorus pentaoxide**

- 8.69 Remember that isoelectronic species have the same electron configuration.
- A chemically unreactive Period 4 element would be Kr in Group 8A(18). Both the Sr^{2+} ion and Br^- ion are isoelectronic with Kr. Their combination results in **SrBr_2 , strontium bromide**.
 - Ar is the Period 3 noble gas. Ca^{2+} and S^{2-} are isoelectronic with Ar. The resulting compound is **CaS , calcium sulfide**.
 - The smallest filled d subshell is the $3d$ shell, so the element must be in Period 4. Zn forms the Zn^{2+} ion by losing its two s subshell electrons to achieve a *pseudo-noble gas* configuration ($[\text{Ar}]3d^{10}$). The smallest halogen is fluorine, whose anion is F^- . The resulting compound is **ZnF_2 , zinc fluoride**.
 - Ne is the smallest element in Period 2, but it is not ionizable. Li is the largest atom whereas F is the smallest atom in Period 2. The resulting compound is **LiF , lithium fluoride**.

- 8.70 Plan: Determine the electron configuration for iron, and then begin removing one electron at a time. Filled subshells give diamagnetic contributions. Any partially filled subshells give a paramagnetic contribution. The more unpaired electrons, the greater the attraction to a magnetic field.

Solution:

Fe	$[\text{Ar}]4s^23d^6$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 4
Fe^+	$[\text{Ar}]4s^13d^6$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 5
Fe^{2+}	$[\text{Ar}]3d^6$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 4
Fe^{3+}	$[\text{Ar}]3d^5$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 5
Fe^{4+}	$[\text{Ar}]3d^4$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 4
Fe^{5+}	$[\text{Ar}]3d^3$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 3
Fe^{6+}	$[\text{Ar}]3d^2$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 2
Fe^{7+}	$[\text{Ar}]3d^1$	partially filled $3d$ = paramagnetic	number of unpaired electrons = 1
Fe^{8+}	$[\text{Ar}]$	filled orbitals = diamagnetic	number of unpaired electrons = 0
Fe^{9+}	$[\text{Ne}]3s^23p^5$	partially filled $3p$ = paramagnetic	number of unpaired electrons = 1
Fe^{10+}	$[\text{Ne}]3s^23p^4$	partially filled $3p$ = paramagnetic	number of unpaired electrons = 2
Fe^{11+}	$[\text{Ne}]3s^23p^3$	partially filled $3p$ = paramagnetic	number of unpaired electrons = 3
Fe^{12+}	$[\text{Ne}]3s^23p^2$	partially filled $3p$ = paramagnetic	number of unpaired electrons = 2
Fe^{13+}	$[\text{Ne}]3s^23p^1$	partially filled $3p$ = paramagnetic	number of unpaired electrons = 1
Fe^{14+}	$[\text{Ne}]3s^2$	filled orbitals = diamagnetic	number of unpaired electrons = 0

Fe^+ and Fe^{3+} would both be most attracted to a magnetic field. They each have 5 unpaired electrons.

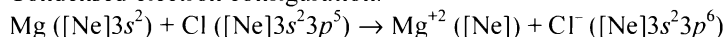
Chapter 9 Models of Chemical Bonding

FOLLOW-UP PROBLEMS

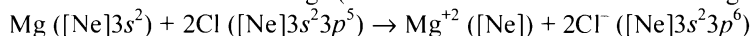
- 9.1 **Plan:** First, write out the condensed electron configuration and electron-dot structure for magnesium atoms and chlorine atoms. In the formation of the ions, each magnesium atom will lose two electrons to form the +2 ion and each chlorine atom will gain one electron to form the -1 ion. Write the condensed electron configuration and electron-dot structure for each of the ions. The formula of the compound is found by combining the ions in a ratio that gives a neutral compound.

Solution:

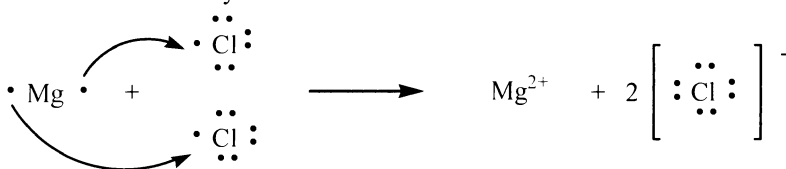
Condensed electron configuration:



In order to balance the charge (or the number of electrons lost and gained) two chlorine atoms are needed:



Lewis electron-dot symbols:



The formula of the compound would contain two chloride ions for each magnesium ion, MgCl_2 .

- 9.2 **Plan:** a) All bonds are single bonds from silicon to a second row element. The trend in bond length can be predicted from the fact that atomic radii decrease across a row, so fluorine will be smaller than oxygen, which is smaller than carbon. Bond length will therefore decrease across the row while bond energy increases.
b) All the bonds are between two nitrogen atoms, but differ in the number of electrons shared between the atoms. The more electrons shared the shorter the bond length and the greater the bond energy.

Solution:

a) Bond length: $\text{Si-F} < \text{Si-O} < \text{Si-C}$

Bond strength: $\text{Si-C} < \text{Si-O} < \text{Si-F}$

b) Bond length: $\text{N}\equiv\text{N} < \text{N}=\text{N} < \text{N-N}$

Bond energy: $\text{N-N} < \text{N}=\text{N} < \text{N}\equiv\text{N}$

Check: (Use the tables in the chapter.)

Bond lengths from Table: $\text{Si-F}, 156 \text{ pm} < \text{Si-O}, 161 \text{ pm} < \text{Si-C}, 186 \text{ pm}$

Bond energies from Table: $\text{Si-C}, 301 \text{ kJ} < \text{Si-O}, 368 \text{ kJ} < \text{Si-F}, 565 \text{ kJ}$

Bond lengths from Table: $\text{N}\equiv\text{N}, 110 \text{ pm} < \text{N}=\text{N}, 122 \text{ pm} < \text{N-N}, 146 \text{ pm}$

Bond energies from Table: $\text{N-N}, 160 \text{ kJ} < \text{N}=\text{N}, 418 \text{ kJ} < \text{N}\equiv\text{N}, 945 \text{ kJ}$

The values from the tables agree with the order predicted.

- 9.3 **Plan:** Assume that all reactant bonds break and all product bonds form. Use Table 9.2 to find the values for the different bonds. Sum the values for the reactants, and sum the values for the products (these are all negative values). Add the sum of product to the values from the sum of the reactant values.

Solution:

Calculating ΔH° for the bonds broken:

$$1 \times \text{N}\equiv\text{N} = (1 \text{ mol}) (945 \text{ kJ/mol}) = 945 \text{ kJ}$$

$$3 \times \text{H-H} = (3 \text{ mol}) (432 \text{ kJ/mol}) = 1296 \text{ kJ}$$

$$\text{Sum broken} = 2241 \text{ kJ}$$

Calculating ΔH° for the bonds formed:

$$1 \times \text{NH}_3 = (3 \text{ mol}) (-391 \text{ kJ/mol}) = -1173 \text{ kJ}$$

$$1 \times \text{NH}_3 = (3 \text{ mol}) (-391 \text{ kJ/mol}) = -1173 \text{ kJ}$$

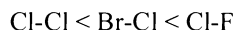
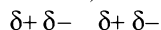
$$\text{Sum formed} = -2346 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^\circ = 2241 \text{ kJ} + (-2346 \text{ kJ}) = -105 \text{ kJ}$$

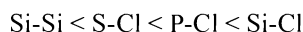
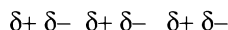
- 9.4 Plan: Bond polarity can be determined from the difference in electronegativity of the two atoms. The more electronegative atom holds the δ^- charge and the other atom holds the δ^+ charge.

Solution:

a) From Figure 9.20, EN of Cl = 3.0, EN of F = 4.0, EN of Br = 2.8. Cl–Cl will be the least polar since there is no difference between the electronegativity of the two chlorine atoms. Cl–F will be more polar than Cl–Br since the electronegativity difference between Cl and F ($4.0 - 3.0 = 1.0$) is greater than the electronegativity difference between Cl and Br ($3.0 - 2.8 = 0.2$)



b) From Figure 9.20, EN of Cl = 3.0, EN of Si = 1.8, EN of P = 2.1, EN of S = 2.5. Si–Si bond is nonpolar, therefore the least polar of the four bonds. The most polar is Si–Cl with an EN difference of 1.2, next is P–Cl with an EN difference of 0.9 and next is S–Cl with an EN of 0.5.

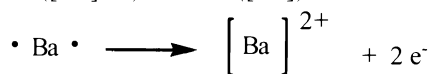
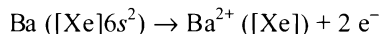


Check: For a) the order follows the increase in electronegativity going up the group of halogens. For b) the order follows the increase in electronegativity across a row. The closer to the end of row 3 (chlorine being at the end of row 3 next to the noble gas argon) that the element that is bonded to chlorine is found, the smaller the electronegativity difference of the bond. Therefore, the order of bond polarity follows the order of elements in row 3: Si, P, S.

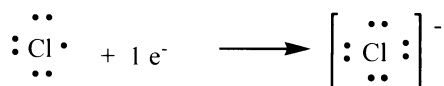
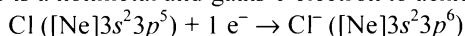
END-OF-CHAPTER PROBLEMS

- 9.1 a) Larger ionization energy decreases metallic character.
b) Larger atomic radius increases metallic character.
c) Larger number of outer electrons decreases metallic character.
d) Larger effective nuclear charge decreases metallic character.
- 9.4 Metallic behavior increases to the left and down on the periodic table.
a) Cs is more metallic since it is further down the alkali metal group than Na.
b) Rb is more metallic since it is both to the left and down from Mg.
c) As is more metallic since it is further down Group 5 A than N.
- 9.6 Ionic bonding occurs between metals and nonmetals and covalent bonding between nonmetals.
a) Bond in CsF is ionic because Cs is a metal and F is a nonmetal.
b) Bonding in N_2 is covalent because N is a nonmetal.
c) Bonding in $\text{H}_2\text{S(g)}$ is covalent because both H and S are nonmetals.
- 9.8 Lewis electron-dot symbols show valence electrons as dots. Place one dot at a time on the four sides (this method explains the structure in b) and then pair up dots until all valence electrons are used.
- a) $\text{Rb} \cdot$ b) $\cdot \overset{\cdot}{\underset{\cdot}{\text{Si}}} \cdot$ c) $\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{I}}}} \cdot$
- 9.10 a) Assuming X is an A-group element, the number of dots (valence electrons) equals the group number. Therefore, X is a 6A(16) element with 6 valence electrons. Its general electron configuration is $[\text{noble gas}]ns^2np^4$, where n is the energy level.
b) X has three valence electrons and is a 3A(13) element with general e^- configuration $[\text{noble gas}]ns^2np^1$.
- 9.13 Because the lattice energy is the result of electrostatic attractions among the oppositely charged ions, its magnitude depends on several factors, including ionic size, ionic charge, and the arrangement of ions in the solid. For a particular arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease.

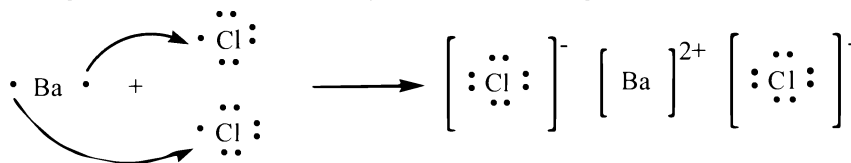
- 9.16 a) Barium is a metal and loses 2 electrons to achieve a noble gas configuration:



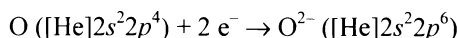
Chlorine is a nonmetal and gains 1 electron to achieve a noble gas configuration:



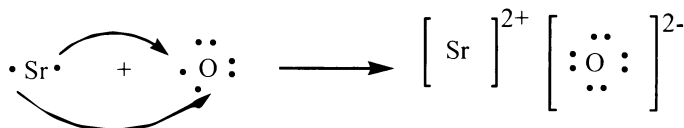
Two Cl atoms gain the two electrons lost by Ba. The ionic compound formed is BaCl_2 .



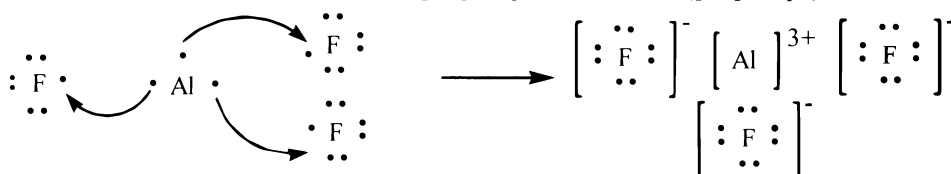
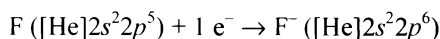
- b) $\text{Sr} ([\text{Kr}]5s^2) \rightarrow \text{Sr}^{2+} ([\text{Kr}]) + 2 e^-$



The ionic compound formed is SrO .

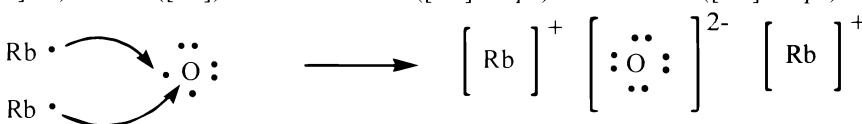
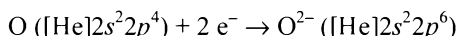


- c) $\text{Al} ([\text{Ne}]3s^23p^1) \rightarrow \text{Al}^{3+} ([\text{Ne}]) + 3 e^-$



The ionic compound formed is AlF_3 .

- d) $\text{Rb} ([\text{Kr}]5s^1) \rightarrow \text{Rb}^+ ([\text{Kr}]) + 1 e^-$



The ionic compound formed is Rb_2O .

- 9.18 a) X in X_2O_3 is a cation with +3 charge. The oxygen in this compound has a -2 charge. To produce an electrically neutral compound, 2 cations with +3 charge bond with 3 anions with -2 charge: $2(+3) + 3(-2) = 0$. Elements in Group 3A(13) form +3 ions.

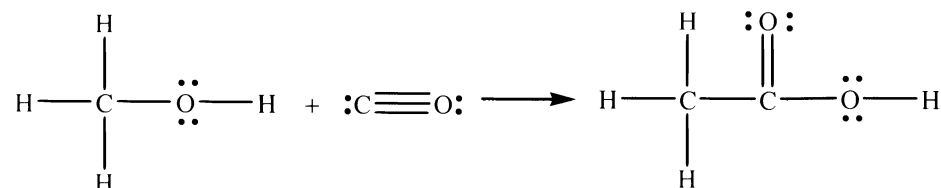
b) The carbonate ion, CO_3^{2-} , has a -2 charge, so X has a +2 charge. Group 2A(2) elements form +2 ions.

c) X in Na_2X has a -2 charge, balanced with the +2 overall charge from the two Na^+ ions. Group 6A(16) elements gain 2 electrons to form -2 ions with a noble gas configuration.

- 9.20 a) BaS has the lower lattice energy because the ionic radius of Ba^{2+} is larger than Ca^{2+} . A larger ionic radius results in a greater distance between ions. The lattice energy decreases with increasing distance between ions.
b) NaF has the lower lattice energy since the charge on each ion (+1, -1) is half the charge on the Mg^{2+} and O^{2-} ions. Lattice energy increases with increasing ion charge.

- 9.23 When two chlorine atoms are far apart, there is no interaction between them. Once the two atoms move closer together, the nucleus of each atom attracts the electrons on the other atom. As the atoms move closer this attraction increases, but the repulsion of the two nuclei also increases. When the atoms are very close together the repulsion between nuclei is much stronger than the attraction between nuclei and electrons. The final internuclear distance for the chlorine molecule is the distance at which maximum attraction is achieved in spite of the repulsion. At this distance, the energy of the molecule is at its lowest value.
- 9.24 The bond energy is the energy required to overcome the attraction between H atoms and Cl atoms in one mole of HCl molecules in the gaseous state. Energy input is needed to break bonds, so bond energy is always endothermic and $\Delta H^\circ_{\text{bond breaking}}$ is positive. The same amount of energy needed to break the bond is released upon its formation, so $\Delta H^\circ_{\text{bond forming}}$ has the same magnitude as $\Delta H^\circ_{\text{bond breaking}}$, but opposite in sign (always exothermic and negative).
- 9.28 a) $\text{I-I} < \text{Br-Br} < \text{Cl-Cl}$. Bond strength increases as the atomic radii of atoms in the bond decreases. Atomic radii decrease up a group in the periodic table, so I is the largest and Cl is the smallest of the three.
 b) $\text{S-Br} < \text{S-Cl} < \text{S-H}$. Radius of H is the smallest and Br is the largest, so the bond strength for S-H is the greatest and that for S-Br is the weakest.
 c) $\text{C-N} < \text{C=N} < \text{C}\equiv\text{N}$. Bond strength increases as the number of electrons in the bond increases. The triple bond is the strongest and the single bond is the weakest.
- 9.30 a) For given pair of atoms, in this case carbon and oxygen, bond strength increases with increasing bond order. The C=O bond (bond order = 2) is stronger than the C-O bond (bond order = 1).
 b) O is smaller than C so the O-H bond is shorter and stronger than the C-H bond.
- 9.33 Reaction between molecules requires the breaking of existing bonds and the formation of new bonds. Substances with weak bonds are more reactive than are those with strong bonds because less energy is required to break weak bonds.
- 9.35 For methane: $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ which requires that 4 C-H bonds and 2 O=O bonds be broken and 2 C=O bonds and 4 O-H bonds be formed.
 For formaldehyde: $\text{CH}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ which requires that 2 C-H bonds, 1 C=O bond and 1 O=O bond be broken and 2 C=O bonds and 2 O-H bonds be formed.
 Methane contains more C-H bonds and fewer C=O bonds than formaldehyde. Since C-H bonds take less energy to break than C=O bonds, more energy is released in the combustion of methane than of formaldehyde.
- 9.37 To find the heat of reaction, add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic.
 Reactant bonds broken: $1(\text{C}=\text{C}) + 4(\text{C}-\text{H}) + 1(\text{Cl}-\text{Cl})$
 $= (1 \text{ mol})(614 \text{ kJ/mol}) + (4 \text{ mol})(413 \text{ kJ/mol}) + (1 \text{ mol})(243 \text{ kJ/mol})$
 $= 2509 \text{ kJ}$
 Product bonds formed: $1(\text{C}-\text{C}) + 4(\text{C}-\text{H}) + 2(\text{C}-\text{Cl})$
 $= (1 \text{ mol})(-347 \text{ kJ/mol}) + (4 \text{ mol})(-413 \text{ kJ/mol}) + (2 \text{ mol})(-339 \text{ kJ/mol})$
 $= -2677 \text{ kJ}$
 $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{bonds broken}} + \Delta H^\circ_{\text{bonds formed}} = 2509 \text{ kJ} + (-2677 \text{ kJ}) = -168 \text{ kJ}$
 Note: It is correct to report the answer in kJ or kJ/mol as long as the value refers to a reactant or product with a molar coefficient of 1.

9.39 The reaction:

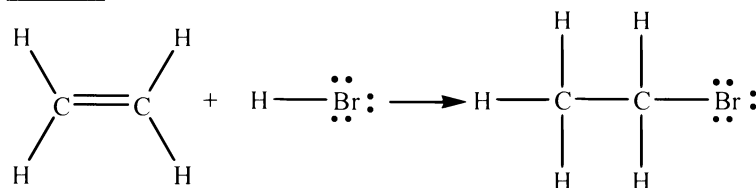


$$\begin{array}{lcl} \Delta H^\circ_{\text{bonds broken}} = & 1 \text{ C-O} & = 1 \text{ mol (358 kJ/mol)} \\ & 3 \text{ C-H} & = 3 \text{ mol (413 kJ/mol)} \\ & 1 \text{ O-H} & = 1 \text{ mol (467 kJ/mol)} \\ & 1 \text{ C}\equiv\text{O} & = 1 \text{ mol (1070 kJ/mol)} \\ & & = 3134 \text{ kJ} \end{array} \quad \begin{array}{lcl} \Delta H^\circ_{\text{bonds formed}} = & 3 \text{ C-H} & = 3 \text{ mol (-413 kJ/mol)} \\ & 1 \text{ C-C} & = 1 \text{ mol (-347 kJ/mol)} \\ & 1 \text{ C=O} & = 1 \text{ mol (-745 kJ/mol)} \\ & 1 \text{ C-O} & = 1 \text{ mol (-358 kJ/mol)} \\ & 1 \text{ O-H} & = 1 \text{ mol (-467 kJ/mol)} \\ & & = -3156 \text{ kJ} \end{array}$$

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{bonds broken}} + \Delta H^\circ_{\text{bonds formed}} = 3134 \text{ kJ} + (-3156 \text{ kJ}) = -22 \text{ kJ}$$

9.40 Plan: Examine the structures for all substances and assume that all reactant bonds are broken and all product bonds are formed. Add the energy required to break all the bonds in the reactants to the energy released to form all bonds in the product. Remember to use a negative sign for the energy of the bonds formed since bond formation is exothermic.

Solution:

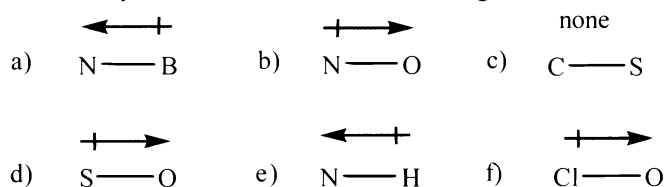


$$\text{Bonds broken: } 1(\text{C}=\text{C}) + 4(\text{C}-\text{H}) + 1(\text{H}-\text{Br}) = 614 + 4(413) + 363 = +2629 \text{ kJ}$$

$$\text{Bonds formed: } 1(\text{C}-\text{C}) + 5(\text{C}-\text{H}) + 1(\text{C}-\text{Br}) = (-347) + 5(-413) + (-276) = -2688 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{bonds broken}} + \Delta H^\circ_{\text{bonds formed}} = 2629 + (-2688) = -59 \text{ kJ}$$

- 9.41 Electronegativity increases from left to right across a period (except for the noble gases) and increases from bottom to top within a group. Fluorine (F) and oxygen (O) are the two most electronegative elements. Cesium (Cs) and francium (Fr) are the two least electronegative elements.
- 9.43 The H-O bond in water is polar covalent, because the two atoms differ in electronegativity which results in an unequal sharing of the bonding electrons. A nonpolar covalent bond occurs between two atoms with identical electronegativities where the sharing of bonding electrons is equal. Although electron sharing occurs to a very small extent in some ionic bonds, the primary force in ionic bonds is attraction of opposite charges resulting from electron transfer between the atoms.
- 9.46 a) $\text{Si} < \text{S} < \text{O}$, sulfur is more electronegative than silicon since it is located further to the right on the table. Oxygen is more electronegative than sulfur since it is located nearer the top of the table.
b) $\text{Mg} < \text{As} < \text{P}$, magnesium is the least electronegative because it lies on the left side of the periodic table and phosphorus and arsenic on the right side. Phosphorus is more electronegative than arsenic because it is higher on the table.
- 9.48 The arrow points toward the more electronegative atom.



9.50 The more polar bond will have a greater difference in electronegativity, ΔEN .

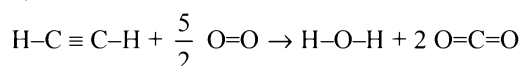
- a) N: EN = 3.0; B: EN = 2.0; $\Delta EN_a = 1.0$ b) N: EN = 3.0; O: EN = 3.5; $\Delta EN_b = 0.5$
 c) C: EN = 2.5; S: EN = 2.5; $\Delta EN_c = 0$ d) S: EN = 2.5; O: EN = 3.5; $\Delta EN_d = 1.0$
 e) N: EN = 3.0; H: EN = 2.1; $\Delta EN_e = 0.9$ f) Cl: EN = 3.0; O: EN = 3.5; $\Delta EN_f = 0.5$
 (a), (d), and (e) have greater bond polarity.

- 9.52 a) Bonds in S_8 are nonpolar covalent. All the atoms are nonmetals so the substance is covalent and bonds are nonpolar because all the atoms are of the same element and thus have the same electronegativity value.
 b) Bonds in $RbCl$ are ionic because Rb is a metal and Cl is a nonmetal.
 c) Bonds in PF_3 are polar covalent. All the atoms are nonmetals so the substance is covalent. The bonds between P and F are polar because their electronegativity differs. (By 1.9 units for P–F)
 d) Bonds in SCl_2 are polar covalent. S and Cl are nonmetals and differ in electronegativity. (By 0.5 unit for S–Cl)
 e) Bonds in F_2 are nonpolar covalent. F is a nonmetal. Bonds between two atoms of the same element are nonpolar since $\Delta EN = 0$.
 f) Bonds in SF_2 are polar covalent. S and F are nonmetals that differ in electronegativity. (By 1.5 units for S–F)
 Increasing bond polarity: $SCl_2 < SF_2 < PF_3$

9.54 Increasing ionic character occurs with increasing ΔEN .

- a) $\Delta EN_{HBr} = 0.7$, $\Delta EN_{HCl} = 0.9$, $\Delta EN_{HI} = 0.4$
 b) $\Delta EN_{HO} = 1.4$, $\Delta EN_{CH} = 0.4$, $\Delta EN_{HF} = 1.9$
 c) $\Delta EN_{SCl} = 0.5$, $\Delta EN_{PCl} = 0.9$, $\Delta EN_{SiCl} = 1.2$
- a) $\begin{array}{c} \text{+} \rightarrow \\ \text{H} \text{---} \text{I} \end{array} < \begin{array}{c} \text{+} \rightarrow \\ \text{H} \text{---} \text{Br} \end{array} < \begin{array}{c} \text{+} \rightarrow \\ \text{H} \text{---} \text{Cl} \end{array}$
- b) $\begin{array}{c} \text{+} \rightarrow \\ \text{H} \text{---} \text{C} \end{array} < \begin{array}{c} \text{+} \rightarrow \\ \text{H} \text{---} \text{O} \end{array} < \begin{array}{c} \text{+} \rightarrow \\ \text{H} \text{---} \text{F} \end{array}$
- c) $\begin{array}{c} \text{+} \rightarrow \\ \text{S} \text{---} \text{Cl} \end{array} < \begin{array}{c} \text{+} \rightarrow \\ \text{P} \text{---} \text{Cl} \end{array} < \begin{array}{c} \text{+} \rightarrow \\ \text{Si} \text{---} \text{Cl} \end{array}$

9.58 a) $C_2H_2 + 5/2 O_2 \rightarrow 2 CO_2 + H_2O$ $\Delta H = -1259 \text{ kJ/mol}$



$$\Delta H_{rxn} = [2 BE_{C-H} + BE_{C \equiv C} + \frac{5}{2} BE_{O_2}] + [4 (-BE_{C=O}) + 2 (-BE_{O-H})]$$

$$-1259 \text{ kJ} = [2(413) + BE_{C \equiv C} + 5/2 (498)] + [4(-799) + 2(-467)]$$

$$-1259 \text{ kJ} = [826 + BE_{C \equiv C} + 1245] + [-4130] \text{ kJ}$$

$$BE_{C \equiv C} = 800. \text{ kJ/mol}$$

Table 9.2 lists the value as 839 kJ/mol

$$\text{b) heat (kJ)} = (500.0 \text{ g } C_2H_2) \left(\frac{1 \text{ mol } C_2H_2}{26.04 \text{ g } C_2H_2} \right) \left(\frac{-1259 \text{ kJ}}{1 \text{ mol } C_2H_2} \right) = -2.4174347 \times 10^4 = -2.417 \times 10^4 \text{ kJ}$$

$$\text{c) } CO_2 \text{ produced (g)} = (500.0 \text{ g } C_2H_2) \left(\frac{1 \text{ mol } C_2H_2}{26.04 \text{ g } C_2H_2} \right) \left(\frac{2 \text{ mol } CO_2}{1 \text{ mol } C_2H_2} \right) \left(\frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} \right)$$

$$= 1690.092 = 1690. \text{ g } CO_2$$

$$\text{d) mol } O_2 = (500.0 \text{ g } C_2H_2) \left(\frac{1 \text{ mol } C_2H_2}{26.04 \text{ g } C_2H_2} \right) \left(\frac{(5/2) \text{ mol } O_2}{1 \text{ mol } C_2H_2} \right) = 48.00307 \text{ mol } O_2 \text{ (unrounded)}$$

$$V = nRT / P = \frac{(48.00307 \text{ mol } O_2) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})}{18.0 \text{ atm}} = 65.2145 = 65.2 \text{ L } O_2$$

- 9.59 a) 1) $\text{Mg}(s) \rightarrow \text{Mg}(g)$ $\Delta H_1^\circ = 148 \text{ kJ}$
 2) $1/2 \text{ Cl}_2(g) \rightarrow \text{Cl}(g)$ $\Delta H_2^\circ = 1/2 (243 \text{ kJ})$
 3) $\text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-$ $\Delta H_3^\circ = 738 \text{ kJ}$
 4) $\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)$ $\Delta H_4^\circ = -349 \text{ kJ}$
 5) $\text{Mg}^+(g) + \text{Cl}^-(g) \rightarrow \text{MgCl}(s)$ $\Delta H_5^\circ = -783.5 \text{ kJ} (= \Delta H_{\text{attice}}^\circ (\text{MgCl}))$
 6) $\text{Mg}(s) + 1/2 \text{ Cl}_2(g) \rightarrow \text{MgCl}(s)$ $\Delta H_f^\circ (\text{MgCl}) = ?$

$$\Delta H_f^\circ (\text{MgCl}) = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$

$$= 148 \text{ kJ} + 1/2 (243 \text{ kJ}) + 738 \text{ kJ} - 349 \text{ kJ} - 783.5 \text{ kJ} = \mathbf{-125 \text{ kJ}}$$

b) **Yes**, since ΔH_f° for MgCl is negative, $\text{MgCl}(s)$ is stable relative to its elements.

- c) $2 \text{ MgCl}(s) \rightarrow \text{MgCl}_2(s) + \text{Mg}(s)$

$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ, \text{MgCl}_2(s)) + 1 \text{ mol } (\Delta H_f^\circ, \text{Mg}(s))] - [2 \text{ mol } (\Delta H_f^\circ, \text{MgCl}(s))]$$

$$= [1 \text{ mol } (-641.6 \text{ kJ/mol}) + 1 \text{ mol } (0)] - [2 \text{ mol } (-125 \text{ kJ/mol})]$$

$$= -391.6 = \mathbf{-392 \text{ kJ}}$$

d) No, ΔH_f° for MgCl_2 is much more negative than that for MgCl . This makes the ΔH° value for the above reaction very negative, and the formation of MgCl_2 would be favored.

- 9.60 a) Find the bond energy for an H-I bond from Table 9.2. Calculate wavelength from this energy using the relationship from Chapter 7: $E = hc / \lambda$.
 Bond energy for H-I is 295 kJ/mol (Table 9.2).

$$\lambda = hc / E = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{\left(295 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = 405.7807 = \mathbf{406 \text{ nm}}$$

b) Calculate the energy for a wavelength of 254 nm and then subtract the energy from part a) to get the excess energy.

$$E(\text{HI}) = \left(295 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right) = 4.8987 \times 10^{-19} \text{ J (unrounded)}$$

$$E(254 \text{ nm}) = hc / \lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{254 \text{ nm}} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = 7.82598 \times 10^{-19} \text{ J (unrounded)}$$

$$\text{Excess energy} = 7.82598 \times 10^{-19} \text{ J} - 4.8987 \times 10^{-19} \text{ J} = 2.92728 \times 10^{-19} \text{ J} = \mathbf{2.93 \times 10^{-19} \text{ J}}$$

c) Speed can be calculated from the excess energy since $E_k = 1/2 mu^2$.

$$E_k = 1/2 mu^2 \text{ thus, } u = \sqrt{\frac{2E}{m}} \quad m = \left(\frac{1.008 \text{ g H}}{\text{mol}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = 1.67386 \times 10^{-27} \text{ kg (unrounded)}$$

$$u = \sqrt{\frac{2(2.92728 \times 10^{-19} \text{ J})}{1.67386 \times 10^{-27} \text{ kg}} \left(\frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{J}}\right)} = 1.8701965 \times 10^4 = \mathbf{1.87 \times 10^4 \text{ m/s}}$$

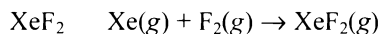
- 9.63 Find the appropriate bond energies in Table 9.2. Calculate the wavelengths using $E = hc / \lambda$.
 C-Cl bond energy = 339 kJ/mol

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{\left(339 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)} = 3.53113 \times 10^{-7} = \mathbf{3.53 \times 10^{-7} \text{ m}}$$

O₂ bond energy = 498 kJ/mol

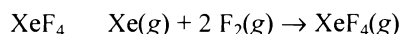
$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{\left(498 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)} = 2.40372 \times 10^{-7} = 2.40 \times 10^{-7} \text{ m}$$

- 9.64 Write balanced chemical equations for the formation of each of the compounds. Obtain the bond energy of fluorine from Table 9.2 (159 kJ/mol). Determine the average bond energy from $\Delta H = \text{bonds broken} + \text{bonds formed}$. Remember that the bonds formed (Xe–F) have negative values since bond formation is exothermic.



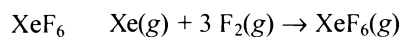
$$\Delta H = [1 \text{ mol F}_2 (159 \text{ kJ/mol})] + [2 (-\text{Xe-F})] = -105 \text{ kJ/mol}$$

$$\text{Xe-F} = 132 \text{ kJ/mol}$$



$$\Delta H = [2 \text{ mol F}_2 (159 \text{ kJ/mol})] + [4 (-\text{Xe-F})] = -284 \text{ kJ/mol}$$

$$\text{Xe-F} = 150.5 = 150. \text{ kJ/mol}$$



$$\Delta H = [3 \text{ mol F}_2 (159 \text{ kJ/mol})] + [6 (-\text{Xe-F})] = -402 \text{ kJ/mol}$$

$$\text{Xe-F} = 146.5 = 146 \text{ kJ/mol}$$

- 9.66 a) The presence of the very electronegative fluorine atoms bonded to one of the carbons makes the C–C bond polar. This polar bond will tend to undergo heterolytic rather than homolytic cleavage. More energy is required to force homolytic cleavage.
b) Since one atom gets both of the bonding electrons in heterolytic bond breakage, this results in the formation of ions. In heterolytic cleavage a cation is formed, involving ionization energy; an anion is also formed, involving electron affinity.

$$\Delta H = (\text{homolytic cleavage} + \text{electron affinity} + \text{first ionization energy})$$

$$\Delta H = (249.2 \text{ kJ/mol} + (-141 \text{ kJ/mol}) + 1.31 \times 10^3 \text{ kJ/mol}) = 1420 \text{ kJ/mol}$$

It would require 1420 kJ to heterolytically cleave 1 mol of O₂.

- 9.69 Use the equations $E = h\nu$, and $E = hc / \lambda$.

$$\nu = \frac{E}{h} = \frac{\left(347 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 8.6963556 \times 10^{14} = 8.70 \times 10^{14} \text{ s}^{-1}$$

$$\lambda = hc / E = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{\left(347 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23}}\right)} = 3.44972 \times 10^{-7} = 3.45 \times 10^{-7} \text{ m}$$

This is in the ultraviolet region of the electromagnetic spectrum.

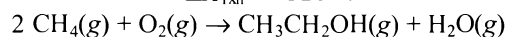
- 9.71 a) $2 \text{ CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OCH}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$

$$\Delta H_{\text{rxn}} = \Sigma \text{BE}_{\text{reactants}} + \Sigma \text{BE}_{\text{products}}$$

$$\Delta H_{\text{rxn}} = [2 \times 4 \text{ BE}_{\text{C-H}} + \text{BE}_{\text{O=O}}] + [6 (-\text{BE}_{\text{C-H}}) + 2 (-\text{BE}_{\text{C-O}}) + 2 (-\text{BE}_{\text{O-H}})]$$

$$\Delta H_{\text{rxn}} = [8 (413 \text{ kJ}) + 498 \text{ kJ}] + [6 (-413 \text{ kJ}) + 2 (-358 \text{ kJ}) + 2 (-467)]$$

$$\Delta H_{\text{rxn}} = -326 \text{ kJ}$$



$$\Delta H_{\text{rxn}} = \Sigma \text{BE}_{\text{reactants}} + \Sigma \text{BE}_{\text{products}}$$

$$\Delta H_{\text{rxn}} = [2 \times 4 \text{ BE}_{\text{C-H}} + \text{BE}_{\text{O=O}}] + [5(-\text{BE}_{\text{C-H}}) + (-\text{BE}_{\text{C-C}}) + (-\text{BE}_{\text{C-O}}) + 3(-\text{BE}_{\text{O-H}})]$$

$$\Delta H_{\text{rxn}} = [8 (413 \text{ kJ}) + 498 \text{ kJ}] + [5 (-413 \text{ kJ}) + (-347 \text{ kJ}) + (-358 \text{ kJ}) + 3 (-467)]$$

$$\Delta H_{\text{rxn}} = -369 \text{ kJ}$$

- b) The formation of gaseous ethanol is more exothermic.

$$\text{c) } \Delta H_{\text{rxn}} = -326 \text{ kJ} - (-369 \text{ kJ}) = 43 \text{ kJ}$$

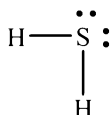
Chapter 10 The Shapes of Molecules

FOLLOW-UP PROBLEMS

10.1 Plan: Follow the steps outlined in the sample problem.

Solution:

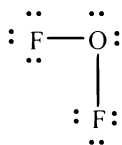
a) The sulfur is the central atom, as the hydrogen is never central. Each of the hydrogens is placed around the sulfur. The actual positions of the hydrogens are not important. The total number of valence electrons available is $[2 \times \text{H}(1 \text{ e}^-)] + [1 \times \text{S}(6 \text{ e}^-)] = 8 \text{ e}^-$. Connect each hydrogen atom to the sulfur with a single bond. These bonds use 4 of the electrons leaving 4 electrons. The last 4 e^- go to the sulfur because the hydrogens can take no more electrons.



Check: Count the electrons. The sulfur has an octet (4 from two lone pairs and 4 from two bonding pairs). Each hydrogen has its 2 electrons (from the bonding pair).

Solution:

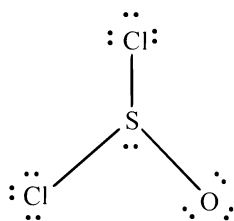
b) The oxygen has the lower group number so it is the central atom. Each of the fluorine atoms will be attached to the central oxygen. The total number of valence electrons available is $[2 \times \text{F}(7 \text{ e}^-)] + [1 \times \text{O}(6 \text{ e}^-)] = 20 \text{ e}^-$. Connecting the two fluorine atoms to the oxygen with single bonds uses $2 \times 2 = 4 \text{ e}^-$, leaving $20 - 4 = 16 \text{ e}^-$. The more electronegative fluorine atoms each need 6 electrons to complete their octets. This requires $2 \times 6 = 12 \text{ e}^-$. The 4 remaining electrons go to the oxygen.



Check: Count the electrons. Each of the three atoms has an octet.

Solution:

c) Both S and O have a lower group number than Cl, thus, one of these two elements must be central. Between S and O, S has the higher period number so it is the central atom. The total number of valence electrons available is $[2 \times \text{Cl}(7 \text{ e}^-)] + [1 \times \text{S}(6 \text{ e}^-)] + [1 \times \text{O}(6 \text{ e}^-)] = 26 \text{ e}^-$. Begin by distributing the two chlorine atoms and the oxygen atom around the central sulfur atom. Connect each of the three outlying atoms to the central sulfur with single bonds. This uses $3 \times 2 = 6 \text{ e}^-$, leaving $26 - 6 = 20 \text{ e}^-$. Each of the outlying atoms still needs 6 electrons to complete their octets. Completing these octets uses $3 \times 6 = 18$ electrons. The remaining 2 electrons are all the sulfur needs to complete its octet.

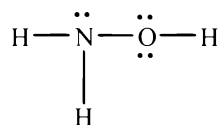


Check: Count the electrons. Each of the four atoms has an octet. Note: Later we will see that the presence of sulfur may lead to some complications.

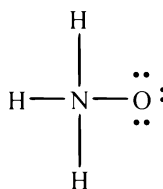
10.2 Plan: Follow the steps outlined in the sample problem.

Solution:

a) As in CH_4O , the N and O both serve as “central” atoms. The N is placed next to the O and the H’s are distributed around them. The N needs more electrons so it gets two of the three hydrogens. You can try placing the N in the center with all the other atoms around it, but you will quickly see that you will have trouble with the oxygen. The number of valence electrons is: $[3 \times \text{H}(1 \text{ e}^-)] + [1 \times \text{N}(5 \text{ e}^-)] + [1 \times \text{O}(6 \text{ e}^-)] = 14 \text{ e}^-$. Four single bonds are needed ($4 \times 2 = 8 \text{ e}^-$). This leaves 6 electrons. The oxygen needs 4 electrons, and the nitrogen needs 2. These last 6 electrons serve as three lone pairs.



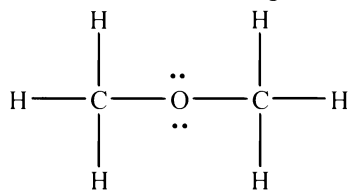
correct



incorrect

Solution:

b) The hydrogens cannot be the central atoms. The problem states that there are no O–H bonds, so the oxygen must be connected to the carbon atoms. Place the O atom between the two C’s, and then distribute the H’s equally around each of the C’s. The total number of valence electrons is $[6 \times \text{H}(1 \text{ e}^-)] + [2 \times \text{C}(4 \text{ e}^-)] + [1 \times \text{O}(6 \text{ e}^-)] = 20 \text{ e}^-$. Draw single bonds between each of the atoms. This creates six C–H bonds, and two C–O bonds, and uses $8 \times 2 = 16$ electrons. The four remaining electrons will become two lone pairs on the O atom.

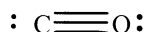


Check: Count the electrons. Both the C’s and the O have octets. Each H has its pair.

10.3 Plan: Follow the steps in the example, and pay attention to the hint for CO.

Solution:

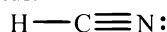
a) In CO there are a total of $[1 \times \text{C}(4 \text{ e}^-)] + [1 \times \text{O}(6 \text{ e}^-)] = 10 \text{ e}^-$. The hint states that carbon has three bonds. Since oxygen is the only other atom present, these bonds must be between the C and the O. This uses 6 of the 10 electrons. The remaining 4 electrons become two lone pairs, one pair for each of the atoms.



Check: Count the electrons. Both the C and the O have octets.

Solution:

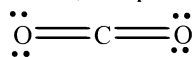
b) In HCN there are a total of $[1 \times \text{H}(1 \text{ e}^-)] + [1 \times \text{C}(4 \text{ e}^-)] + [1 \times \text{N}(5 \text{ e}^-)] = 10$ electrons. Carbon has a lower group number, so it is the central atom. Place the C between the other two atoms and connect each of the atoms to the central C with a single bond. This uses 4 of the 10 electrons, leaving 6 electrons. Distribute these 6 to nitrogen to complete its octet. However, the carbon atom is 4 electrons short of an octet. Change two lone pairs on the nitrogen atom to bonding pairs to form two more bonds between carbon and nitrogen for a total of three bonds.



Check: Count the electrons. Both the C and the N have octets. The H has its pair.

Solution:

c) In CO_2 there are a total of $[1 \times \text{C}(4 \text{ e}^-)] + [2 \times \text{O}(6 \text{ e}^-)] = 16$ electrons. Carbon has a lower group number, so it is the central atom. Placing the C between the two O’s and adding single bonds uses 4 electrons, leaving $16 - 4 = 12 \text{ e}^-$. Distributing these 12 electrons to the oxygen atoms completes those octets, but the carbon atom does not have an octet. Change one lone pair on each oxygen atom to a bonding pair to form two double bonds to the carbon atom, completing its octet.

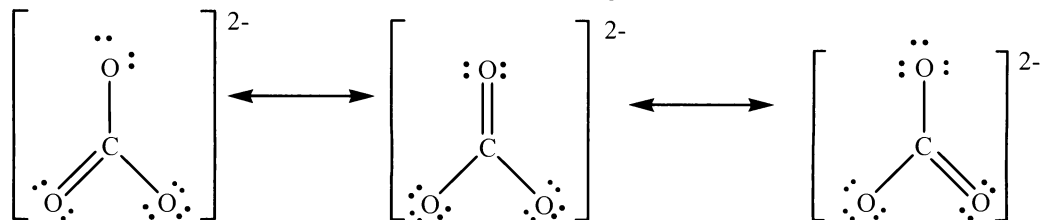


Check: Count the electrons. Both the C and the O’s have octets.

10.4 Plan: Modify the structure shown in the text to produce additional resonance structures.

Solution:

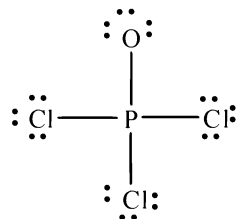
The structure drawn in the text is shown below on the right. Just shift the double bond and electron pairs.



10.5 Plan: The presence of available *d* orbitals makes checking formal charges more important.

Solution:

a) In POCl_3 , the P is the most likely central atom because all the other elements have higher group numbers. The molecule contains: $[1 \times \text{P}(5 \text{ e}^-)] + [1 \times \text{O}(6 \text{ e}^-)] + [3 \times \text{Cl}(7 \text{ e}^-)] = 32$ electrons. Placing the P in the center with single bonds to all the surrounding atoms uses 8 electrons and gives P an octet. The remaining 24 can be split into 12 pairs with each of the surrounding atoms receiving three pairs. At this point, structure I below, all the atoms have an octet. The central atom is P (smallest group number, highest period number) and can have more than an octet. To see how reasonable this structure is, calculate the formal (FC) for each atom. The +1 and -1 formal charges are not too unreasonable, however, 0 charges are better. If one of the lone pairs is moved from the O (the atom with the negative FC) to form a double bond to the P (the atom with the positive FC), structure II results. The calculated formal charges in structure II are all 0, thus, this is a better structure even though P has 10 electrons.

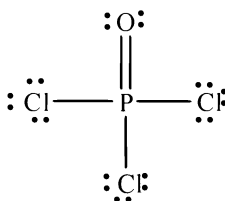


I

$$\text{FC}_\text{P} = 5 - (0 + 1/2(8)) = +1$$

$$\text{FC}_\text{O} = 6 - (6 + 1/2(2)) = -1$$

$$\text{FC}_\text{Cl} = 7 - (6 + 1/2(2)) = 0$$



II

$$\text{FC}_\text{P} = 5 - (0 + 1/2(10)) = 0$$

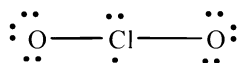
$$\text{FC}_\text{O} = 6 - (4 + 1/2(4)) = 0$$

$$\text{FC}_\text{Cl} = 7 - (6 + 1/2(2)) = 0$$

Check: Count the electrons. All the atoms in structure II, except P, have an octet. The P can have more than an octet, because it has readily available *d* orbitals.

Solution:

b) In ClO_2 , the Cl is probably the central atom because the O's have a lower period. The molecule contains: $[1 \times \text{Cl}(7 \text{ e}^-)] + [2 \times \text{O}(6 \text{ e}^-)] = 19$ electrons. The presence of an odd number of electrons means that there will be an exception to the octet rule. Placing the O's about the Cl and using 4 electrons to form single bonds leaves 15 electrons, 14 of which may be separated into 7 pairs. If 3 of these pairs are given to each O, and the remaining pair plus the lone electron are given to the Cl, we have the following structure:

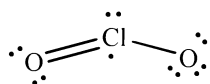


Calculating formal charges:

$$\text{FC}_\text{Cl} = 7 - (3 + 1/2(4)) = +2$$

$$\text{FC}_\text{O} = 6 - (6 + 1/2(2)) = -1$$

The +2 charge on the Cl is a little high, so other structures should be tried. Moving a lone pair from one of the O atoms (negative FC) to form a double bond between the Cl and one of the oxygens gives either structure I or II below. If both O's donate a pair of electrons to form a double bond, then structure III results. The next step is to calculate the formal charges.

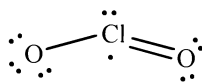


I

$$FC_{Cl} = 7 - (3 + 1/2(6)) = +1$$

$$\text{Left } FC_O = 6 - (4 + 1/2(4)) = 0$$

$$\text{Right } FC_O = 6 - (6 + 1/2(2)) = -1$$

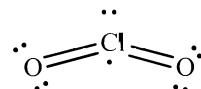


II

$$FC_{Cl} = 7 - (3 + 1/2(6)) = +1$$

$$FC_O = 6 - (6 + 1/2(4)) = -1$$

$$FC_O = 6 - (4 + 1/2(2)) = 0$$



III

$$FC_{Cl} = 7 - (3 + 1/2(8)) = 0$$

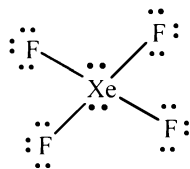
$$FC_O = 6 - (4 + 1/2(8)) = 0$$

$$FC_O = 6 - (4 + 1/2(8)) = 0$$

Check: Pick the structure with the best distribution of formal charges (structure III).

Solution:

c) XeF_4 is a noble gas compound, thus, there will be an exception to the octet rule. The molecule contains: $[1 \times \text{Xe}(8 e^-)] + [4 \times \text{F}(7 e^-)] = 36$ electrons. The Xe is in a higher period than F so Xe is the central atom. If it is placed in the center with a single bond to each of the four fluorine atoms, 8 electrons are used, and 28 electrons remain. The remaining electrons can be divided into 14 pairs with 3 pairs given to each F and the last 2 pairs being given to the Xe. This gives the structure:



Check: Determine the formal charges for each atom:

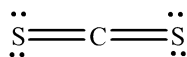
$$FC_{Xe} = 8 - (4 + 1/2(8)) = 0$$

$$FC_F = 7 - (6 + 1/2(2)) = 0$$

- 10.6 Plan: Draw a Lewis structure. Determine the electron arrangement by counting the electron pairs around the central atom.

Solution:

a) The Lewis structure for CS_2 is shown below. The central atom, C, has two pairs (double bonds only count once). The two pair arrangement is **linear** with the designation, AX_2 . The absence of lone pairs on the C means there is no deviation in the bond angle (**180°**).



Check: Compare the results in the figures in the chapter.

Solution:

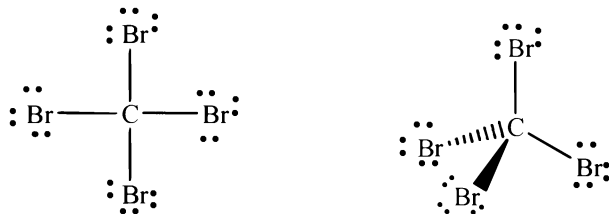
b) Even though this is a combination of a metal with a nonmetal, it may be treated as a molecular species. The Lewis structure for PbCl_2 is shown below. The molecule is of the AX_2E type; the central atom has three pairs of electrons (1 lone pair and two bonding pairs). This means the *electron-group arrangement* is trigonal planar (**120°**), with a lone pair giving a **bent or V-shaped** molecule. The lone pair causes the ideal bond angle to decrease.



Check: Compare the results in the figures in the chapter.

Solution:

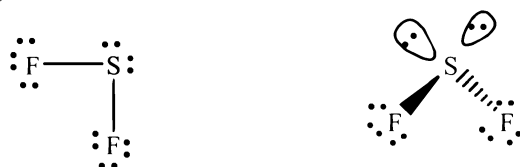
c) The Lewis structure for the CBr_4 molecule is shown above. It has the AX_4 type formula which is a perfect **tetrahedron** (with 109.5° bond angles) because all bonds are identical, and there are no lone pairs.



Check: Compare the results in the figures in the chapter.

Solution:

d) The SF_2 molecule has the Lewis structure shown below. This is a AX_2E_2 molecule; the central atom is surrounded by four electron pairs, two of which are lone pairs and two of which are bonding pairs. The *electron group arrangement* is tetrahedral. The two lone pairs give a **V-shaped or bent** arrangement. The ideal tetrahedral bond angle is **decreased from the ideal 109.5°** value.

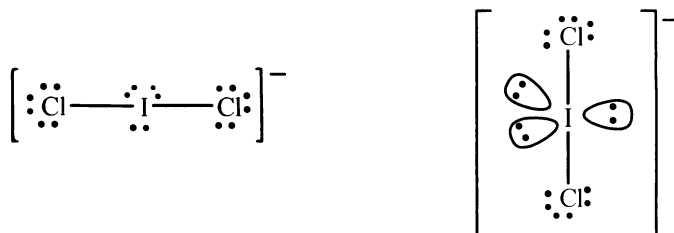


Check: Compare the results in the figures in the chapter.

- 10.7 Plan: Draw a Lewis structure. Determine the electron arrangement by counting the electron pairs around the central atom.

Solution:

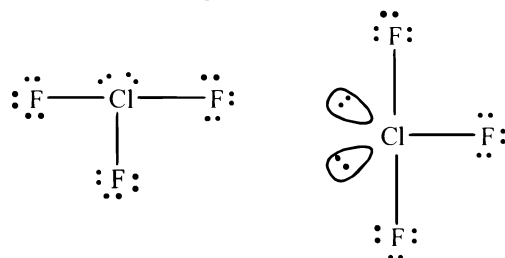
a) The Lewis structure for the ICl_2^- is shown below. This is a AX_2E_3 type structure. The five pairs give a trigonal bipyramidal arrangement of electron groups. The presence of 3 lone pairs leads to a **linear shape (180°)**. The usual distortions caused by lone pairs cancel in this case. In the trigonal bipyramidal geometry, lone pairs always occupy equatorial positions.



Check: Compare the results in the figures in the chapter.

Solution:

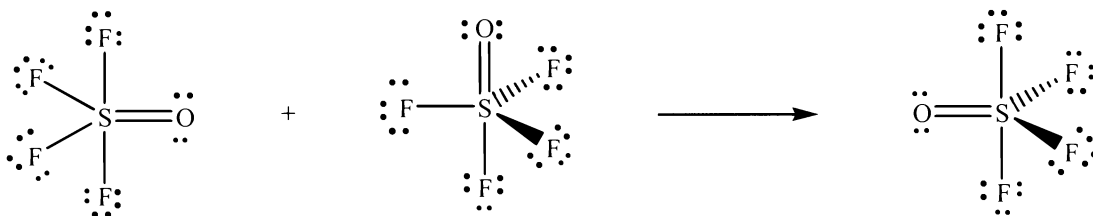
b) The Lewis structure for the ClF_3 molecule is given below. Like ICl_2^- there are 5 pairs around the central atom; however, there are only 2 lone pairs. This gives a molecule that is **T-shaped**. The presence of the lone pairs decreases the ideal bond angles to **less than 90°** .



Check: Compare the results in the figures in the chapter.

Solution:

c) The SOF_4 molecule has several possible Lewis structures, two of which are shown below. In both cases, the central atom has 5 atoms attached with no lone pairs. The formal charges work out the same in both structures. The structure on the right has an equatorial double bond. Double bonds require more room than single bonds, and equatorial positions have this extra room.



The molecule is **trigonal bipyramidal**, and the double bond causes deviation from ideal bond angles. All of the F atoms move away from the O. Thus, all angles involving the O are increased, and all other angles are decreased. Check: Compare the results in the figures in the chapter.

10.8 Plan: Draw the Lewis structure for each of the substances, and determine the molecular geometry of each.

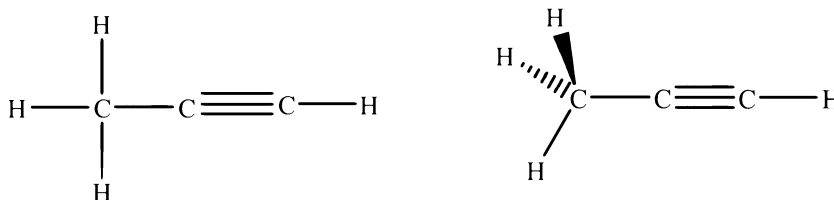
Solution:

a) The Lewis structure for H_2SO_4 is shown below. The double bonds ease the problem of a high formal charge on the sulfur. Sulfur is allowed to exceed an octet. The S has 4 groups around it, making it **tetrahedral**. The ideal angles around the S are 109.5° . The double bonds move away from each other, and force the single bonds away. This opens the angle between the double bonded oxygens, and results in an angle between the single bonded oxygens that is less than ideal.



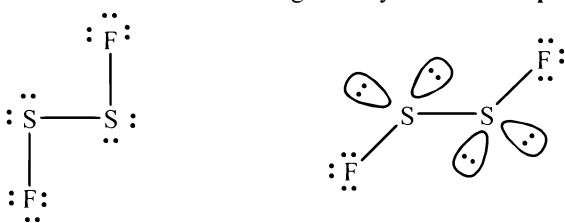
Solution:

b) The hydrogens cannot be central so the carbons must be attached to each other. The problem states that there is a carbon-carbon triple bond. This leaves only a single bond to connect the third carbon to a triple-bonded carbon, and give that carbon an octet. The other triple-bonded carbon needs one hydrogen to complete its octet. The remaining three hydrogens are attached to the single-bonded carbon, which allows it to complete its octet. This structure is shown below. The single-bonded carbon has four groups tetrahedrally around it leading to bond angles $\sim 109.5^\circ$ (little or no deviation). The triple-bonded carbons each have two groups (the triple bond counts as one electron group) so they should be **linear** (180°).



Solution:

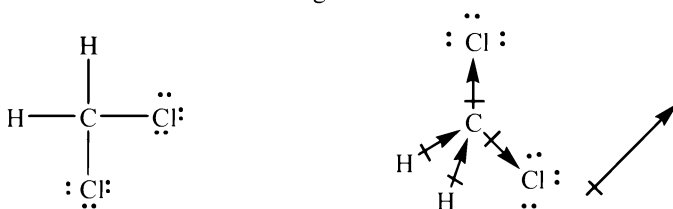
c) Fluorine, like hydrogen, is never a central atom. Thus, the sulfurs must be bonded to each other. Each F ends with 3 lone pairs, and the sulfurs end with 2 lone pairs. All 4 atoms now have an octet. This structure is shown below. Each sulfur has four groups around it, so the electron arrangement is **tetrahedral**. The presence of the lone pairs on the sulfurs results in a geometry that is **V-shaped or bent** and in a bond angle that is **< 109.5°**.



- 10.9 Plan: Draw the Lewis structures, predict the shapes, and then examine the positions of the bond dipoles.

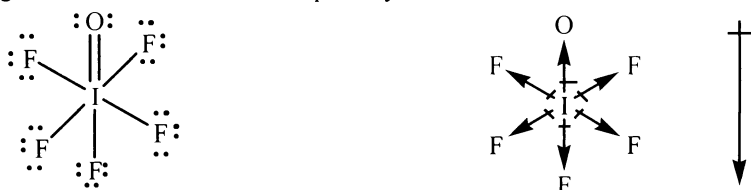
Solution:

a) Dichloromethane, CH₂Cl₂, has the Lewis structure shown below. It is tetrahedral, and if the outlying atoms were identical, it would be nonpolar. However, the chlorines are more electronegative than hydrogen so there is a general shift in their direction resulting in the arrows shown.



Solution:

b) Iodine oxide pentafluoride, IOF₅, has the Lewis structure shown below. The overall geometry is octahedral. All six bonds are polar, with the more electronegative O and F atoms shifting electron density away from the I. The 4 equatorial fluorines counterbalance each other. The axial F is not equivalent to the axial O. The more electronegative F results in an overall polarity in the direction of the axial F.



The lone electron pairs are left out for simplicity.

Solution:

c) Nitrogen tribromide, NBr₃, has the trigonal pyramidal Lewis structure shown below. The nitrogen is more electronegative than the Br, so the shift in electron density is towards the N, resulting in the dipole indicated below.



END-OF-CHAPTER PROBLEMS

- 10.1 To be the central atom in a compound, the atom must be able to simultaneously bond to at least two other atoms. He, F, and H cannot serve as central atoms in a Lewis structure. Helium (1s²) is a noble gas, and as such, it does not need to bond to any other atoms. Hydrogen (1s¹) and fluorine (1s²2s²2p⁵) only need one electron to complete their valence shells. Thus, they can only bond to one other atom, and they do not have *d* orbitals available to expand their valence shells.

- 10.3 For an element to obey the octet rule it must be surrounded by 8 electrons. To determine the number of electrons present (1) count the individual electrons actually shown adjacent to a particular atom, and (2) add two times the number of bonds to that atom. Using this method the structures shown give: (a) $0 + 2(4) = 8$; (b) $2 + 2(3) = 8$; (c) $0 + 2(5) = 10$; (d) $2 + 2(3) = 8$; (e) $0 + 2(4) = 8$; (f) $2 + 2(3) = 8$; (g) $0 + 2(3) = 6$; (h) $8 + 2(0) = 8$. All the structures obey the octet rule except: c and g.

- 10.5 **Plan:** Count the valence electrons and draw Lewis structures.

Solution:

Total valence electrons: SiF_4 : $[1 \times \text{Si}(4e^-)] + [4 \times \text{F}(7e^-)] = 32$; SeCl_2 : $[1 \times \text{Se}(6e^-)] + [2 \times \text{Cl}(7e^-)] = 20$; COF_2 : $[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [2 \times \text{F}(7e^-)] = 24$. The Si, Se, and the C are the central atoms, because these are the elements in their respective compounds with the lower group number (in addition, we are told C is central). Place the other atoms around the central atoms and connect each to the central atom with a single bond.

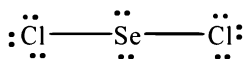
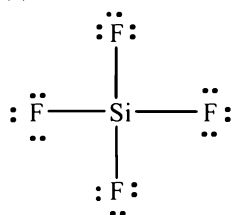
SiF_4 : At this point, 8 electrons ($2e^-$ in 4 Si–F bonds) have been used with $32 - 8 = 24$ remaining; the remaining electrons are placed around the fluorines (3 pairs each). All atoms have an octet.

SeCl_2 : The 2 bonds use $4e^-$ ($2e^-$ in 2 Se–Cl bonds) leaving $20 - 4 = 16e^-$. These $16e^-$ are used to complete the octets on Se and the Cl atoms.

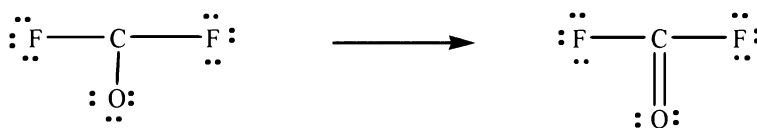
COF_2 : The 3 bonds to the C use $6e^-$ ($2e^-$ in 3 bonds) leaving $24 - 6 = 18e^-$. These $18e^-$ are distributed to the surrounding atoms first to complete their octets. After the $18e^-$ are used, the central C is 2 electrons short of an octet. Forming a double bond to the O (change a lone pair on O to a bonding pair on C) completes the C octet.

(a) SiF_4

(b) SeCl_2



(c) COF_2



- 10.7 **Plan:** Count the valence electrons and draw Lewis structures.

Solution:

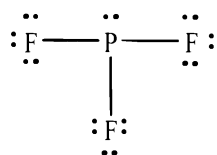
a) PF_3 : $[1 \times \text{P}(5e^-)] + [3 \times \text{F}(7e^-)] = 26$ valence electrons. P is the central atom. Draw single bonds from P to the 3 F atoms, using $2e^- \times 3 \text{ bonds} = 6e^-$. Remaining e^- : $26 - 6 = 20e^-$. Distribute the $20e^-$ around the P and F atoms to complete their octets.

b) H_2CO_3 : $[2 \times \text{H}(2e^-)] + [1 \times \text{C}(4e^-)] + [3 \times \text{O}(6e^-)] = 24$ valence electrons. C is the central atom with the H atoms attached to the O atoms. Place appropriate single bonds between all atoms using $2e^- \times 5 \text{ bonds} = 10e^-$ so that

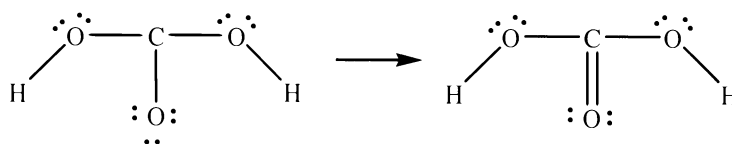
$24 - 10 = 14e^-$ remain. Use these $14e^-$ to complete the octets of the O atoms (the H atoms already have their two electrons). After the $14e^-$ are used, the central C is 2 electrons short of an octet. Forming a double bond to the O that does not have a H bonded to it (change a lone pair on O to a bonding pair on C) completes the C octet.

c) CS_2 : $[1 \times \text{C}(4e^-)] + [2 \times \text{S}(6e^-)] = 16$ valence electrons. C is the central atom. Draw single bonds from C to the 2 S atoms, using $2e^- \times 2 \text{ bonds} = 4e^-$. Remaining e^- : $16 - 4 = 12e^-$. Use these $12e^-$ to complete the octets of the surrounding S atoms; this leaves C 4 electrons short of an octet. Form a double bond from each S to the C by changing a lone pair on each S to a bonding pair on C.

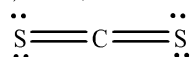
a) PF_3 (26 valence e^-)



b) H_2CO_3 (24 valence e^-)



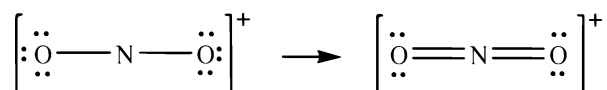
c) CS_2 (16 valence e^-)



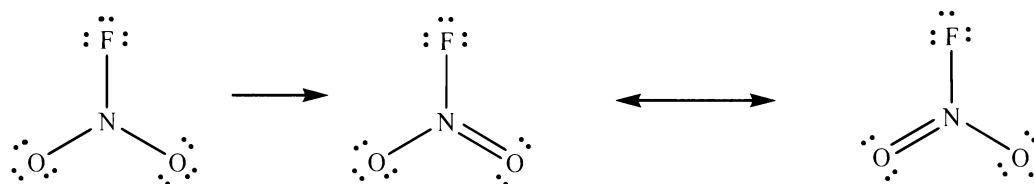
10.9 **Plan:** The problem asks for resonance structures, so there must be more than one answer for each part.

Solution:

a) NO_2^+ has $[1 \times \text{N}(5 e^-)] + [2 \times \text{O}(6 e^-)] - 1 e^-$ (+ charge) = 16 valence electrons. Draw a single bond from N to each O, using $2e^- \times 2 \text{ bonds} = 4 e^-$; $16 - 4 = 12 e^-$ remain. Distribute these $12 e^-$ to the O atoms to complete their octets. This leaves N $4 e^-$ short of an octet. Form a double bond from each O to the N by changing a lone pair on each O to a bonding pair on N. No resonance is required as all atoms can achieve an octet with double bonds.



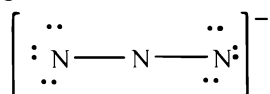
b) NO_2F has $[1 \times \text{N}(5 e^-)] + [2 \times \text{O}(6 e^-)] + [1 \times \text{F}(7e^-)] = 24$ valence electrons. Draw a single bond from N to each surrounding atom, using $2e^- \times 3 \text{ bonds} = 6 e^-$; $24 - 6 = 18 e^-$ remain. Distribute these $18 e^-$ to the O and F atoms to complete their octets. This leaves N $2 e^-$ short of an octet. Form a double bond from either O to the N by changing a lone pair on O to a bonding pair on N. There are two resonance structures since a lone pair from either of the two O atoms can be moved to a bonding pair with N:



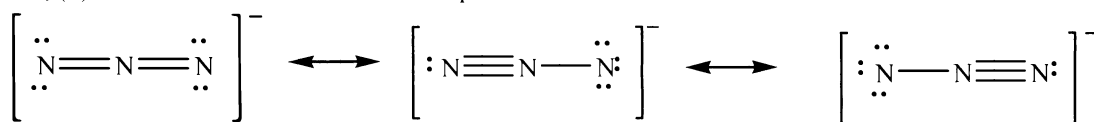
10.11 **Plan:** Count the valence electrons and draw Lewis structures. Additional structures are needed to show resonance.

Solution:

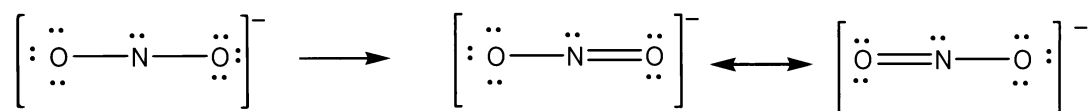
a) N_3^- has $[3 \times \text{N}(5e^-)] + [1 e^- (\text{from charge})] = 16$ valence electrons. Place a single bond between the nitrogen atoms. This uses $2e^- \times 2 \text{ bonds} = 4$ electrons, leaving $16 - 4 = 12$ electrons (6 pairs). Giving 3 pairs on each end nitrogen gives them an octet, but leaves the central N with only 4 electrons as shown below:



The central N needs 4 electrons. There are three options to do this: (1) each of the end N's could form a double bond to the central N by sharing one of its pairs; (2) one of the end N's could form a triple bond by sharing two of its lone pairs; (3) the other end N could form the triple bond instead.



b) NO_2^- has $[1 \times \text{N}(5e^-)] + [2 \times \text{O}(6e^-)] + [1e^- \text{ (from charge)}] = 18$ valence electrons. The nitrogen should be the central atom with each of the oxygens attached to it by a single bond ($2e^- \times 2 \text{ bonds} = 4$ electrons). This leaves $18 - 4 = 14$ electrons (7 pairs). If 3 pairs are given to each O and 1 pair is given to the N, then both O's have an octet, but the N only has 6. To complete an octet the N needs to gain a pair of electrons from one O or the other (from a double bond). The resonance structures are:

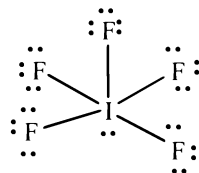


- 10.13 Plan: Initially, the method used in the preceding problems may be used to establish a Lewis structure. The total of the formal charges must equal the charge on an ion or be equal to 0 for a compound. The FC only needs to be calculated once for a set of identical atoms.

Solution:

a) IF_5 has $[1 \times \text{I}(7e^-)] + [5 \times \text{F}(7e^-)] = 42$ valence electrons.

The presence of 5 F's around the central I means that the I will have a minimum of 10 electrons; thus, this is an exception to the octet rule. The 5 I-F bonds use $2e^- \times 5 \text{ bonds} = 10$ electrons leaving $42 - 10 = 32$ electrons (16 pairs). Each F needs 3 pairs to complete an octet. The 5 F's use 15 of the 16 pairs, so there is 1 pair left for the central I. This gives:



Calculating formal charges:

FC = valence electrons - (lone electrons + 1/2 (bonded electrons))

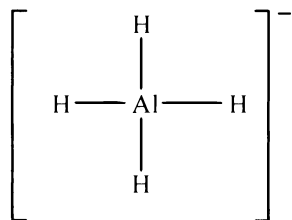
For iodine: $\text{FC}_\text{I} = 7 - (2 + 1/2(10)) = 0$

For each fluorine: $\text{FC}_\text{F} = 7 - (6 + 1/2(2)) = 0$

Total formal charge = 0 = charge on the compound.

b) AlH_4^- has $[1 \times \text{Al}(3e^-)] + [4 \times \text{H}(1e^-)] + [1e^- \text{ (from charge)}] = 8$ valence electrons.

The 4 Al-H bonds use all the electrons and leave the Al with an octet.



For aluminum: $\text{FC}_\text{Al} = 3 - (0 + 1/2(8)) = -1$

For each hydrogen $\text{FC}_\text{H} = 1 - (0 + 1/2(2)) = 0$

Total formal charge = -1 = charge on the ion.

- 10.15 Plan: The general procedure is similar to the preceding problems, plus the oxidation number determination.

Solution:

a) BrO_3^- has $[1 \times \text{Br}(7e^-)] + 3 \times \text{O}(6e^-)] + [1e^- \text{ (from charge)}] = 26$ valence electrons.

Placing the O's around the central Br and forming 3 Br-O bonds uses $2e^- \times 3 \text{ bonds} = 6$ electrons and leaves $26 - 6 = 20$ electrons (10 pairs). Placing 3 pairs on each O ($3 \times 3 = 9$ total pairs) leaves 1 pair for the Br and yields structure I below. In structure I, all the atoms have a complete octet. Calculating formal charges:

$\text{FC}_\text{Br} = 7 - (2 + 1/2(6)) = +2$ $\text{FC}_\text{O} = 6 - (6 + 1/2(2)) = -1$

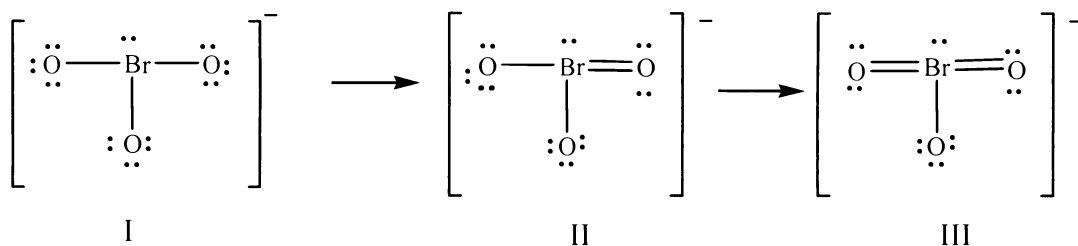
The FC_O is acceptable, but FC_Br is larger than is usually acceptable. Forming a double bond between any one of the O's gives Structure II. Calculating formal charges:

$\text{FC}_\text{Br} = 7 - (2 + 1/2(8)) = +1$ $\text{FC}_\text{O} = 6 - (6 + 1/2(2)) = -1$

$\text{FC}_\text{O} = 6 - (4 + 1/2(4)) = 0$
Double bonded O

The FC_{Br} can be improved further by forming a second double bond to one of the other O's (structure III).
 $\text{FC}_{\text{Br}} = 7 - (2 + 1/2(10)) = 0$ $\text{FC}_{\text{O}} = 6 - (6 + 1/2(2)) = -1$ $\text{FC}_{\text{O}} = 6 - (4 + 1/2(4)) = 0$
 Double bonded O's

Structure III has the more reasonable distribution of formal charges.



The oxidation numbers (O.N.) are: $\text{O.N.}_{\text{Br}} = +5$ and $\text{O.N.}_{\text{O}} = -2$.
Check: The total formal charge equals the charge on the ion (-1).
 BrO_3^-

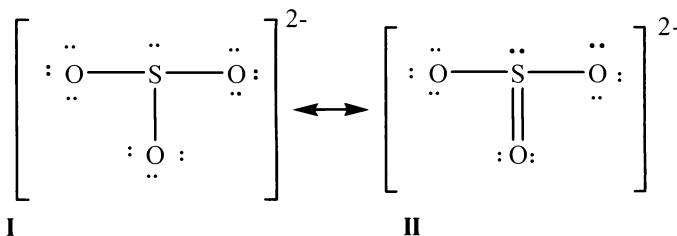
b) SO_3^{2-} has $[1 \times \text{S}(6 e^-)] + 3 \times \text{O}(6 e^-) + [2e^- \text{ (from charge)}] = 26$ valence electrons.

Placing the O's around the central S and forming 3 S–O bonds uses $2e^- \times 3 \text{ bonds} = 6$ electrons and leaves $26 - 6 = 20$ electrons (10 pairs). Placing 3 pairs on each O ($3 \times 3 = 9$ total pairs) leaves 1 pair for the S and yields structure I below. In structure I all the atoms have a complete octet. Calculating formal charges:

$\text{FC}_{\text{S}} = 6 - (2 + 1/2(6)) = +1$; $\text{FC}_{\text{O}} = 6 - (6 + 1/2(2)) = -1$

The FC_{O} is acceptable, but FC_{S} is larger than is usually acceptable. Forming a double bond between any one of the O's (Structure II) gives:

$\text{FC}_{\text{S}} = 6 - (2 + 1/2(8)) = 0$ $\text{FC}_{\text{O}} = 6 - (6 + 1/2(2)) = -1$ $\text{FC}_{\text{O}} = 6 - (4 + 1/2(4)) = 0$
 Double bonded O



Structure II has the more reasonable distribution of formal charges.

The oxidation numbers (O.N.) are: $\text{O.N.}_{\text{S}} = +4$ and $\text{O.N.}_{\text{O}} = -2$.

Check: The total formal charge equals the charge on the ion (-2).

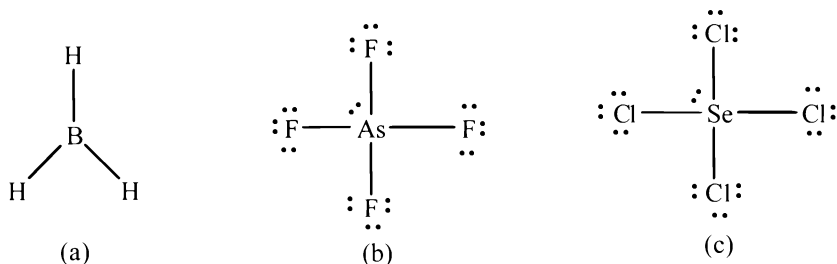
10.17 Plan: We know that each of these compounds does not obey the octet rule.

Solution:

a) BH_3 has $[1 \times \text{B}(3e^-)] + [3 \times \text{H}(1e^-)] = 6$ valence electrons. These are used in 3 B–H bonds. The B has 6 electrons instead of an octet – electron deficient.

b) AsF_4^- has $[1 \times \text{As}(5e^-)] + [4 \times \text{F}(7e^-)] + [1e^- \text{ (from charge)}] = 34$ valence electrons. Four As–F bonds use 8 electrons leaving $34 - 8 = 26$ electrons (13 pairs). Each F needs 3 pairs to complete its octet and the remaining pair goes to the As. The As has an expanded octet with 10 electrons. The F cannot expand its octet.

c) SeCl_4 has $[1 \times \text{Se}(6e^-)] + 4 \times \text{Cl}(7e^-) = 34$ valence electrons. The SeCl_4 is isoelectronic (has the same electron structure) as AsF_4^- , and so its Lewis structure looks the same. Se has an expanded octet of 10 electrons.



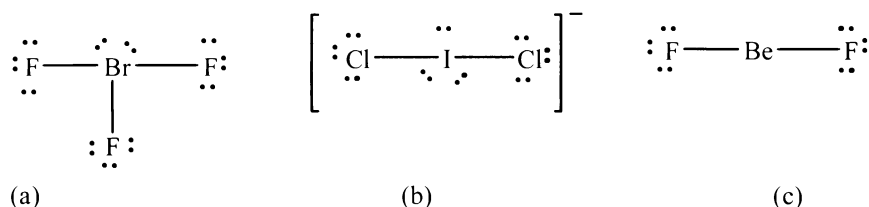
10.19 Plan: We know that each of these compounds does not obey the octet rule.

Solution:

a) BrF_3 has $[1 \times \text{Br}(7e^-)] + [3 \times \text{F}(7e^-)] = 28$ valence electrons. Placing a single bond between Br and each F uses $2e^- \times 3 \text{ bonds} = 6e^-$, leaving $28 - 6 = 22$ electrons (11 pairs). After the F's complete their octets with 3 pairs each, the Br gets the last 2 lone pairs. The Br expands its octet to 10 electrons.

b) ICl_2^- has $[1 \times \text{I}(7e^-)] + [2 \times \text{Cl}(7e^-)] + [1e^- \text{ (from charge)}] = 22$ valence electrons. Placing a single bond between I and each Cl uses $2e^- \times 2 \text{ bonds} = 4e^-$, leaving $22 - 4 = 18$ electrons (9 pairs). After the Cl's complete their octets with 3 pairs each, the iodine finishes with the last 3 lone pairs. The iodine has an expanded octet of 10 electrons.

c) BeF_2 , $[1 \times \text{Be}(2e^-)] + [2 \times \text{F}(7e^-)] = 16$ valence electrons. Placing a single bond between Be and each of the F atoms uses $2e^- \times 2 \text{ bonds} = 4e^-$, leaving $16 - 4 = 12$ electrons (6 pairs). The F's complete their octets with 3 pairs each, and there are no electrons left for the Be. Formal charges work against the formation of double bonds. Be, with only 4 electrons, is electron deficient.



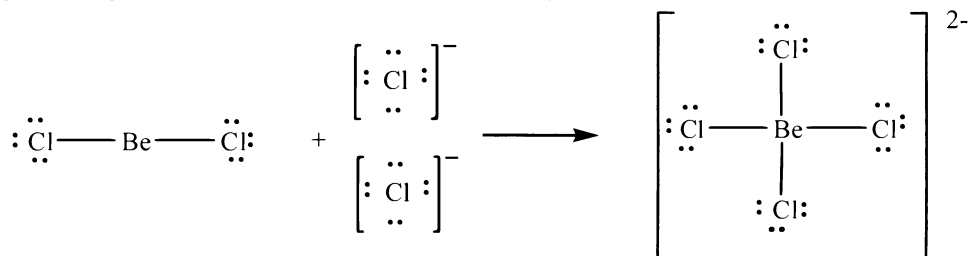
10.21 Plan: Draw Lewis structures for the reactants and products.

Solution:

Beryllium chloride has the formula BeCl_2 . BeCl_2 has $[1 \times \text{Be}(2e^-)] + [2 \times \text{Cl}(7e^-)] = 16$ valence electrons. 4 of these electrons are used to place a single bond between Be and each of the Cl atoms, leaving $16 - 4 = 12$ electrons (6 pairs). These 6 pairs are used to complete the octets of the Cl atoms, but Be does not have an octet – it is electron deficient.

Chloride ion has the formula Cl^- with an octet of electrons.

BeCl_4^{2-} has $[1 \times \text{Be}(2e^-)] + [4 \times \text{Cl}(7e^-)] + [2e^- \text{ (from charge)}] = 32$ valence electrons. 8 of these electrons are used to place a single bond between Be and each Cl atom, leaving $32 - 8 = 24$ electrons (12 pairs). These 12 pairs complete the octet of the Cl atoms (Be already has an octet).



10.24 Plan: Use the structures in the text to determine the formal charges.

Solution:

Structure **A**: $FC_C = 4 - (0 + 1/2(8)) = 0$; $FC_O = 6 - (4 + 1/2(4)) = 0$; $FC_{Cl} = 7 - (6 + 1/2(2)) = 0$

Total FC = 0

Structure **B**: $FC_C = 4 - (0 + 1/2(8)) = 0$; $FC_O = 6 - (6 + 1/2(2)) = -1$;

$FC_{Cl} = 7 - (4 + 1/2(4)) = +1$ (double bonded); $FC_{Cl} = 7 - (6 + 1/2(2)) = 0$ (single bonded)

Total FC = 0

Structure **C**: $FC_C = 4 - (0 + 1/2(8)) = 0$; $FC_O = 6 - (6 + 1/2(2)) = -1$;

$FC_{Cl} = 7 - (4 + 1/2(4)) = +1$ (double bonded); $FC_{Cl} = 7 - (6 + 1/2(2)) = 0$ (single bonded)

Total FC = 0

Structure **A** has the most reasonable set of formal charges.

10.26 The molecular shape and the electron-group arrangement are the same when there are no lone pairs on the central atom.

10.28 Plan: Examine a list of all possible structures, and choose the ones with four electron groups.

Solution:

Tetrahedral

AX_4

Trigonal pyramidal

AX_3E

Bent or V-shaped

AX_2E_2

10.30 Plan: Begin with the basic structures and redraw them.

Solution:

a) A molecule that is V-shaped has two bonds and generally has either one (AX_2E) or two (AX_2E_2) lone electron pairs.

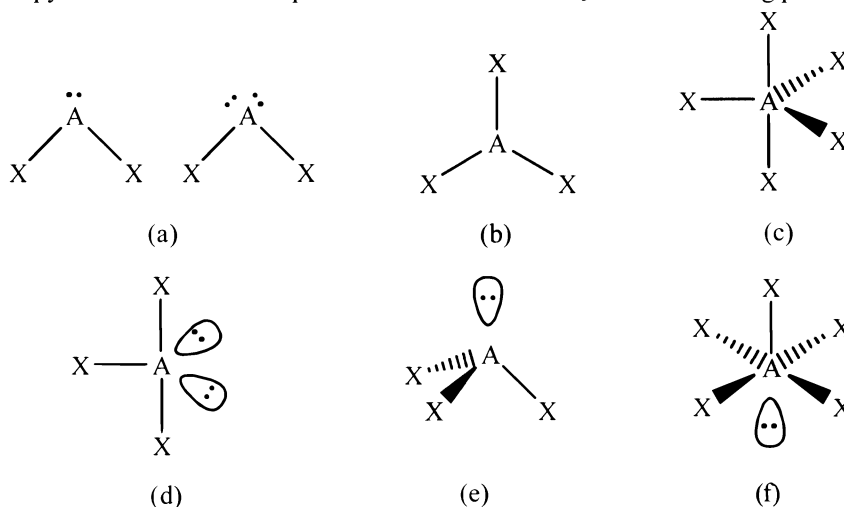
b) A trigonal planar molecule follows the formula AX_3 with three bonds and no lone electron pairs.

c) A trigonal bipyramidal molecule contains five bonding pairs (single bonds) and no lone pairs (AX_5).

d) A T-shaped molecule has three bonding groups and two lone pairs (AX_3E_2).

e) A trigonal pyramidal molecule follows the formula AX_3E with three bonding pairs and one lone pair.

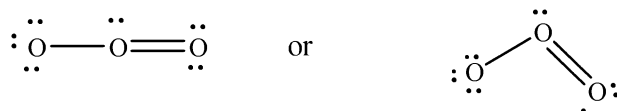
f) A square pyramidal molecule shape follows the formula AX_5E with 5 bonding pairs and one lone pair.



10.32 **Plan:** First, draw a Lewis structure, and then apply VSEPR.

Solution:

a) O_3 : The molecule has $[3 \times \text{O}(6e^-)] = 18$ valence electrons. 4 electrons are used to place a single bond between the oxygen atoms, leaving $18 - 4 = 14e^-$ (7 pairs). 6 pairs are required to give the end oxygen atoms an octet; the last pair is distributed to the central oxygen, leaving this atom 2 electrons short of an octet. Form a double bond from one of the end O atoms to the central O by changing a lone pair on the end O to a bonding pair on the central O. This gives the following Lewis structure:



There are three groups around the central O, one of which is a lone pair. This gives a **trigonal planar** electron-group arrangement, a **bent** molecular shape, and an ideal bond angle of 120° .

b) H_3O^+ : This ion has $[3 \times \text{H}(1e^-)] + [1 \times \text{O}(6e^-)] - [1e^- \text{ (due to + charge)}] = 8$ valence electrons. 6 electrons are used to place a single bond between O and each H, leaving $8 - 6 = 2e^-$ (1 pair). Distribute this pair to the O atom, giving it an octet (the H atoms only get 2 electrons). This gives the following Lewis structure:



There are four groups around the O, one of which is a lone pair. This gives a **tetrahedral** electron-group arrangement, a **trigonal pyramidal** molecular shape, and an ideal bond angle of 109.5° .

c) NF_3 : The molecule has $[1 \times \text{N}(5e^-)] + [3 \times \text{F}(7e^-)] = 26$ valence electrons. 6 electrons are used to place a single bond between N and each F, leaving $26 - 6 = 20e^-$ (10 pairs). These 10 pairs are distributed to all of the F atoms and the N atoms to give each atom an octet. This gives the following Lewis structure:

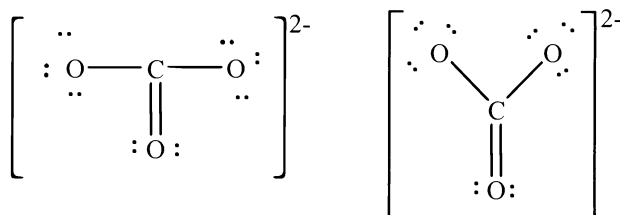


There are four groups around the N, one of which is a lone pair. This gives a **tetrahedral** electron-group arrangement, a **trigonal pyramidal** molecular shape, and an ideal bond angle of 109.5° .

10.34 **Plan:** First, draw a Lewis structure, and then apply VSEPR.

Solution:

a) CO_3^{2-} : This ion has $[1 \times \text{C}(4e^-)] + [3 \times \text{O}(6e^-)] + [2e^- \text{ (from charge)}] = 24$ valence electrons. 6 electrons are used to place single bonds between C and each O atom, leaving $24 - 6 = 18e^-$ (9 pairs). These 9 pairs are used to complete the octets of the three O atoms, leaving C 2 electrons short of an octet. Form a double bond from one of the O atoms to C by changing a lone pair on an O to a bonding pair on C. This gives the following Lewis structure:



+ 2 additional resonance forms. There are three groups of electrons around the C, none of which are lone pairs. This gives a **trigonal planar** electron-group arrangement, a **trigonal planar** molecular shape, and an ideal bond angle of 120° .

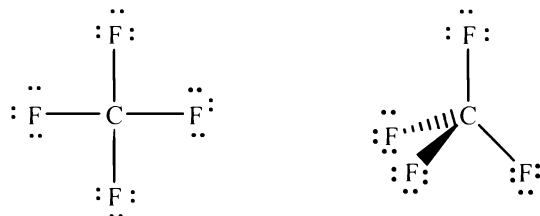
(b) SO_2 : This molecule has $[1 \times \text{S}(6 \text{ e}^-)] + [2 \times \text{O}(6 \text{ e}^-)] = 18$ valence electrons. 4 electrons are used to place a single bond between S and each O atom, leaving $18 - 4 = 14 \text{ e}^-$ (7 pairs). 6 pairs are needed to complete the octets of the O atoms, leaving a pair of electrons for S. S needs one more pair to complete its octet. Form a double bond from one of the end O atoms to the S by changing a lone pair on the O to a bonding pair on the S. This gives the following Lewis structure:



There are three groups of electrons around the C, one of which is a lone pair.

This gives a **trigonal planar** electron-group arrangement, a **bent (V-shaped)** molecular shape, and an ideal bond angle of **120°** .

(c) CF_4 : This molecule has $[1 \times \text{C}(4 \text{ e}^-)] + [4 \times \text{F}(7 \text{ e}^-)] = 32$ valence electrons. 8 electrons are used to place a single bond between C and each F, leaving $32 - 8 = 24 \text{ e}^-$ (12 pairs). Use these 12 pairs to complete the octets of the F atoms (C already has an octet). This gives the following Lewis structure:



There are four groups of electrons around the C, none of which is a lone pair.

This gives a **tetrahedral** electron-group arrangement, a **tetrahedral** molecular shape, and an ideal bond angle of **109.5°** .

10.36 Plan: Examine the structure shown, and then apply VSEPR.

Solution:

a) This structure shows three electron groups with three bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **trigonal planar**, the classification is **AX_3** , with an ideal bond angle of **120°** .

b) This structure shows three electron groups with three bonds around the central atom.

The bonds are distorted down indicating the presence of a lone pair. The shape of the molecule is **trigonal pyramidal** and the classification is **AX_3E** , with an ideal bond angle of **109.5°** .

c) This structure shows five electron groups with five bonds around the central atom.

There appears to be no distortion of the bond angles so the shape is **trigonal bipyramidal** and the classification is **AX_5** , with ideal bond angles of **90° and 120°** .

10.38 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures.

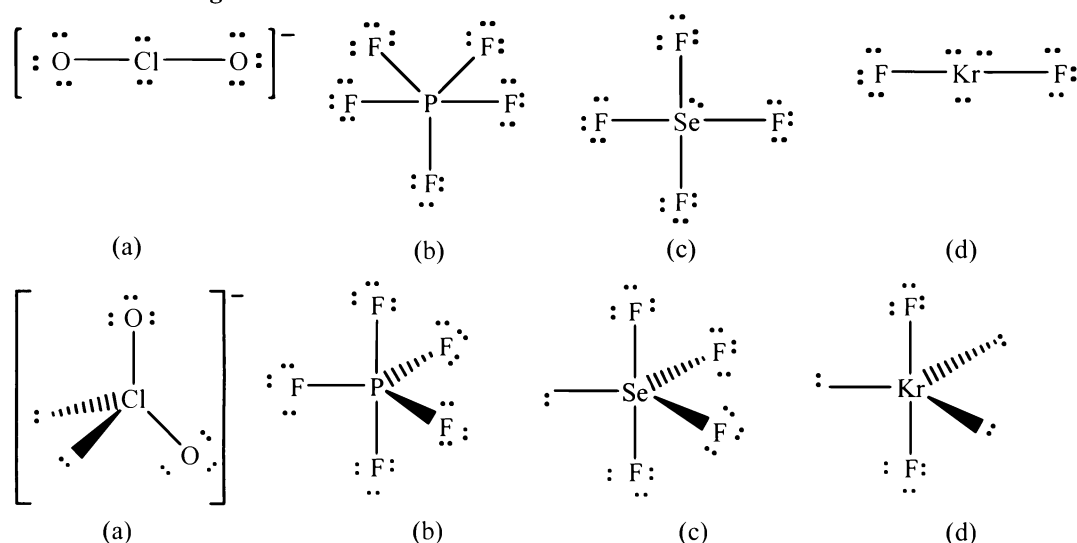
Solution:

a) The ClO_2^- ion has $[1 \times \text{Cl}(7 \text{ e}^-)] + [2 \times \text{O}(6 \text{ e}^-)] + [1 \text{ e}^- \text{ (from charge)}] = 20$ valence electrons. 4 electrons are used to place a single bond between the Cl and each O, leaving $20 - 4 = 16$ electrons (8 pairs). All 8 pairs are used to complete the octets of the Cl and O atoms. There are two bonds (to the O's) and two lone pairs on the Cl for a total of 4 electron groups (**AX_2E_2**). The structure is based on a tetrahedral electron-group arrangement with an ideal bond angle of **109.5°** . The shape is **bent** (or V-shaped). The presence of the lone pairs will cause the remaining angles to be **less than 109.5°** .

b) The PF_5 molecule has $[1 \times \text{P}(5 \text{ e}^-)] + [5 \times \text{F}(7 \text{ e}^-)] = 40$ valence electrons. 10 electrons are used to place single bonds between P and each F atom, leaving $40 - 10 = 30 \text{ e}^-$ (15 pairs). The 15 electrons are used to complete the octets of the F atoms. There are 5 bonds to the P and no lone pairs (**AX_5**). The electron-group arrangement and the shape is **trigonal bipyramidal**. The ideal bond angles are **90° and 120°** . The absence of lone pairs means the **angles are ideal**.

c) The SeF_4 molecule has $[1 \times \text{Se}(6 e^-)] + [4 \times \text{F}(7 e^-)] = 34$ valence electrons. 8 electrons are used to place single bonds between Se and each F atom, leaving $34 - 8 = 26 e^-$ (13 pairs). 12 pairs are used to complete the octets of the F atoms which leaves 1 pair of electrons. This pair is placed on the central Se atom. There are 4 bonds to the Se which also has a lone pair (AX_4E). The structure is based on a trigonal bipyramidal structure with ideal angles of 90° and 120° . The shape is **see-saw**. The presence of the lone pairs means the angles are **less than ideal**.

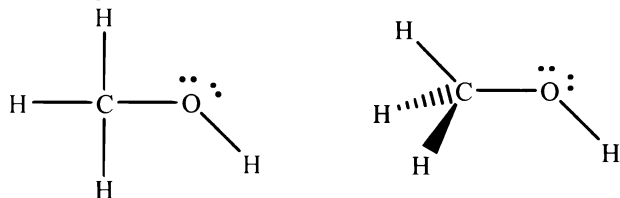
d) The KrF_2 molecule has $[1 \times \text{Kr}(8 e^-)] + [2 \times \text{F}(7 e^-)] = 22$ valence electrons. 4 electrons are used to place a single bond between the Kr atom and each F atom, leaving $22 - 4 = 18 e^-$ (9 pairs). 6 pairs are used to complete the octets of the F atoms. The remaining 3 pairs of electrons are placed on the Kr atom. The Kr is the central atom. There are 2 bonds to the Kr and 3 lone pairs (AX_2E_3). The structure is based on a trigonal bipyramidal structure with ideal angles of 90° and 120° . The shape is **linear**. The placement of the F's makes their ideal bond angle to be $2 \times 90^\circ = 180^\circ$. The placement of the lone pairs is such that they cancel each other's repulsion, thus the actual **bond angle is ideal**.



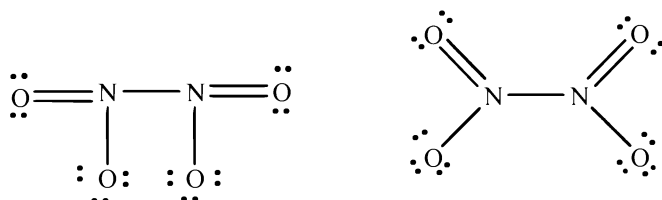
10.40 **Plan:** The Lewis structures must be drawn, and VSEPR applied to the structures.

Solution:

a) CH_3OH : This molecule has $[1 \times \text{C}(4 e^-)] + [4 \times \text{H}(1 e^-)] + [1 \times \text{O}(6 e^-)] = 14$ valence electrons. In the CH_3OH molecule, both carbon and oxygen serve as central atoms. (H can never be central.) Use 8 electrons to place a single bond between the C and the O atom and 3 of the H atoms and another 2 electrons to place a single bond between the O and the last H atom. This leaves $14 - 10 = 4 e^-$ (2 pairs). Use these two pairs to complete the octet of the O atom. C already has an octet and each H only gets 2 electrons. The carbon has 4 bonds and no lone pairs (AX_4), so it is **tetrahedral with no deviation** (no lone pairs) from the ideal angle of 109.5° . The oxygen has 2 bonds and 2 lone pairs (AX_2E_2), so it is **V-shaped** or **bent** with the angles **less than the ideal** angle of 109.5° .



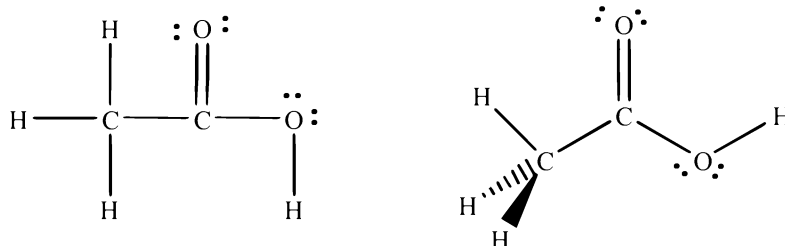
b) N_2O_4 : This molecule has $[2 \times \text{N}(5 \text{ e}^-)] + [4 \times \text{O}(6 \text{ e}^-)] = 34$ valence electrons. Use 10 electrons to place a single bond between the two N atoms and between each N and two of the O atoms. This leaves $34 - 10 = 24 \text{ e}^-$ (12 pairs). Use the 12 pairs to complete the octets of the oxygen atoms. Neither N atom has an octet however. Form a double bond from one O atom to one N atom by changing a lone pair on the O to a bonding pair on the N. Do this for the other N atom as well. In the N_2O_4 molecule, both nitrogens serve as central atoms. This is the arrangement given in the problem. Both nitrogens are equivalent with 3 groups and no lone pairs (AX_3), so the arrangement is **trigonal planar** with **no deviation** (no lone pairs) from the ideal angle of 120° . The same results arise from the other resonance structures.



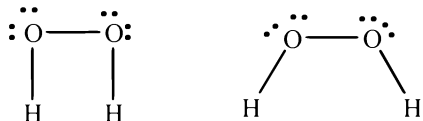
10.42 Plan: The Lewis structures must be drawn, and VSEPR applied to the structures.

Solution:

a) CH_3COOH has $[2 \times \text{C}(4 \text{ e}^-)] + [4 \times \text{H}(1 \text{ e}^-)] + [2 \times \text{O}(6 \text{ e}^-)] = 24$ valence electrons. Use 14 electrons to place a single bond between all of the atoms. This leaves $24 - 14 = 10 \text{ e}^-$ (5 pairs). Use these 5 pairs to complete the octets of the O atoms; the C atom bonded to the H atoms has an octet but the other C atom does not have a complete octet. Form a double bond from the O atom (not bonded to H) to the C by changing a lone pair on the O to a bonding pair on the C. In the CH_3COOH molecule, the carbons and the O with H attached serve as central atoms. The carbon bonded to the H atoms has 4 groups and no lone pairs (AX_4), so it is **tetrahedral** with **no deviation** from the ideal angle of 109.5° . The carbon bonded to the O atoms has 3 groups and no lone pairs (AX_3), so it is **trigonal planar** with **no deviation** from the ideal angle of 120° . The H bearing O has 2 bonds and 2 lone pairs (AX_2E_2), so the arrangement is **V-shaped** or **bent** with an angle **less than the ideal** values of 109.5° .

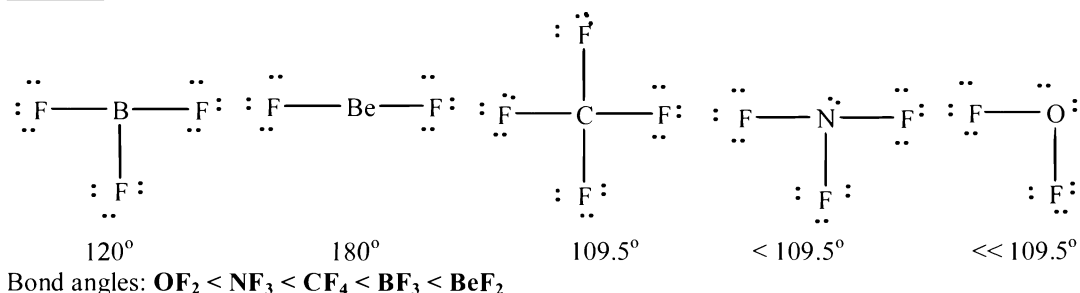


b) H_2O_2 has $[2 \times \text{H}(1 \text{ e}^-)] + [2 \times \text{O}(6 \text{ e}^-)] = 14$ valence electrons. Use 6 electrons to place single bonds between the O atoms and between each O atom and a H atom. This leaves $14 - 6 = 8 \text{ e}^-$ (4 pairs). Use these 4 pairs to complete the octets of the O atoms. In the H_2O_2 molecule, both oxygens serve as central atoms. Both O's have 2 bonds and 2 lone pairs (AX_2E_2), so they are **V-shaped** or **bent** with angles **less than the ideal** values of 109.5° .



10.44 Plan: First, draw a Lewis structure, and then apply VSEPR.

Solution:



BeF_2 is an AX_2 type molecule, so the angle is the ideal 180° . BF_3 is an AX_3 molecule, so the angle is the ideal 120° . CF_4 , NF_3 , and OF_2 all have tetrahedral electron-group arrangements of the following types: AX_4 , AX_3E , and AX_2E_2 , respectively. The ideal tetrahedral bond angle is 109.5° , which is present in CF_4 . The one lone pair in NF_3 decreases the angle a little. The two lone pairs in OF_2 decrease the angle even more.

10.46 Plan: The ideal bond angles depend on the electron-group arrangement. Deviations depend on lone pairs.

Solution:

a) The C and N have 3 groups, so they are **ideally 120°** , and the O has 4 groups, so **ideally the angle is 109.5°** . The N and O have lone pairs, so the **angles are less than ideal**.

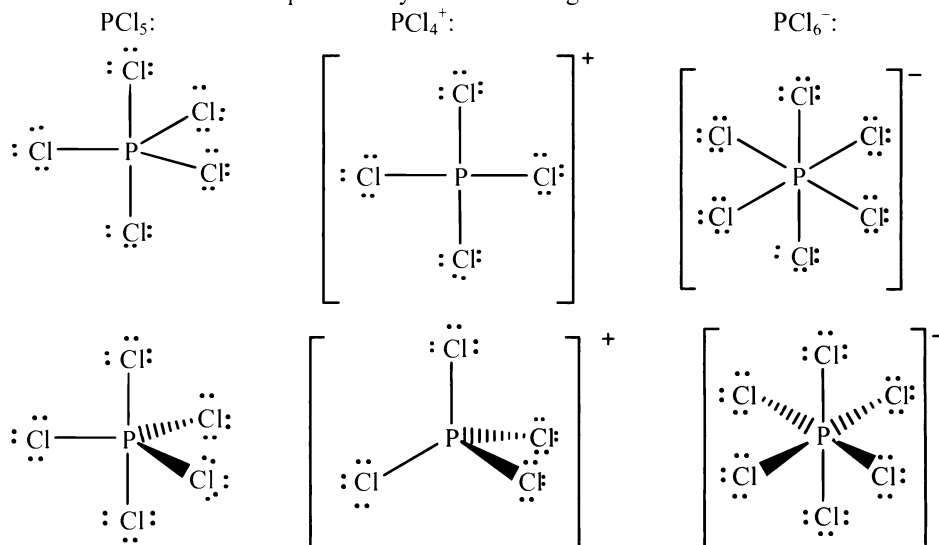
b) All central atoms have 4 pairs, so ideally all the angles are **109.5°** . The lone pairs on the O **reduce** this value.

c) The B has 3 groups (no lone pairs) leading to an **ideal bond angle of 120°** . All the O's have 4 pairs (**ideally 109.5°**), 2 of which are lone, and **reduce the angle**.

10.49 Plan: The Lewis structures are needed to predict the ideal bond angles.

Solution:

The P atoms have no lone pairs in any case so the angles are ideal.



The original PCl_5 is AX_5 , so the shape is trigonal bipyramidal, and the angles are 120° and 90° .

The PCl_4^+ is AX_4 , so the shape is tetrahedral, and the angles are 109.5° .

The PCl_6^- is AX_6 , so the shape is octahedral, and the angles are 90° .

Half the PCl_5 (trigonal bipyramidal, 120° and 90°) become tetrahedral PCl_4^+ (tetrahedral, 109.5°), and the other half become octahedral PCl_6^- (octahedral, 90°).

10.51 Plan: To determine if a bond is polar, determine the electronegativity difference of the atoms participating in the bond. To determine if a molecule is polar, it must have polar bonds, and a certain shape determined by VSEPR.

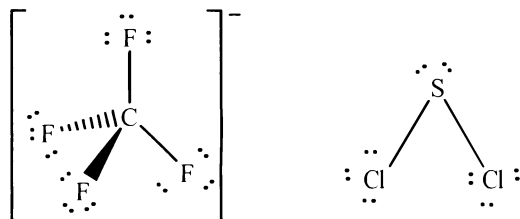
Solution:

a) The greater the difference in electronegativity the more polar the bond:

Molecule	Bond	Electronegativities	Electronegativity difference
SCl_2	S–Cl	S = 2.5 Cl = 3.0	$3.0 - 2.5 = 0.5$
F_2	F–F	F = 4.0 F = 4.0	$4.0 - 4.0 = 0.0$
CS_2	C–S	C = 2.5 S = 2.5	$2.5 - 2.5 = 0.0$
CF_4	C–F	C = 2.5 F = 4.0	$4.0 - 2.5 = 1.5$
BrCl	Br–Cl	Br = 2.8 Cl = 3.0	$3.0 - 2.8 = 0.2$

The polarities of the bonds increases in the order: $\text{F–F} = \text{C–S} < \text{Br–Cl} < \text{S–Cl} < \text{C–F}$. Thus, **CF_4** has the most polar bonds.

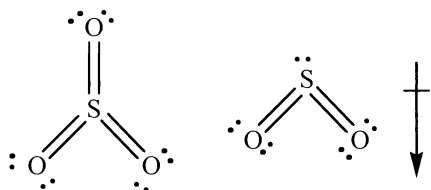
b) The F_2 and CS_2 cannot be polar since they do not have polar bonds. CF_4 is a AX_4 molecule, so it is tetrahedral with the 4 polar C–F bonds arranged to cancel each other giving an overall nonpolar molecule. **BrCl has a dipole moment** since there are no other bonds to cancel the polar Br–Cl bond. **SCl_2 has a dipole moment** (is polar) because it is a bent molecule, AX_2E_2 , and the S–Cl bonds both pull to one side.



- 10.53 Plan: If only 2 atoms are involved, only an electronegativity difference is needed. If there are more than 2 atoms, the structure must be determined.

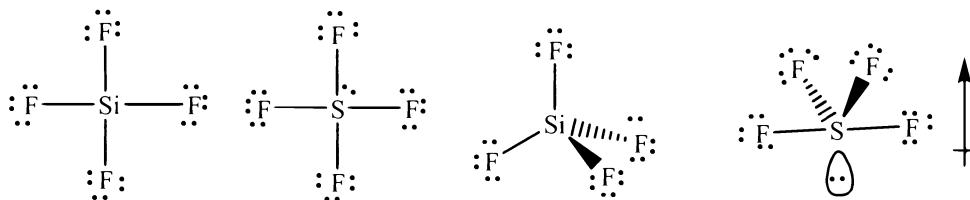
Solution:

a) All the bonds are polar covalent. The SO_3 molecule is trigonal planar, AX_3 , so the bond dipoles cancel leading to a nonpolar molecule (no dipole moment). The SO_2 molecule is bent, AX_2E , so the polar bonds both pull to one side. **SO_2 has a greater dipole moment** because it is the only one of the pair that is polar.



b) ICl and IF are polar, as are all diatomic molecules composed of atoms with differing electronegativities. The electronegativity difference for ICl ($3.0 - 2.5 = 0.5$) is less than that for IF ($4.0 - 2.5 = 1.5$). The greater difference means that **IF has a greater dipole moment**.

c) All the bonds are polar covalent. The SiF_4 molecule is nonpolar (has no dipole moment) because the bonds are arranged tetrahedrally, AX_4 . SF_4 is AX_4E , so it has a see-saw shape, where the bond dipoles do not cancel. **SF_4 has the greater dipole moment**.

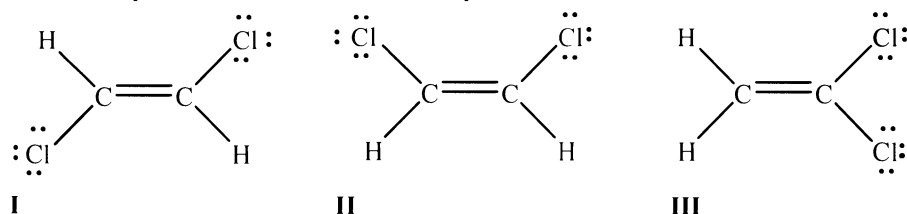


d) H_2O and H_2S have the same basic structure. They are both bent molecules, AX_2E_2 , and as such, they are polar. The electronegativity difference in H_2O ($3.5 - 2.1 = 1.4$) is greater than the electronegativity difference in H_2S ($2.5 - 2.1 = 0.4$) so **H_2O has a greater dipole moment**.

- 10.55 Plan: Draw Lewis structures, and then apply VSEPR.

Solution:

There are 3 possible structures for the compound $C_2H_2Cl_2$:



The presence of the double bond prevents rotation about the C=C bond, so the structures are “fixed.” The C–Cl bonds are more polar than the C–H bonds, so the key to predicting the polarity is the positioning of the C–Cl bonds. Compound I has the C–Cl bonds arranged so that they cancel leaving I as a nonpolar molecule. Both II and III have C–Cl bonds on the same side so the bonds work together making both molecules polar. Both I and II will react with H₂ to give a compound with a Cl attached to each C (same product). Compound III will react with H₂ to give a compound with 2 Cl's on one C and none on the other (different product). **Compound I must be X** as it is the only one that is nonpolar (has no dipole moment). **Compound II must be Z** because it is polar and gives the same product as compound X. This means that compound III must be the remaining compound — Y. **Compound Y (III) has a dipole moment.**

10.56 Plan: The Lewis structures are needed to do this problem. For part (b), obtain bond energy values from Table 9.2.

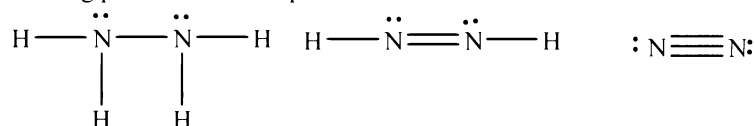
Solution:

a) The H atoms cannot be central, and they are evenly distributed on the N's.

N₂H₄ has [2 x N(5 e⁻)] + [4 x H(1 e⁻)] = 14 valence electrons, 10 of which are used in the bonds between the atoms. The remaining two pairs are used to complete the octets of the N atoms.

N₂H₂ has [2 x N(5 e⁻)] + (2 x H(1 e⁻)) = 12 valence electrons, 6 of which are used in the bonds between the atoms. The remaining three pairs of electrons are not enough to complete the octets of both N atoms, so one lone pair is moved to a bonding pair between the N atoms.

N₂ has [2 x N(5 e⁻)] = 10 valence electrons, 2 of which are used to place a single bond between the two N atoms. Since only 4 pairs of electrons remain and 6 pairs are required to complete the octets, two lone pairs become bonding pairs to form a triple bond.



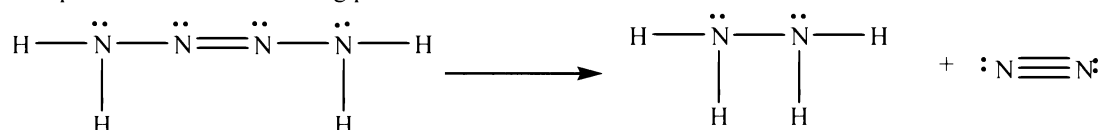
Hydrazine

Diazene

Nitrogen

The single (bond order = 1) N–N bond is **weaker and longer** than any of the others are. The **triple bond (bond order = 3) is stronger and shorter** than any of the others. The **double bond (bond order = 2) has an intermediate strength and length.**

b) N₄H₄ has [4 x N(5 e⁻)] + [4 x H(1 e⁻)] = 24 valence electrons, 14 of which are used for single bonds between the atoms. When the remaining 5 pairs are distributed to complete the octets, one N atom lacks two electrons. A lone pair is moved to a bonding pair for a double bond.



$$\Delta H^\circ_{\text{bonds broken}} = 4 \text{ N-H} = 4 \text{ mol (391 kJ/mol)}$$

$$2 \text{ N-N} = 2 \text{ mol (160 kJ/mol)}$$

$$1 \text{ N=N} = 1 \text{ mol (418 kJ/mol)}$$

$$= 2302 \text{ kJ}$$

$$\Delta H^\circ_{\text{bonds formed}} = 4 \text{ N-H} = 4 \text{ mol (391 kJ/mol)}$$

$$1 \text{ N-N} = 1 \text{ mol (160 kJ/mol)}$$

$$1 \text{ N}\equiv\text{N} = 1 \text{ mol (945 kJ/mol)}$$

$$= 2669 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{bonds broken}} - \Delta H^\circ_{\text{bonds formed}} = 2302 \text{ kJ} - (2669 \text{ kJ}) = -367 \text{ kJ}$$

Note: It is correct to report the answer in kJ or kJ/mol as long as the value refers to a reactant or product with a molar coefficient of 1.

10.57 Plan: Use the Lewis structures shown in the text.

FC = valence electrons – [lone electrons + 1/2 (bonded electrons)]

Solution:

a) Formal charges for Al₂Cl₆:

$$\text{FC}_{\text{Al}} = 3 - (0 + 1/2(8)) = -1$$

$$\text{FC}_{\text{Cl, ends}} = 7 - (6 + 1/2(2)) = 0$$

$$\text{FC}_{\text{Cl, bridging}} = 7 - (4 + 1/2(4)) = +1$$

(Check: Formal charges add to zero, the charge on the compound.)

Formal charges for I_2Cl_6 :

$$\text{FC}_\text{I} = 7 - (4 + 1/2(8)) = -1$$

$$\text{FC}_{\text{Cl, ends}} = 7 - (6 + 1/2(2)) = 0$$

$$\text{FC}_{\text{Cl, bridging}} = 7 - (4 + 1/2(4)) = +1$$

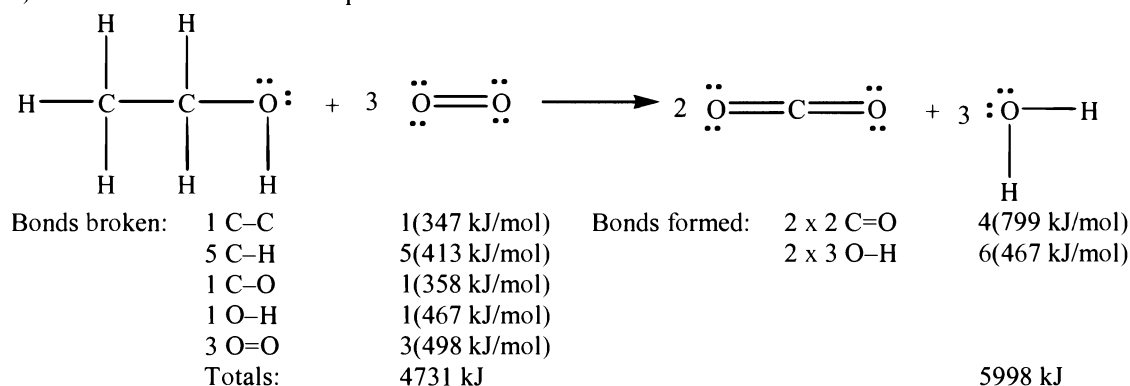
(Check: Formal charges add to zero, the charge on the compound.)

b) The aluminum atoms have no lone pairs and are AX_4 , so they are tetrahedral. The 2 tetrahedral Al's cannot give a planar structure. The iodine atoms have two lone pairs each and are AX_4E_2 so they are square planar. Placing the square planar I's adjacent can give a planar molecule.

10.65 Plan: Assume all reactants and products are assumed to be gaseous. Ethanol burns (combusts) with O_2 to produce CO_2 and H_2O .

Solution:

a) To save time the balanced equation includes the Lewis structures:



$$\Delta H = \text{Bonds broken} - \text{Bonds formed}$$

$$= 4731 \text{ kJ} - 5998 \text{ kJ} = -1267 \text{ kJ for each mole of ethanol burned.}$$

b) If it takes 40.5 kJ/mol to vaporize the ethanol, part of the heat of combustion must be used to convert liquid ethanol to gaseous ethanol. The new value becomes:

$$\Delta H_{\text{comb(liquid)}} = -1267 \text{ kJ} + (1 \text{ mol})(40.5 \text{ kJ/mol}) = -1226.5 = -1226 \text{ kJ per mol of liquid ethanol burned}$$

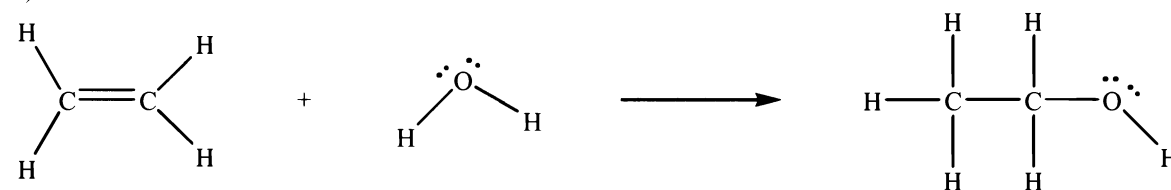
$$\text{c) } \Delta H_{\text{comb(liquid)}} = \sum n\Delta H_f^\circ (\text{products}) - \sum m\Delta H_f^\circ (\text{reactants})$$

$$\Delta H_{\text{comb(liquid)}} = [2(\Delta H_f^\circ (\text{CO}_2(\text{g}))) + 3(\Delta H_f^\circ (\text{H}_2\text{O}(\text{g}))) - [(\Delta H_f^\circ (\text{C}_2\text{H}_5\text{OH}(\text{l}))) + 3(\Delta H_f^\circ (\text{O}_2(\text{g})))]$$

$$\Delta H_{\text{comb(liquid)}} = [2(-393.5 \text{ kJ}) + 3(-241.826 \text{ kJ})] - [(-277.63 \text{ kJ}) + 3(0 \text{ kJ})] = -1234.848 = -1234.8 \text{ kJ}$$

The two answers differ by less than 10 kJ. This is a very good agreement since average bond energies were used to calculate answers a and b.

d) The Lewis structures for the reaction are:



$$\begin{aligned} \text{The energy to break the reactant bonds is: } & \text{BE}(\text{C}=\text{C}) + 4 \text{ BE}(\text{C}-\text{H}) + 2 \text{ BE}(\text{O}-\text{H}) \\ & = (1 \text{ mol})(614 \text{ kJ/mol}) + (4 \text{ mol})(413 \text{ kJ/mol}) + (2 \text{ mol})(467 \text{ kJ/mol}) \\ & = 3200. \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{The energy from forming the product bonds is: } & \text{BE}(\text{C}-\text{C}) + 5 \text{ BE}(\text{C}-\text{H}) + \text{BE}(\text{C}-\text{O}) + \text{BE}(\text{O}-\text{H}) \\ & = (1 \text{ mol})(347 \text{ kJ/mol}) + (5 \text{ mol})(413 \text{ kJ/mol}) + (1 \text{ mol})(358 \text{ kJ/mol}) + (1 \text{ mol})(467 \text{ kJ/mol}) \\ & = 3237 \text{ kJ} \end{aligned}$$

$$\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{bonds broken}}^\circ - \Delta H_{\text{bonds formed}}^\circ = 3200. \text{ kJ} - (3237 \text{ kJ}) = -37 \text{ kJ}$$

- 10.67 **Plan:** Determine the empirical formula from the percent composition (assuming 100 grams of compound). Use the titration data to determine the mole ratio of acid to the NaOH. This ratio relates the number of acidic H's to the formula of the acid. Finally, combine this information to construct the Lewis structure.

Solution:

$$\text{H} \quad (2.24 \text{ g H}) \left(\frac{1 \text{ mol}}{1.008 \text{ g H}} \right) = 2.222 \text{ mol H} \quad \frac{2.222 \text{ mol}}{2.222 \text{ mol}} = 1.00$$

$$\text{C} \quad (26.7 \text{ g C}) \left(\frac{1 \text{ mol}}{12.01 \text{ g C}} \right) = 2.223 \text{ mol C} \quad \frac{2.223 \text{ mol}}{2.222 \text{ mol}} = 1.00$$

$$\text{O} \quad (71.1 \text{ g O}) \left(\frac{1 \text{ mol}}{16.00 \text{ g O}} \right) = 4.444 \text{ mol O} \quad \frac{4.444 \text{ mol}}{2.222 \text{ mol}} = 2.00$$

The empirical formula is HCO_2 .

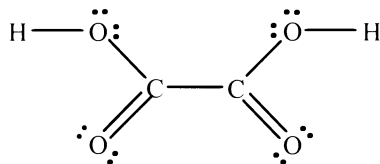
The titration required:

$$\left(\frac{0.040 \text{ mol NaOH}}{\text{L}} \right) \left(\frac{50.0 \text{ mL}}{1000 \text{ mL}} \right) \left(\frac{1 \text{ mmol}}{0.001 \text{ mol}} \right) = 2.0 \text{ mmole NaOH}$$

Thus, the ratio is 2.0 mmole base / 1.0 mmole acid, or each acid molecule has two hydrogens to react (diprotic).

The empirical formula indicates a monoprotic acid, so the formula must be doubled to: $\text{H}_2\text{C}_2\text{O}_4$.

There are 34 valence electrons to be used in the Lewis structure. 14 of these electrons are used to bond the atoms with single bonds, leaving 10 pairs of electrons. When these 10 pairs of electrons are distributed to the atoms to complete octets, neither C atom has an octet; a lone pair from the oxygen without hydrogen is changed to a bonding pair on C.

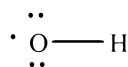


- 10.68 **Plan:** Draw the Lewis structure of the OH species. Find the additional bond energy information in Table 9.2.

Solution:

a) The OH molecule has 7 valence electrons. Thus, no atom can have an octet, and one electron is left unpaired.

The Lewis structure is:



b) The formation reaction is: $1/2 \text{ O}_2(\text{g}) + 1/2 \text{ H}_2(\text{g}) \rightarrow \text{OH}(\text{g})$. The heat of reaction is:

$$\Delta H_{\text{reaction}} = \Delta H_{\text{broken}} - \Delta H_{\text{formed}} = 39.0 \text{ kJ}$$

$$[\text{BE}_{\text{O}=\text{O}} + \text{BE}_{\text{H}-\text{H}}] - [\text{BE}_{\text{O}-\text{H}}] = 39.0 \text{ kJ}$$

$$[(1/2 \text{ mol}) (498 \text{ kJ/mol}) + (1/2 \text{ mol}) (432 \text{ kJ/mol})] - [\text{BE}_{\text{O}-\text{H}}] = 39.0 \text{ kJ}$$

$$\text{BE}_{\text{O}-\text{H}} = \mathbf{426 \text{ kJ}}$$

c) The average bond energy (from the bond energy table) is 467 kJ/mol. There are 2 O–H bonds in water for a total of $2 \times 467 \text{ kJ/mol} = 934 \text{ kJ}$. The answer to part b accounts for 426 kJ of this, leaving:

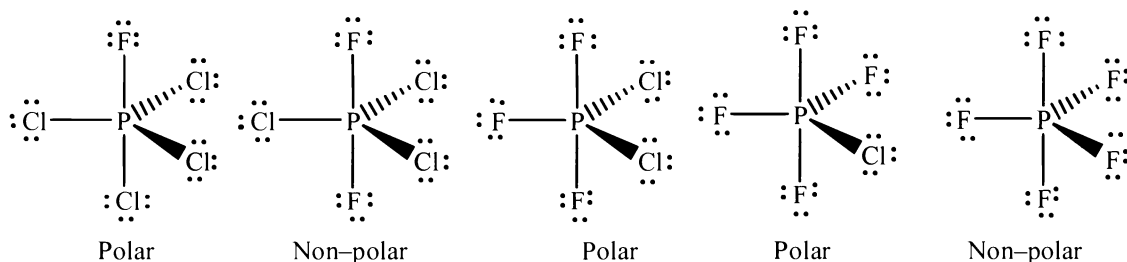
$$934 \text{ kJ} - 426 \text{ kJ} = \mathbf{508 \text{ kJ}}$$

- 10.70 **Plan:** The basic Lewis structure will be the same for all species. The Cl atoms are larger than the F atoms.

Solution:

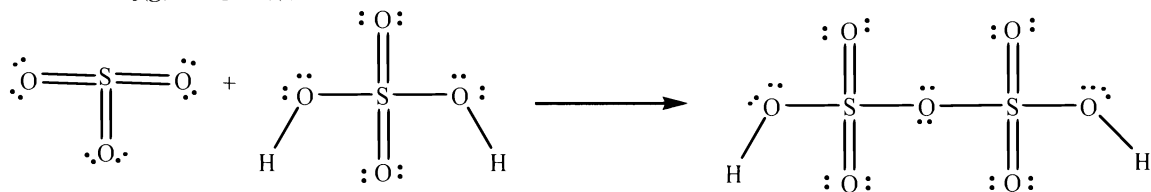
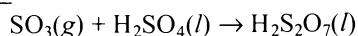
a) The F atoms will occupy the smaller axial positions first. The molecules containing only F or only Cl are nonpolar, as all the polar bonds would cancel. The molecules with one F or one Cl would be polar since there would be no corresponding bond to cancel the polarity. The presence of 2 axial F's means that their polarities will cancel (as would the 3 Cl's) giving a nonpolar molecule. The molecule with 3 F's is also polar.

b)



10.73 Plan: Draw the Lewis structures and look for potential problems. Calculate the heat of reaction from the bond energies.

Solution:



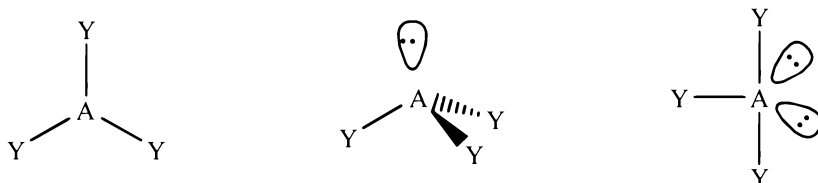
Bonds broken:	5 S=O	5(552 kJ/mol)	Bonds formed:	4 S=O	4(552 kJ/mol)
	2 S-O	2(265 kJ/mol)		4 S-O	4(265 kJ/mol)
	2 O-H	2(467 kJ/mol)		2 O-H	2(467 kJ/mol)
Totals:		4224 kJ			4202 kJ

$$\Delta H = \text{Bonds broken} - \text{Bonds formed}$$

$$= 4224 \text{ kJ} - 4202 \text{ kJ} = \mathbf{22 \text{ kJ}}$$

10.75 Plan: Pick the VSEPR structures for AY_3 substances. Then determine which are polar.

Solution:



(a)

3 groups

(AX_3)

Trigonal planar

(b)

4 groups

(AX_3E)

trigonal pyramidal

(c)

5 groups

(AX_3E_2)

T-shaped

The trigonal planar molecules, such as (a), are nonpolar, so it cannot be AY_3 . Trigonal pyramidal molecules (b) and T-shaped molecules (c) are polar, so either could represent AY_3 .

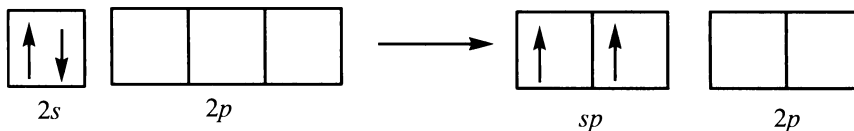
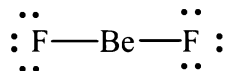
Chapter 11 Theories of Covalent Bonding

FOLLOW-UP PROBLEMS

- 11.1 Plan: Draw a Lewis structure. Determine the number and arrangement of the electron pairs about the central atom. This process leads to the hybridization.

Solution:

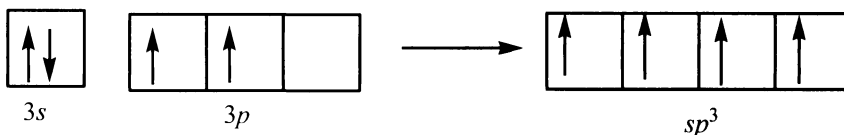
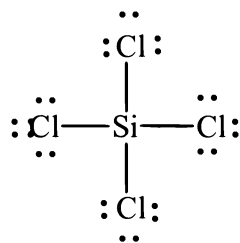
- a) In BeF_2 , Be is surrounded by two electron groups (two single bonds) so hybridization around Be is sp .



Isolated Be atom

Hybridized Be atom

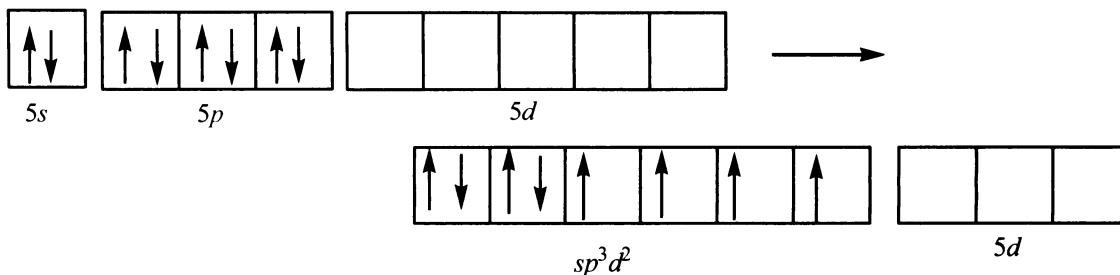
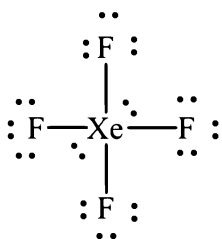
- b) In SiCl_4 , Si is surrounded by four electron groups (four single bonds) so its hybridization is sp^3 .



Isolated Si atom

Hybridized Si atom

- c) In XeF_4 , xenon is surrounded by 6 electron groups (4 bonds and 2 lone pairs) so the hybridization is sp^3d^2 .



Isolated Xe atom

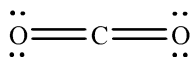
Hybridized Xe atom

- 11.2 Plan: First, determine the Lewis structure for the molecule. Then count the number of electron groups around each atom. Hybridization is sp if there are two groups, sp^2 if there are three groups and sp^3 if there are four groups. No hybridization occurs with only one group of electrons. The bonds are then designated as sigma or pi. A single bond is a sigma bond. A double bond consists of one sigma and one pi bond. A triple bond includes one sigma bond and two pi bonds. Hybridized orbitals overlap head on to form sigma bonds whereas pi bonds form through the sideways overlap of p or d orbitals.

Solution:

a) Hydrogen cyanide has $\text{H}-\text{C}\equiv\text{N}$: as its Lewis structure. The single bond between carbon and hydrogen is a sigma bond formed by the overlap of a hybridized sp orbital on carbon with the $1s$ orbital from hydrogen. Between carbon and nitrogen are three bonds. One is a sigma bond formed by the overlap of a hybridized sp orbital on carbon with a hybridized sp orbital on nitrogen. The other two bonds between carbon and nitrogen are pi bonds formed by the overlap of p orbitals from carbon and nitrogen. One sp orbital on nitrogen is filled with a lone pair of electrons.

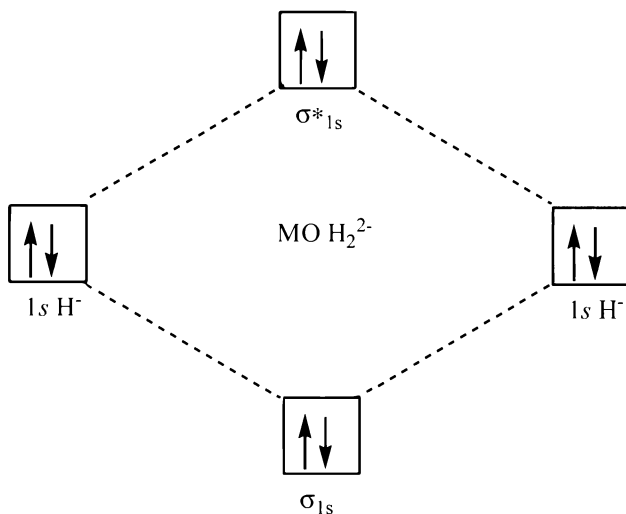
b) The Lewis structure of carbon dioxide, CO_2 , is



Both oxygen atoms are sp^2 hybridized (the O atoms have three electron groups – one double bond and two lone pairs) and form a sigma bond and a pi bond with carbon. The sigma bonds are formed by the overlap of a hybridized sp orbital on carbon with a hybridized sp^2 orbital on oxygen. The pi bonds are formed by the overlap of an oxygen p orbital with a carbon p orbital. Two sp^2 orbitals on each oxygen are filled with a lone pair of electrons.

- 11.3 Plan: Draw the molecular orbital diagram. Determine the bond order from calculation:
 $\text{BO} = 1/2(\# \text{ e}^- \text{ in bonding orbitals} - \# \text{ e}^- \text{ in antibonding orbitals})$. A bond order of zero indicates the molecule will not exist. A bond order greater than zero indicates that the molecule is at least somewhat stable and is likely to exist. H_2^{2-} has 4 electrons (1 from each hydrogen and two from the -2 charge).

Solution:



Configuration for H_2^{2-} is $(\sigma_{1s})^2(\sigma_{1s}^*)^2$. Bond order of H_2^{2-} is $1/2(2 - 2) = 0$. Thus, it is not likely that two H^- ions would combine to form the ion H_2^{2-} .

- 11.4 Plan: To find bond order it is necessary to determine the molecular orbital electron configuration from the total number of electrons. Bond order is calculated from the configuration as $1/2(\# \text{ e}^- \text{ in bonding orbitals} - \# \text{ e}^- \text{ in antibonding orbitals})$.

Solution:

F_2^{2-} : total electrons = $9 + 9 + 2 = 20$

Configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$

Bond order = $1/2(10 - 10) = 0$

F_2^- : total electrons = 9 + 9 + 1 = 19

Configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^1$

Bond order = $1/2(10 - 9) = 0.5$

F_2 : total electrons = 9 + 9 = 18

Configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$

Bond order = $1/2(10 - 8) = 1$

F_2^+ : total electrons = 9 + 9 - 1 = 17

Configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

Bond order = $1/2(10 - 7) = 1.5$

F_2^{2+} : total electrons = 9 + 9 - 2 = 16

Configuration: $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

Bond order = $1/2(10 - 6) = 2$

Bond energy increases as bond order increases: $F_2^{2+} < F_2^+ < F_2 < F_2^-$

Bond length decreases as bond energy increases, so the order of increasing bond length will be opposite that of increasing bond energy.

Increasing bond length: $F_2^{2+} < F_2^+ < F_2 < F_2^-$.

F_2^{2-} will not form a bond, so it has no bond length and is not included in the list.

Check: Since the highest energy orbitals are antibonding orbitals, it makes sense that the bond order increases as electrons are removed from the antibonding orbitals.

END-OF-CHAPTER PROBLEMS

11.1 Table 11.1 describes the types of shapes that form from a given set of hybrid orbitals.

- a) trigonal planar: three electron groups – three hybrid orbitals: sp^2
- b) octahedral: six electron groups – six hybrid orbitals: sp^3d^2
- c) linear: two electron groups – two hybrid orbitals: sp
- d) tetrahedral: four electron groups – four hybrid orbitals: sp^3
- e) trigonal bipyramidal: five electron groups – five hybrid orbitals: sp^3d

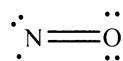
11.3 Carbon and silicon have the same number of valence electrons, but the outer level of electrons is $n = 2$ for carbon and $n = 3$ for silicon. Thus, silicon has $3d$ orbitals in addition to $3s$ and $3p$ orbitals available for bonding in its outer level, to form up to 6 hybrid orbitals, whereas carbon has only $2s$ and $2p$ orbitals available in its outer level to form up to 4 hybrid orbitals.

11.5 The *number* of orbitals remains the same as the number of orbitals before hybridization. The *type* depends on the orbitals mixed.

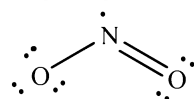
- a) There are six unhybridized orbitals, and therefore **six** hybrid orbitals result. The type is sp^3d^2 .
- b) **Four** sp^3 hybrid orbitals form from three p and one s atomic orbitals.

11.7 To determine hybridization, draw the Lewis structure and count the number of electron groups. Hybridize that number of orbitals.

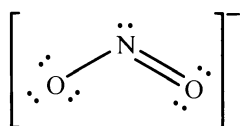
- a) The three electron groups (one double bond, one lone pair and one unpaired electron) around nitrogen require three hybrid orbitals. The hybridization is sp^2 .



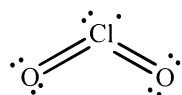
- b) The nitrogen has three electron groups (one single bond, one double bond and one unpaired electron), requiring three hybrid orbitals so hybridization is sp^2 .



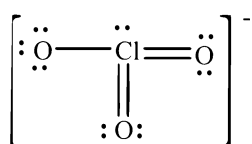
c) The nitrogen has three electron groups (one single bond, one double bond and one lone pair so hybridization is sp^2 .



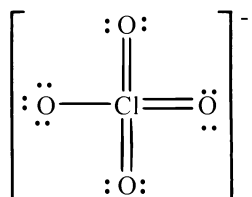
- 11.9 a) sp^3 The Cl has four electron groups (1 lone pair, 1 lone electron, and 2 double bonds) and therefore four hybrid orbitals are required; the hybridization is sp^3 . Note that in ClO_2 , the π bond is formed by the overlap of d -orbitals from chlorine with p -orbitals from oxygen.



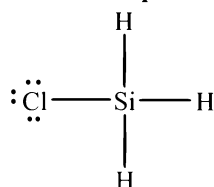
- b) sp^3 The Cl has four electron groups (1 lone pair and 3 bonds) and therefore four hybrid orbitals are required; the hybridization is sp^3 .



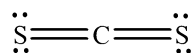
- c) sp^3 The Cl has four electron groups (4 bonds) and therefore four hybrid orbitals are required; the hybridization is sp^3 .



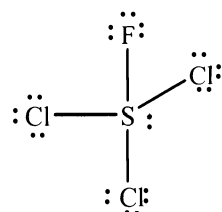
- 11.11 a) Silicon has four electron groups (four bonds) requiring four hybrid orbitals; four sp^3 hybrid orbitals are made from **one s and three p atomic orbitals**.



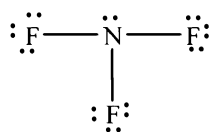
- b) Carbon has two electron groups (two double bonds) requiring two hybrid orbitals; two sp hybrid orbitals are made from **one s and one p orbital**.



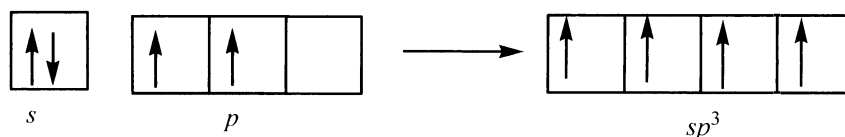
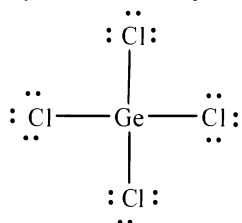
- 11.13 a) Sulfur is surrounded by 5 electron groups (4 bonding pairs, 1 lone pair) requiring five hybrid orbitals; five sp^3d hybrid orbitals are formed from **one s orbital, three p orbitals, and one d orbital**.



b) Nitrogen is surrounded by 4 electron groups (3 bonding pairs, 1 lone pair) requiring four hybrid orbitals; four sp^3 hybrid orbitals are formed from **one s orbital and three p orbitals**.



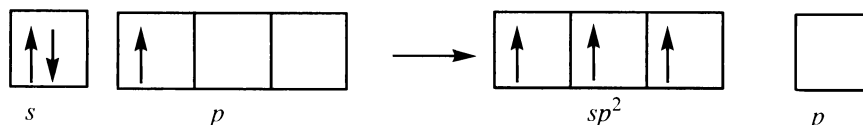
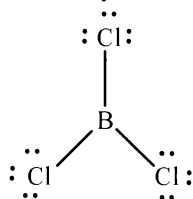
- 11.15 a) Germanium is the central atom in GeCl_4 . Ge has four electron groups (four bonds), requiring four hybrid orbitals. Hybridization is sp^3 around Ge.



Isolated Ge atom

Hybridized Ge atom

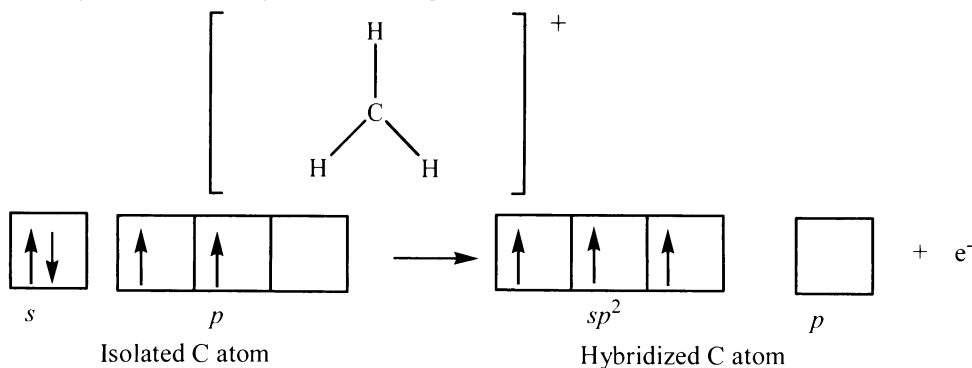
- c) Boron is the central atom in BCl_3 . B has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is sp^2 around B.



Isolated B atom

Hybridized B atom

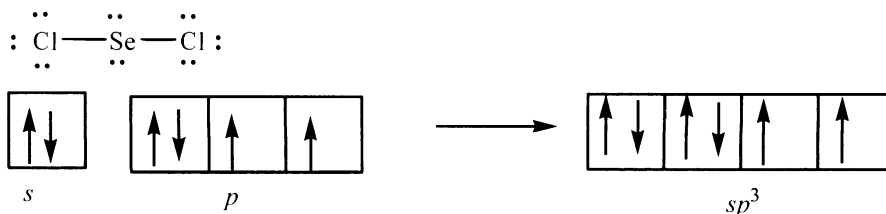
- d) Carbon is the central atom in CH_3^+ . C has three electron groups (three bonds), requiring three hybrid orbitals. Hybridization is sp^2 around C.



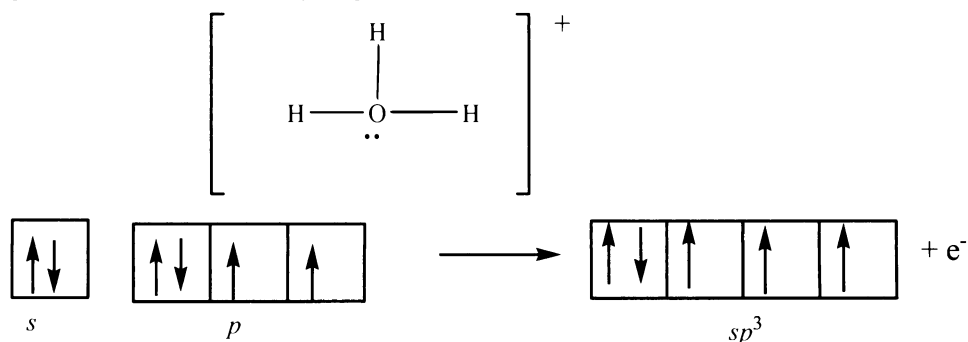
Isolated C atom

Hybridized C atom

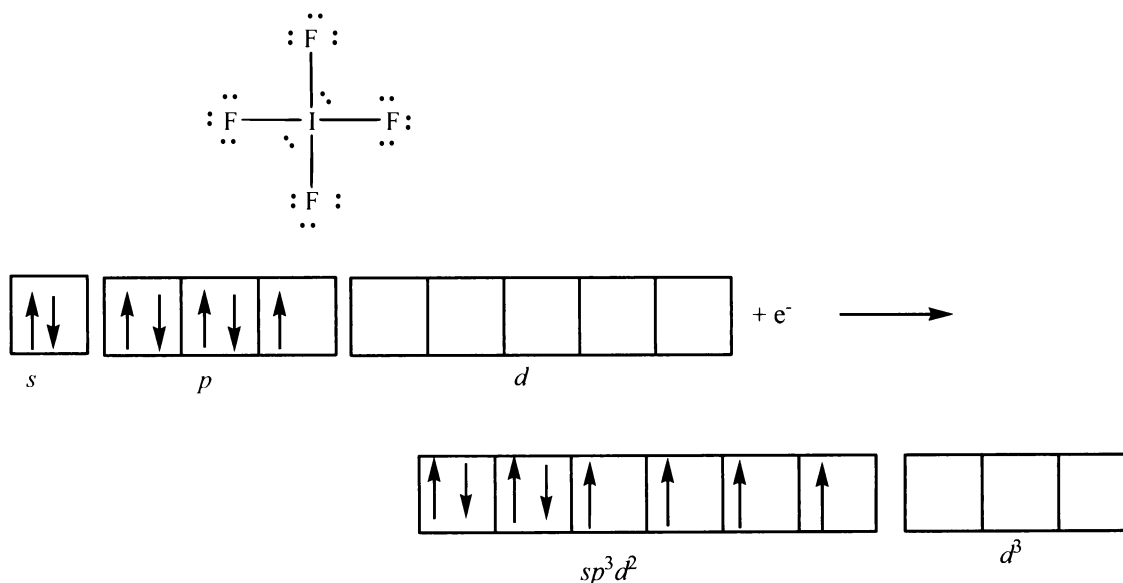
- 11.17 a) In SeCl_2 , Se is the central atom and has four electron groups (two single bonds and two lone pairs), requiring four hybrid orbitals. Se is sp^3 hybridized. Two sp^3 orbitals are filled with lone electron pairs and two sp^3 orbitals bond with the chlorine atoms.



- b) In H_3O^+ , O is the central atom and has four electron groups (three single bonds and one lone pair), requiring four hybrid orbitals. O is sp^3 hybridized. One sp^3 orbital is filled with a lone electron pair and three sp^3 orbitals bond with the hydrogen atoms.

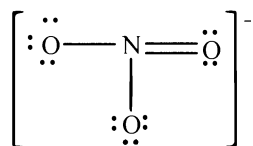


- c) I is the central atom in IF_4^- with 6 electron groups (four single bonds and two lone pairs) surrounding it. Six hybrid orbitals are required and I has sp^3d^2 hybrid orbitals. The sp^3d^2 hybrid orbitals are composed of one *s* orbital, three *p* orbitals, and two *d* orbitals. Two sp^3d^2 orbitals are filled with a lone pair and four sp^3d^2 orbitals bond with the fluorine atoms.

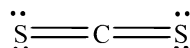


- 11.20 a) **False**, a double bond is one sigma and one pi bond.
 b) **False**, a triple bond consists of one sigma (σ) and two pi (π) bonds.
 c) **True**
 d) **True**
 e) **False**, a π bond consists of one pair of electrons; it occurs after a σ bond has been previously formed.
 f) **False**, end-to-end overlap results in a bond with electron density along the bond axis.

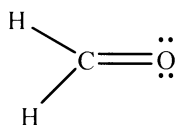
- 11.21 a) Nitrogen is the central atom in NO_3^- . Nitrogen has 3 surrounding electron groups (two single bonds and one double bond), so it is sp^2 hybridized. Nitrogen forms **three σ bonds** (one each for the N–O bonds) and **one π bond** (part of the N=O double bond).



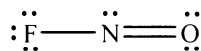
- b) Carbon is the central atom in CS_2 . Carbon has 2 surrounding electron groups (two double bonds), so it is sp hybridized. Carbon forms **two σ bonds** (one each for the C–S bonds) and **two π bonds** (part of the two C=S double bonds).



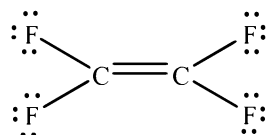
- c) Carbon is the central atom in CH_2O . Carbon has 3 surrounding electron groups (two single bonds and one double bond), so it is sp^2 hybridized. Carbon forms **three σ bonds** (one each for the two C–H bonds and one C–O bond) and **one π bond** (part of the C=O double bond).



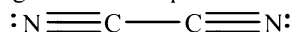
- 11.23 a) Examine the Lewis structure. Three electron groups (one lone pair, one single bond and one double bond) surround the central N atom. Hybridization is sp^2 around nitrogen. One sigma bond exists between F and N, and one sigma and one pi bond exists between N and O. Nitrogen participates in a total of **2 σ and 1 π bonds**.



- b) Examine the Lewis structure. Each carbon has three electron groups (two single bonds and one double bond) with sp^2 hybridization. The bonds between C and F are sigma bonds. The C–C bond consists of one sigma and one pi bond. Each carbon participates in a total of **3 σ and 1 π bonds**.



- c) Examine the Lewis structure. Each carbon has two electron groups (1 single bond and one triple bond) and is sp hybridized with a sigma bond between the two carbons and a sigma and two pi bonds comprising each C–N triple bond. Each carbon participates in a total of **2 σ and 2 π bonds**.

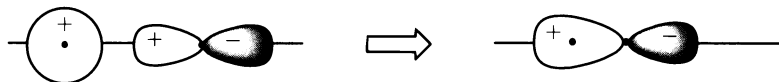


- 11.25 Four molecular orbitals form from the four p atomic orbitals. In forming molecular orbitals, the total number of molecular orbitals must equal the number of atomic orbitals. Two of the four molecular orbitals formed are bonding orbitals and two are antibonding.
- 11.27 a) Bonding MO's have lower energy than antibonding MO's. The bonding MO's lower energy, even lower than its constituent atomic orbitals, accounts for the stability of a molecule in relation to its individual atoms. However, the sum of energy of the MO's must equal the sum of energy of the AO's.
- b) The node is the region of an orbital where the probability of finding the electron is zero, so the nodal plane is the plane that bisects the node perpendicular to the bond axis. According to Figure 11.13A, there is no node along the bond axis (probability is positive between the two nuclei) for the bonding MO. The antibonding MO does have a nodal plane, shown as "waves cancel" on Figure 11.13B.
- c) The bonding MO has higher electron density between nuclei than the antibonding MO.

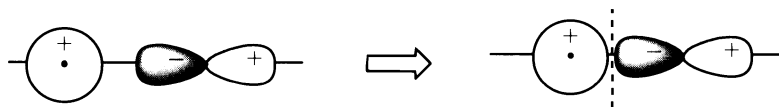
- 11.29 a) **Two** electrons are required to fill a σ -bonding molecular orbital. Each molecular orbital requires two electrons.
 b) **Two** electrons are required to fill a π -antibonding molecular orbital. There are two π -antibonding orbitals, each holding a maximum of two electrons.
 c) **Four** electrons are required to fill the two σ molecular orbitals (two electrons to fill the σ -bonding and two to fill the σ -antibonding) formed from two $1s$ atomic orbitals.

11.31 The horizontal line in all cases represents the bond axis.

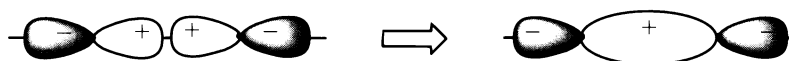
a) Bonding $s + p$



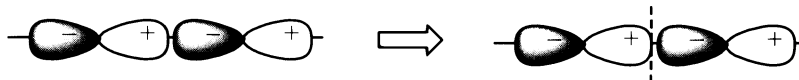
Antibonding $s - p$



b) Bonding $p + p$



Antibonding $p - p$



- 11.33 a) The molecular orbital configuration for Be_2^+ with a total of 7 electrons is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$ and bond order = $1/2(4 - 3) = 1/2$. With a bond order of $1/2$ the Be_2^+ ion will be **stable**. (Bond order = $1/2(\text{number of electrons in bonding MO} - \text{number of electrons in antibonding MO})$)
 b) No, the ion has one unpaired electron in the σ_{2s}^* MO, so it is **paramagnetic**, not diamagnetic.
 c) Valence electrons would be those in the molecular orbitals at the $n = 2$ level, so the valence electron configuration is $(\sigma_{2s})^2((\sigma_{2s}^*)^1)$.

11.35 The sequence of MO's for C_2 is shown in Figure 11.19 (the $(\sigma_{1s})^2$ and $(\sigma_{1s}^*)^2$ MO's are not shown for convenience). For each species, determine the total number of electrons, the valence molecular orbital electron configuration and bond order. Bond order = $1/2(\text{number of electrons in bonding MO} - \text{number of electrons in antibonding MO})$

C_2^- Total valence electrons = $4 + 4 + 1 = 9$

Valence configuration: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$

Bond order = $1/2(7 - 2) = 2.5$

C_2 Total valence electrons = $4 + 4 = 8$

Valence configuration: $(\sigma_{2s})^2((\sigma_{2s}^*)^2)(\pi_{2p})^4$

Bond order = $1/2(6 - 2) = 2$

C_2^+ Total valence electrons = $4 + 4 - 1 = 7$

Valence configuration: $(\sigma_{2s})^2((\sigma_{2s}^*)^2)(\pi_{2p})^3$

Bond order = $1/2(5 - 2) = 1.5$

a) Bond energy increases as bond order increases: $\text{C}_2^+ < \text{C}_2 < \text{C}_2^-$

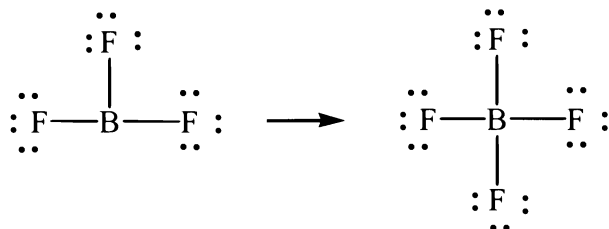
b) Bond length decreases as bond energy increases, so the order of increasing bond length will be opposite that of increasing bond energy. Increasing bond length: $\text{C}_2^- < \text{C}_2 < \text{C}_2^+$

- 11.39 a) Each of the six C atoms in the ring has three electron groups (two single bonds and a double bond) and has sp^2 hybridization; all of the other C atoms have four electron groups (four single bonds) and have sp^3 hybridization; all of the O atoms have four electron groups (two single bonds and two lone pairs) and have sp^3 hybridization; the N atom has four electron groups (three single bonds and a lone pair) and has sp^3 hybridization.
 b) Each of the single bonds is a sigma bond; each of the double bonds has one sigma bond for a total of **26 sigma bonds**.

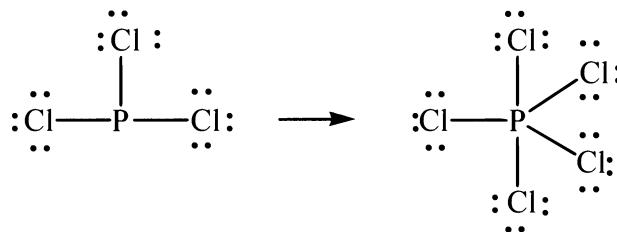
c) The ring has three double bonds each of which is composed of one sigma bond and one pi bond; so there are three pi bonds each with 2 electrons for a total of **6 pi electrons**.

- 11.41 a) Every single bond is a sigma bond. There is one sigma bond in each double bond as well. There are **17 σ bonds** in isoniazid. Every atom-to-atom connection contains a σ bond.
 b) All carbons have three surrounding electron groups (two single and one double bond), so their hybridization is sp^2 . The ring N also has three surrounding electron groups (one single bond, one double bond and one lone pair), so its hybridization is also sp^2 . The other two N's have four surrounding electron groups (three single bonds and one lone pair) and are sp^3 hybridized.

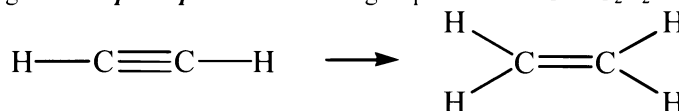
- 11.43 a) B changes from $sp^2 \rightarrow sp^3$. Boron in BF_3 has three electron groups with sp^2 hybridization. In BF_4^- , 4 electron groups surround B with sp^3 hybridization.



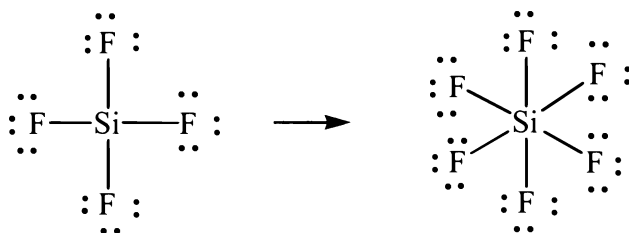
- b) P changes from $sp^3 \rightarrow sp^3d$. Phosphorus in PCl_3 is surrounded by 4 electron groups (3 bonds to Cl and 1 lone pair) for sp^3 hybridization. In PCl_5 , phosphorus is surrounded by 5 electron groups for sp^3d hybridization.



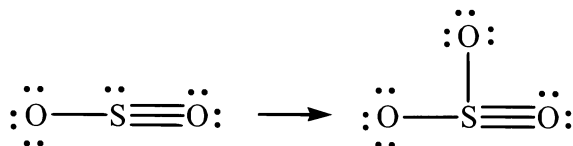
- c) C changes from $sp \rightarrow sp^2$. Two electron groups surround C in C_2H_2 and 3 electron groups surround C in C_2H_4 .



- d) Si changes from $sp^3 \rightarrow sp^3d^2$. Four electron groups surround Si in SiF_4 and 6 electron groups surround Si in SiF_6^{2-} .



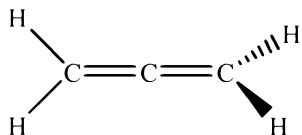
- e) **No change**, S in SO_2 is surrounded by three electron groups (one single bond, one double bond and one lone pair) and in SO_3 is surrounded by 3 electron groups (two single bonds and one double bond); both have sp^2 hybridization.



11.44 Count the electron groups, both bonds and lone pairs, about each atom. (Do not forget to count double bonds only once.)

P (3 single bonds and one double bond)	AX ₄	tetrahedral	<i>sp</i>³
N (3 single bonds and one lone pair)	AX ₃ E	trigonal pyramid	<i>sp</i>³
C ₁ and C ₂ (4 single bonds)	AX ₄	tetrahedral	<i>sp</i>³
C ₃ (2 single bonds and one double bond)	AX ₃	trigonal planar	<i>sp</i>²

11.48



The central C is *sp* hybridized, and the other two C's are *sp*².

11.53 a) The 6 carbons in the ring each have three surrounding electron groups (two single bonds and one double bond) with *sp*² hybrid orbitals. The two carbons participating in the C=O bond are also *sp*² hybridized. The single carbon in the -CH₃ group has 4 electron groups (four single bonds) and is *sp*³ hybridized. There are only 2 central oxygen atoms, one in a C-O-H configuration and the other in a C-O-C configuration. Both of these atoms have 4 surrounding electron groups (two single bonds and two lone pairs) and are *sp*³ hybridized.

Summary: C in -CH₃: *sp*³, all other C atoms (8 total): *sp*², O (2 total): *sp*³

b) The **two** C=O bonds are localized; the double bonds on the ring are delocalized as in benzene.

c) Each carbon with three surrounding groups has *sp*² hybridization and trigonal planar shape; therefore, **8** carbons have this shape. Only **1** carbon in the CH₃ group has four surrounding groups with *sp*³ hybridization and tetrahedral shape.

Chapter 12 Intermolecular Forces: Liquids, Solids, and Phase Changes

FOLLOW-UP PROBLEMS

- 12.1 **Plan:** The variables ΔH_{vap} , P_1 , T_1 , and T_2 are given, so substitute them into Equation 12.1 and solve for P_2 . Convert both temperatures from $^{\circ}\text{C}$ to K. Convert ΔH_{vap} to J so that the units cancel with R.

Solution:

$$T_1 = 34.1 + 273.15 = 307.2 \text{ K}$$

$$T_2 = 85.5 + 273.15 = 358.6 \text{ K}$$

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_2}{40.1 \text{ torr}} = \frac{-40.7 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{358.6 \text{ K}} - \frac{1}{307.2 \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 2.28410 \text{ (unrounded)}$$

$$\frac{P_2}{40.1 \text{ torr}} = 9.81689 \text{ (unrounded)}$$

$$P_2 = (9.81689)(40.1 \text{ torr}) = 393.657 = \mathbf{394 \text{ torr}}$$

Note: Watch significant figures when subtracting numbers:

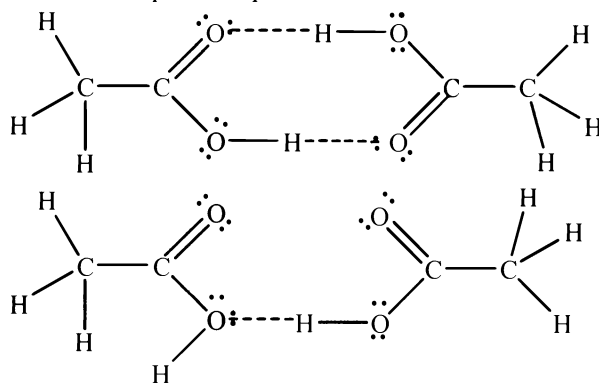
$$1/358.6 = 0.002789 \text{ and } 1/307.2 = 0.003255$$

$$0.002789 - 0.003255 = 0.000466$$

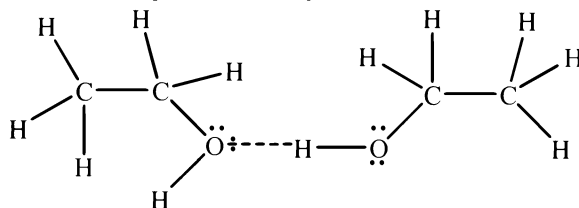
In the subtraction, the number of significant figures decreased from 4 to 3.

Check: The temperature increased, so the vapor pressure should be higher.

- 12.2 a) The $-\text{A}:\cdots\text{H}-\text{B}-$ sequence is present in both structures below:



- b) The $-\text{A}:\cdots\text{H}-\text{B}-$ sequence can only be achieved in one arrangement.



The hydrogens attached to the carbons cannot form H bonds because they do not satisfy the $-\text{A}:\cdots\text{H}-\text{B}-$ sequence.

- c) Hydrogen bonding is not possible because there are no O–H, N–H, or F–H bonds.

- 12.3 a) Both CH_3Br and CH_3F are polar molecules that experience dipole-dipole and dispersion intermolecular interactions. Because CH_3Br ($\mathcal{M} = 94.9 \text{ g/mol}$) is ~ 3 times larger than CH_3F ($\mathcal{M} = 34.0 \text{ g/mol}$), dispersion forces result in a higher boiling point (BP) for **CH_3Br** .
 b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, n-propanol, forms hydrogen bonds and has dispersion forces whereas $\text{CH}_3\text{CH}_2\text{OCH}_3$, ethyl methyl ether, has only dipole-dipole and dispersion attractions. **$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$** has the higher BP.
 c) Both C_2H_6 and C_3H_8 are nonpolar and experience dispersion forces only. **C_3H_8** , with the higher molar mass, experiences greater dispersion forces and has the higher boiling point.
- 12.4 Plan: The density of Fe is 7.874 g/cm^3 , but Fe atoms occupy only 68% of the volume in a body-centered cubic structure. Calculate the volume/mole Fe ratio, and multiply by 0.68 to determine the volume/mol Fe atoms ratio. Dividing by the volume of a single Fe will yield the units of atoms/mol, which is Avogadro's number.
Solution:
 Molar volume of Fe = $(55.85 \text{ g/mol}) / (7.874 \text{ g/cm}^3) = 7.09296 \text{ cm}^3/\text{mol Fe}$ (unrounded)
 The volume of just the atoms (not including the empty spaces between atoms) is:
 Volume/mole Fe atoms = $(7.09296 \text{ cm}^3/\text{mol Fe})(68\% / 100\%) = 4.82321 \text{ cm}^3/\text{mol Fe atoms}$ (unrounded)
 The number of atoms in one mole of Fe is obtained by dividing by the volume of one Fe atom:
 Atoms/mol = $(4.82321 \text{ cm}^3/\text{mol Fe atoms}) (1 \text{ Fe atom} / 8.38 \times 10^{-24} \text{ cm}^3)$
 $= 5.7556 \times 10^{23} = \mathbf{5.8 \times 10^{23} \text{ atoms/mol}}$
Check: The calculated value is within 4.4% error of the true value,
 $6.02 \times 10^{23} \text{ atoms/mol}$ (% error = $(\text{true} - \text{measured}) \div \text{true}$).

END-OF-CHAPTER PROBLEMS

- 12.1 The energy of attraction is a *potential* energy and denoted E_p . The energy of motion is *kinetic* energy and denoted E_k . The relative strength of E_p vs. E_k determines the phase of the substance. In the gas phase, $E_p \ll E_k$ because the gas particles experience little attraction for one another and the particles are moving very fast. In the solid phase, $E_p \gg E_k$ because the particles are very close together and are only vibrating in place.
- Two properties that differ between a gas and a solid are the volume and density. The volume of a gas expands to fill the container it is in while the volume of a solid is constant no matter what container holds the solid. Density of a gas is much less than the density of a solid. The density of a gas also varies significantly with temperature and pressure changes. The density of a solid is only slightly altered by changes in temperature and pressure. Compressibility and ability to flow are other properties that differ between gases and solids.
- 12.4 a) Heat of fusion refers to the change between the solid and the liquid states and heat of vaporization refers to the change between liquid and gas states. In the change from solid to liquid, the kinetic energy of the molecules must increase only enough partially to offset the intermolecular attractions between molecules. In the change from liquid to gas, the kinetic energy of the molecules must increase enough to overcome the intermolecular forces. The energy to overcome the intermolecular forces for the molecules to move freely in the gaseous state is much greater than the amount of energy needed to allow the molecules to move more easily past each other but still stay very close together.
 b) The net force holding molecules together in the solid state is greater than that in the liquid state. Thus, to change solid molecules to gaseous molecules in sublimation requires more energy than to change liquid molecules to gaseous molecules in vaporization.
 c) At a given temperature and pressure, the magnitude of ΔH_{vap} is the same as the magnitude of ΔH_{cond} . The only difference is in the sign: $\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$.
- 12.5 a) **Condensation** The water vapor in the air condenses to liquid when the temperature drops during the night.
 b) **Fusion** (melting) Solid ice melts to liquid water.
 c) **Evaporation** Liquid water on clothes evaporates to water vapor.
- 12.7 The propane gas molecules slow down as the gas is compressed. Therefore, much of the **kinetic energy** lost by the propane molecules is released to the surroundings upon liquefaction.

12.11 In closed containers, two processes, evaporation and condensation occur simultaneously. Initially there are few molecules in the vapor phase, so more liquid molecules evaporate than gas molecules condense. Thus, the numbers of molecules in the gas phase increases causing the vapor pressure of hexane to increase. Eventually, the number of molecules in the gas phase reaches a maximum where the number of liquid molecules evaporating equals the number of gas molecules condensing. In other words, the evaporation rate equals the condensation rate. At this point, there is no further change in the vapor pressure.

12.14 The total heat required is the sum of three processes:

1) Warming the ice from -5.00°C to 0.00°C

$$q_1 = Cm\Delta T = (2.09 \text{ J/g}^{\circ}\text{C}) (12.00 \text{ g}) [0.0 - (-5.00)]^{\circ}\text{C} = 125.4 \text{ J (unrounded)}$$

2) Phase change of ice at 0.00°C to water at 0.00°C

$$q_2 = n\Delta H_{\text{fus}} = (12.0 \text{ g}) \left(\frac{1 \text{ mol}}{18.02 \text{ g}} \right) \left(\frac{6.02 \text{ kJ}}{\text{mol}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 4008.879 \text{ J (unrounded)}$$

3) Warming the liquid from 0.00°C to 0.500°C

$$q_3 = Cm\Delta T = (4.21 \text{ J/g}^{\circ}\text{C}) (12.00 \text{ g}) [0.500 - (0.0)]^{\circ}\text{C} = 25.26 \text{ J (unrounded)}$$

The three heats are positive because each process takes heat from the surroundings (endothermic). The phase change requires much more energy than the two temperature change processes. The total heat is $q_1 + q_2 + q_3 = (125.4 \text{ J} + 4008.879 \text{ J} + 25.26 \text{ J}) = 4160 \text{ J} = 4159.539 = \mathbf{4.16 \times 10^3 \text{ J}}$.

12.16 The Clausius-Clapeyron equation gives the relationship between vapor pressure and temperature. Boiling point is defined as the temperature when vapor pressure of liquid equals atmospheric pressure, usually assumed to be exactly 1 atm. So, the number of significant figures in the pressure of 1 atm given is not one, but is unlimited since it is an exact number. In the calculation below, 1.00 atm is used to emphasize the additional significant figures.

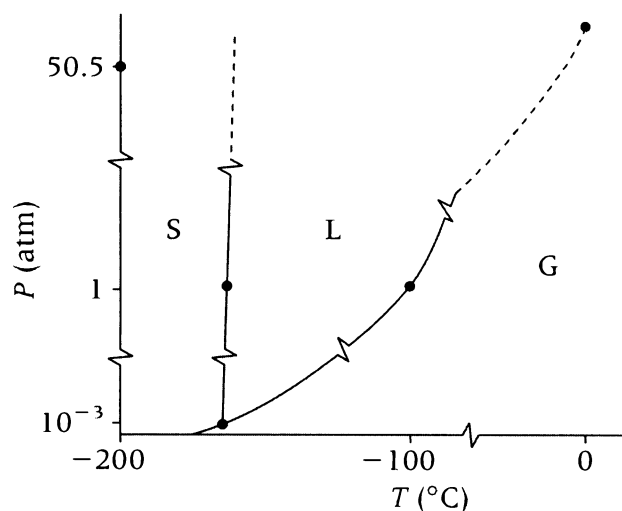
$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 1.00 \text{ atm}; \quad T_1 = 122^{\circ}\text{C} + 273 = 395 \text{ K};$$

$$T_2 = 109^{\circ}\text{C} + 273 = 382 \text{ K}; \quad P_2 = ?$$

$$\ln \frac{P_2}{1.00 \text{ atm}} = \frac{-35.5 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{382 \text{ K}} - \frac{1}{395 \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -0.3678758 \text{ (unrounded)}$$

$$\frac{P_2}{1.00 \text{ atm}} = 0.692203 \text{ (unrounded)}$$

$$P_2 = (0.692203) (1.00 \text{ atm}) = 0.692203 = \mathbf{0.692 \text{ atm}}$$



The pressure scale is distorted to represent the large range in pressures given in the problem, so the liquid–solid curve looks different from the one shown in Figure 12.8. The important features of the graph include the distinction between the gas, liquid and solid states, and the melting point T , which is located directly above the critical T . Solid ethylene is denser than liquid ethylene since the solid–liquid line slopes to the right with increasing pressure.

- 12.20 This problem is also an application of the Clausius-Clapeyron equation. Convert the temperatures from $^{\circ}\text{C}$ to K and ΔH_{vap} from kJ/mol to J/mol to allow cancellation with the units in R.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 2.3 \text{ atm}; \quad T_1 = 25.0^{\circ}\text{C} + 273 = 298 \text{ K};$$

$$T_2 = 150^{\circ}\text{C} + 273 = 423 \text{ K}; \quad P_2 = ?$$

$$\ln \frac{P_2}{2.3 \text{ atm}} = \frac{-24.3 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{423 \text{ K}} - \frac{1}{298 \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 2.89834$$

$$\frac{P_2}{2.3 \text{ atm}} = 18.14404$$

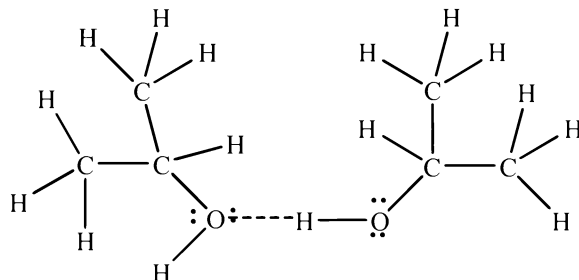
$$P_2 = (18.14404) (2.3 \text{ atm}) = 41.731 = \mathbf{42 \text{ atm}}$$

- 12.24 To form hydrogen bonds, the atom bonded to hydrogen must have two characteristics: small size and high electronegativity (so that the atom has a very high electron density). With this high electron density, the attraction for a hydrogen on another molecule is very strong. Selenium is much larger than oxygen (atomic radius of 119 pm vs. 73 pm) and less electronegative than oxygen (2.4 for Se and 3.5 for O) resulting in an electron density on Se in H_2Se that is too small to form hydrogen bonds.
- 12.25 All particles (atoms and molecules) exhibit dispersion forces, but these are the weakest of intermolecular forces. The dipole-dipole forces in polar molecules dominate the dispersion forces.
- 12.28
- Hydrogen bonding** will be the strongest force between methanol molecules since they contain O–H bonds. Dipole-dipole and dispersion forces also exist.
 - Dispersion forces** are the only forces between nonpolar carbon tetrachloride molecules and, thus, are the strongest forces.
 - Dispersion forces** are the only forces between nonpolar chlorine molecules and, thus, are the strongest forces.

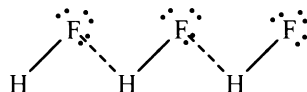
- 12.30 a) **Dipole-dipole** interactions will be the strongest forces between methyl bromide molecules because the C–Br bond has a dipole moment.
 b) **Dispersion** forces dominate because CH_3CH_3 (ethane) is a symmetrical nonpolar molecule.
 c) **Hydrogen bonding** dominates because hydrogen is bonded to nitrogen, which is one of the 3 atoms (N, O, or F) that participate in hydrogen bonding.

12.32 Hydrogen bonds are formed when a hydrogen atom is bonded to N, O, or F.

- a) The presence of an OH group leads to the formation of hydrogen bonds in $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. There are no hydrogen bonds in CH_3SCH_3 .



- b) The presence of H attached to F in HF leads to the formation of hydrogen bonds. There are no hydrogen bonds in HBr.



12.34 Polarizability increases down a group and decreases from left to right because as atomic size increases, polarizability increases.

- a) **Iodide ion** has greater polarizability than the bromide ion because the iodide ion is larger. The electrons can be polarized over a larger volume in a larger atom or ion.
 b) **Ethene ($\text{CH}_2=\text{CH}_2$)** has greater polarizability than ethane (CH_3CH_3) because π orbitals are more easily polarized than σ orbitals.
 c) **H_2Se** has greater polarizability than water because the selenium atom is larger than the oxygen atom.

12.36 Weaker attractive forces result in a higher vapor pressure because the molecules have a smaller energy barrier in order to escape the liquid and go into the gas phase.

- a) **C_2H_6** C_2H_6 is a smaller molecule exhibiting weaker dispersion forces than C_4H_{10} .
 b) **$\text{CH}_3\text{CH}_2\text{F}$** $\text{CH}_3\text{CH}_2\text{F}$ has no H–F bonds (F is bonded to C, not to H), so it only exhibits dipole-dipole forces, which are weaker than the hydrogen bonding in $\text{CH}_3\text{CH}_2\text{OH}$.
 c) **PH_3** PH_3 has weaker intermolecular forces (dipole-dipole) than NH_3 (hydrogen bonding).

12.38 The stronger the intermolecular forces, the higher the boiling point.

- a) **LiCl** would have a higher boiling point than HCl because the ions in lithium chloride are held together by ionic forces, which are stronger than the dipole-dipole intermolecular forces between hydrogen chloride molecules in the liquid phase.
 b) **Ammonia, NH_3** , would have a higher boiling point than phosphine (PH_3) because the intermolecular forces in ammonia are stronger than those in phosphine are. Hydrogen bonding exists between ammonia molecules but weaker dipole-dipole forces hold phosphine molecules together.
 c) **Iodine** would have a higher boiling point than xenon. Both are nonpolar with dispersion forces, but the forces between iodine molecules would be stronger than between xenon atoms are since the iodine molecules are more polarizable because of their larger size.

- 12.40 The molecule in the pair with the weaker intermolecular attractive forces will have the lower boiling point.
 a) **C₄H₈**, the cyclic molecule, cyclobutane, has less surface area exposed, so its dispersion forces are less than the straight chain molecule, C₄H₁₀.
 b) **PBr₃**, the dipole-dipole forces of phosphorous tribromide are weaker than the ionic forces of sodium bromide.
 c) **HBr**, the dipole-dipole forces of hydrogen bromide are weaker than the hydrogen bonding forces of water.
- 12.45 The shape of the drop depends upon the competing cohesive forces (attraction of molecules within the drop itself) and adhesive forces (attraction between molecules in the drop and the molecules of the waxed floor). If the cohesive forces are strong and outweigh the adhesive forces, the drop will be as spherical as gravity will allow. If, on the other hand, the adhesive forces are significant, the drop will spread out. Both water (hydrogen bonding) and mercury (metallic bonds) have strong cohesive forces, whereas cohesive forces in oil (dispersion) are relatively weak. Figure 12.19 explains the difference between these forces when *glass*, not *wax*, is used. Neither water nor mercury will have significant adhesive forces to the nonpolar wax molecules, so these drops will remain nearly spherical. The adhesive forces between the oil and wax can compete with the weak, cohesive forces of the oil (dispersion) and so the oil drop spreads out.
- 12.47 The stronger the intermolecular force, the greater the surface tension. All three molecules exhibit hydrogen bonding, but the extent of hydrogen bonding increases with the number of O–H bonds present in each molecule. Molecule b) with 3 O–H groups can form more hydrogen bonds than molecule c) with 2 O–H groups, which in turn can form more hydrogen bonds than molecule a) with only 1 O–H group.
CH₃CH₂CH₂OH < HOCH₂CH₂OH < HOCH₂CH(OH)CH₂OH
 The greater the number of hydrogen bonds, the greater the energy requirements.
- 12.51 Water is a good solvent for polar and ionic substances and a poor solvent for nonpolar substances. Water is a polar molecule and dissolves polar substances because their intermolecular forces are of similar strength. Water is also able to dissolve ionic compounds and keep ions separated in solution through ion-dipole interactions. Nonpolar substances will not be very soluble in water since their dispersion forces are much weaker than the hydrogen bonds in water. A solute whose intermolecular attraction to a solvent molecule is less than the attraction between two solvent molecules will not dissolve because its attraction cannot replace the attraction between solvent molecules.
- 12.52 A single water molecule can form 4 hydrogen bonds. The two hydrogen atoms form a hydrogen bond each to oxygen atoms on neighboring water molecules. The two lone pairs on the oxygen atom form hydrogen bonds with hydrogen atoms on neighboring molecules.
- 12.54 Water exhibits strong capillary action, which allows it to be easily absorbed by the plant's roots and transported to the leaves.
- 12.60 A solid metal is a shiny solid that conducts heat, is malleable, and melts at high temperatures. (Other answers include relatively high boiling point and good conductor of electricity.)
- 12.63 The energy gap is the energy difference between the highest filled energy level (valence band) and the lowest unfilled energy level (conduction band). In conductors and superconductors, the energy gap is zero because the valence band overlaps the conduction band. In semiconductors, the energy gap is small but greater than zero. In insulators, the energy gap is large and thus insulators do not conduct electricity.
- 12.64 The simple cubic structure unit cell contains 1 atom since the atoms at the 8 corners are shared by eight cells for a total of 8 atoms x 1/8 atom per cell = 1 atom.; the body-centered cell also has an atom in the center, for a total of 2 atoms; the face-centered cell has 6 atoms in the faces which are shared by two cells: 6 atoms x 1/2 atom per cell = 3 atoms plus another atom from the 8 corners for a total of 4 atoms.
 a) Ni is **face-centered cubic** since there are 4 atoms/unit cell.
 b) Cr is **body-centered cubic** since there are 2 atoms/unit cell.
 c) Ca is **face-centered cubic** since there are 4 atoms/unit cell.

- 12.66 a) Tin is a metal (malleable, excellent electrical conductor) that forms **metallic** bonds.
 b) Silicon is in the same group as carbon, so it exhibits similar bonding properties. Since diamond and graphite are both **network covalent** solids, it makes sense that Si forms the same type of bonds.
 c) Xenon, Xe, is a noble gas and is monatomic. Xe is an **atomic** solid.
- 12.68 Figure P12.68 shows the face-centered cubic array of zinc blende, ZnS. Both ZnS and ZnO have a 1:1 ion ratio, so the ZnO unit cell will also contain **four Zn²⁺ ions**.
- 12.70 a) To determine the number of Zn²⁺ ions and Se²⁻ ions in each unit cell count the number of ions at the corners, faces, and center of unit cell. Looking at selenide ions, there is one ion at each corner and one ion on each face. The total number of selenide ions is 1/8 (8 corner ions) + 1/2 (6 face ions) = **4 Se²⁻ ions**. There are also **4 Zn²⁺ ions** due to the 1:1 ratio of Se ions to Zn ions.
 b) Mass of unit cell = (4 x mass of Zn atom) + (4 x mass of Se atom)

$$= (4 \times 65.41 \text{ amu}) + (4 \times 78.96 \text{ amu}) = \mathbf{577.48 \text{ amu}}$$

 c) Given the mass of one unit cell and the ratio of mass to volume (density) divide the mass, converted to grams (conversion factor is 1 amu = 1.66054 x 10⁻²⁴ g), by the density to find the volume of the unit cell.

$$\text{Volume} = \left(\frac{\text{cm}^3}{5.42 \text{ g}} \right) \left(\frac{1.66054 \times 10^{-24} \text{ g}}{1 \text{ amu}} \right) (577.48 \text{ amu})$$

$$= 1.76924 \times 10^{-22} = \mathbf{1.77 \times 10^{-22} \text{ cm}^3}$$

 d) The volume of a cube equals (length of side)³.

$$\text{Side} = \sqrt[3]{1.76924 \times 10^{-22} \text{ cm}^3} = 5.6139 \times 10^{-8} = \mathbf{5.61 \times 10^{-8} \text{ cm}}$$
- 12.72 To classify a substance according to its electrical conductivity, first locate it on the periodic table as a metal, metalloid, or nonmetal. In general, metals are conductors, metalloids are semiconductors, and nonmetals are insulators.
 a) Phosphorous is a nonmetal and an **insulator**.
 b) Mercury is a metal and a **conductor**.
 c) Germanium is a metalloid in Group 4A(14) and is beneath carbon and silicon in the periodic table. Pure germanium crystals are **semiconductors** and are used to detect gamma rays emitted by radioactive materials. Germanium can also be doped with phosphorous (similar to the doping of silicon) to form an n-type semiconductor or be doped with lithium to form a p-type semiconductor.
- 12.73 First, classify the substance as an insulator, conductor, or semiconductor. The electrical conductivity of conductors decreases with increasing temperature, whereas that of semiconductors increases with temperature. Temperature increases have little impact on the electrical conductivity of insulators.
 a) Antimony, Sb, is a metalloid, so it is a semiconductor. Its electrical conductivity **increases** as the temperature increases.
 b) Tellurium, Te, is a metalloid, so it is a semiconductor. Its electrical conductivity **increases** as temperature increases.
 c) Bismuth, Bi, is a metal, so it is a conductor. Its electrical conductivity **decreases** as temperature increases.
- 12.77 The Clausius-Clapeyron equation can be solved for the temperature that will give a vapor pressure of 5.0x10⁻⁵ torr.
- $$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad P_1 = 1.20 \times 10^{-3} \text{ torr}; \quad T_1 = 20.0^\circ\text{C} + 273 = 293 \text{ K};$$
- $$P_2 = 5.0 \times 10^{-5} \text{ torr}; \quad T_2 = ?$$
- $$\ln \frac{5.0 \times 10^{-5} \text{ torr}}{1.20 \times 10^{-3} \text{ torr}} = \frac{-59.1 \frac{\text{kJ}}{\text{mol}}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{T_2} - \frac{1}{293 \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

$$-3.17805 = -7108.49 \left(\frac{1}{(T)K} - \frac{1}{(293)K} \right) \text{ (unrounded)}$$

$$(-3.17805) / (-7108.49) = 4.47078 \times 10^{-4} = \left(\frac{1}{(T)K} - \frac{1}{(293)K} \right) \text{ (unrounded)}$$

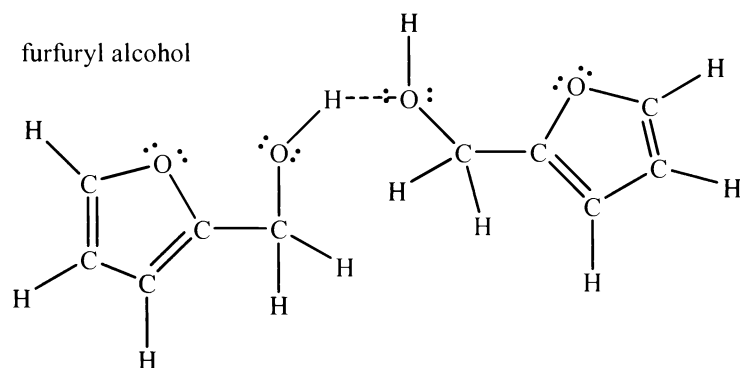
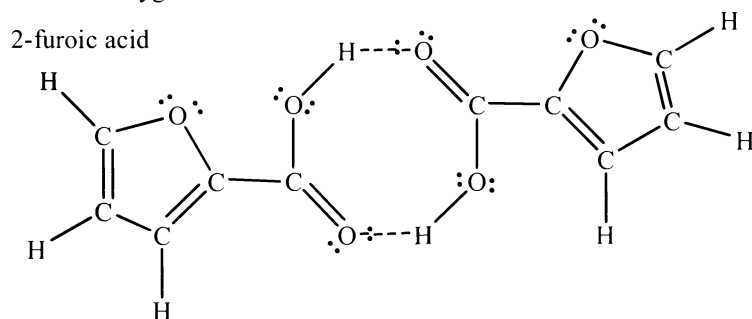
$$4.47078 \times 10^{-4} + 1 / 293 = 1 / T$$

$$T = 259.064 = \mathbf{259\text{ K}}$$

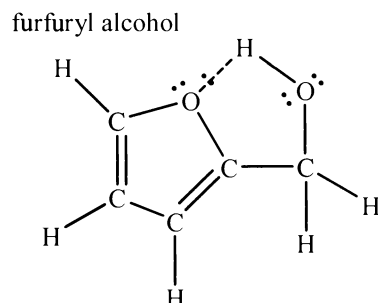
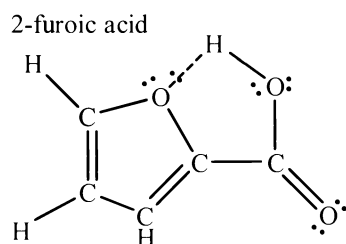
- 12.79 a) The cell contents are one Ca, $8 \times (1/8) = 1$ Ti, and $12 \times (1/4) = 3$ O, or one CaTiO_3 formula unit. The presence of one formula unit per unit cell indicates a **simple cubic** unit cell.

$$\text{b) Density} = \frac{\left(\frac{1 \text{ CaTiO}_3}{\text{Unit Cell}} \right) \left(\frac{1 \text{ mol CaTiO}_3}{6.022 \times 10^{23} \text{ CaTiO}_3} \right) \left(\frac{135.96 \text{ g CaTiO}_3}{1 \text{ mol CaTiO}_3} \right)}{\left(\frac{(3.84 \text{ \AA})^3}{\text{Unit Cell}} \right) \left(\frac{10^{-8} \text{ cm}}{1 \text{ \AA}} \right)^3} = 3.98728 = \mathbf{3.99 \text{ g/cm}^3}$$

- 12.81 a) Both furfuryl alcohol and 2-furoic acid can form hydrogen bonds since these two molecules have hydrogen directly bonded to oxygen.



b) Both furfuryl alcohol and 2-furoic acid can form internal hydrogen bonds by forming a hydrogen bond between the O–H and the O in the ring.



- 12.85 This problem involves carefully examining the figures showing the different cells pictured in the chapter.
- a) The atoms touch along the body diagonal. The two corner atoms each contribute one radius (r), and the center atom contributes a diameter ($2r$). The total for the body diagonal = $4r$.
- b) The face diagonal is the hypotenuse of a right triangle with the other two sides being the unit cell edge (a). Using the Pythagorean Theorem ($a^2 + b^2 = c^2$) with $a = b =$ the unit cell edge, and $c =$ the face diagonal:

$$a^2 + b^2 = c^2$$

$$a^2 + a^2 = 2a^2 = c^2$$

$$c = \text{face diagonal} = \sqrt{2} a$$

- c) The body-diagonal is the hypotenuse (c) of a triangle with one of the other sides being a face-diagonal (b) and the remaining side being a unit cell edge (a). Again, the Pythagorean Theorem is applied.

$$a^2 + b^2 = c^2$$

From part a:

$$a^2 + b^2 = (4r)^2$$

From part b:

$$a^2 + (\sqrt{2} a)^2 = (4r)^2 \quad \text{or} \quad a^2 + 2a^2 = 16r^2$$

Rearranging:

$$3a^2 = 16r^2 \quad a^2 = \frac{16r^2}{3} \quad a = \frac{4r}{\sqrt{3}}$$

- d) A body-centered cubic unit cell contains **2 atoms** (eight atoms in the corners are each $1/8$ in the cell (i.e., shared by eight cells), so there is a net of one atom – $1/8 \times 8$ and one atom in the center of the cell.

- e) Fraction filled = (volume of atoms present) / (volume of unit cell)
 = [2 atoms x volume of one atom] / (answer from part c)

Find the volume of one atom using the equation for the volume of a sphere: $\frac{4}{3}\pi r^3$

Find the volume of the unit cell by cubing the value of the edge length from part c:

Volume of a cube = length x width x height

$$\text{Fraction filled} = \frac{2 \left[\frac{4}{3} \pi r^3 \right]}{\left[\frac{4r}{\sqrt{3}} \right]^3} = \frac{8.37758r^3}{12.3168r^3} = \mathbf{0.68017}$$

Chapter 13 The Properties of Mixtures:

Solutions and Colloids

FOLLOW-UP PROBLEMS

- 13.1 Plan: Compare the intermolecular forces in the solutes with the intermolecular forces in the solvent. The intermolecular forces for the more soluble solute will be more similar to the intermolecular forces in the solvent than the forces in the less soluble solute.
Solution:
 a) 1,4-Butanediol is more soluble in water than butanol. Intermolecular forces in water are primarily hydrogen bonding. The intermolecular forces in both solutes also involve hydrogen bonding with the hydroxyl groups. Compared to butanol, each 1,4-butanediol molecule will form more hydrogen bonds with water because 1,4-butanediol contains two hydroxyl groups in each molecule, whereas butanol contains only one -OH group. Since 1,4-butanediol has more hydrogen bonds to water than butanol, it will be more soluble than butanol.
 b) Chloroform is more soluble in water than carbon tetrachloride because chloroform is a polar molecule and carbon tetrachloride is nonpolar. Polar molecules are more soluble in water, a polar solvent.
- 13.2 Plan: Solubility of a gas can be found from Henry's law: $S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$. The problem gives k_{H} for N_2 but not its partial pressure. To calculate the partial pressure, use the relationship from Chapter 5: $P_{\text{gas}} = X_{\text{gas}} \times P_{\text{total}}$ where X represents the mole fraction of the gas.
Solution:
 To find partial pressure use the 78% N_2 given for the mole fraction:
 $P_{\text{N}_2} = 0.78 \times 1 \text{ atm} = 0.78 \text{ atm}$
 Use Henry's law to find solubility at this partial pressure:
 $S_{\text{N}_2} = 7 \times 10^{-4} \text{ mol/L} \cdot \text{atm} \times 0.78 \text{ atm} = 5.46 \times 10^{-4} \text{ mol/L} = \mathbf{5 \times 10^{-4} \text{ mol/L}}$
Check: The solubility should be close to the value of k_{H} since the partial pressure is close to 1 atm.
- 13.3 Plan: Molality (m) is defined as amount (mol) of solute per kg of solvent. Use the molality and the mass of solvent given to calculate the amount of glucose. Then convert amount (mol) of glucose to mass (g) of glucose.
Solution:
 Mass of solvent must be converted to kg: $563 \text{ g} \times (1 \text{ kg}/1000 \text{ g}) = 0.563 \text{ kg}$

$$(0.563 \text{ kg}) \left(\frac{2.40 \times 10^{-2} \text{ mol C}_6\text{H}_{12}\text{O}_6}{1 \text{ kg}} \right) \left(\frac{180.16 \text{ C}_6\text{H}_{12}\text{O}_6}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \right) = 2.4343 = \mathbf{2.43 \text{ g C}_6\text{H}_{12}\text{O}_6}$$

Check: To check these results estimate the molality from the calculated mass of glucose and given mass of solvent. The number of moles of glucose is approximately $(2.4 \text{ g}) (1 \text{ mol} / 180 \text{ g}) = 0.013 \text{ mol}$ glucose. Using the calculated value for amount of glucose and the given mass of solvent, calculate the molality: $(0.013) / (0.56 \text{ kg}) = 0.023 \text{ m}$, which is close to the given value of 0.0240 m.
- 13.4 Plan: Mass percent is the mass (g) of solute per 100 g of solution. For each alcohol, divide the mass of the alcohol by the total mass. Multiply this number by 100 to obtain mass percent. To find mole fraction, first find the amount (mol) of each alcohol, then divide by the total moles.
Solution:
 Mass percent:

$$\text{Mass\% propanol} = \frac{35.0 \text{ g}}{(35.0 + 150.) \text{ g}} \times 100\% = 18.9189 = \mathbf{18.9\% \text{ propanol}}$$

$$\text{Mass\% ethanol} = \frac{150. \text{ g}}{(35.0 + 150.) \text{ g}} \times 100\% = 81.08108 = \mathbf{81.1\% \text{ ethanol}}$$

Mole fraction:

$$\text{Moles propanol} = (35.0 \text{ g C}_3\text{H}_7\text{OH}) \left(\frac{1 \text{ mol C}_3\text{H}_7\text{OH}}{60.09 \text{ g C}_3\text{H}_7\text{OH}} \right) = 0.5824596 \text{ mol propanol (unrounded)}$$

$$\text{Moles ethanol} = (150. \text{ g C}_2\text{H}_5\text{OH}) \left(\frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} \right) = 3.2559149 \text{ mol ethanol (unrounded)}$$

$$X_{\text{propanol}} = \frac{0.5824596 \text{ mol propanol}}{0.5824596 \text{ mol propanol} + 3.2559149 \text{ mol ethanol}} = 0.151746 = \mathbf{0.152}$$

$$X_{\text{ethanol}} = \frac{3.2559149 \text{ mol ethanol}}{0.5824596 \text{ mol propanol} + 3.2559149 \text{ mol ethanol}} = 0.84825 = \mathbf{0.848}$$

Check: Since the mass of ethanol is 4 times that of propanol, the mass percent of ethanol should be about 4 times greater. 81% is about 4 times 19%. The mole fraction should be similar, but the fraction that is ethanol should be slightly greater than the mass fraction of 0.81 – and it is at 0.85.

13.5 Plan: To find the mass percent, molality and mole fraction of HCl, the following is needed.

- 1) Moles of HCl in 1 L solution (from molarity)
- 2) Mass of HCl in 1 L solution (from molarity times molar mass of HCl)
- 3) Mass of 1 L solution (from volume times density)
- 4) Mass of solvent in 1 L solution (by subtracting mass of solute from mass of solution)
- 5) Moles of solvent (by multiplying mass of solvent by molar mass of water)

Mass percent is calculated by dividing mass of HCl by mass of solution.

Molality is calculated by dividing moles of HCl by mass of solvent in kg.

Mole fraction is calculated by dividing mol of HCl by the sum of mol of HCl plus mol of solvent.

Solution:

Assume the volume is exactly 1 L.

$$1) \text{ Mole HCl in 1 L solution} = (1.0 \text{ L}) \left(\frac{11.8 \text{ mol HCl}}{1.0 \text{ L}} \right) = 11.8 \text{ mol HCl}$$

$$2) \text{ Mass HCl in 1 L solution} = (11.8 \text{ mol HCl}) \left(\frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} \right) = 430.228 \text{ g HCl}$$

$$3) \text{ Mass of 1 L solution} = (1.0 \text{ L}) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1.190 \text{ g}}{1 \text{ mL}} \right) = 1190. \text{ g solution}$$

$$(1190 \text{ g}) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 1.190 \text{ kg solution}$$

$$4) \text{ Mass of solvent in 1 L solution} = 1190. \text{ g} - 430.228 \text{ g} = 759.772 \text{ g solvent (H}_2\text{O)}$$

$$(759.772 \text{ g}) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 0.759772 \text{ kg solvent}$$

$$5) \text{ Mole of solvent in 1 L solution} = (759.772 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 42.1627 \text{ mol solvent}$$

$$\text{Mass percent of HCl} = \frac{\text{Mass HCl}}{\text{Mass solution}} (100) = \frac{430.228 \text{ g HCl}}{1190 \text{ g solution}} (100) = 36.1536 = \mathbf{36.2\%}$$

$$\text{Molality of HCl} = \frac{\text{Mole HCl}}{\text{Kg solvent}} = \frac{11.8 \text{ mol HCl}}{0.759772 \text{ kg}} = 15.530975 = \mathbf{15.5 \text{ m}}$$

$$\text{Mole fraction of HCl} = \frac{\text{Mol HCl}}{\text{Mol HCl} + \text{Mol H}_2\text{O}} = \frac{11.8 \text{ mol}}{11.8 \text{ mol} + 42.1627 \text{ mol}} = 0.21866956 = \mathbf{0.219}$$

Check: The mass of HCl is about 1/3 of the mass of the solution, so 36% is in the ballpark for the mass% HCl. Since the moles of HCl is about 1/4 the moles of water, the mole fraction of HCl should come out around 0.2.

- 13.6 Plan: Raoult's law states that the vapor pressure of a solvent is proportional to the mole fraction of the solvent: $P_{\text{solvent}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$. To calculate the drop in vapor pressure, a similar relationship is used with the mole fraction of the solute substituted for that of the solvent.

Solution:

Mole fraction of aspirin in methanol:

$$\frac{(2.00 \text{ g}) \left(\frac{1 \text{ mol Aspirin}}{180.15 \text{ g Aspirin}} \right)}{(2.00 \text{ g}) \left(\frac{1 \text{ mol Aspirin}}{180.15 \text{ g Aspirin}} \right) + (50.0 \text{ g}) \left(\frac{1 \text{ mol Methanol}}{32.04 \text{ g Methanol}} \right)}$$

$$X_{\text{aspirin}} = 7.06381 \times 10^{-3} \text{ (unrounded)}$$

$$\Delta P = X_{\text{aspirin}} P^{\circ}_{\text{methanol}} = (7.06381 \times 10^{-3})(101 \text{ torr}) = 0.71344 = \mathbf{0.713 \text{ torr}}$$

Check: The drop in vapor pressure is expected to be insignificant since the amount of aspirin in solution is so small – only 0.01 mol aspirin in 1.5 mol solvent.

- 13.7 Plan: The question asks for the concentration of ethylene glycol that would prevent freezing at 0.00°F. First, convert 0.00°F to °C. The change in freezing point of water will then be this temperature subtracted from the freezing point of pure water, 0.00°C. Use this value for ΔT in $\Delta T_f = 1.86^{\circ}\text{C}/m \times \text{molality of solution}$ and solve for molality.

Solution:

Temperature conversion

$$T(^{\circ}\text{C}) = (T(^{\circ}\text{F}) - 32^{\circ}\text{F}) \left(\frac{5^{\circ}\text{C}}{9^{\circ}\text{F}} \right) = (0.00^{\circ}\text{F} - 32^{\circ}\text{F}) \left(\frac{5^{\circ}\text{C}}{9^{\circ}\text{F}} \right) = -17.7778^{\circ}\text{C} \text{ (unrounded)}$$

$$\Delta T_f = m K_f$$

$$m = \frac{\Delta T_f}{K_f} = \frac{-17.7778^{\circ}\text{C}}{1.86^{\circ}\text{C}/m} = 9.557956 = \mathbf{9.56 \text{ } m}$$

The minimum concentration of ethylene glycol would have to be 9.56 *m* in order to prevent the water from freezing at 0.00°F.

Check: In Sample Problem 13.7, a 3.6 *m* solution lowered the freezing point by about 7 degrees. Thus, to lower the temperature by 18 degrees, the concentration must be 18/7 times 3.6 or 9.3 *m*. Calculated value of 9.56 *m* is close to the estimated value.

- 13.8 Plan: The osmotic pressure is calculated as the product of molarity, temperature, and the gas constant.

Solution:

$$\Pi = MRT = \left(\frac{0.30 \text{ mol}}{\text{L}} \right) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 37) \text{ K}) = 7.6353 = \mathbf{7.6 \text{ atm}}$$

Check: The answer, 7.6 atm, is a significant osmotic pressure, which is expected from a relatively concentrated solution of 0.3 *M*.

- 13.9 Plan: Calculate the molarity of the solution, then calculate the osmotic pressure of the magnesium chloride solution. Do not forget that MgCl_2 is a strong electrolyte, and ionizes to yield three ions per formula unit. This will result in a pressure three times as great as a nonelectrolyte (glucose) solution of equal concentration.

Solution:

$$\text{a) Liters of solution} = (100. + 0.952 \text{ g solution}) \left(\frac{1 \text{ mL}}{1.006 \text{ g}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.1003499 \text{ L (unrounded)}$$

$$\text{Moles } \text{MgCl}_2 = (0.952 \text{ g } \text{MgCl}_2) \left(\frac{1 \text{ mol } \text{MgCl}_2}{95.21 \text{ g } \text{MgCl}_2} \right) = 9.9989 \times 10^{-3} \text{ mol } \text{MgCl}_2 \text{ (unrounded)}$$

$$\text{Molarity } \text{MgCl}_2 = \frac{\text{Mol } \text{MgCl}_2}{\text{Volume solution}} = \frac{0.0099989 \text{ mol}}{0.1003499 \text{ L}} = 0.099640 \text{ M } \text{MgCl}_2 \text{ (unrounded)}$$

$$\Pi = iMRT = 3 \left(\frac{0.099640 \text{ mol}}{\text{L}} \right) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273.2 + 20.0) \text{ K}) = 7.1955 = 7.20 \text{ atm}$$

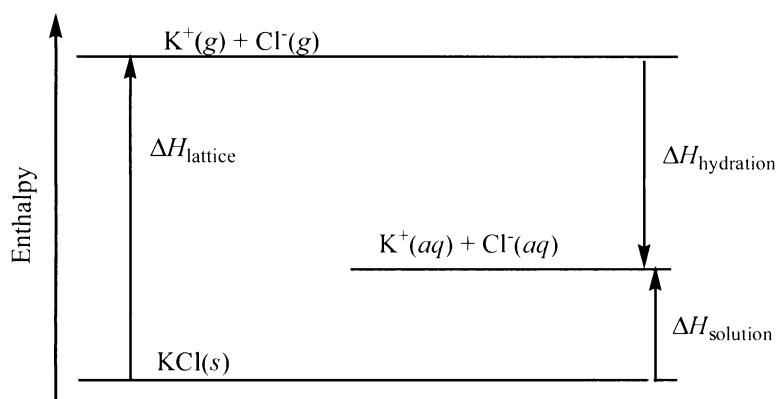
b) The magnesium chloride solution has a higher osmotic pressure, thus, liquid will diffuse from the glucose solution into the magnesium chloride solution. The glucose side will lower and the magnesium chloride side will rise. **Scene C** represents this situation.

Check: Repeat the calculations using approximate values ($M = 0.1$, $R = 0.08$, and $T = 300$).

END-OF-CHAPTER PROBLEMS

- 13.2 When a salt such as NaCl dissolves, ion-dipole forces cause the ions to separate, and many water molecules cluster around each of them in hydration shells. Ion-dipole forces hold the first shell. Additional shells are held by hydrogen bonding to inner shells.
- 13.4 a) A more concentrated solution will have more solute dissolved in the solvent. Potassium nitrate, KNO_3 , is an ionic compound and therefore soluble in a polar solvent like water. Potassium nitrate is not soluble in the nonpolar solvent CCl_4 . Because potassium nitrate dissolves to a greater extent in water, **KNO_3 in H_2O** will result in the more concentrated solution.
- 13.6 To identify the strongest type of intermolecular force, check the formula of the solute and identify the forces that could occur. Then look at the formula for the solvent and determine if the forces identified for the solute would occur with the solvent. The strongest force is ion-dipole followed by dipole-dipole (including H bonds). Next in strength is ion-induced dipole force and then dipole-induced dipole force. The weakest intermolecular interactions are dispersion forces.
- a) **Ion-dipole forces** are the strongest intermolecular forces in the solution of the ionic substance cesium chloride in polar water.
- b) **Hydrogen bonding** (type of dipole-dipole force) is the strongest intermolecular force in the solution of polar propanone (or acetone) in polar water.
- c) **Dipole-induced dipole forces** are the strongest forces between the polar methanol and nonpolar carbon tetrachloride.
- 13.8 a) **Hydrogen bonding** occurs between the H atom on water and the lone electron pair on the O atom in dimethyl ether (CH_3OCH_3). However, none of the hydrogen atoms on dimethyl ether participates in hydrogen bonding because the C–H bond does not have sufficient polarity.
- b) The dipole in water induces a dipole on the Ne(g) atom, so **dipole-induced dipole** interactions are the strongest intermolecular forces in this solution.
- c) Nitrogen gas and butane are both nonpolar substances, so **dispersion forces** are the principal attractive forces.
- 13.10 $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ is polar with dipole-dipole interactions as the dominant intermolecular forces. Examine the solutes to determine which has intermolecular forces more similar to those for the diethyl ether. This solute is the one that would be more soluble.
- a) **HCl** would be more soluble since it is a covalent compound with dipole-dipole forces, whereas NaCl is an ionic solid. Dipole-dipole forces between HCl and diethyl ether are more similar to the dipole forces in diethyl ether than the ion-dipole forces between NaCl and diethyl ether.
- b) **CH_3CHO** (acetaldehyde) would be more soluble. The dominant interactions in H_2O are hydrogen bonding, a stronger type of dipole-dipole force. The dominant interactions in CH_3CHO are dipole-dipole. The solute-solvent interactions between CH_3CHO and diethyl ether are more similar to the solvent intermolecular forces than the forces between H_2O and diethyl ether.
- c) **$\text{CH}_3\text{CH}_2\text{MgBr}$** would be more soluble. $\text{CH}_3\text{CH}_2\text{MgBr}$ has a polar end ($-\text{MgBr}$) and a nonpolar end (CH_3CH_2-), whereas MgBr_2 is an ionic compound. The nonpolar end of $\text{CH}_3\text{CH}_2\text{MgBr}$ and diethyl ether would interact with dispersion forces, while the polar end of $\text{CH}_3\text{CH}_2\text{MgBr}$ and the dipole in diethyl ether would interact with dipole-dipole forces. Recall, that if the polarity continues to increase, the bond will eventually become ionic. There is a continuous sequence from nonpolar covalent to ionic.

- 13.12 Gluconic acid is a very polar molecule because it has -OH groups attached to every carbon. The abundance of -OH bonds allows gluconic acid to participate in extensive H-bonding with water, hence its great solubility in water. On the other hand, caproic acid has a 5-carbon, nonpolar, hydrophobic ("water hating") tail that does not easily dissolve in water. The dispersion forces in the nonpolar tail are more similar to the dispersion forces in hexane, hence its greater solubility in hexane.
- 13.17 This compound would be very soluble in water. A large exothermic value in $\Delta H_{\text{solution}}$ (enthalpy of solution) means that the solution has a much lower energy state than the isolated solute and solvent particles, so the system tends to the formation of the solution. Entropy that accompanies dissolution always favors solution formation. Entropy becomes important when explaining why solids with an endothermic $\Delta H_{\text{solution}}$ (and higher energy state) are still soluble in water.
- 13.18



Lattice energy values are always positive as energy is required to separate the ions from each other. Hydration energy values are always negative as energy is released when intermolecular forces between ions and water form. Since the heat of solution for KCl is endothermic, the lattice energy must be greater than the hydration energy for an overall input of energy.

- 13.20 Charge density is the ratio of an ion's charge (regardless of sign) to its volume. An ion's volume is related to its radius. For ions whose charges have the same sign (+ or -), ion size decreases as a group in the periodic table is ascended and as you proceed from left to right in the periodic table.
- Both ions have a +1 charge, but the volume of Na^+ is smaller, so it has the greater charge density.
 - Sr^{2+} has a greater ionic charge and a smaller size (because it has a greater Z_{eff}), so it has the greater charge density.
 - Na^+ has a smaller ion volume than Cl^- , so it has the greater charge density.
 - O^{2-} has a greater ionic charge and similar ion volume, so it has the greater charge density.
 - OH^- has a smaller ion volume than SH^- , so it has the greater charge density.
- 13.22 The ion with the greater charge density will have the larger $\Delta H_{\text{hydration}}$.
- Na^+ would have a larger $\Delta H_{\text{hydration}}$ than Cs^+ since its charge density is greater than that of Cs^+ .
 - Sr^{2+} would have a larger $\Delta H_{\text{hydration}}$ than Rb^+ .
 - Na^+ would have a larger $\Delta H_{\text{hydration}}$ than Cl^- .
 - O^{2-} would have a larger $\Delta H_{\text{hydration}}$ than F^- .
 - OH^- would have a larger $\Delta H_{\text{hydration}}$ than SH^- .
- 13.24
- The two ions in potassium bromate are K^+ and BrO_3^- . The heat of solution for ionic compounds is $\Delta H_{\text{soln}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydr of the ions}}$. Therefore, the combined heats of hydration for the ions is $(\Delta H_{\text{soln}} - \Delta H_{\text{lattice}})$ or $41.1 \text{ kJ/mol} - 745 \text{ kJ/mol} = -703.9 = \mathbf{-704 \text{ kJ/mol}}$.
 - K^+ ion contributes more to the heat of hydration because it has a smaller size and, therefore, a greater charge density.

- 13.26 Entropy increases as the possible states for a system increases.
- Entropy **increases** as the gasoline is burned. Gaseous products at a higher temperature form.
 - Entropy **decreases** as the gold is separated from the ore. Pure gold has only the arrangement of gold atoms next to gold atoms, while the ore mixture has a greater number of possible arrangements among the components of the mixture.
 - Entropy **increases** as a solute dissolves in the solvent.
- 13.29 Add a pinch of the solid solute to each solution. A saturated solution contains the maximum amount of dissolved solute at a particular temperature. When additional solute is added to this solution, it will remain undissolved. An unsaturated solution contains less than the maximum amount of dissolved solute and so will dissolve added solute. A supersaturated solution is unstable and addition of a “seed” crystal of solute causes the excess solute to crystallize immediately, leaving behind a saturated solution.
- 13.31
- Increasing pressure for a gas **increases** the solubility of the gas according to Henry’s law.
 - Increasing the volume of a gas causes a decrease in its pressure (Boyle’s Law), which **decreases** the solubility of the gas.
- 13.33 a) Solubility for a gas is calculated from Henry’s law: $S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$. S_{gas} is expressed as mol/L, so convert moles of O_2 to mass of O_2 using the molar mass.

$$S_{\text{gas}} = \left(1.28 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}} \right) (1.00 \text{ atm}) = 1.28 \times 10^{-3} \text{ mol/L}$$

$$\left(\frac{1.28 \times 10^{-3} \text{ mol O}_2}{\text{L}} \right) \left(\frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} \right) (2.00 \text{ L}) = 0.08192 = \mathbf{0.0819 \text{ g O}_2}$$

b) The amount of gas that will dissolve in a given volume decreases proportionately with the partial pressure of the gas, so

$$S_{\text{gas}} = \left(1.28 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}} \right) (0.209 \text{ atm}) = 2.6752 \times 10^{-4} \text{ mol/L}$$

$$\left(\frac{2.6752 \times 10^{-4} \text{ mol O}_2}{\text{L}} \right) \left(\frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} \right) (2.00 \text{ L}) = 0.01712 = \mathbf{0.0171 \text{ g O}_2}$$

- 13.36 Solubility for a gas is calculated from Henry’s law: $S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$.
- $$S_{\text{gas}} = (3.7 \times 10^{-2} \text{ mol/L} \cdot \text{atm}) (5.5 \text{ atm}) = 0.2035 = \mathbf{0.20 \text{ mol/L}}$$

- 13.39 Converting between molarity and molality involves conversion between volume of solution and mass of solution. Both of these quantities are given so interconversion is possible. To convert to mole fraction requires that the mass of solvent be converted to moles of solvent. Since the identity of the solvent is not given, conversion to mole fraction is not possible if the molar mass is not known. Why is the identity of the solute not necessary for conversion?

- 13.41 Convert the masses to moles and the volumes to liters and use the definition of molarity: $M = \frac{\text{mol of solute}}{V(\text{L}) \text{ of solution}}$

$$\text{a) Molarity} = \left(\frac{42.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{100. \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} \right) = 1.235758 = \mathbf{1.24 \text{ M C}_{12}\text{H}_{22}\text{O}_{11}}$$

$$\text{b) Molarity} = \left(\frac{5.50 \text{ g LiNO}_3}{505 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol LiNO}_3}{68.95 \text{ g LiNO}_3} \right) = 0.157956 = \mathbf{0.158 \text{ M LiNO}_3}$$

- 13.43 Dilution calculations can be done using $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$
 a) $M_{\text{conc}} = 0.250 \text{ M NaOH}$ $V_{\text{conc}} = 75.0 \text{ mL}$ $M_{\text{dil}} = ?$ $V_{\text{dil}} = 0.250 \text{ L}$

$$M_{\text{dil}} = M_{\text{conc}} V_{\text{conc}} / V_{\text{dil}} = \frac{(0.250 \text{ M})(75.0 \text{ mL})}{(0.250 \text{ L})} \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = \mathbf{0.0750 \text{ M}}$$

- b) $M_{\text{conc}} = 1.3 \text{ M HNO}_3$ $V_{\text{conc}} = 35.5 \text{ mL}$ $M_{\text{dil}} = ?$ $V_{\text{dil}} = 0.150 \text{ L}$

$$M_{\text{dil}} = M_{\text{conc}} V_{\text{conc}} / V_{\text{dil}} = \frac{(1.3 \text{ M})(35.5 \text{ mL})}{(0.150 \text{ L})} \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.3076667 = \mathbf{0.31 \text{ M}}$$

- 13.45 a) Find the number of moles KH_2PO_4 needed to make 355 mL of this solution. Convert moles to mass using the molar mass of KH_2PO_4 (Molar mass = 136.09 g/mol)

$$\begin{aligned} \text{Mass KH}_2\text{PO}_4 &= (355 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{8.74 \times 10^{-2} \text{ mol KH}_2\text{PO}_4}{\text{L}} \right) \left(\frac{136.09 \text{ g KH}_2\text{PO}_4}{1 \text{ mol KH}_2\text{PO}_4} \right) \\ &= 4.22246 = 4.22 \text{ g KH}_2\text{PO}_4 \end{aligned}$$

Add **4.22 g KH_2PO_4** to enough water to make 355 mL of aqueous solution.

- b) Use the relationship $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$ to find the volume of 1.25 M NaOH needed.

$$M_{\text{conc}} = 1.25 \text{ M NaOH} \quad V_{\text{conc}} = ? \quad M_{\text{dil}} = 0.315 \text{ M NaOH} \quad V_{\text{dil}} = 425 \text{ mL}$$

$$V_{\text{conc}} = M_{\text{dil}} V_{\text{dil}} / M_{\text{conc}} = (0.315 \text{ M})(425 \text{ mL}) / (1.25 \text{ M}) = 107.1 = 107 \text{ mL}$$

Add **107 mL** of 1.25 M NaOH to enough water to make 425 mL of solution.

- 13.47 Molality, $m = \frac{\text{moles of solute}}{\text{kg of solvent}}$

$$\text{a) } m \text{ glycine} = \frac{88.4 \text{ g Glycine} \left(\frac{1 \text{ mol Glycine}}{75.07 \text{ g Glycine}} \right)}{(1.250 \text{ kg})} = 0.942054 = \mathbf{0.942 \text{ m glycine}}$$

$$\text{b) } m \text{ glycerol} = \frac{8.89 \text{ g Glycerol} \left(\frac{1 \text{ mol Glycerol}}{92.09 \text{ g Glycerol}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right)}{(75.0 \text{ g})} = 1.2871466 = \mathbf{1.29 \text{ m glycerol}}$$

- 13.49 Molality, $m = \frac{\text{moles of solute}}{\text{kg of solvent}}$ Use density to convert volume to mass.

$$m \text{ benzene} = \frac{(34.0 \text{ mL C}_6\text{H}_6) \left(\frac{0.877 \text{ g}}{\text{mL}} \right) \left(\frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right)}{(187 \text{ mL C}_6\text{H}_{14}) \left(\frac{0.660 \text{ g}}{\text{mL}} \right)} = 3.0930 = \mathbf{3.09 \text{ m C}_6\text{H}_6}$$

- 13.51 a) The total weight of the solution is $3.00 \times 10^2 \text{ g}$, so $\text{mass}_{\text{solute}} + \text{mass}_{\text{solvent}} = 3.00 \times 10^2 \text{ g}$

$$\text{Mass of C}_2\text{H}_6\text{O}_2 \text{ in } 1000 \text{ g (1 kg) of H}_2\text{O} = \left(\frac{0.115 \text{ mol C}_2\text{H}_6\text{O}_2}{1 \text{ kg H}_2\text{O}} \right) \left(\frac{62.07 \text{ g C}_2\text{H}_6\text{O}_2}{1 \text{ mol C}_2\text{H}_6\text{O}_2} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right)$$

$$= 7.13805 \text{ g C}_2\text{H}_6\text{O}_2 \text{ in } 1000 \text{ g H}_2\text{O (unrounded)}$$

$$\text{Grams of this solution} = 1000 \text{ g H}_2\text{O} + 7.13805 \text{ g C}_2\text{H}_6\text{O}_2 = 1007.13805 \text{ (unrounded)}$$

$$\text{Mass C}_2\text{H}_6\text{O}_2 = \left(\frac{7.13805 \text{ g C}_2\text{H}_6\text{O}_2}{1007.13805 \text{ g solution}} \right) (3.00 \times 10^2 \text{ g solution}) = 2.1262378 = 2.13 \text{ g C}_2\text{H}_6\text{O}_2$$

$\text{Mass}_{\text{solvent}} = 3.00 \times 10^2 \text{ g} - \text{mass}_{\text{solute}} = 3.00 \times 10^2 \text{ g} - 2.1262378 \text{ g C}_2\text{H}_6\text{O}_2 = 297.87376 = 2.98 \times 10^2 \text{ g H}_2\text{O}$
 Therefore, add **2.13 g $\text{C}_2\text{H}_6\text{O}_2$ to 298 g of H_2O** to make a 0.115 m solution.

b) This is a disguised dilution problem. First, determine the amount of solute in your target solution:

$$\left(\frac{2.00\%}{100\%}\right)(1.00 \text{ kg}) = 0.0200 \text{ kg HNO}_3 \text{ (solute)}$$

Then determine the amount of the concentrated acid solution needed to get 0.0200 kg solute:

$$\left(\frac{62.0\%}{100\%}\right)(\text{mass needed}) = 0.0200 \text{ kg}$$

Mass solute needed = 0.032258 = 0.0323 kg

Mass solvent = Mass solution – Mass solute = 1.00 kg – 0.032258 kg = 0.96774 = 0.968 kg

Add 0.0323 kg of the 62.0% (w/w) HNO₃ to 0.968 kg H₂O to make 1.00 kg of 2.00% (w/w) HNO₃

13.53 a) Mole fraction is moles of isopropanol per total moles.

$$X_{\text{isopropanol}} = \frac{0.30 \text{ mol Isopropanol}}{(0.30 + 0.80) \text{ mol}} = 0.2727272 = \mathbf{0.27} \text{ (Notice that mole fractions have no units.)}$$

b) Mass percent is the mass of isopropanol per 100 g of solution. From the mole amounts, find the masses of isopropanol and water:

$$\text{Mass isopropanol} = (0.30 \text{ mol C}_3\text{H}_7\text{OH})\left(\frac{60.09 \text{ g C}_3\text{H}_7\text{OH}}{1 \text{ mol C}_3\text{H}_7\text{OH}}\right) = 18.027 \text{ g isopropanol (unrounded)}$$

$$\text{Mass water} = (0.80 \text{ mol H}_2\text{O})\left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right) = 14.416 \text{ g water (unrounded)}$$

$$\text{Percent isopropanol} = \frac{(18.027 \text{ g Isopropanol})}{(18.027 + 14.416) \text{ g}} \times 100\% = 55.5651 = \mathbf{56\%} \text{ isopropanol}$$

c) Molality of isopropanol is moles of isopropanol per kg of solvent.

$$\text{Molality isopropanol} = \frac{0.30 \text{ mol Isopropanol}}{14.416 \text{ g Water}}\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 20.8102 = \mathbf{21 \text{ m}} \text{ isopropanol}$$

13.55 The information given is 8.00 mass % NH₃ solution with a density of 0.9651 g/mL.

For convenience, choose exactly 100.00 grams of solution.

Determine some fundamental quantities:

$$\text{Mass of NH}_3 = (100 \text{ g solution})\left(\frac{8.00\% \text{ NH}_3}{100\% \text{ solution}}\right) = 8.00 \text{ g NH}_3$$

$$\text{Mass H}_2\text{O} = \text{mass of solution} - \text{mass NH}_3 = (100.00 - 8.00) \text{ g} = 92.00 \text{ g H}_2\text{O}$$

$$\text{Moles NH}_3 = (8.00 \text{ g NH}_3)\left(\frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3}\right) = 0.469759 \text{ mol NH}_3 \text{ (unrounded)}$$

$$\text{Moles H}_2\text{O} = (92.00 \text{ g H}_2\text{O})\left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}}\right) = 5.1054 \text{ mol H}_2\text{O (unrounded)}$$

$$\text{Volume solution} = (100.00 \text{ g solution})\left(\frac{1 \text{ mL solution}}{0.9651 \text{ g solution}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.103616 \text{ L (unrounded)}$$

Using the above fundamental quantities and the definitions of the various units:

$$\text{Molality} = \frac{\text{Moles solute}}{\text{kg solvent}} = \left(\frac{0.469759 \text{ mol NH}_3}{92.00 \text{ g H}_2\text{O}}\right)\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 5.106076 = \mathbf{5.11 \text{ m NH}_3}$$

$$\text{Molarity} = \frac{\text{Moles solute}}{\text{L solution}} = \left(\frac{0.469759 \text{ mol NH}_3}{0.103616 \text{ L}}\right) = 4.53365 = \mathbf{4.53 \text{ M NH}_3}$$

$$\text{Mole fraction} = X = \frac{\text{Moles substance}}{\text{total moles}} = \frac{0.469759 \text{ mol NH}_3}{(0.469759 + 5.1054) \text{ mol}} = 0.084259 = \mathbf{0.0843}$$

$$13.57 \quad \text{ppm} = \left(\frac{\text{mass solute}}{\text{mass solution}} \right) \times 10^6$$

The mass of 100.0 L of waste water solution is $(100.0 \text{ L solution}) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1.001 \text{ g}}{1 \text{ mL}} \right) = 1.001 \times 10^5 \text{ g}$.

$$\text{ppm Ca}^{2+} = \left(\frac{0.22 \text{ g Ca}^{2+}}{1.001 \times 10^5 \text{ g solution}} \right) \times 10^6 = 2.1978 = \mathbf{2.2 \text{ ppm Ca}^{2+}}$$

$$\text{ppm Mg}^{2+} = \left(\frac{0.066 \text{ g Mg}^{2+}}{1.001 \times 10^5 \text{ g solution}} \right) \times 10^6 = 0.65934 = \mathbf{0.66 \text{ ppm Mg}^{2+}}$$

13.60 The boiling point temperature is higher and the freezing point temperature is lower for the solution compared to the solvent because the addition of a solute lowers the freezing point and raises the boiling point of a liquid.

13.64 Strong electrolytes are substances that produce a large number of ions when dissolved in water; strong acids and bases and soluble salts are strong electrolytes. Weak electrolytes produce few ions when dissolved in water; weak acids and bases are weak electrolytes. Nonelectrolytes produce no ions when dissolved in water. Molecular compounds other than acids and bases are nonelectrolytes.

a) **Strong electrolyte** When hydrogen chloride is bubbled through water, it dissolves and dissociates completely into H^+ (or H_3O^+) ions and Cl^- ions.

b) **Strong electrolyte** Potassium nitrate is a soluble salt.

c) **Nonelectrolyte** Glucose solid dissolves in water to form individual $\text{C}_6\text{H}_{12}\text{O}_6$ molecules, but these units are not ionic and therefore do not conduct electricity.

d) **Weak electrolyte** Ammonia gas dissolves in water, but is a weak base that forms few NH_4^+ and OH^- ions.

13.66 To count solute particles in a solution of an ionic compound, count the number of ions per mole and multiply by the number of moles in solution. For a covalent compound, the number of particles equals the number of molecules.

$$\text{a) } \left(\frac{0.2 \text{ mol KI}}{\text{L}} \right) \left(\frac{2 \text{ mol particles}}{1 \text{ mol KI}} \right) (1 \text{ L}) = \mathbf{0.4 \text{ mol of particles}}$$

KI consists of K^+ ions and I^- ions, 2 particles for each KI.

$$\text{b) } \left(\frac{0.070 \text{ mol HNO}_3}{\text{L}} \right) \left(\frac{2 \text{ mol particles}}{1 \text{ mol HNO}_3} \right) (1 \text{ L}) = \mathbf{0.14 \text{ mol of particles}}$$

HNO_3 is a strong acid that forms hydronium ions and nitrate ions in aqueous solution.

$$\text{c) } \left(\frac{10^{-4} \text{ mol K}_2\text{SO}_4}{\text{L}} \right) \left(\frac{3 \text{ mol particles}}{1 \text{ mol K}_2\text{SO}_4} \right) (1 \text{ L}) = \mathbf{3 \times 10^{-4} \text{ mol of particles}}$$

Each K_2SO_4 forms 2 potassium ions and 1 sulfate ion in aqueous solution.

$$\text{d) } \left(\frac{0.07 \text{ mol C}_2\text{H}_5\text{OH}}{\text{L}} \right) \left(\frac{1 \text{ mol particles}}{1 \text{ mol C}_2\text{H}_5\text{OH}} \right) (1 \text{ L}) = \mathbf{0.07 \text{ mol of particles}}$$

Ethanol is not an ionic compound so each molecule dissolves as one particle. The number of moles of particles is the same as the number of moles of molecules, **0.07 mol** in 1 L.

13.68 The magnitude of freezing point depression is directly proportional to molality.

$$\text{a) Molality of CH}_3\text{OH} = \frac{(10.0 \text{ g CH}_3\text{OH})}{(100. \text{ g H}_2\text{O})} \left(\frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 3.1210986 = \mathbf{3.12 \text{ m CH}_3\text{OH}}$$

$$\begin{aligned} \text{Molality of CH}_3\text{CH}_2\text{OH} &= \frac{(20.0 \text{ g CH}_3\text{CH}_2\text{OH})}{(200. \text{ g H}_2\text{O})} \left(\frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g CH}_3\text{CH}_2\text{OH}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \\ &= 2.1706 = \mathbf{2.17 \text{ m CH}_3\text{CH}_2\text{OH}} \end{aligned}$$

The molality of methanol, CH₃OH, in water is 3.12 *m* whereas the molality of ethanol, CH₃CH₂OH, in water is 2.17 *m*. Thus, **CH₃OH/H₂O solution** has the lower freezing point.

$$\text{b) Molality of H}_2\text{O} = \frac{(10.0 \text{ g H}_2\text{O})}{(1.00 \text{ kg CH}_3\text{OH})} \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 0.5549 = 0.55 \text{ } m \text{ H}_2\text{O}$$

$$\text{Molality of CH}_3\text{CH}_2\text{OH} = \frac{(10.0 \text{ g CH}_3\text{CH}_2\text{OH})}{(1.00 \text{ kg CH}_3\text{OH})} \left(\frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g CH}_3\text{CH}_2\text{OH}} \right) = 0.21706 = 0.217 \text{ } m \text{ CH}_3\text{CH}_2\text{OH}$$

The molality of H₂O in CH₃OH is 0.555 *m*, whereas CH₃CH₂OH in CH₃OH is 0.217 *m*. Therefore, **H₂O/CH₃OH solution** has the lower freezing point.

- 13.70 To rank the solutions in order of increasing osmotic pressure, boiling point, freezing point, and vapor pressure, convert the molality of each solute to molality of particles in the solution. The higher the molality of particles the higher the osmotic pressure, the higher the boiling point, the lower the freezing point, and the lower the vapor pressure at a given temperature.

$$\text{(I)} (0.100 \text{ } m \text{ NaNO}_3) \left(\frac{2 \text{ mol particles}}{1 \text{ mol NaNO}_3} \right) = 0.200 \text{ } m \text{ ions}$$

NaNO₃ consists of Na⁺ ions and NO₃⁻ ions, 2 particles for each NaNO₃.

$$\text{(II)} (0.200 \text{ } m \text{ glucose}) \left(\frac{1 \text{ mol particles}}{1 \text{ mol glucose}} \right) = 0.200 \text{ } m \text{ molecules}$$

Ethanol is not an ionic compound so each molecule dissolves as one particle. The number of moles of particles is the same as the number of moles of molecules.

$$\text{(III)} (0.100 \text{ } m \text{ CaCl}_2) \left(\frac{3 \text{ mol particles}}{1 \text{ mol CaCl}_2} \right) = 0.300 \text{ } m \text{ ions}$$

CaCl₂ consists of Ca⁺² ions and Cl⁻ ions, 3 particles for each CaCl₂.

- | | |
|----------------------------|---|
| a) Osmotic pressure: | $\Pi_{\text{I}} = \Pi_{\text{II}} < \Pi_{\text{III}}$ |
| b) Boiling point: | $\text{bp}_{\text{I}} = \text{bp}_{\text{II}} < \text{bp}_{\text{III}}$ |
| c) Freezing point: | $\text{fp}_{\text{III}} < \text{fp}_{\text{I}} = \text{fp}_{\text{II}}$ |
| d) Vapor pressure at 50°C: | $\text{vp}_{\text{III}} < \text{vp}_{\text{I}} = \text{vp}_{\text{II}}$ |

- 13.72 The mol fraction of solvent affects the vapor pressure according to the equation: $P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$

$$\text{Moles C}_3\text{H}_8\text{O}_3 = (44.0 \text{ g C}_3\text{H}_8\text{O}_3) \left(\frac{1 \text{ mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3} \right) = 0.47779 \text{ mol C}_3\text{H}_8\text{O}_3 \text{ (unrounded)}$$

$$\text{Moles H}_2\text{O} = (500.0 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 27.7469 \text{ mol H}_2\text{O} \text{ (unrounded)}$$

$$X_{\text{solvent}} = \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol glycerol}} = \frac{27.7469 \text{ mol H}_2\text{O}}{27.7469 \text{ mol H}_2\text{O} + 0.47779 \text{ mol glycerol}} = 0.98307 \text{ (unrounded)}$$

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} = (0.98307) (23.76 \text{ torr}) = 23.35774 = \mathbf{23.36 \text{ torr}}$$

- 13.74 The change in freezing point is calculated from $\Delta T_f = i K_f m$, where K_f is 1.86°C/*m* for aqueous solutions, *i* is the van't Hoff factor, and *m* is the molality of particles in solution. Since urea is a covalent compound and does not ionize in water, *i* = 1. Once ΔT_f is calculated, the freezing point is determined by subtracting it from the freezing point of pure water (0.00°C).

$$\Delta T_f = i K_f m = (1) (1.86^{\circ}\text{C}/m) (0.111 \text{ } m) = 0.20646^{\circ}\text{C} \text{ (unrounded)}$$

The freezing point is 0.00°C – 0.20646°C = –0.20646 = **–0.206°C**.

- 13.76 The boiling point of a solution is increased relative to the pure solvent by the relationship $\Delta T_b = iK_b m$. Vanillin is a nonelectrolyte so $i = 1$. The molality must be calculated, and K_b is given ($1.22^\circ\text{C} / m$).

$$\text{Molality of Vanillin} = \frac{(3.4 \text{ g Vanillin}) \left(\frac{1 \text{ mol Vanillin}}{152.14 \text{ g Vanillin}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right)}{(50.0 \text{ g Ethanol})}$$

$$= 0.44695675 \text{ } m \text{ Vanillin (unrounded)}$$

$$\Delta T_b = iK_b m = (1) (1.22^\circ\text{C} / m) (0.44695675 \text{ } m) = 0.545287^\circ\text{C (unrounded)}$$

The boiling point is $78.5^\circ\text{C} + 0.545287^\circ\text{C} = 79.045287 = \mathbf{79.0^\circ\text{C}}$.

- 13.78 The molality of the solution can be determined from the relationship $\Delta T_f = iK_f m$ with the value $1.86^\circ\text{C}/m$ inserted for K_f and $i = 1$ for the nonelectrolyte ethylene glycol (ethylene glycol is a covalent compound that will form one particle per molecule when dissolved). Convert the freezing point of the solution to $^\circ\text{C}$ and find ΔT_f :

$$^\circ\text{C} = (5/9) (^\circ\text{F} - 32.0) = (5/9) ((-10.0)^\circ\text{F} - 32.0) = -23.3333^\circ\text{C (unrounded)}$$

$$\Delta T_f = (0.00 - (-23.3333))^\circ\text{C} = 23.3333^\circ\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{23.3333^\circ\text{C}}{1.86^\circ\text{C}/m} = 12.54478 \text{ } m \text{ (unrounded)}$$

Ethylene glycol will be abbreviated as EG

Multiply the molality by the given mass of solvent to find the mass of ethylene glycol that must be in solution.

$$\text{Mass ethylene glycol} = \left(\frac{12.54478 \text{ mol EG}}{1 \text{ kg H}_2\text{O}} \right) (14.5 \text{ kg H}_2\text{O}) \left(\frac{62.07 \text{ g EG}}{1 \text{ mol EG}} \right)$$

$$= 1.129049 \times 10^4 = \mathbf{1.13 \times 10^4 \text{ g ethylene glycol}}$$

To prevent the solution from freezing, dissolve a minimum of $1.13 \times 10^4 \text{ g}$ ethylene glycol in 14.5 kg water.

- 13.80 Convert the mass percent to molality and use $\Delta T = iK_b m$ to find the van't Hoff factor.

a) Assume exactly 100 grams of solution.

$$\text{Mass NaCl} = (100 \text{ g solution}) \left(\frac{1.00\% \text{ NaCl}}{100\% \text{ solution}} \right) = 1.00 \text{ g NaCl}$$

$$\text{Moles NaCl} = (1.00 \text{ g NaCl}) \left(\frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) = 0.0171116 \text{ mol NaCl}$$

$$\text{Mass H}_2\text{O} = 100.00 \text{ g solution} - 1.00 \text{ g NaCl} = 99.00 \text{ g H}_2\text{O}$$

$$\text{Molality NaCl} = \frac{\text{mole NaCl}}{\text{kg H}_2\text{O}} = \frac{0.0171116 \text{ mol NaCl}}{99.00 \text{ g H}_2\text{O}} \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 0.172844 = \mathbf{0.173 \text{ } } m \text{ NaCl}$$

$$\text{Calculate } \Delta T = (0.000 - (-0.593))^\circ\text{C} = 0.593^\circ\text{C}$$

$$\Delta T_f = iK_f m$$

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.593^\circ\text{C}}{(1.86^\circ\text{C}/m)(0.172844 \text{ } m)} = 1.844537 = \mathbf{1.84}$$

The value of i should be close to 2 because NaCl dissociates into 2 particles when dissolving in water.

b) For acetic acid, CH_3COOH :

Assume exactly 100 grams of solution.

$$\text{Mass CH}_3\text{COOH} = (100 \text{ g solution}) \left(\frac{0.500\% \text{ CH}_3\text{COOH}}{100\% \text{ solution}} \right) = 0.500 \text{ g CH}_3\text{COOH}$$

$$\text{Moles CH}_3\text{COOH} = (0.500 \text{ g CH}_3\text{COOH}) \left(\frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \text{ g CH}_3\text{COOH}} \right) = 0.0083264 \text{ mol CH}_3\text{COOH}$$

$$\text{Mass H}_2\text{O} = 100.00 \text{ g solution} - 0.500 \text{ g CH}_3\text{COOH} = 99.500 \text{ g H}_2\text{O}$$

$$\text{Molality CH}_3\text{COOH} = \frac{\text{mole CH}_3\text{COOH}}{\text{kg H}_2\text{O}} = \frac{0.0083264 \text{ mol CH}_3\text{COOH}}{99.500 \text{ g H}_2\text{O}} \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right)$$

$$= 0.083682 = \mathbf{0.0837 \text{ } m \text{ CH}_3\text{COOH}}$$

$$\text{Calculate } \Delta T = (0.000 - (-0.159))^\circ\text{C} = 0.159^\circ\text{C}$$

$$\Delta T_f = iK_f m$$

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.159^\circ\text{C}}{(1.86^\circ\text{C}/m)(0.083682 \text{ } m)} = 1.02153 = \mathbf{1.02}$$

Acetic acid is a weak acid and dissociates to a small extent in solution, hence a van't Hoff factor that is close to 1.

- 13.83 The pressure of each compound is proportional to its mole fraction according to Raoult's law: $P_A = X_A P_A^\circ$

$$X_{\text{CH}_2\text{Cl}_2} = \frac{\text{moles CH}_2\text{Cl}_2}{\text{moles CH}_2\text{Cl}_2 + \text{mol CCl}_4} = \frac{1.50 \text{ mol}}{1.50 + 1.00 \text{ mol}} = 0.600$$

$$X_{\text{CCl}_4} = \frac{\text{moles CCl}_4}{\text{moles CH}_2\text{Cl}_2 + \text{mol CCl}_4} = \frac{1.00 \text{ mol}}{1.50 + 1.00 \text{ mol}} = 0.400$$

$$P_A = X_A P_A^\circ$$

$$= (0.600) (352 \text{ torr}) = 211.2 = \mathbf{211 \text{ torr CH}_2\text{Cl}_2}$$

$$= (0.400) (118 \text{ torr}) = \mathbf{47.2 \text{ torr CCl}_4}$$

- 13.85 To find the volume of seawater needed, substitute the given information into the equation that describes the ppb concentration, account for extraction efficiency, and convert mass to volume using the density of seawater.

$$1.1 \times 10^{-2} \text{ ppb} = \frac{\text{mass Gold}}{\text{mass seawater}} \times 10^9$$

$$1.1 \times 10^{-2} \text{ ppb} = \frac{31.1 \text{ g Au}}{\text{mass seawater}} \times 10^9$$

$$\text{mass seawater} = \left[\frac{31.1 \text{ g}}{1.1 \times 10^{-2}} \times 10^9 \right] = 2.827273 \times 10^{12} \text{ g (with 100\% efficiency)}$$

$$\text{Mass of seawater} = \left(2.827273 \times 10^{12} \text{ g} \right) \left(\frac{100\%}{79.5\%} \right) = 3.5563 \times 10^{12} \text{ g seawater (unrounded) (79.5\% efficiency)}$$

$$\text{Volume seawater} = \left(3.5563 \times 10^{12} \text{ g} \right) \left(\frac{1 \text{ mL}}{1.025 \text{ g}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 3.46956 \times 10^9 = \mathbf{3.5 \times 10^9 \text{ L}}$$

- 13.90 a) First, find the molality from the freezing point depression and then use the molality, given mass of solute and volume of water to calculate the molar mass of the solute compound. Assume the solute is a nonelectrolyte ($i = 1$). $\Delta T_f = iK_f m = (0.000 - (-0.201)) = 0.201^\circ\text{C}$

$$m = \frac{\Delta T_f}{K_f i} = \frac{0.201^\circ\text{C}}{(1.86^\circ\text{C}/m)(1)} = 0.1080645 \text{ } m \text{ (unrounded)}$$

$$m = \frac{\text{moles solute}}{\text{kg solvent}} \quad (25.0 \text{ mL}) \left(\frac{1.00 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 0.0250 \text{ kg water}$$

$$\text{moles solute} = (m)(\text{kg solvent}) = (0.1080645 \text{ } m)(0.0250 \text{ kg}) = 0.0027016 \text{ mol}$$

$$\text{molar mass} = \frac{0.243 \text{ g}}{0.0027016 \text{ mol}} = 89.946698 = \mathbf{89.9 \text{ g/mol}}$$

b) Assume that 100.00 g of the compound gives 53.31 g carbon, 11.18 g hydrogen and $100.00 - 53.31 - 11.18 = 35.51$ g oxygen.

$$\text{Moles C} = (53.31 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 4.43880 \text{ mol C (unrounded)}$$

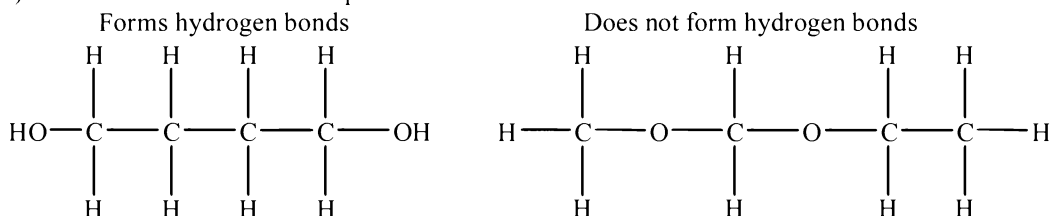
$$\text{Moles H} = (11.18 \text{ g H}) \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 11.09127 \text{ mol H (unrounded)}$$

$$\text{Moles O} = (35.51 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 2.219375 \text{ mol O (unrounded)}$$

Dividing the values by the lowest amount of moles (2.219375) will give 2 mol C, 5 mol H and 1 mol O for an **empirical formula** $\text{C}_2\text{H}_5\text{O}$ with molar mass 45.06 g/mol.

Since the molar mass of the compound, 89.9 g/mol from part (a), is twice the molar mass of the empirical formula, the **molecular formula is** $2(\text{C}_2\text{H}_5\text{O})$ or $\text{C}_4\text{H}_{10}\text{O}_2$.

c) There is more than one example in each case. Possible Lewis structures:



- 13.92 a) Use the boiling point elevation of 0.45°C to calculate the molality of the solution. Then, with molality, the mass of solute, and volume of water calculate the molar mass.

$$\Delta T = iK_b m \quad i = 1 \text{ (nonelectrolyte)}$$

$$\Delta T = (100.45 - 100.00)^\circ\text{C} = 0.45^\circ\text{C}$$

$$m = \frac{\Delta T_b}{K_b i} = \frac{0.45^\circ\text{C}}{(0.512^\circ\text{C}/m)(1)} = 0.878906 \text{ } m = 0.878906 \text{ mol/kg (unrounded)}$$

$$m = \frac{\text{moles solute}}{\text{kg solvent}} \quad (25.0 \text{ mL}) \left(\frac{0.997 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 0.0249250 \text{ kg water}$$

$$\text{moles solute} = (m)(\text{kg solvent}) = (0.878906 \text{ } m)(0.0249250 \text{ kg}) = 0.0219067 \text{ mol}$$

$$\text{molar mass} = \frac{1.50 \text{ g}}{0.0219067 \text{ mol}} = 68.4722 = \mathbf{68 \text{ g/mol}}$$

b) The molality calculated would be the moles of ions per kg of solvent. If the compound consists of three ions the molality of the compound would be $1/3$ of $0.878906 \text{ } m$ and the calculated molar mass would be three times greater: $3 \times 68.4722 = 205.417 = \mathbf{2.1 \times 10^2 \text{ g/mol}}$.

c) The molar mass of CaN_2O_6 is 164.10 g/mol. This molar mass is less than the $2.1 \times 10^2 \text{ g/mol}$ calculated when the compound is assumed to be a strong electrolyte and is greater than the 68 g/mol calculated when the compound is assumed to be a nonelectrolyte. Thus, the compound is an electrolyte, since it dissociates into ions in solution. However, the ions do not dissociate completely in solution.

d) Use the molar mass of CaN_2O_6 to calculate the molality of the compound. Then calculate i in the boiling point elevation formula.

$$m = \left(\frac{1.50 \text{ g CaN}_2\text{O}_6}{25.0 \text{ mL}} \right) \left(\frac{\text{mL}}{0.997 \text{ g}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol}}{164.10 \text{ g CaN}_2\text{O}_6} \right) = 0.3667309 \text{ } m \text{ (unrounded)}$$

$$\Delta T = iK_b m$$

$$i = \frac{\Delta T_b}{K_b m} = \frac{(0.45^\circ\text{C})}{(0.512^\circ\text{C}/m)(0.3667309 \text{ } m)} = 2.396597 = \mathbf{2.4}$$

- 13.95 a) From the osmotic pressure, the molarity of the solution can be found. The ratio of mass per volume to moles per volume gives the molar mass of the compound.

$$\Pi V = nRT$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{(0.340 \text{ torr})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 25) \text{ K}) \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right)} = 1.828546 \times 10^{-5} M (\text{unrounded})$$

$$(M)(V) = \text{moles}$$

$$\text{Moles} = (1.828546 \times 10^{-5} M)(30.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 5.48564 \times 10^{-7} \text{ mol}$$

$$\text{Molar mass} = \frac{(10.0 \text{ mg}) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right)}{5.48564 \times 10^{-7} \text{ mol}} = 1.82294 \times 10^4 = \mathbf{1.82 \times 10^4 \text{ g/mol}}$$

- b) To find the freezing point depression, the molarity of the solution must be converted to molality.

Then use $\Delta T_f = iK_f m$. ($i = 1$)

Mass solvent = mass of solution – mass of solute

$$\text{Mass solvent} = \left[(30.0 \text{ mL}) \left(\frac{0.997 \text{ g}}{1 \text{ mL}}\right) - (10.0 \text{ mg}) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \right] \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = 0.0299 \text{ kg}$$

$$\text{Moles solute} = \left(\frac{1.828546 \times 10^{-5} \text{ mol}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (30.0 \text{ mL}) = 5.485638 \times 10^{-7} \text{ mol (unrounded)}$$

$$\text{Molality} = \frac{5.485638 \times 10^{-7} \text{ mol}}{0.0299 \text{ kg}} = 1.83466 \times 10^{-5} m (\text{unrounded})$$

$$\Delta T_f = iK_f m = (1)(1.86^\circ\text{C}/m)(1.83466 \times 10^{-5} m) = 3.412 \times 10^{-5} = \mathbf{3.41 \times 10^{-5}^\circ\text{C}}$$

(So the solution would freeze at $0 - 3.41 \times 10^{-5}^\circ\text{C} = -3.41 \times 10^{-5}^\circ\text{C}$.)

- 13.101 a) Assume a 100 g sample of urea. This leads to the mass of each element being equal to the percent of that element.

$$\text{Moles C} = (20.1 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 1.6736 \text{ mol C (unrounded)}$$

$$\text{Moles H} = (6.7 \text{ g H}) \left(\frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 6.6468 \text{ mol H (unrounded)}$$

$$\text{Moles N} = (46.5 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 3.31906 \text{ mol N (unrounded)}$$

$$\text{Moles O} = ((100 - 20.1 - 6.7 - 46.5) \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 1.66875 \text{ mol O (unrounded)}$$

Dividing all by the smallest value (1.66875 mol O) gives: C = 1, H = 4, N = 2, O = 1. Thus, the empirical formula is $\mathbf{CH_4N_2O}$. The empirical formula weight is 60.06 g/mol.

- b) Use $\Pi = MRT$ to solve for the molarity of the urea solution. The solution molarity is related to the concentration expressed in % w/v by using the molar mass.

$$M = \Pi / RT = \frac{(2.04 \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 25) \text{ K})} = 0.0833817 M (\text{unrounded})$$

$$\text{Molar mass} = \frac{\left(\frac{5.0 \text{ g}}{\text{L}} \right)}{\left(\frac{0.0833817 \text{ mol}}{\text{L}} \right)} = 59.965 = \mathbf{60. \text{ g/mol}}$$

Because the molecular weight equals the empirical weight, the molecular formula is also **CH₄N₂O**.

Chapter 14 Periodic Patterns in the Main-Group Elements

FOLLOW-UP PROBLEMS

There are no follow-up problems for this chapter.

END-OF-CHAPTER PROBLEMS

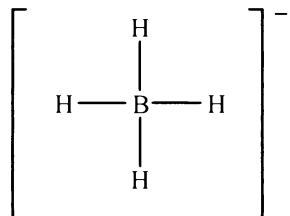
- 14.1 Ionization energy is defined as the energy required to remove the outermost electron from an atom. The further the outermost electron is from the nucleus, the less energy is required to remove it from the attractive force of the nucleus. In hydrogen, the outermost electron is in the $n = 1$ level and in lithium the outermost electron is in the $n = 2$ level. Therefore, the outermost electron in lithium requires less energy to remove, resulting in a lower ionization energy.

- 14.2 a) $2 \text{Al}(s) + 6 \text{HCl}(aq) \rightarrow 2 \text{AlCl}_3(aq) + 3 \text{H}_2(g)$
Active metals displace hydrogen from HCl by reducing the H^+ to H_2 .
b) $\text{LiH}(s) + \text{H}_2\text{O}(l) \rightarrow \text{LiOH}(aq) + \text{H}_2(g)$
In water, H^- (here in LiH) reacts as a strong base to form H_2 and OH^- .

- 14.4 a)

Na = +1	B = +3	H = -1 in NaBH_4
Al = +3	B = +3	H = -1 in $\text{Al}(\text{BH}_4)_3$
Li = +1	Al = +3	H = -1 in LiAlH_4

b) The polyatomic ion in NaBH_4 is $[\text{BH}_4]^-$. Boron is the central atom and has four surrounding electron groups; therefore, its shape is **tetrahedral**.



- 14.7 a) Alkali metals generally lose electrons (act as **reducing agents**) in their reactions.
b) Alkali metals have relatively low ionization energies, meaning they easily lose the outermost electron. The electron configurations of alkali metals have one more electron than a noble gas configuration, so losing an electron gives a stable electron configuration.
c) $2 \text{Na}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Na}^+(aq) + 2 \text{OH}^-(aq) + \text{H}_2(g)$
 $2 \text{Na}(s) + \text{Cl}_2(g) \rightarrow 2 \text{NaCl}(s)$
- 14.9 a) Density increases down a group. The increasing atomic size (volume) is not offset by the increasing size of the nucleus (mass), so m/V increases.
b) Ionic size increases down a group. Electron shells are added down a group, so both atomic and ionic size increase.
c) E-E bond energy decreases down a group. Shielding of the outer electron increases as the atom gets larger, so the attraction responsible for the E-E bond decreases.
d) IE_1 decreases down a group. Increased shielding of the outer electron is the cause of the decreasing IE_1 .
e) ΔH_{hydr} decreases down a group. ΔH_{hydr} is the heat released when the metal salt dissolves in, or is hydrated by, water. Hydration energy decreases as ionic size increases.

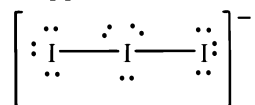
Increasing down **a and b**
Decreasing down **c, d, and e**

- 14.11 Peroxides are oxides in which oxygen has a -1 oxidation state. Sodium peroxide has the formula Na_2O_2 and is formed from the elements Na and O_2 .
- $$2 \text{Na}(s) + \text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s)$$
- 14.13 The problem specifies that an alkali halide is the desired product. The alkali metal is K (comes from potassium carbonate, $\text{K}_2\text{CO}_3(s)$) and the halide is I (comes from hydroiodic acid, $\text{HI}(aq)$). Treat the reaction as a double displacement reaction.
- $$\text{K}_2\text{CO}_3(s) + 2 \text{HI}(aq) \rightarrow 2 \text{KI}(aq) + \text{H}_2\text{CO}_3(aq)$$
- However, $\text{H}_2\text{CO}_3(aq)$ is unstable and decomposes to $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$, so the final reaction is:
- $$\text{K}_2\text{CO}_3(s) + 2 \text{HI}(aq) \rightarrow 2 \text{KI}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$$
- 14.17 Metal atoms are held together by metallic bonding, a sharing of valence electrons. Alkaline earth metal atoms have one more valence electron than alkali metal atoms, so the number of electrons shared is greater. Thus, metallic bonds in alkaline earth metals are stronger than in alkali metals. Melting requires overcoming the metallic bonds. To overcome the stronger alkaline earth metal bonds requires more energy (higher temperature) than to overcome the alkali earth metal bonds. First ionization energy, density, and boiling points will be larger for alkaline earth metals than for alkali metals.
- 14.18 a) A base forms when a basic oxide, such as CaO , is added to water.
- $$\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s)$$
- b) Alkaline earth metals reduce O_2 to form the oxide.
- $$2 \text{Ca}(s) + \text{O}_2(g) \rightarrow 2 \text{CaO}(s)$$
- 14.20 Beryllium is generally the exception to properties exhibited by other alkaline earth elements.
- a) Here, Be does not behave like other alkaline earth metals: $\text{BeO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NR}$. The oxides of alkaline earth metals are strongly basic, but BeO is amphoteric. BeO will react with both acids and bases to form salts, but an amphoteric substance does not react with water.
- b) Here, Be does behave like other alkaline earth metals:
- $$\text{BeCl}_2(l) + 2 \text{Cl}^-(\text{solvated}) \rightarrow \text{BeCl}_4^{2-}(\text{solvated})$$
- Each chloride ion donates a lone pair of electrons to form a covalent bond with the Be in BeCl_2 . Metal ions form similar covalent bonds with ions or molecules containing a lone pair of electrons. The difference in beryllium is that the orbital involved in the bonding is a p orbital, whereas in metal ions it is usually the d orbitals that are involved.
- 14.22 For period 2 elements in the first four groups, the number of covalent bonds equals the number of electrons in the outer level, so it increases from 1 covalent bond for lithium in group 1A(1) to 4 covalent bonds for carbon in group 4A(14). For the rest of period 2 elements, the number of covalent bonds equals the difference between 8 and the number of electrons in the outer level. So for nitrogen, $8 - 5 = 3$ covalent bonds; for oxygen, $8 - 6 = 2$ covalent bonds; for fluorine, $8 - 7 = 1$ covalent bond; and for neon, $8 - 8 = 0$, no bonds. For elements in higher periods, the same pattern exists but with exceptions for groups 3A(13) to 7A(17) when an expanded octet allows for more covalent bonds.
- 14.25 The electron removed in Group 2A(2) atoms is from the outer level s orbital, whereas in Group 3A(13) atoms the electron is from the outer level p orbital. For example, the electron configuration for Be is $1s^2 2s^2$ and for B is $1s^2 2s^2 2p^1$. It is easier to remove the p electron of B than the s electron of Be, because the energy of a p orbital is slightly higher than that of the s orbital from the same level. Even though the atomic size decreases from increasing Z_{eff} , the IE decreases from 2A(2) to 3A(13).
- 14.26 a) Compounds of Group 3A(13) elements, like boron, have only six electrons in their valence shell when combined with halogens to form three bonds. Having six electrons, rather than an octet, results in an "electron deficiency."
- b) As an electron deficient central atom, B is trigonal planar. Upon accepting an electron pair to form a bond, the shape changes to tetrahedral.
- $$\text{BF}_3(g) + \text{NH}_3(g) \rightarrow \text{F}_3\text{B}-\text{NH}_3(g)$$
- $$\text{B}(\text{OH})_3(aq) + \text{OH}^-(aq) \rightarrow \text{B}(\text{OH})_4^-(aq)$$

14.28 Acidity of oxides increases up a group: $\text{In}_2\text{O}_3 < \text{Ga}_2\text{O}_3 < \text{Al}_2\text{O}_3$.

14.30 Halogens typically have a -1 oxidation state in metal-halide combinations, so the apparent oxidation state of $\text{I} = +3$. However, the anion I_3^- combines with TI in the $+1$ oxidation state. The anion I_3^- has $[3 \times (1)7e^-] + [1e^- \text{ from the charge}] = 22$ valence electrons; 4 of these electrons are used to form the two single bonds between iodine atoms and 16 electrons are used to give every atom an octet. The remaining two electrons belong to the central I atom; therefore the central iodine has five electron groups (2 single bonds and 3 lone pairs) and has a general formula of AX_2E_3 . The electrons are arranged in a trigonal bipyramid with the three lone pairs in the trigonal plane. It is a linear molecule with bond angles $= 180^\circ$. $(\text{TI}^{3+})(\text{I})_3$ does not exist because of the low strength of the $\text{TI}-\text{I}$ bond.

O.N. = +3 (apparent); = +1 (actual)



14.35 Network covalent solids differ from molecular solids in that they are harder and have higher melting points than molecular solids. A network solid is held together by covalent bonds while intermolecular forces hold molecules in molecular solids together. Covalent bonds are much stronger than intermolecular forces and require more energy to break. To melt a network solid, more energy (higher temperature) is required to break the covalent bonds than is required to break the intermolecular forces in the molecular solid, so the network solid has a higher melting point. The covalent bonds also hold the atoms in a much more rigid structure than the intermolecular forces hold the molecules. Thus, a network solid is much harder than a molecular solid.

14.36 Oxide basicity is greater for the oxide of a metal atom. Tin(IV) oxide is more basic than carbon dioxide since tin has more metallic character than carbon.

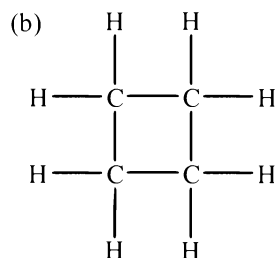
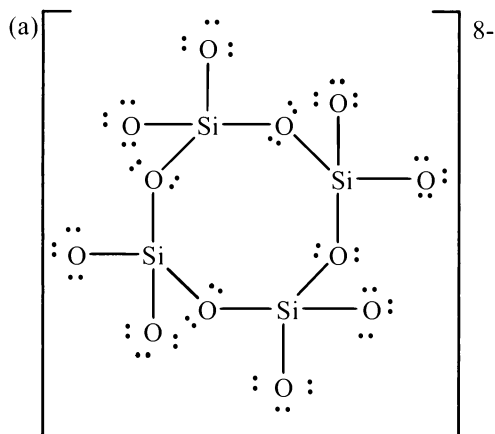
14.38 a) IE_1 values generally decreases down a group.

b) The increase in Z_{eff} from Si to Ge is larger than the increase from C to Si because more protons have been added. Between C and Si an additional 8 protons have been added, whereas between Si and Ge an additional 18 (includes the protons for the d -block) protons have been added. The same type of change takes place when going from Sn to Pb, when the 14 f -block protons are added.

c) Group 3A(13) would show greater deviations because the single p electron receives no shielding effect offered by other p electrons.

14.41 Atomic size increases moving down a group. As atomic size increases, ionization energy decreases so that it is easier to form a positive ion. An atom that is easier to ionize exhibits greater metallic character.

14.43



There is another answer possible for C_4H_8 .

- 14.46 a) **Diamond, C**, a network covalent solid of carbon
 b) **Calcium carbonate, CaCO_3** (brands that use this compound as an antacid also advertise them as an important source of calcium)
 c) **Carbon dioxide, CO_2** , is the most widely known greenhouse gas; CH_4 is also implicated.
 d) **CO binds to Fe(II) in blood, preventing the normal binding of O_2 .**
 e) **Lead, Pb** (in old plumbing as lead solder, and in paint as a pigment)
- 14.50 a) In Group 5A(15), all elements except bismuth have a range of oxidation states from -3 to $+5$.
 b) For nonmetals, the range of oxidation states is from the lowest at group number (A) -8 , which is $5 - 8 = -3$ for Group 5A, to the highest equal to the group number (A), which is $+5$ for Group 5A.
- 14.51 a) Element oxides are either ionic or covalent molecules. Elements with low electronegativity (metals) form ionic oxides, whereas elements with relatively high electronegativity (nonmetals) form covalent oxides. The greater the electronegativity of the element, the more covalent the bonding is in its oxide.
 b) Oxide acidity increases to the right across a period and decreases down a group, so increasing acidity directly correlates with increasing electronegativity.
- 14.54 a) With excess oxygen arsenic will form the oxide with arsenic in its highest possible oxidation state, $+5$.

$$4 \text{As}(s) + 5 \text{O}_2(g) \rightarrow 2 \text{As}_2\text{O}_5(s)$$

 b) Trihalides are formed by direct combination of the elements (except N).

$$2 \text{Bi}(s) + 3 \text{F}_2(g) \rightarrow 2 \text{BiF}_3(s)$$

 c) Metal phosphides, arsenides, and antimonides react with water to form Group 5A hydrides.

$$\text{Ca}_3\text{As}_2(s) + 6 \text{H}_2\text{O}(l) \rightarrow 3 \text{Ca}(\text{OH})_2(s) + 2 \text{AsH}_3(g)$$
- 14.60 a) Both groups have elements that range from gas to metalloid to metal. Thus, their boiling points and conductivity vary in similar ways down a group.
 b) The degree of metallic character and methods of bonding vary in similar ways down a group.
 c) Both P and S have allotropes and both bond covalently with almost every other nonmetal.
 d) Both N and O are diatomic gases at normal temperatures and pressures. Both N and O have very low melting and boiling points.
 e) Oxygen, O_2 , is a reactive gas whereas nitrogen, N_2 , is not. Nitrogen can exist in multiple oxidation states, whereas oxygen has 2 oxidation states.
- 14.62 a) To decide what type of reaction will occur, examine the reactants. Notice that sodium hydroxide is a strong base. Is the other reactant an acid? If we separate the salt, sodium hydrogen sulfate, into the two ions, Na^+ and HSO_4^- , then it is easier to see the hydrogen sulfate ion as the acid. The sodium ions could be left out for the net ionic reaction.

$$\text{NaHSO}_4(aq) + \text{NaOH}(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l)$$

 b) As mentioned in the book, hexafluorides are known to exist for sulfur. These will form when excess fluorine is present.

$$\text{S}_8(s) + 24 \text{F}_2(g) \rightarrow 8 \text{SF}_6(g)$$

 c) Group 6A(16) elements, except oxygen, form hydrides in the following reaction.

$$\text{FeS}(s) + 2 \text{HCl}(aq) \rightarrow \text{H}_2\text{S}(g) + \text{FeCl}_2(aq)$$
- 14.64 a) Se is a nonmetal; its oxide is **acidic**.
 b) N is a nonmetal; its oxide is **acidic**.
 c) K is a metal; its oxide is **basic**.
 d) Be is an alkaline earth metal, but all of its bonds are covalent; its oxide is **amphoteric**.
 e) Ba is a metal; its oxide is **basic**.
- 14.66 a) **O_3 , ozone**
 b) **SO_3 , sulfur trioxide** ($+6$ oxidation state)
 c) **SO_2 , sulfur dioxide**

- 14.67 $\text{S}_2\text{F}_{10}(\text{g}) \rightarrow \text{SF}_4(\text{g}) + \text{SF}_6(\text{g})$
 O.N. of S in S_2F_{10} : $-(10 \times -1 \text{ for F}) / 2 = +5$
 O.N. of S in SF_4 : $-(4 \times -1 \text{ for F}) = +4$
 O.N. of S in SF_6 : $-(6 \times -1 \text{ for F}) = +6$
- 14.68 a) Polarity is the molecular property that is responsible for the difference in boiling points between iodine monochloride and bromine. The stronger the intermolecular forces holding molecules together, the higher the boiling point. More polar molecules have stronger intermolecular forces and higher boiling points. Molecular polarity is a result of the difference in electronegativity, an atomic property, of the atoms in the molecule.
 b) ICl is a polar molecule while Br_2 is nonpolar. The dipole-dipole forces between polar molecules are stronger than the dispersion forces between nonpolar molecules. The boiling point of the polar ICl is higher than the boiling point of Br_2 .
- 14.70 a) Bonding with very electronegative elements: **+1, +3, +5, +7**. Bonding with other elements: **-1**
 b) The electron configuration for Cl is $[\text{Ne}]3s^23p^5$. By adding on electron, Cl achieves an octet similar to the noble gas Ar. By forming covalent bonds, Cl completes or expands its octet by maintaining its electrons paired in bonds or lone pairs.
 c) Fluorine only forms the -1 oxidation state because its small size and no access to d orbitals prevent it from forming multiple covalent bonds. Fluorine's high electronegativity also prevents it from sharing its electrons.
- 14.71 a) The Cl-Cl bond is stronger than the Br-Br bond since the chlorine atoms are smaller than the bromine atoms, so the shared electrons are held more tightly by the two nuclei.
 b) The Br-Br bond is stronger than the I-I bond since the bromine atoms are smaller than the iodine atoms.
 c) The Cl-Cl bond is stronger than the F-F bond. The fluorine atoms are smaller than the chlorine but they are so small that electron-electron repulsion of the lone pairs decreases the strength of the bond.
- 14.72 a) A substance that disproportionates serves as both an oxidizing and reducing agent. Assume that OH^- serves as the base. Write the reactants and products of the reaction, and balance like a redox reaction.

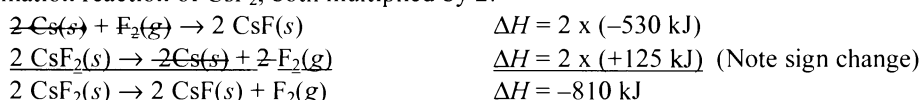
$$3 \text{Br}_2(\text{l}) + 6 \text{OH}^-(\text{aq}) \rightarrow 5 \text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$$
- 14.73 a) $\text{I}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HI}(\text{aq}) + \text{HIO}(\text{aq})$
 b) $\text{Br}_2(\text{l}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{s}) + 2 \text{Br}^-(\text{aq})$
 c) $\text{CaF}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{CaSO}_4(\text{s}) + 2 \text{HF}(\text{g})$
- 14.76 **Helium** is the second most abundant element in the universe. **Argon** is the most abundant noble gas in Earth's atmosphere, the third most abundant constituent after N_2 and O_2 .
- 14.77 Whether a boiling point is high or low is a result of the strength of the forces between particles. Dispersion forces, the weakest of all the intermolecular forces, hold atoms of noble gases together. Only a relatively low temperature is required for the atoms to have enough kinetic energy to break away from the attractive force of other atoms and go into the gas phase. The boiling points are so low that all the noble gases are gases at room temperature.
- 14.79 a) Alkali metals have an outer electron configuration of ns^1 . The first electron lost by the metal is the ns electron, giving the metal a noble gas configuration. Second ionization energies for alkali metals are high because the electron being removed is from the next lower energy level and electrons in a lower level are more tightly held by the nucleus. The metal would also lose its noble gas configuration.
 b) The reaction is $2 \text{CsF}_2(\text{s}) \rightarrow 2 \text{CsF}(\text{s}) + \text{F}_2(\text{g})$
 You know the ΔH_f for the formation of CsF :

$$\text{Cs}(\text{s}) + 1/2 \text{F}_2(\text{g}) \rightarrow \text{CsF}(\text{s}) \quad \Delta H_f = -530 \text{ kJ/mol}$$

 You also know the ΔH_f for the formation of CsF_2 :

$$\text{Cs}(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{CsF}_2(\text{s}) \quad \Delta H_f = -125 \text{ kJ/mol}$$

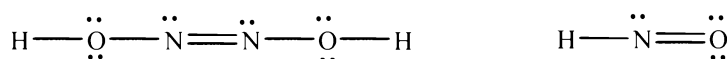
To obtain the heat of reaction for the breakdown of CsF_2 to CsF , combine the formation reaction of CsF with the reverse of the formation reaction of CsF_2 , both multiplied by 2:



810 kJ of energy are released when 2 moles of CsF_2 convert to 2 moles of CsF , so heat of reaction for one mole of CsF is $-810/2$ or **-405 kJ/mol** .

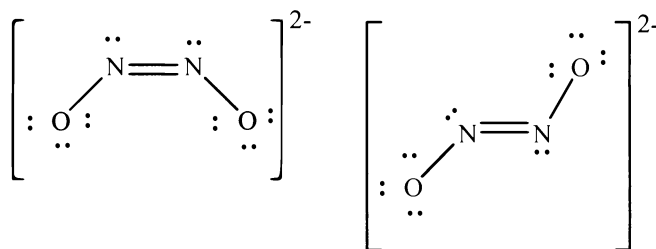
- 14.81 a) Empirical formula HNO has a molar mass of 31.02, so hyponitrous acid with a molar mass of 62.04 g/mol which is twice 31.02 would have a molecular formula twice the empirical formula, $\text{H}_2\text{N}_2\text{O}_2$. In addition, the molecular formula of nitroxyl would be the same as the empirical formula, HNO , since the molar mass of nitroxyl is the same as the empirical formula.

b)

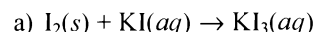


c) In both hyponitrous acid and nitroxyl, the nitrogens are surrounded by 3 electron groups (one single bond, one double bond and one unshared pair), so the electron arrangement is trigonal planar and the molecular shape is **bent**.

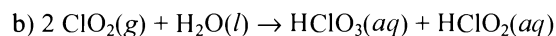
d)



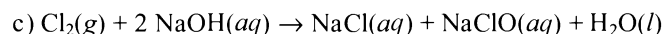
- 14.84 In a disproportionation reaction, a substance acts as both a reducing agent and oxidizing agent because an atom within the substance reacts to form atoms with higher and lower oxidation states.



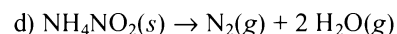
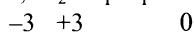
I in I_2 reduces to I in KI_3 . I in KI oxidizes to I in KI_3 . This is not a disproportionation reaction since different substances have atoms that reduce or oxidize. The *reverse* direction would be a disproportionation reaction because a single substance (I in KI) both oxidizes and reduces.



Yes, ClO_2 disproportionates, as the chlorine reduces from +4 to +3 and oxidizes from +4 to +5.



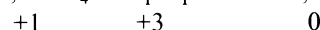
Yes, Cl_2 disproportionates, as the chlorine reduces from 0 to -1 and oxidizes from 0 to +1.



Yes, NH_4NO_2 disproportionates, the ammonium (NH_4^+) nitrogen oxidizes from -3 to 0, and the nitrite (NO_2^-) nitrogen reduces from +3 to 0.



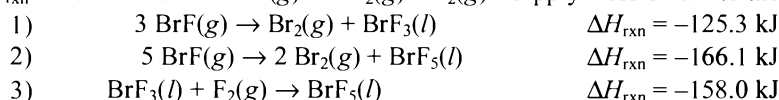
Yes, MnO_4^{2-} disproportionates, the manganese oxidizes from +6 to +7 and reduces from +6 to +4.



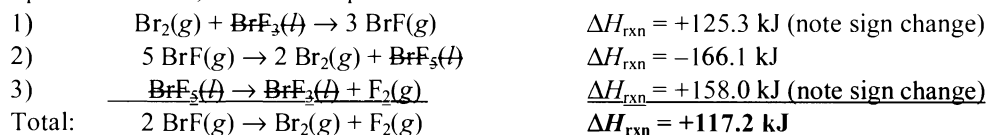
Yes, AuCl disproportionates, the gold oxidizes from +1 to +3 and reduces from +1 to 0.

- 14.85 a) Group **5A(15)** elements have 5 valence electrons and typically form three bonds with a lone pair to complete the octet. An example is NH_3 .
 b) Group **7A(17)** elements readily gain an electron causing the other reactant to be oxidized. They form monatomic ions of formula X^- and oxoanions. Examples would be Cl^- and ClO^- .
 c) Group **6A(16)** elements have six valence electrons and gain a complete octet by forming two covalent bonds. An example is H_2O .
 d) Group **1A(1)** elements are the strongest reducing agents because they most easily lose an electron. As the least electronegative and most metallic of the elements, they are not likely to form covalent bonds. Group **2A(2)** have similar characteristics. Thus, either Na or Ca could be an example.
 e) Group **3A(13)** elements have only three valence electrons to share in covalent bonds, but with an empty orbital they can accept an electron pair from another atom. Boron would be an example of an element of this type.
 f) Group **8A(18)**, the noble gases, are the least reactive of all the elements. Xenon is an example that forms compounds, while helium does not form compounds.

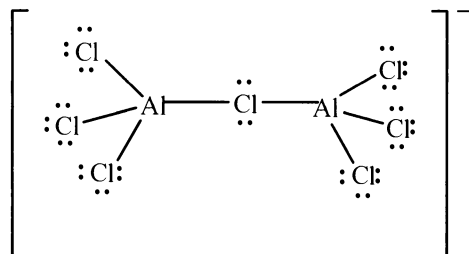
14.86 Find ΔH_{rxn} for the reaction $2 \text{BrF}(g) \rightarrow \text{Br}_2(g) + \text{F}_2(g)$. Apply Hess's Law to the equations given:



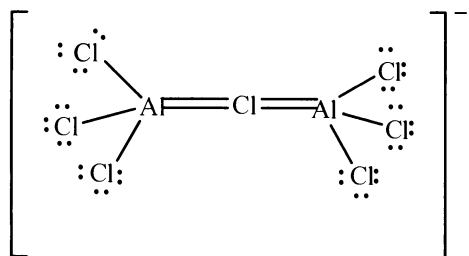
Reverse equations 1 and 3, and add to equation 2:



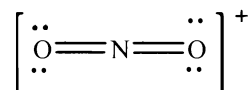
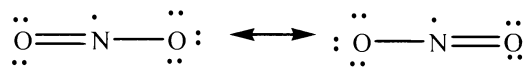
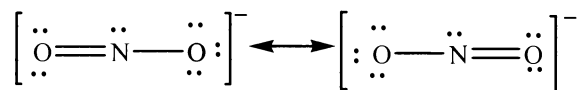
14.87 To answer these questions, draw an initial structure for Al_2Cl_7^- :



- a) Aluminum uses its $3s$ and $3p$ valence orbitals to form sp^3 hybrid orbitals for bonding.
 b) With formula AX_4 , the shape is tetrahedral around each aluminum atom.
 c) It is sp , since the ion is linear, the central atom must be sp hybridized.
 d) The sp hybridization suggests that there are no lone pairs on the central chlorine. Instead, the extra four electrons participate in bonding with the empty d -orbitals on the aluminum to form double bonds between the chlorine and each aluminum.



14.88 The Lewis structures are



The nitronium ion (NO_2^{+}) has a linear shape because the central N atom has 2 surrounding electron groups, which achieve maximum repulsion at 180° . Both the nitrite ion (NO_2^{-}) and nitrogen dioxide (NO_2) have a central N surrounded by three electron groups. The electron group arrangement would be trigonal planar with an ideal bond angle of 120° . The bond angle in NO_2 is more compressed than that in NO_2^{-} since the lone pair of electrons in NO_2^{-} takes up more space than the lone electron in NO_2 .

14.90 a) Determine the mass of As in a formula mass of the compound.

$$\% \text{ As in CuHAsO}_3 = \frac{74.92 \text{ g As}}{187.48 \text{ g CuHAsO}_3} \times 100\% = 39.96160 = \mathbf{39.96\% \text{ As}}$$

$$\% \text{ As in (CH}_3)_3\text{As} = \frac{74.92 \text{ g As}}{120.02 \text{ g (CH}_3)_3\text{As}} \times 100\% = 62.4229 = \mathbf{62.42\% \text{ As}}$$

$$\text{b) Mass As} = \left(\frac{0.50 \text{ mg As}}{\text{m}^3} \right) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) ((12.35 \text{ m})(7.52 \text{ m})(2.98 \text{ m})) = 0.13838 \text{ g As}$$

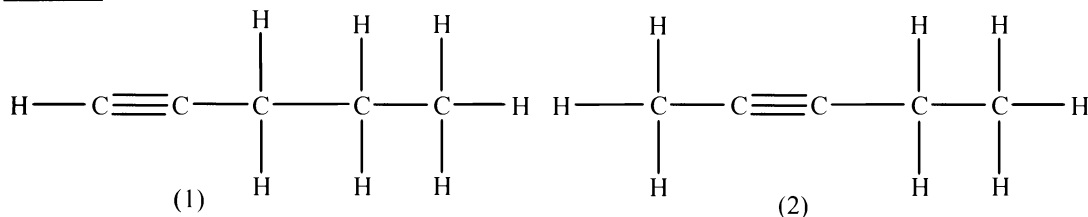
$$\text{Mass CuHAsO}_3 = (0.13838 \text{ g As}) \left(\frac{100 \text{ g CuHAsO}_3}{39.96160 \text{ g As}} \right) = 0.346282 = \mathbf{0.35 \text{ g CuHAsO}_3}$$

Chapter 15 Organic Compounds and the Atomic Properties of Carbon

FOLLOW-UP PROBLEMS

- 15.1 Plan: a) For a five-carbon compound start with 5 C atoms in a chain and place the triple bond in as many unique places as possible.

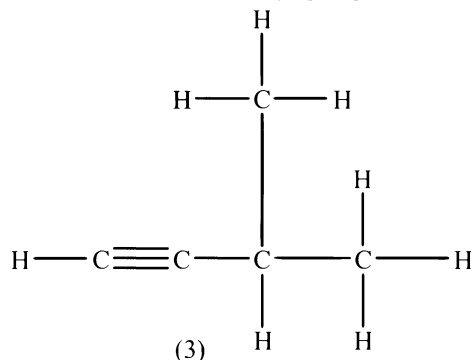
Solution:



4 C atoms in chain: There are two unique placements for the triple bond: one between the first and second carbons and one between the second and third carbons in the chain.



The fifth carbon is added as a methyl group branched off the chain. With the triple bond between the first and second carbons, the methyl group is attached to the third carbon to give structure (3).

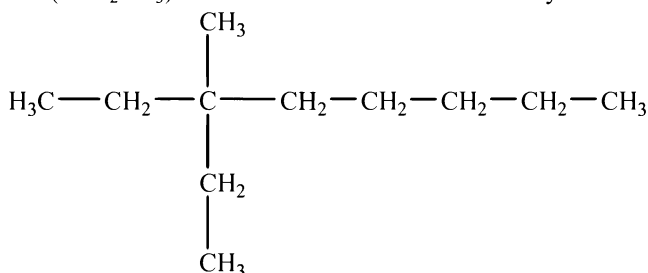


With the triple bond between the second and third carbons, the methyl group cannot be attached to either the second or the third carbons because that would create 5 bonds to a carbon and carbon has only 4 bonds. Thus, a unique structure cannot be formed with a 4 C chain where the triple bond is between the second and third carbons. There are only 3 structures with 5 carbon atoms, one triple bond, and no rings.

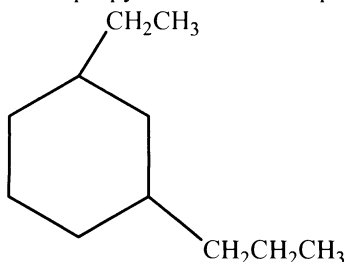
15.2 Plan: Analyze the name for chain length and side groups, then draw the structure.

Solution:

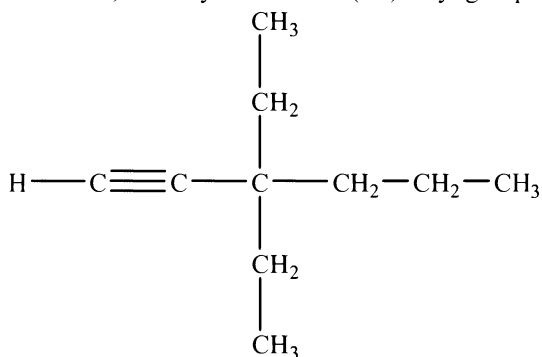
- a) 3-ethyl-3-methyloctane. The end of the name, octane, indicates an 8 C chain (oct- represents 8 C) with only single bonds between the carbons (-ane represents alkanes, only single bonds). 3-ethyl means an ethyl group ($-\text{CH}_2\text{CH}_3$) attached to carbon #3 and 3-methyl means a methyl group ($-\text{CH}_3$) attached to carbon #3.



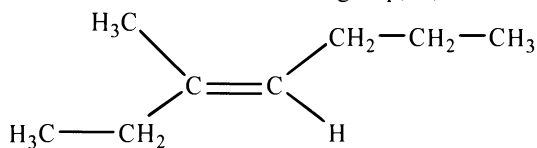
- b) 1-ethyl-3-propylcyclohexane. The hexane indicates 6 C chain (hex-) and only single bonds (-ane). The cyclo- indicates that the 6 carbons are in a ring. The 1-ethyl indicates that an ethyl group ($-\text{CH}_2\text{CH}_3$) is attached to carbon #1. Select any carbon atom in the ring as carbon #1 since all the carbon atoms in the ring are equivalent. The 3-propyl indicates that a propyl group ($-\text{CH}_2\text{CH}_2\text{CH}_3$) is attached to carbon #3.



- c) 3,3-diethyl-1-hexyne. The 1-hexyne indicates a 6 C chain with a triple bond (-yne) between C #1 and C #2. The 3,3-diethyl means two (di-) ethyl groups ($-\text{CH}_2\text{CH}_3$) both attached to C #3.



- d) *trans*-3-methyl-3-heptene. The 3-heptene indicates a 7 C chain (hept-) with one double bond (-ene) between the 3rd and 4th carbons. The 3-methyl indicates a methyl group ($-\text{CH}_3$) attached to carbon #3. The *trans* indicates that the arrangement around the two carbons in the double bond gives the two smaller groups on opposite sides of the double bond. Therefore, the smaller group on the third carbon (which would be the methyl group) is above the double bond while the smaller group, H, on the fourth carbon is below the double bond.

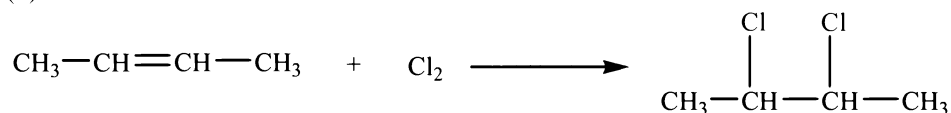


15.3 Plan:

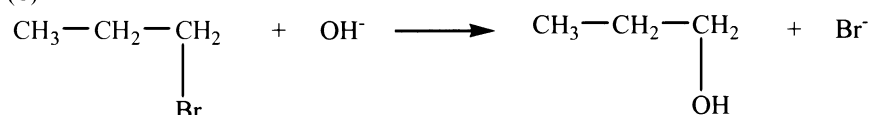
- a) An addition reaction involves breaking a multiple bond, in this case the double bond in 2-butene, and adding the other reactant to the carbons in the double bond. The reactant Cl_2 will add $-\text{Cl}$ to one of the carbons and $-\text{Cl}$ to the other carbon.
- b) A substitution reaction involves removing one atom or group from a carbon chain and replacing it with another atom or group. For 1-bromopropane the bromine will be replaced by hydroxide.
- c) An elimination reaction involves removing two atoms or groups, one from each of two adjacent carbon atoms, and forming a double bond between the two carbon atoms. For 2-methyl-2-propanol, the $-\text{OH}$ group from the center carbon and a hydrogen from one of the terminal carbons will be removed and a double bond formed between the two carbon atoms.

Solution:

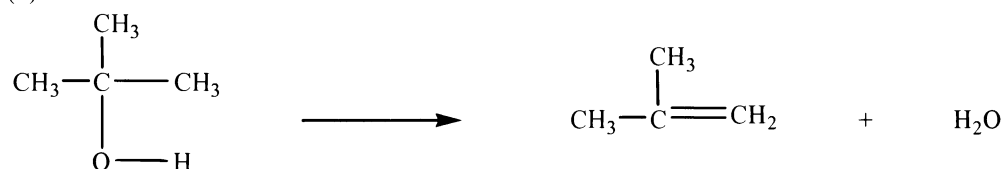
(a)



(b)



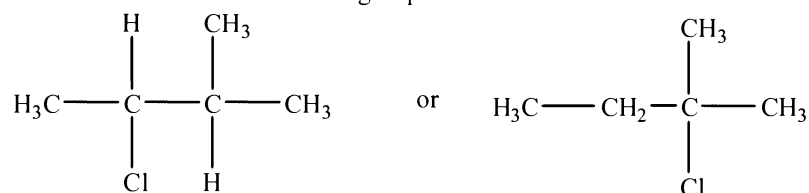
(c)



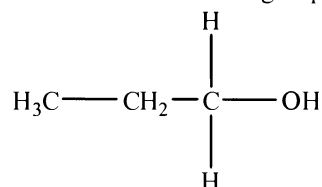
- 15.4 Plan: Reaction a) is an elimination reaction where H and Cl are eliminated from the organic reactant and a double bond is formed. Determine which carbons were involved in formation of the double bond and those two carbons would have been bonded to the H and Cl. Reaction b) is an oxidation reaction because $\text{Cr}_2\text{O}_7^{2-}$ and H_2SO_4 are oxidizing agents. An alcohol group ($-\text{OH}$) is oxidized to an acid group ($-\text{COOH}$), so determine which carbon in the product is in the acid group and attach an alcohol group to it for the reactant.

Solution:

- a) The organic reactant must contain a single bond between the second and third carbons and the second and third carbons each have an additional group: an H atom on one carbon and a Cl atom on the other carbon.

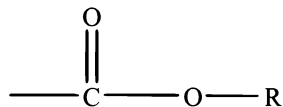


- b) The third carbon from the left in the product contains the acid group. Therefore, in the reactant this carbon should have an alcohol group.



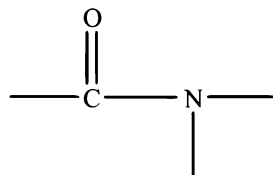
Check: When the reactants are combined, the products are identical to those given.

15.5 Plan: a) The product is an ester because it contains the unit:



Reacting an alcohol with an acid forms an ester. Since the reactant shown is an alcohol the other reactant must be the acid. Take the ---OR group off the carbon in the ester product and replace with a hydroxyl group to get the structure of the acid.

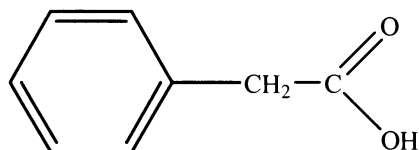
b) The product is an amide because it contains the unit:



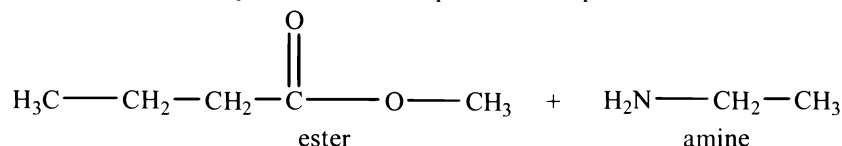
An amide forms from the reaction between an ester and an amine. This is the indicated reaction because the other product is an alcohol that results when the ---OR group on the ester breaks off. To draw the reactants first take the ---NH---R group off the amide and add another hydrogen to the nitrogen to form the amine. Attach the ---OR group to the remaining carbonyl (---C=O) group of the amide molecule so that an ester linkage is formed.

Solution:

a) The ---OR group attached to the oxygen in the product is ---OCH_3 . Removing this and adding the ---OH gives the acid reactant:



b) Take the $\text{---NHCH}_2\text{CH}_3$ group off the amide product, attach a hydrogen to the nitrogen to make the amine reactant, and attach the ---OCH_3 from the alcohol product in its place to make the ester reactant.

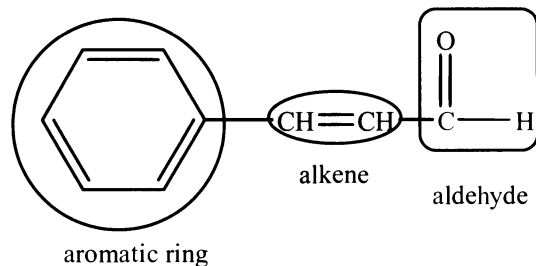


Check: When the reactants are combined, the products are identical to those given.

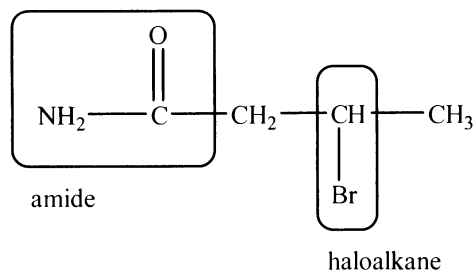
15.6 Plan: Examine the structures for known functional groups: alkenes (C=C), alkynes ($\text{C}\equiv\text{C}$), haloalkanes (C---X , where X is a halogen), alcohols (C---OH), esters (---COOR), ethers (C---O---C), amines (NR_3), carboxylic acids (---COOH), amides (---CONR_2), aldehydes (O=CHR), and ketones (O=CR_2 where R cannot be a H).

Solution:

a) The structure contains an aromatic ring, alkene bond, and an aldehyde group.



b) The structure contains an amide and a haloalkane.



END-OF-CHAPTER PROBLEMS

- 15.1
- Carbon's electronegativity is midway between the most metallic and nonmetallic elements of period 2. To attain a filled outer shell, carbon forms covalent bonds to other atoms in molecules (e.g., methane, CH_4), network covalent solids (e.g., diamond), and polyatomic ions (e.g., carbonate, CO_3^{2-}).
 - Since carbon has 4 valence shell electrons, it forms four covalent bonds to attain an octet.
 - Two noble gas configurations, He and Ne, are equally near carbon's configuration. To reach the He configuration, the carbon atom must lose 4 electrons, requiring too much energy to form the C^{4+} cation. This is confirmed by the fact that the value of the ionization energy for carbon is very high. To reach the Ne configuration, the carbon atom must gain 4 electrons, also requiring too much energy to form the C^{4-} anion. The fact that a carbon anion is unlikely to form is supported by carbon's electron affinity. The other possible ions would not have a stable noble gas configuration.
 - Carbon is able to bond to itself extensively because carbon's small size allows for closer approach and greater orbital overlap. The greater orbital overlap results in a strong, stable bond.
 - The C-C bond is short enough to allow the sideways overlap of unhybridized p orbitals on neighboring C atoms. The sideways overlap of p orbitals results in double and triple bonds.
- 15.2
- The elements that most frequently bond to carbon are other carbon atoms, hydrogen, oxygen, nitrogen, phosphorus, sulfur, and the halogens, F, Cl, Br, and I.
 - In organic compounds, heteroatoms are defined as atoms of any element other than carbon and hydrogen. The elements **O, N, P, S, F, Cl, Br, and I** listed in part a) are heteroatoms.
 - Elements more electronegative than carbon are N, O, F, Cl, and Br. Elements less electronegative than carbon are H and P. Sulfur and iodine have the same electronegativity as carbon.
 - The more types of atoms that can bond to carbon, the greater the variety of organic compounds that are possible.
- 15.4
- Chemical reactivity occurs when unequal sharing of electrons in a covalent bond results in regions of high and low electron density. The C-H, C-C and C-I bonds are unreactive because electron density is shared equally between the two atoms. The C=O bond is reactive because oxygen is more electronegative than carbon and the electron rich pi bond is above and below the C-O bond axis, making it very attractive to electron-poor atoms. The C-Li bond is also reactive because the bond polarity results in an electron-rich region around carbon and an electron-poor region around Li.
- 15.5
- An alkane is an organic compound consisting of carbon and hydrogen in which there are no multiple bonds between carbons, only single bonds. A cycloalkane is an alkane in which the carbon chain is arranged in a ring. An alkene is a hydrocarbon with at least one double bond between two carbons. An alkyne is a hydrocarbon with at least one triple bond between two carbons.

b) The general formula for an alkane is C_nH_{2n+2} .

The general formula for a cycloalkane is C_nH_{2n} . Elimination of two hydrogen atoms is required to form the additional bond between carbons in the ring.

For an alkene, assuming only one double bond, the general formula is C_nH_{2n} . When a double bond is formed in an alkane, two hydrogen atoms are removed.

For an alkyne, assuming only one triple bond, the general formula is C_nH_{2n-2} . Forming a triple bond from a double bond causes the loss of two hydrogen atoms.

c) For hydrocarbons, "saturated" is defined as a compound that cannot add more hydrogen. An unsaturated hydrocarbon contains multiple bonds that react with H_2 to form single bonds. The **alkanes and cycloalkanes** are saturated hydrocarbons since they contain only single C–C bonds.

15.8 An asymmetric molecule has no plane of symmetry.

a) A circular clock face numbered 1 to 12 o'clock is **asymmetric**. Imagine that the clock is cut in half, from 12 to 6 or from 9 to 3. The one-half of the clock could never be superimposed on the other half, so the halves are not identical. Another way to visualize symmetry is to imagine cutting an object in half and holding the half up to a mirror. If the original object is "re-created" in the mirror, then the object has a plane of symmetry.

b) A football is symmetric and has two planes of symmetry – one axis along the length and one axis along the fattest part of the football.

c) A dime is **asymmetric**. Either cutting it in half or slicing it into two thin diameters results in two pieces that cannot be superimposed on one another.

d) A brick, assuming that it is perfectly shaped, is symmetric and has three planes of symmetry at right angles to each other.

e) A hammer is symmetric and has one plane of symmetry, slicing through the metal head and down through the handle.

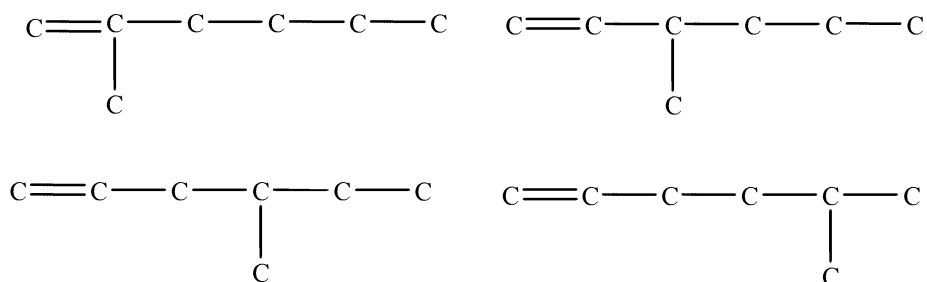
f) A spring is **asymmetric**. Every coil of the spring is identical to the one before it, so a spring can be cut in half and the two pieces can be superimposed on one another by sliding (not flipping) the second half over the first. However, if the cut spring is held up to a mirror, the resulting image is not the same as the uncut spring.

Disassemble a ballpoint pen and cut the spring inside to verify this explanation.

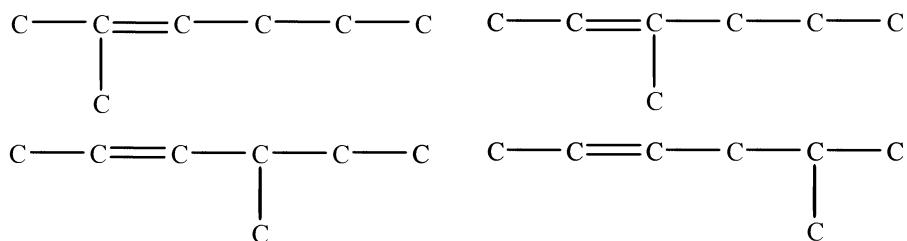
15.9 To draw the possible skeletons it is useful to have a systematic approach to make sure no structures are missed.

a) Since there are 7 C atoms but only a 6 C chain, there is one C branch off of the chain. First, draw the skeleton with the double bond between the first and second carbons and place the branched carbon in all possible positions starting with C #2. Then move the double bond to between the second and third carbon and place the branched carbon in all possible positions. Then move the double bond to between the third and fourth carbons and place the branched carbon in all possible positions. The double bond does not need to be moved further in the chain since the placement between the second and third carbon is equivalent to placement between the fourth and fifth carbons and placement between the first and second carbons is equivalent to placement between the fifth and sixth carbons. The only position to consider for the double bond is between the branched carbon and the 6 C chain.

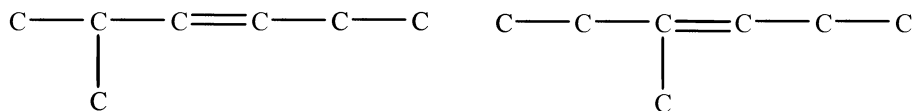
Double bond between first and second carbons:



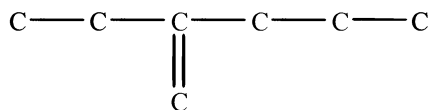
Double bond between second and third carbons:



Double bond between third and fourth carbons:



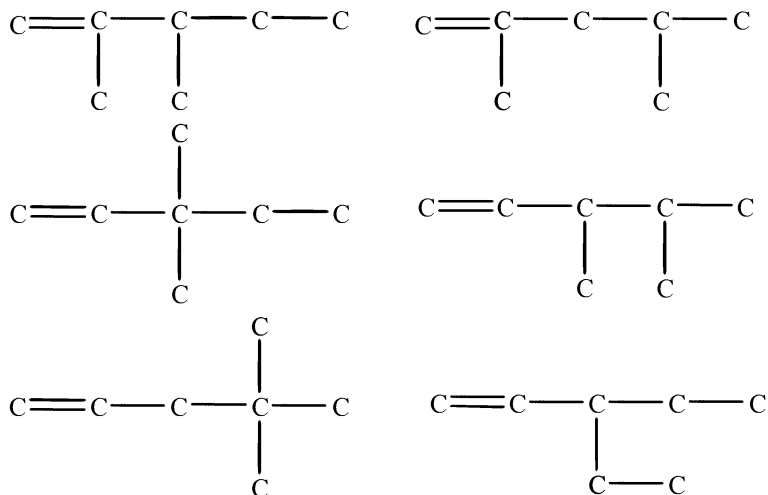
Double bond between branched carbon and chain:



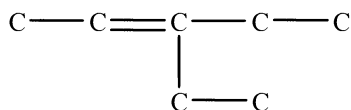
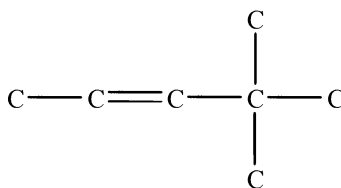
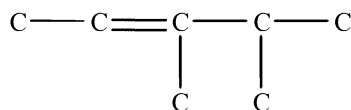
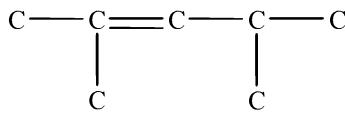
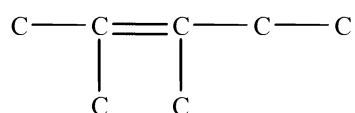
The total number of unique skeletons is 11. To determine if structures are the same, build a model of one skeleton and see if you can match the structure of the other skeleton by rotating the model and without breaking any bonds. If bonds must be broken to make the other skeleton, the structures are not the same.

b) The same approach can be used here with placement of the double bond first between C #1 and C #2, then between C #2 and C #3. Since there are 7 C atoms but only 5 C atoms in the chain, there are two C branches.

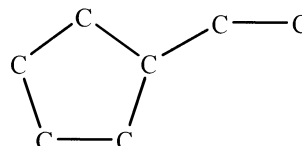
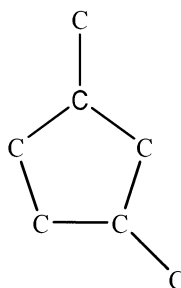
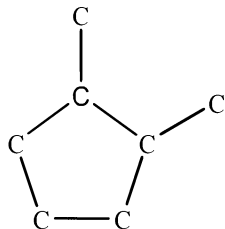
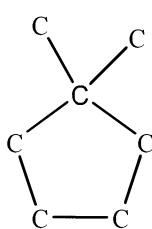
Double bond between first and second carbons:



Double bond between second and third carbons:

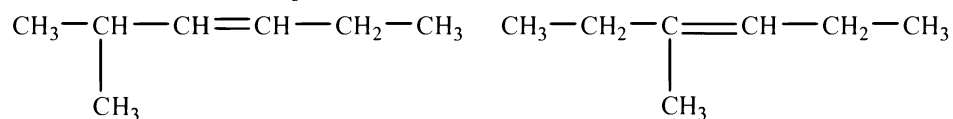
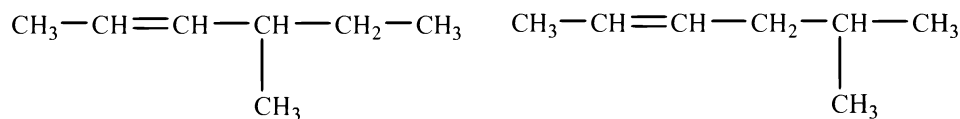
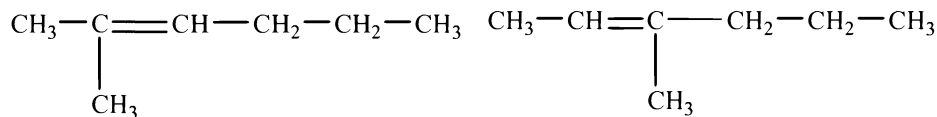
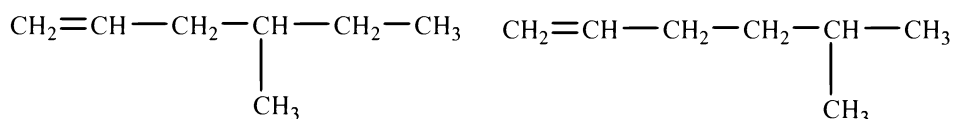
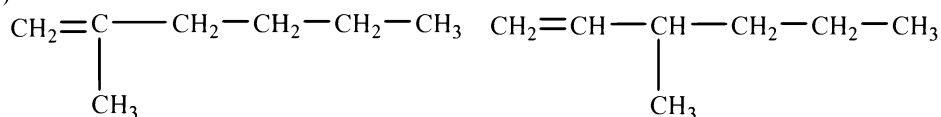


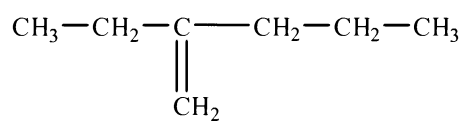
c) Five of the carbons are in the ring and two are branched off the ring. Remember that all the carbons in the ring are equivalent and there are two groups bonded to each carbon in the ring.



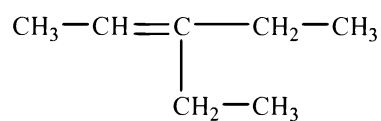
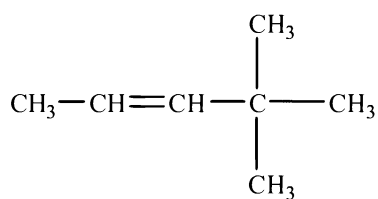
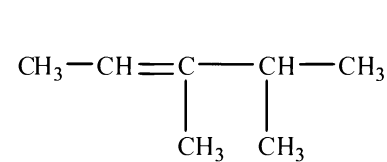
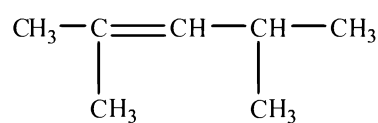
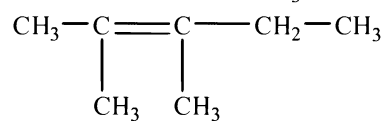
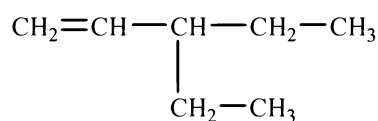
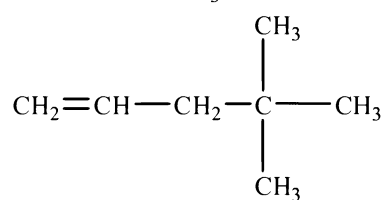
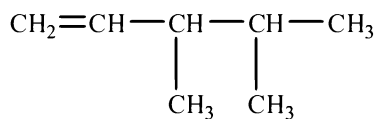
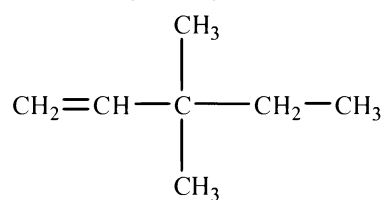
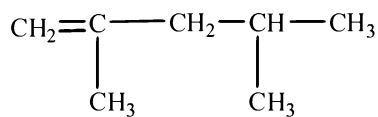
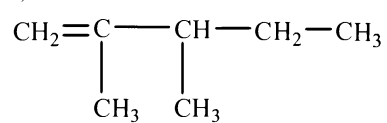
15.11 Add hydrogen atoms to make a total of 4 bonds to each carbon.

a)

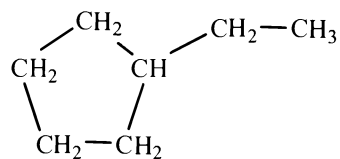
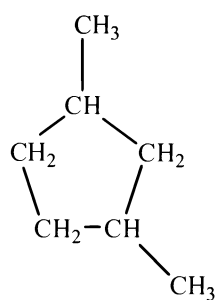
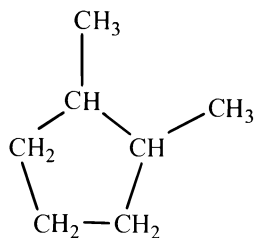
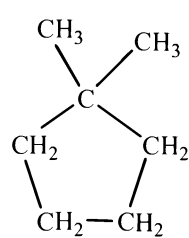




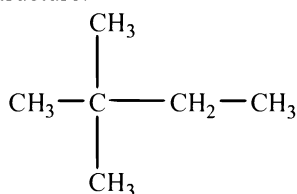
b)



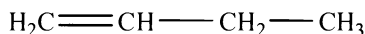
c)



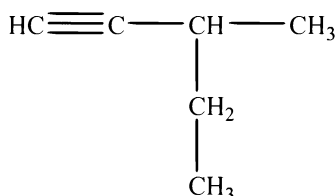
- 15.13 a) The second carbon from the left in the chain is bonded to five groups. Removing one of the groups gives a correct structure.



- b) The first carbon in the chain has five bonds, so remove one of the hydrogens on this carbon.

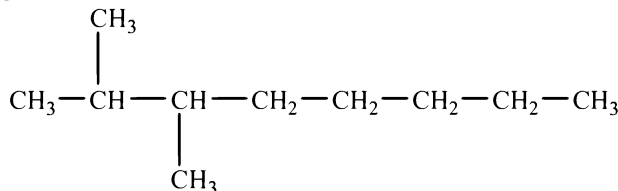


- c) The second carbon in the chain has five bonds, so move the ethyl group from the second carbon to the third. To do this, a hydrogen atom must be removed from the third carbon atom.

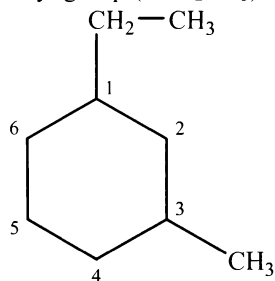


- d) Structure is correct.

- 15.15 a) *Octane* denotes an eight carbon alkane chain. A methyl group ($-\text{CH}_3$) is located at the second and third carbon position from the left.



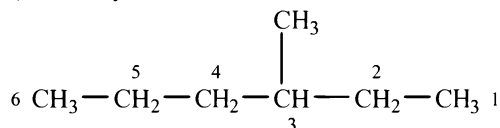
- b) *Cyclohexane* denotes a six-carbon ring containing only single bonds. Numbering of the carbons on the ring could start at any point, but typically numbering starts at the top carbon atom of the ring for convenience. The ethyl group ($-\text{CH}_2\text{CH}_3$) is located at position 1 and the methyl group is located at position 3.



- c) The longest continuous chain contains seven carbon atoms, so the root name is “hept”. The molecule contains only single bonds, so the suffix is “ane”. Numbering the carbon chain from the left results in side groups (methyl groups) at positions 3 and 4. Numbering the carbon chain from the other will result in side groups at positions 4 and 5. Since the goal is to obtain the lowest numbering position for a side group, the correct name is **3,4-dimethylheptane**. Note that the prefix “di” is used to denote that two methyl side groups are present in this molecule.

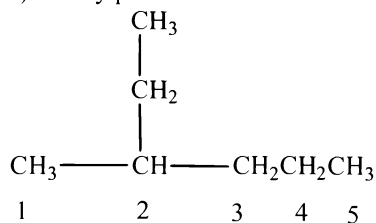
- d) At first glance, this molecule looks like a 4 carbon *ring*, but the two $-\text{CH}_3$ groups mean that they cannot be bonded to each other. Instead, this molecule is a 4-carbon *chain*, with two methyl groups (dimethyl) located at the position 2 carbon. The correct name is **2,2-dimethylbutane**.

15.17 a) 4-methylhexane means a 6C chain with a methyl group on the 4th carbon:

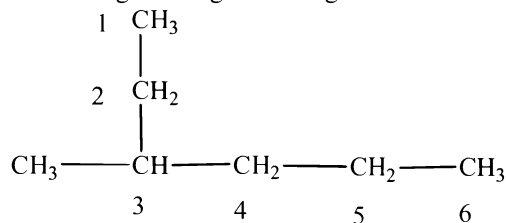


Numbering from the end carbon to give the lowest value for the methyl group gives correct name of 3-methylhexane.

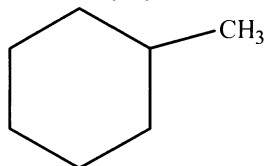
b) 2-ethylpentane means a 5 C chain with an ethyl group on the 2nd carbon:



Numbering the longest chain gives the correct name, **3-methylhexane**.

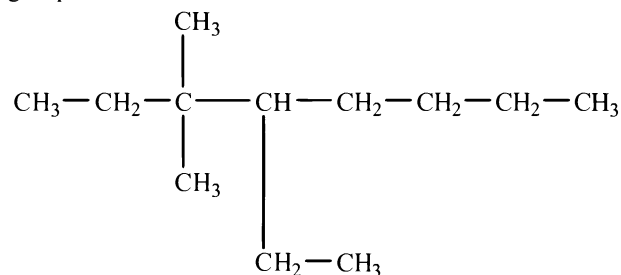


c) 2-methylcyclohexane means a 6 C ring with a methyl group on carbon #2:



In a ring structure, whichever carbon is bonded to the methyl group is automatically assigned as carbon #1. Since this is automatic, it is not necessary to specify 1-methyl in the name. Correct name is **methylcyclohexane**.

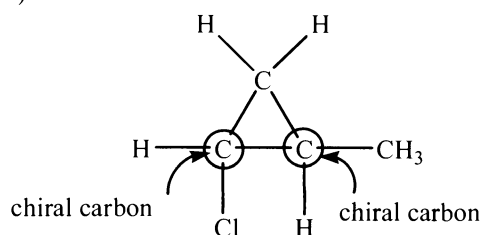
d) 3,3-methyl-4-ethyloctane means an 8 C chain with 2 methyl groups attached to the 3rd carbon and one ethyl group to the 4th carbon.



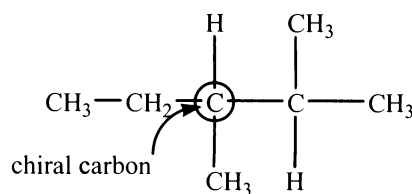
Numbering is good for this structure, but the fact that there are two methyl groups must be indicated by the prefix di- in addition to listing 3,3. The branch names appear in alphabetical order. Correct name is **4-ethyl-3,3-dimethyloctane**.

15.19 A carbon atom is chiral if it is attached to four different groups. The circled atoms below are chiral.

a)



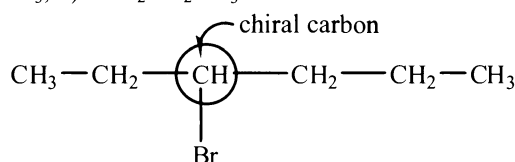
b)



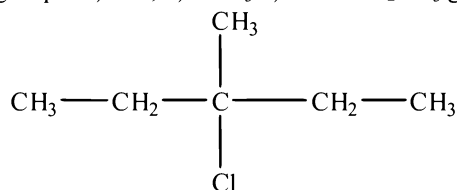
Both can exhibit optical activity.

15.21 An optically active compound will contain at least one chiral center, a carbon with four distinct groups bonded to it.

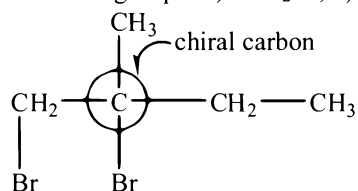
a) This compound is a 6 carbon chain with a Br on the third carbon. 3-bromohexane is optically active because carbon #3 has four distinct groups bonded to it: 1) -Br, 2) -H, 3) -CH₂CH₃, 4) -CH₂CH₂CH₃.



b) This compound is a 5 carbon chain with a Cl and a methyl (CH₃) group on the third carbon. 3-chloro-3-methylpentane is not optically active because no carbon has four distinct groups. The third carbon has three distinct groups: 1) -Cl, 2) -CH₃, 3) two -CH₂CH₃ groups.

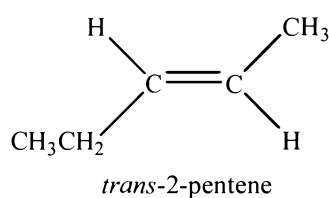
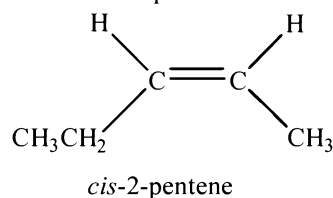


c) This compound is a 4 carbon chain with Br atoms on the first and second carbon atoms and a methyl group on the second carbon. 1,2-dibromo-2-methylbutane is optically active because the 2nd carbon is chiral, bonded to the four groups: 1) -CH₂Br, 2) -CH₃, 3) -Br, 4) -CH₂CH₃.

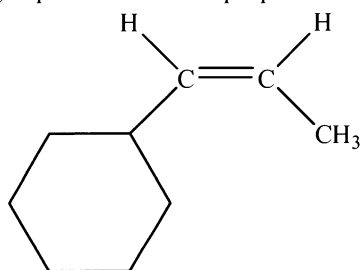


15.23 Geometric isomers are defined as compounds with the same atom sequence but different arrangements of the atoms in space. The *cis-trans* geometric isomers occur when rotation is restricted around a bond, as in a double bond or a ring structure, and when two different groups are bonded to each atom in the restricted bond.

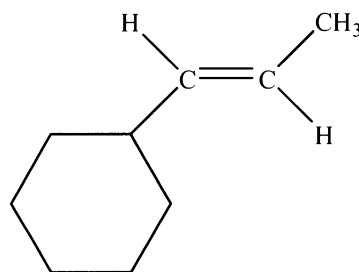
a) Both carbons in the double bond are bonded to two distinct groups, so geometric isomers will occur. The double bond occurs at position 2 in a five-carbon chain.



b) *Cis-trans* geometric isomerism occurs about the double bond. The ring is named as a side group (cyclohexyl) occurring at position 1 on the propene main chain.



cis-1-cyclohexylpropene

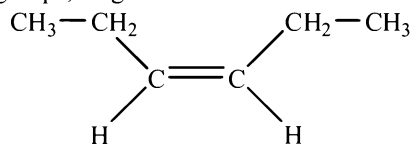


trans-1-cyclohexylpropene

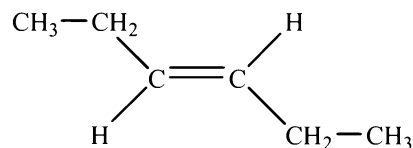
c) No geometric isomers occur because the left carbon participating in the double bond is attached to two identical methyl ($-\text{CH}_3$) groups.

15.25 a) The structure of propene is $\text{CH}_2=\text{CH}-\text{CH}_3$. The first carbon that is involved in the double bond is bonded to two of the same type of group, hydrogen. Geometric isomers will not occur in this case.

b) The structure of 3-hexene is $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$. Both carbons in the double bond are bonded to two distinct groups, so geometric isomers will occur.



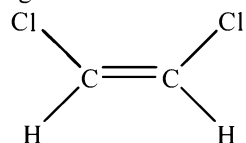
cis-3-hexene



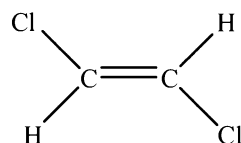
trans-3-hexene

c) The structure of 1,1-dichloroethene is $\text{CCl}_2=\text{CH}_2$. Both carbons in the double bond are bonded to two identical groups, so no geometric isomers occur.

d) The structure of 1,2-dichloroethene is $\text{CHCl}=\text{CHCl}$. Each carbon in the double bond is bonded to two distinct groups, so geometric isomers do exist.

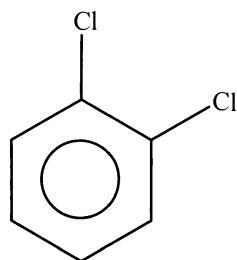


cis-1,2-dichloroethene

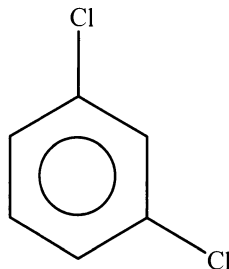


trans-1,2-dichloroethene

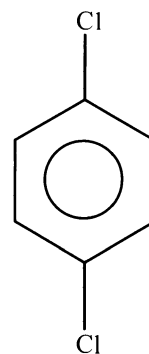
15.27 Benzene is a planar, aromatic hydrocarbon. It is commonly depicted as a hexagon with a circle in the middle to indicate that the π bonds are delocalized around the ring and that all ring bonds are identical. The *ortho*, *meta*, *para* naming system is used to denote the location of attached groups in benzene compounds only, not other ring structures like the cycloalkanes.



1,2-dichlorobenzene
(*o*-dichlorobenzene)

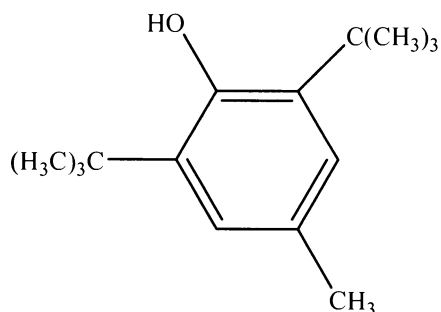


1,3-dichlorobenzene
(*m*-dichlorobenzene)

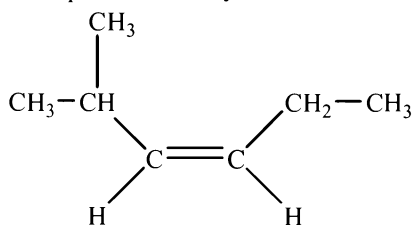


1,4-dichlorobenzene
(*p*-dichlorobenzene)

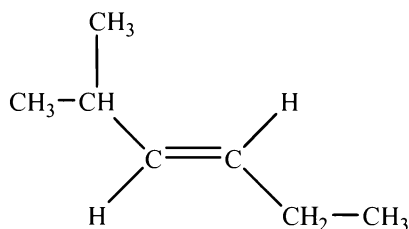
- 15.29 Analyzing the name gives benzene as the base structure with the following groups bonded to it: 1) on carbon #1 a hydroxy group, $-\text{OH}$; 2) on carbons #2 and #6 a *tert*-butyl group, $-\text{C}(\text{CH}_3)_3$; and 3) on carbon #4 a methyl group, $-\text{CH}_3$.



- 15.30 The compound 2-methyl-3-hexene has *cis-trans* isomers.

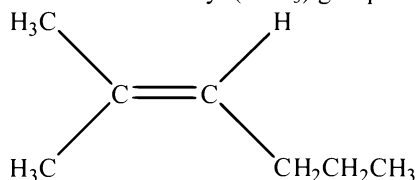


cis-2-methyl-3-hexene



trans-2-methyl-3-hexene

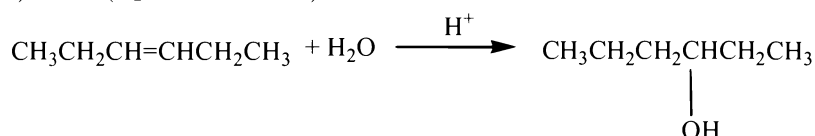
The compound 2-methyl-2-hexene does not have *cis-trans* isomers because the #2 carbon atom is attached to two identical methyl ($-\text{CH}_3$) groups:



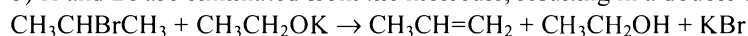
2-methyl-2-hexene

- 15.32 a) HBr is removed in this **elimination reaction**, and an unsaturated product is formed.
b) This is an **addition reaction** in which hydrogen is added to the double bond, resulting in a saturated product.

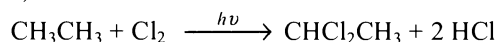
- 15.34 a) Water (H_2O or H and OH) is added to the double bond:



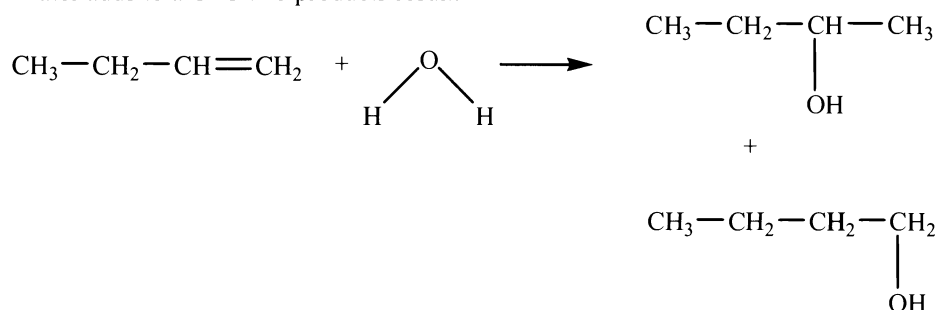
b) H and Br are eliminated from the molecule, resulting in a double bond:



c) Two chlorine atoms are substituted for two hydrogen atoms in ethane:

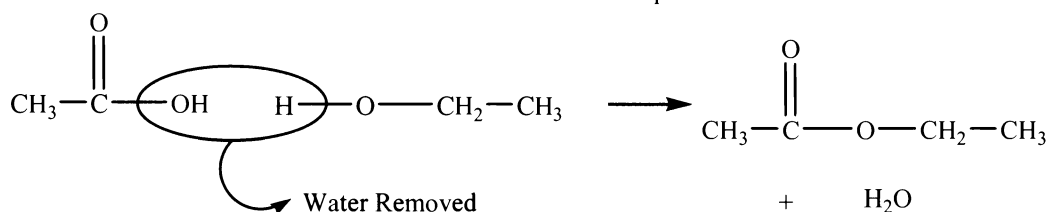


But when water adds to a C=C two products result:



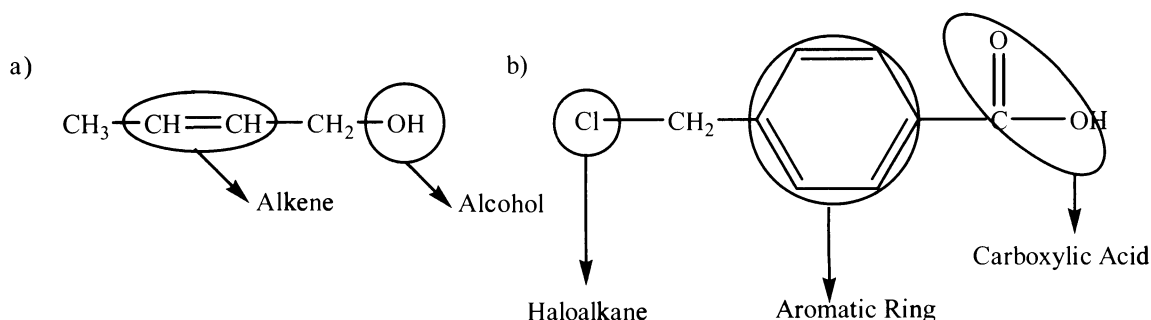
In this reaction very little of the second product forms.

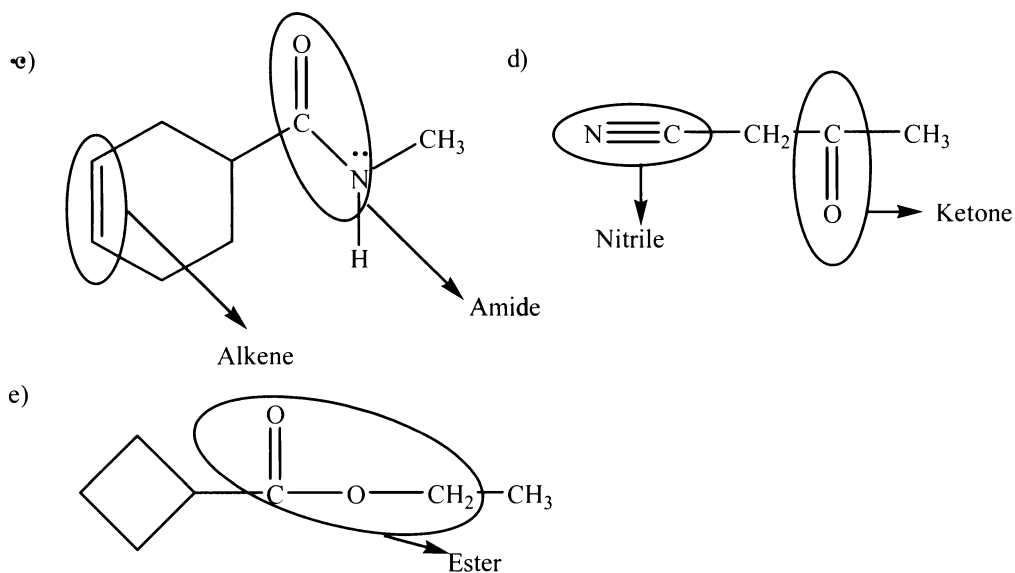
- 15.41 Esters and acid anhydrides form through **dehydration-condensation** reactions. Dehydration indicates that the other product is **water**. In the case of ester formation, condensation refers to the combination of the carboxylic acid and the alcohol. The ester forms and water is the other product.



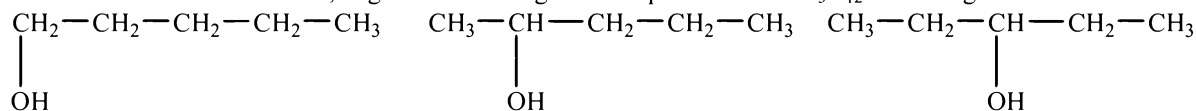
- 15.43 a) Halogens, except iodine, differ from carbon in electronegativity and form a single bond with carbon. The organic compound is an **alkyl halide**.
 b) Carbon forms triple bonds with itself and nitrogen. For the bond to be polar, it must be between carbon and nitrogen. The compound is a **nitrile**.
 c) **Carboxylic acids** contain a double bond to oxygen and a single bond to oxygen. Carboxylic acids dissolve in water to give acidic solutions.
 d) Oxygen is commonly double-bonded to carbon. A carbonyl group (C=O) that is at the end of a chain is found in an **aldehyde**.

15.45



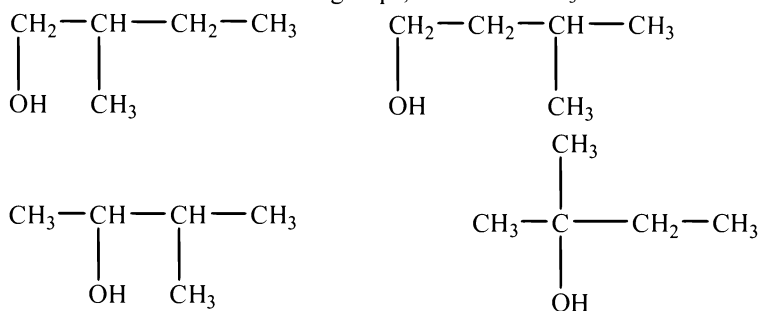


15.47 To draw all structural isomers, begin with the longest chain possible. For $C_5H_{12}O$ the longest chain is 5 carbons:

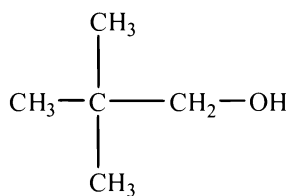


The three structures represent all the unique positions for the alcohol group on a 5 C chain.

Next use a 4 C chain and attach to side groups, $-\text{OH}$ and $-\text{CH}_3$.

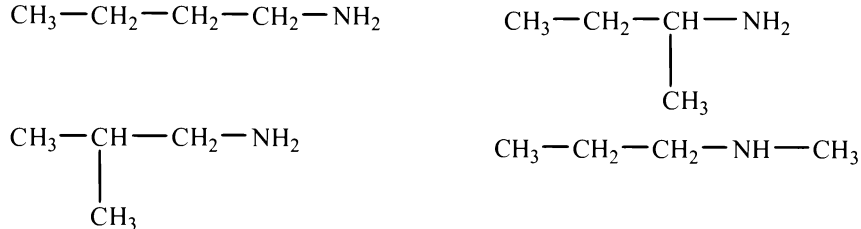


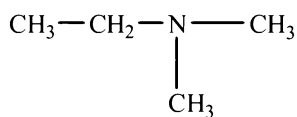
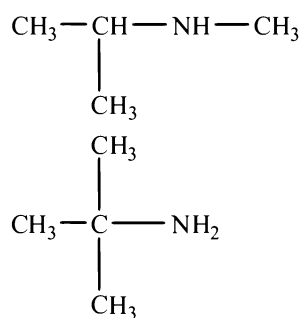
Next use a 3 C chain with three side groups:



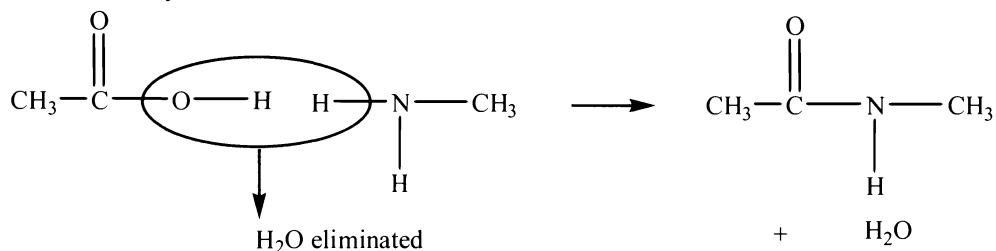
The total number of different structures is eight.

15.49 First, draw all primary amines (formula $\text{R}-\text{NH}_2$). Next, draw all secondary amines (formula $\text{R}-\text{NH}-\text{R}'$). There is only one possible tertiary amine structure (formula R_3-N). Eight amines with the formula $\text{C}_4\text{H}_{11}\text{N}$ exist.

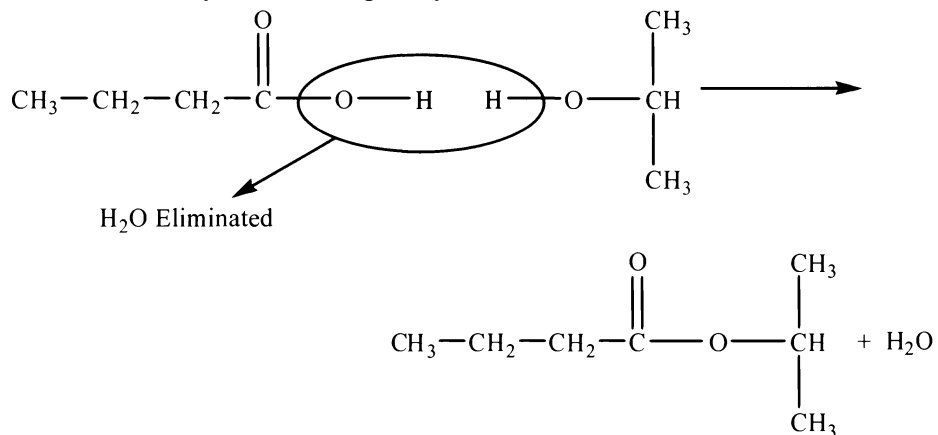




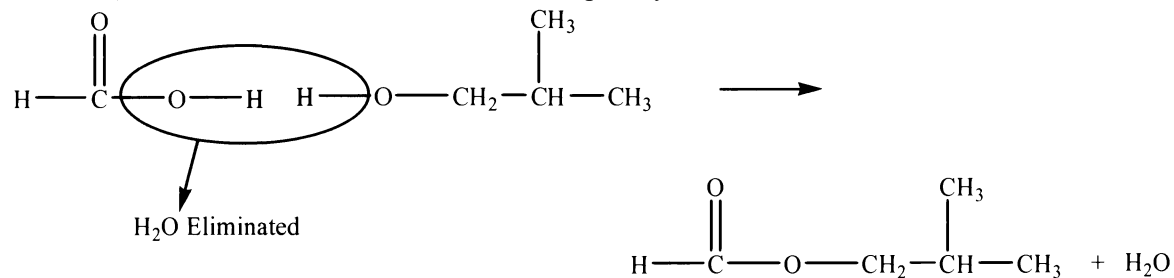
15.51 a) This reaction is a dehydration-condensation reaction.



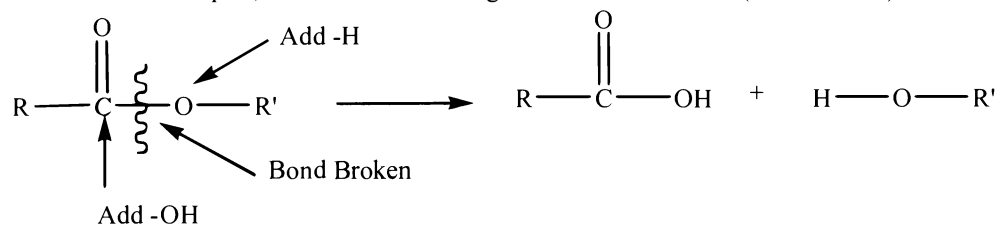
b) An alcohol and a carboxylic acid undergo dehydration-condensation to form an ester.



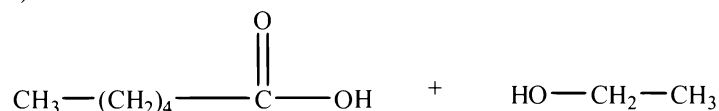
c) This reaction is also ester formation through dehydration-condensation.



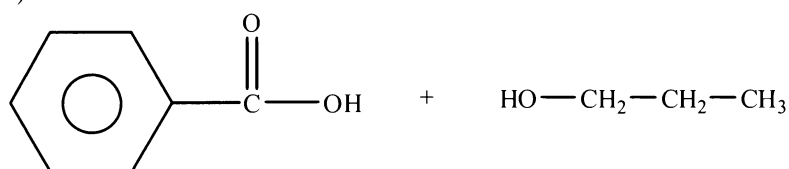
15.53 To break an ester apart, break the --C--O-- single bond and add water (--H and --OH) as shown.



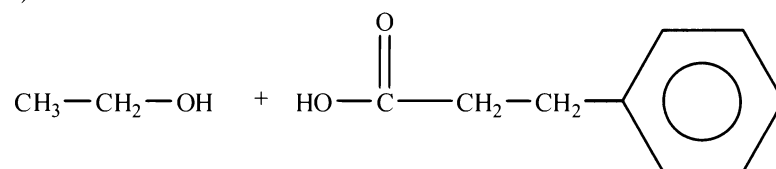
a)



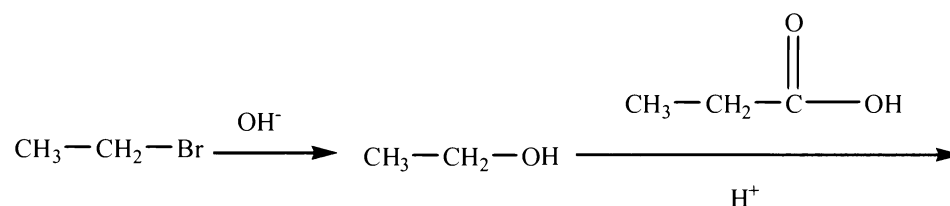
b)



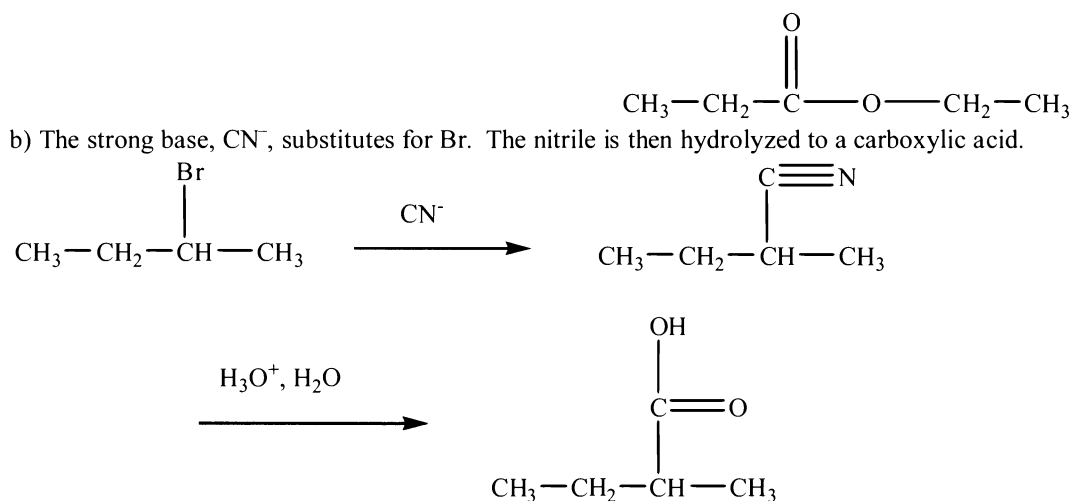
c)



15.55 a) Substitution of Br^- occurs by the stronger base, OH^- . Then a substitution reaction between the alcohol and carboxylic acid produces an ester:

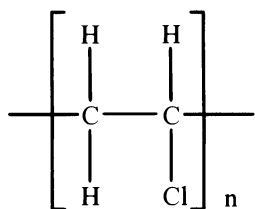


b) The strong base, CN^- , substitutes for Br. The nitrile is then hydrolyzed to a carboxylic acid.

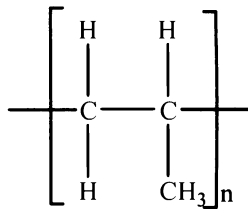


- 15.59 **Addition reactions** and **condensation reactions** are the two reactions that lead to the two types of synthetic polymers that are named for the reactions that form them.
- 15.61 Polyethylene comes in a range of strengths and flexibilities. The intermolecular dispersion forces (also called London forces) that attract the long, unbranched chains of high-density polyethylene (HDPE) are strong due to the large size of the polyethylene chains. Low-density polyethylene (LDPE) has increased branching that prevents packing and weakens intermolecular dispersion forces.
- 15.63 Nylon is formed by the condensation reaction between an **amine** and a **carboxylic acid** resulting in an amide bond. Polyester is formed by the condensation reaction between a **carboxylic acid** and an **alcohol** to form an ester bond.
- 15.64 Both PVC and polypropylene are addition polymers. The general formula for creating repeating units from a monomer is given in the chapter.

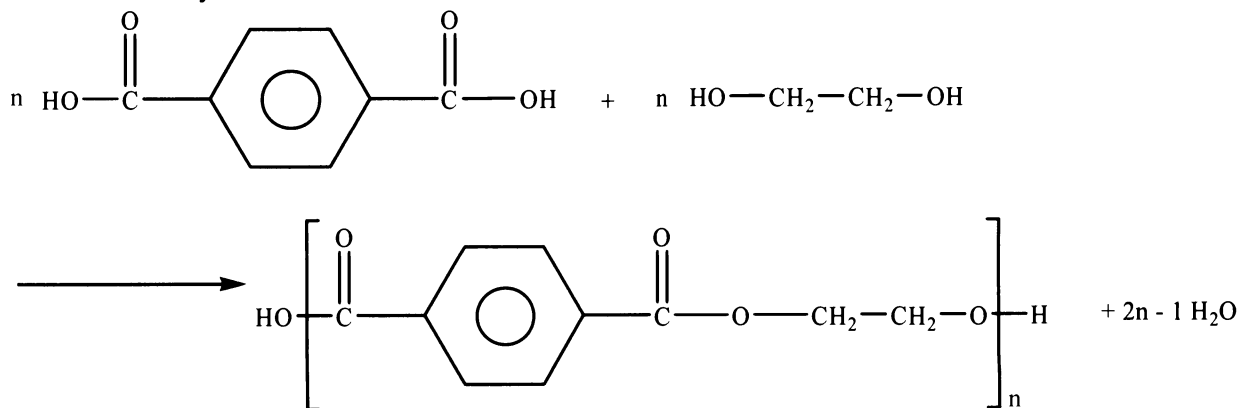
a)



(b)



- 15.66 A carboxylic acid and an alcohol react to form an ester bond.



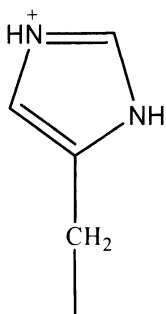
- 15.68 a) Amino acids form **condensation** polymers called proteins.
 b) Alkenes form **addition** polymers, the simplest of which is polyethylene.
 c) Simple sugars form **condensation** polymers called polysaccharides.
 d) Mononucleotides form **condensation** polymers called nucleic acids.
- 15.70 The amino acid sequence in a protein determines its shape and structure, which determine its function.

15.72 Locate the specific amino acids in Figure 15.28.

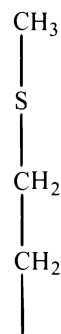
a) alanine



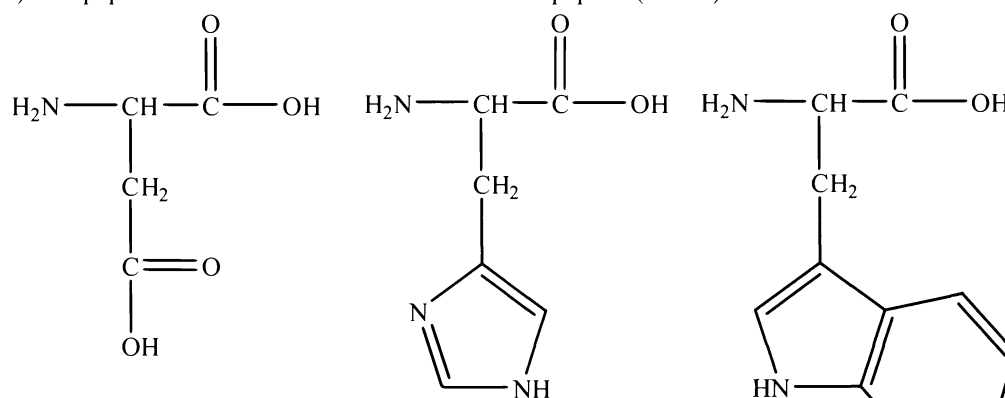
b) histidine



c) methionine



15.74 a) A tripeptide contains three amino acids and two peptide (amide) bonds.

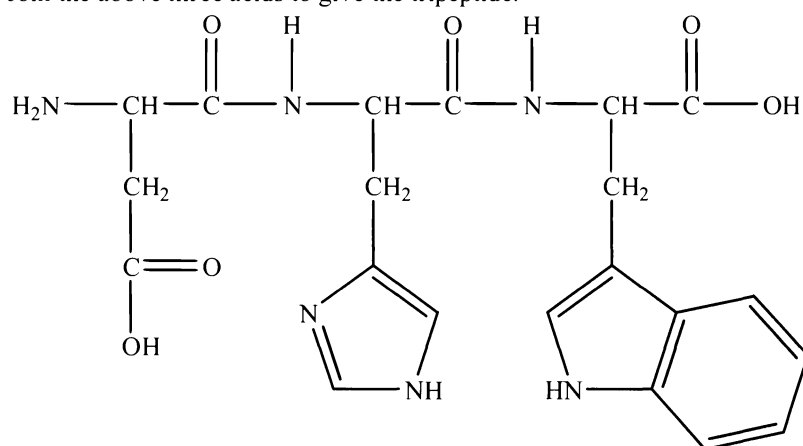


aspartic acid

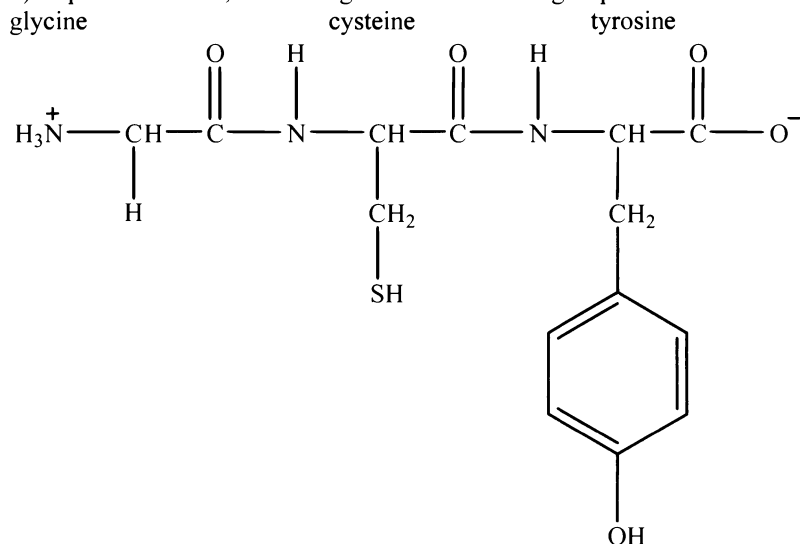
histidine

tryptophan

Join the above three acids to give the tripeptide:



b) Repeat the above, with charges on the terminal groups.



15.76 Base A always pairs with Base T; Base C always pairs with Base G.

a) Complementary DNA strand is **AATCGG**.

b) Complementary DNA strand is **TCTGTA**.

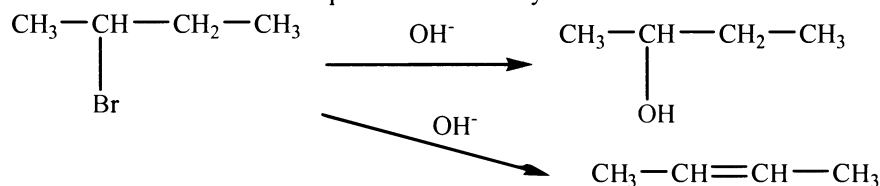
15.78 a) Both side chains are part of the amino acid **cysteine**. Two cysteine R groups can form a **disulfide bond** (covalent bond).

b) The R group $-(\text{CH}_2)_4-\text{NH}_3^+$ is found in the amino acid **lysine** and the R group $-\text{CH}_2\text{COO}^-$ is found in the amino acid **aspartic acid**. The positive charge on the amine group in lysine is attracted to the negative charge on the acid group in aspartic acid to form a **salt link**.

c) The R group in the amino acid **asparagine** and the R group in the amino acid **serine**. The $-\text{NH}-$ and $-\text{OH}$ groups will **hydrogen bond**.

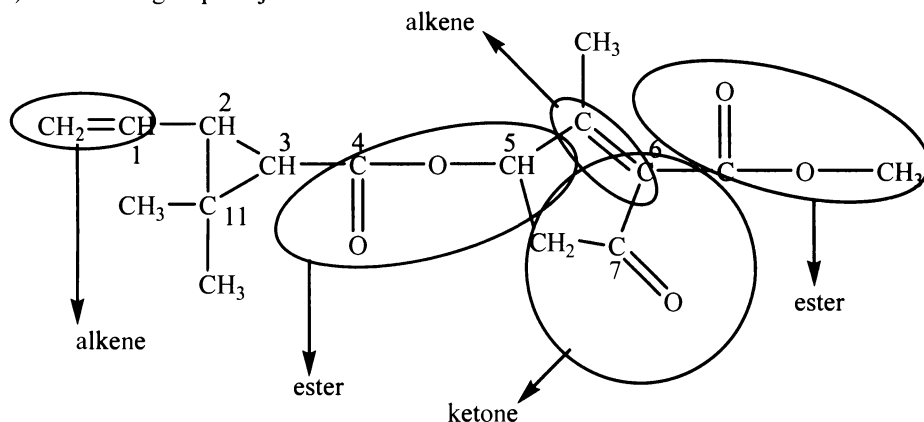
d) Both the R group $-\text{CH}(\text{CH}_3)-\text{CH}_3$ from **valine** and the R group $\text{C}_6\text{H}_5-\text{CH}_2-$ from **phenylalanine** are nonpolar so their interaction is **through dispersion forces**.

15.80 The desired reaction is the displacement of Br^- by OH^- :



However, the elimination of HX also occurs in the presence of a strong base to give the second product, 2-butene.

15.81 a) Functional groups in jasmolin II



b) Carbon atoms surrounded by four electron regions (4 single bonds) are sp^3 hybridized. Carbon atoms surrounded by three electron regions (2 single bonds and 1 double bond) are sp^2 hybridized.

Carbon 1 is sp^2 hybridized.

Carbon 2 is sp^3 hybridized.

Carbon 3 is sp^3 hybridized.

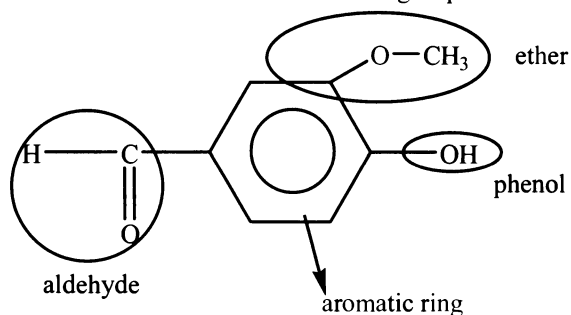
Carbon 4 is sp^2 hybridized.

Carbon 5 is sp^3 hybridized.

Carbon 6 and 7 are sp^2 hybridized.

c) Carbons 2, 3, and 5 are chiral centers as they are each bonded to four different groups.

15.83 A vanillin molecule includes three functional groups containing oxygen:



The shortest carbon-oxygen bond is the double bond in the aldehyde group. Bond length decreases as the number of bonds increases.

Chapter 16 Kinetics: Rates and Mechanisms of Chemical Reactions

FOLLOW-UP PROBLEMS

- 16.1 a) Plan: The balanced equation is $4 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{N}_2\text{O}_3$. Choose O_2 as the reference because its coefficient is 1. Four molecules of NO (nitrogen monoxide) are consumed for every one O_2 molecule, so the rate of O_2 disappearance is 1/4 the rate of NO decrease. By similar reasoning, the rate of O_2 disappearance is 1/2 the rate of N_2O_3 (dinitrogen trioxide) increase. A negative sign is associated with the rate in terms of the reactant concentrations since these concentrations are decreasing.

Solution:

$$\text{Rate} = -\frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_3]}{\Delta t}$$

- b) Plan: Because NO is decreasing, its rate of concentration change is negative. Substitute the negative value into the expression and solve for $\Delta[\text{O}_2]/\Delta t$.

Solution:

$$\text{Rate} = -\frac{1}{4}(-1.60 \times 10^{-4} \text{ mol/L} \cdot \text{s}) = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -4.00 \times 10^{-5} \text{ mol/L} \cdot \text{s}$$

Check: a) Verify that the general formula shown in Equation 16.2 produces the same result when $a = 4$, $b = 1$, and $c = 2$. b) The rate should be negative because O_2 is disappearing. The rate can also be expressed as $-\Delta[\text{O}_2]/\Delta t = 4.00 \times 10^{-5} \text{ mol/L} \cdot \text{sec}$, where the negative sign on the left side of the equation denote reactant disappearance as well. It makes sense that the rate of NO disappearance is 4 times greater than the rate of O_2 disappearance, because 4 molecules of NO disappear for every one O_2 molecule.

- 16.2 The exponent of $[\text{Br}^-]$ is 1, so the reaction is **first order with respect to Br^-** . Similarly, the reaction is **first order with respect to BrO_3^-** , and **second order with respect to H^+** since the exponent of H^+ is 2. The overall reaction order is $(1 + 1 + 2) = 4$, or **fourth order overall**.

- 16.3 Solution: Assume that the rate law takes the general form $\text{rate} = k[\text{H}_2]^m[\text{I}_2]^n$. To find how the rate varies with respect to $[\text{H}_2]$, find two experiments in which $[\text{H}_2]$ changes but $[\text{I}_2]$ remains constant. Take the ratio of rate laws for Experiments 1 and 3 to find m .

$$\begin{aligned} \frac{\text{rate 3}}{\text{rate 1}} &= \frac{[\text{H}_2]_3^m}{[\text{H}_2]_1^m} \\ \frac{9.3 \times 10^{-23}}{1.9 \times 10^{-23}} &= \frac{[0.0550]_3^m}{[0.0113]_1^m} \\ 4.8947 &= (4.8672566)^m \end{aligned}$$

Therefore, $m = 1$

If the reaction order was more complex, an alternate method of solving for m is:

$$\log(4.8947) = m \log(4.8672566); m = \log(4.8947)/\log(4.8672566) = 1$$

Take the ratio of rate laws for Experiments 2 and 4 to find n.

$$\frac{\text{rate 4}}{\text{rate 2}} = \frac{[\text{I}_2]_4^n}{[\text{I}_2]_2^n}$$

$$\frac{1.9 \times 10^{-22}}{1.1 \times 10^{-22}} = \frac{[0.0056]_4^n}{[0.0033]_2^n}$$

$$1.72727 = (1.69697)^n$$

Therefore, n = 1

The rate law is rate = $k[\text{H}_2][\text{I}_2]$ and is second order overall.

Check: The rate is first order with respect to each reactant. If one reactant doubles, the rate doubles; if one reactant triples, the rate triples. If *both* reactants double (each reactant x 2), the rate quadruples (2 x 2). Comparing reactions 1 and 4, the $[\text{H}_2]$ doubles (x 2) and the $[\text{I}_2]$ increases by 5 times (x 5). Accordingly, the rate increases by 10 (2 x 5). This exercise verifies that the determined rate law exponents are correct.

- 16.4 **Plan:** The rate expression indicates that the reaction order is two (exponent of $[\text{HI}] = 2$), so use the integrated second-order law. Substitute the given concentrations and the rate constant into the expression and solve for time.
Solution:

$$\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = kt$$

$$\frac{1}{[0.00900 \text{ mol/L}]_t} - \frac{1}{[0.0100 \text{ mol/L}]_0} = (2.4 \times 10^{-21} \text{ L/mol}\cdot\text{s}) t$$

$$t = \frac{\frac{1}{0.00900 \text{ mol/L}} - \frac{1}{0.0100 \text{ mol/L}}}{2.4 \times 10^{-21} \text{ L/mol}\cdot\text{s}}$$

$$t = 4.6296 \times 10^{21} \text{ s} = \mathbf{4.6 \times 10^{21} \text{ s}}$$

Check: The problem indicates this decomposition reaction is very slow, so it should take a long time to decrease the HI concentration. The incredibly small rate constant also indicates that the reaction rate is very slow. A hundred thousand billion years is indeed a long time.

- 16.5 **Plan:** Rearrange the first-order half-life equation to solve for k .
Solution: $k = \ln 2 / t_{1/2} = \ln 2 / 13.1 \text{ h} = 0.052911998 = \mathbf{0.0529 \text{ h}^{-1}}$
Check: Verify that the units on k reflect the data given.

- 16.6 **Plan:** Activation energy, rate constant at T_1 , and a second temperature, T_2 , are given. Substitute these values into Equation 16.9 and solve for k_2 , the rate constant at T_2 .
Solution: Rearranging Equation 16.9 to solve for k_2 :

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\begin{array}{lll} k_1 = 0.286 \text{ L/mol}\cdot\text{s} & T_1 = 500. \text{ K} & E_a = 1.00 \times 10^2 \text{ kJ/mol} \\ k_2 = ? \text{ L/mol}\cdot\text{s} & T_2 = 490. \text{ K} & \end{array}$$

$$\ln \frac{k_2}{0.286 \text{ L/mol}\cdot\text{s}} = -\frac{1.00 \times 10^2 \text{ kJ/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{490. \text{ K}} - \frac{1}{500. \text{ K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

$$\ln \frac{k_2}{0.286 \text{ L/mol}\cdot\text{s}} = -0.49093 \quad \text{Raise each side to } e^x \text{ to eliminate the } \ln \text{ term}$$

$$\frac{k_2}{0.286 \text{ L/mol}\cdot\text{s}} = 0.612054$$

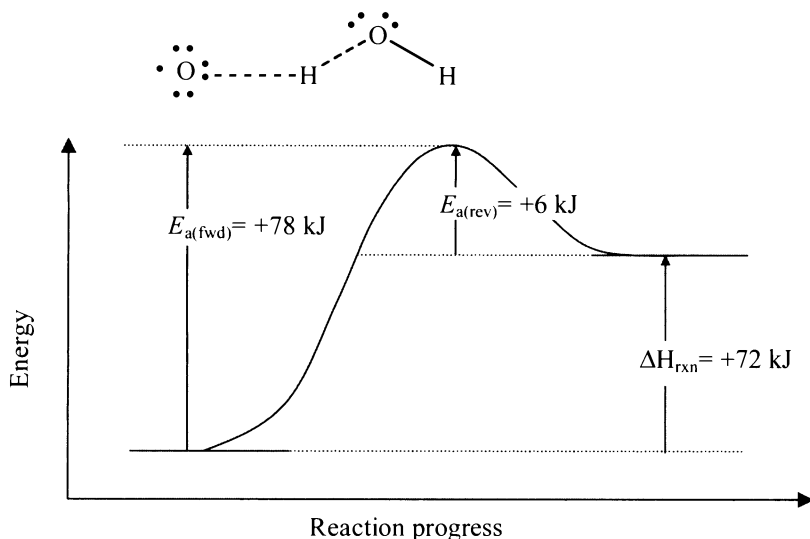
$$k_2 = (0.612054)(0.286 \text{ L/mol}\cdot\text{s}) = 0.175047423 = \mathbf{0.175 \text{ L/mol}\cdot\text{s}}$$

Check: The temperature only changes by 10 K degrees, so it is likely that the rate constant at T_2 would not change by orders of magnitude; 0.175 s^{-1} is in the same “ballpark” as 0.286 s^{-1} . Furthermore, the rate should decrease at the lower temperature, so the lower rate of 0.175 s^{-1} at 490 K is expected.

16.7 Plan: Begin by using Figure 16.16 as a guide for labeling the diagram.

Solution: The reaction energy diagram indicates that $\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{OH}(\text{g})$ is an endothermic process, because the energy of the product is higher than the energy of the reactants. The highest point on the curve indicates the transition state. In the transition state, an oxygen atom forms a bond with one of the hydrogen atoms on the H_2O molecule (hashed line) and the O–H bond (dashed line) in H_2O weakens. $E_{\text{a}(\text{fwd})}$ is the sum of ΔH_{rxn} and $E_{\text{a}(\text{rev})}$.

Transition state:



16.8 Plan: Sum the elementary steps to obtain the overall equation. Think of the individual steps as reactions along the “reaction progress” axis, i.e., sum each equation as written (this is different from the application of Hess’s law in which reactions are reversed as necessary to reach a final reaction).

Solution:

	b) Molecularity	c) Rate law
(1) $2 \text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}_2(\text{g})$	2	$\text{rate}_1 = k_1[\text{NO}]^2$
(2) $2[\text{H}_2(\text{g}) \rightarrow 2 \text{H}(\text{g})]$	1	$\text{rate}_2 = k_2[\text{H}_2]$
(3) $\text{N}_2\text{O}_2(\text{g}) + \text{H}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{HO}(\text{g})$	2	$\text{rate}_3 = k_3[\text{N}_2\text{O}_2][\text{H}]$
(4) $2[\text{HO}(\text{g}) + \text{H}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})]$	2	$\text{rate}_4 = k_4[\text{HO}][\text{H}]$
(5) $\text{H}(\text{g}) + \text{N}_2\text{O}(\text{g}) \rightarrow \text{HO}(\text{g}) + \text{N}_2(\text{g})$	2	$\text{rate}_5 = k_5[\text{H}][\text{N}_2\text{O}]$

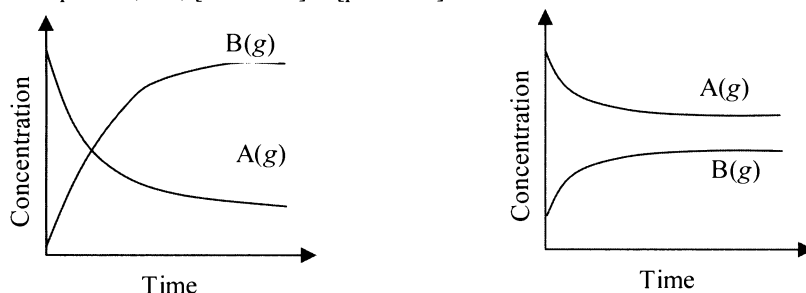
a) $2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$

Check: The overall equation is balanced.

END-OF-CHAPTER PROBLEMS

- 16.2 Rate is proportional to concentration. An increase in pressure will increase in number of gas molecules per unit volume. In other words, the gas concentration increases due to increased pressure, so the **reaction rate increases**. Increased pressure also causes more collisions between gas molecules.
- 16.3 The addition of more water will dilute the concentrations of all solutes dissolved in the reaction vessel. If any of these solutes are reactants, the **rate of the reaction will decrease**.
- 16.5 An increase in temperature affects the rate of a reaction by increasing the number of collisions, but more importantly the energy of collisions increases. As the energy of collisions increase, more collisions result in reaction (i.e., reactants \rightarrow products), so the **rate of reaction increases**.

- 16.8 a) For most reactions, the rate of the reaction changes as a reaction progresses. The instantaneous rate is the rate at one point, or instant, during the reaction. The average rate is the average of the instantaneous rates over a period of time. On a graph of reactant concentration versus time of reaction, the instantaneous rate is the slope of the tangent to the curve at any one point. The average rate is the slope of the line connecting two points on the curve. The closer together the two points (shorter the time interval), the more closely the average rate agrees with the instantaneous rate.
- b) The initial rate is the instantaneous rate at the point on the graph where time = 0, that is when reactants are mixed.
- 16.10 At time $t = 0$, no product has formed, so the $B(g)$ curve must start at the origin. Reactant concentration ($A(g)$) decreases with time; product concentration ($B(g)$) increases with time. Many correct graphs can be drawn. Two examples are shown below. The graph on the left shows a reaction that proceeds nearly to completion, i.e., $[products] \gg [reactants]$ at the end of the reaction. The graph on the right shows a reaction that does not proceed to completion, i.e., $[reactants] > [products]$ at reaction end.

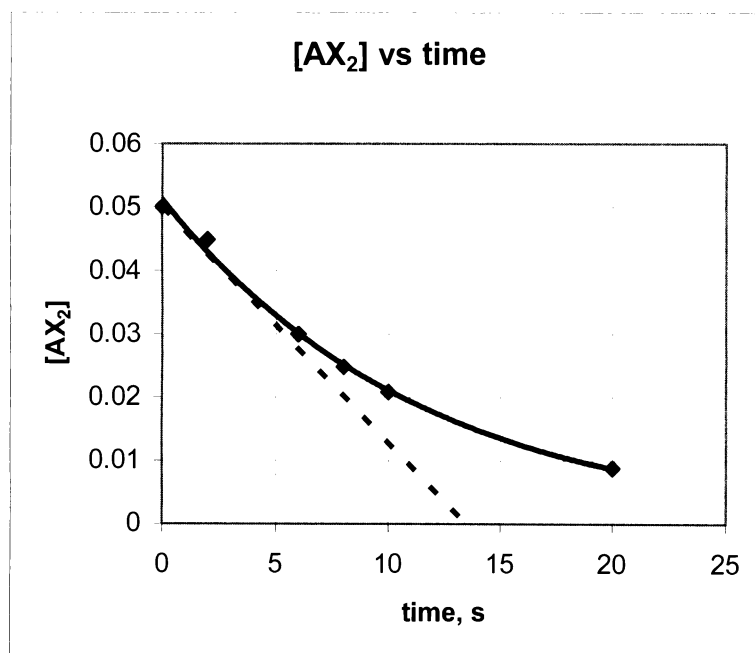


- 16.12 a) The average rate from $t = 0$ to $t = 20.0$ s is proportional to the slope of the line connecting these two points:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[AX_2]}{\Delta t} = -\frac{1}{2} \frac{(0.0088 \text{ M} - 0.0500 \text{ M})}{(20.0 \text{ s} - 0 \text{ s})} = 0.00103 = \mathbf{0.0010 \text{ M/s}}$$

The negative of the slope is used because rate is defined as the change in product concentration with time. If a reactant is used, the rate is the negative of the change in reactant concentration. The $1/2$ factor is included to account for the stoichiometric coefficient of 2 for AX_2 in the reaction.

b)



The slope of the tangent to the curve (dashed line) at $t = 0$ is approximately -0.004 M/s . This initial rate is greater than the average rate as calculated in part (a). The **initial rate is greater than the average rate** because rate decreases as reactant concentration decreases.

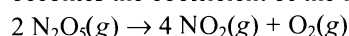
$$16.14 \quad \text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

Rate is defined as the change in product concentration with time. If a reactant is used, the rate is the negative of the change in reactant concentration. The $1/2$ factor is included for reactant B to account for the stoichiometric coefficient of 2 for B in the reaction.

$$-\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} = -\frac{1}{2} \frac{(0.50 \text{ mol/L})}{\text{s}} = -0.25 \text{ mol/L}\cdot\text{s} \text{ (unrounded)}$$

[B] decreases twice as fast as [A], so [A] is decreasing at a rate of $1/2$ ($0.5 \text{ mol/L}\cdot\text{s}$) or $0.2 \text{ mol/L}\cdot\text{s}$.

- 16.16 A term with a negative sign is a reactant; a term with a positive sign is a product. The inverse of the fraction becomes the coefficient of the molecule:



$$16.19 \quad \text{a) Rate} = -\frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t}$$

b) Use the mole ratio in the balanced equation:

$$\left(\frac{2.17 \times 10^{-5} \text{ mol O}_2 / \text{L}\cdot\text{s}}{3 \text{ mol O}_2 / \text{L}\cdot\text{s}} \right) \left(\frac{2 \text{ mol O}_3 / \text{L}\cdot\text{s}}{3 \text{ mol O}_2 / \text{L}\cdot\text{s}} \right) = 1.45 \times 10^{-5} \text{ mol/L}\cdot\text{s}$$

- 16.20 a) k is the rate constant, the proportionality constant in the rate law. k represents the fraction of successful collisions which includes the fraction of collisions with sufficient energy and the fraction of collisions with correct orientation. k is a constant that varies with temperature.
b) m represents the order of the reaction with respect to [A] and n represents the order of the reaction with respect to [B]. The order is the exponent in the relationship between rate and reactant concentration and defines how reactant concentration influences rate.

The order of a reactant does not necessarily equal its stoichiometric coefficient in the balanced equation. If a reaction is an elementary reaction, meaning the reaction occurs in only one-step, and then the orders and stoichiometric coefficients are equal. However, if a reaction occurs in a series of elementary reactions, called a mechanism, then the rate law is based on the slowest elementary reaction in the mechanism. The orders of the reactants will equal the stoichiometric coefficients of the reactants in the slowest elementary reaction but may not equal the stoichiometric coefficients in the overall reaction.

c) For the rate law $\text{rate} = k[\text{A}][\text{B}]^2$ substitute in the units:

$$\begin{aligned} \text{Rate (mol/L}\cdot\text{min)} &= k[\text{A}]^1[\text{B}]^2 \\ k &= \frac{\text{Rate}}{[\text{A}]^1[\text{B}]^2} = \frac{\text{mol/L}\cdot\text{min}}{\left[\frac{\text{mol}}{\text{L}} \right]^1 \left[\frac{\text{mol}}{\text{L}} \right]^2} = \frac{\text{mol/L}\cdot\text{min}}{\frac{\text{mol}^3}{\text{L}^3}} \\ k &= \frac{\text{mol}}{\text{L}\cdot\text{min}} \left(\frac{\text{L}^3}{\text{mol}^3} \right) \\ k &= \text{L}^2/\text{mol}^2\cdot\text{min} \end{aligned}$$

- 16.21 a) The **rate doubles**. If $\text{rate} = k[\text{A}]^1$ and [A] is doubled, then the rate law becomes $\text{rate} = k[2 \times \text{A}]^1$. The rate increases by 2^1 or 2.
b) The **rate decreases by a factor of four**. If $\text{rate} = k[1/2 \times \text{B}]^2$, then rate decreases to $(1/2)^2$ or $1/4$ of its original value.
c) The **rate increases by a factor of nine**. If $\text{rate} = k[3 \times \text{C}]^2$, then rate increases to 3^2 or 9 times its original value.

- 16.22 The order for each reactant is the exponent on the reactant concentration in the rate law. The orders with respect to $[\text{BrO}_3^-]$ and to $[\text{Br}^-]$ are both 1. The order with respect to $[\text{H}^+]$ is 2. The overall reaction order is the sum of each reactant order: $1 + 1 + 2 = 4$.
first order with respect to BrO_3^- , first order with respect to Br^- , second order with respect to H^+ , fourth order overall
- 16.24 a) The rate is first order with respect to $[\text{BrO}_3^-]$. If $[\text{BrO}_3^-]$ is doubled, $\text{rate} = k[2 \times \text{BrO}_3^-]$, then rate increases to 2^1 or 2 times its original value. The rate **doubles**.
 b) The rate is first order with respect to $[\text{Br}^-]$. If $[\text{Br}^-]$ is halved, $\text{rate} = k[1/2 \times \text{Br}^-]$, then rate decreases by a factor of $1/2^1$ or $1/2$ times its original value. The rate is **halved**.
 c) The rate is second order with respect to $[\text{H}^+]$. If $[\text{H}^+]$ is quadrupled, $\text{rate} = k[4 \times \text{H}^+]^2$, then rate increases to 4^2 or **16 times** its original value.
- 16.26 a) To find the order for reactant A, first identify the reaction experiments in which $[\text{A}]$ changes but $[\text{B}]$ is constant. Set up a proportionality: $\frac{\text{rate}_{\text{exp 1}}}{\text{rate}_{\text{exp 2}}} = \left(\frac{[\text{A}]_{\text{exp 1}}}{[\text{A}]_{\text{exp 2}}} \right)^m$. Fill in the values given for rates and concentrations and solve for m , the order with respect to $[\text{A}]$. Repeat the process to find the order for reactant B. Use experiments 1 and 2 (or 3 and 4 would work) to find the order with respect to $[\text{A}]$.
- $$\frac{\text{rate}_{\text{exp 1}}}{\text{rate}_{\text{exp 2}}} = \left(\frac{[\text{A}]_{\text{exp 1}}}{[\text{A}]_{\text{exp 2}}} \right)^m$$
- $$\frac{45.0 \text{ mol/L}\cdot\text{min}}{5.00 \text{ mol/L}\cdot\text{min}} = \left(\frac{0.300 \text{ mol/L}}{0.100 \text{ mol/L}} \right)^m$$
- $$9.00 = (3.00)^m$$
- $$\log(9.00) = m \log(3.00)$$
- $$m = 2$$
- Using experiments 3 and 4 also gives **2nd order with respect to $[\text{A}]$** .
 Use experiments 1 and 3 with $[\text{A}] = 0.100 \text{ M}$ or 2 and 4 with $[\text{A}] = 0.300 \text{ M}$ to find order with respect to $[\text{B}]$.
- $$\frac{\text{rate}_{\text{exp 1}}}{\text{rate}_{\text{exp 2}}} = \left(\frac{[\text{B}]_{\text{exp 1}}}{[\text{B}]_{\text{exp 2}}} \right)^n$$
- $$\frac{10.0 \text{ mol/L}\cdot\text{min}}{5.00 \text{ mol/L}\cdot\text{min}} = \left(\frac{0.200 \text{ mol/L}}{0.100 \text{ mol/L}} \right)^n$$
- $$2.00 = (2.00)^n$$
- $$\log(2.00) = n \log(2.00)$$
- $$n = 1$$
- The reaction is **first order with respect to $[\text{B}]$** .
- b) The rate law, without a value for k , is **$\text{rate} = k[\text{A}]^2[\text{B}]$** .
- c) Using experiment 1 to calculate k :
- $$k = \frac{\text{rate}}{[\text{A}]^2[\text{B}]} = \frac{5.00 \text{ mol/L}\cdot\text{min}}{[0.100 \text{ mol/L}]^2[0.100 \text{ mol/L}]} = 5.00 \times 10^3 \text{ L}^2/\text{mol}^2\cdot\text{min}$$
- 16.29 The integrated rate law can be used to plot a graph. If the plot of $[\text{reactant}]$ versus time is linear, the order is zero. If the plot of $\ln[\text{reactant}]$ versus time is linear, the order is first. If the plot of inverse concentration ($1/[\text{reactant}]$) versus time is linear, the order is second.
- a) The reaction is **first order** since $\ln[\text{reactant}]$ versus time is linear.
 b) The reaction is **second order** since $1/[\text{reactant}]$ versus time is linear.
 c) The reaction is **zero order** since $[\text{reactant}]$ versus time is linear.

- 16.31 The rate expression indicates that this reaction is second order overall (the order of [AB] is 2), so use the second order integrated rate law to find time. ($[AB] = 1/3 [AB]_0 = 1/3 (1.50 \text{ M}) = 0.500 \text{ M}$)

$$\frac{1}{[AB]_t} - \frac{1}{[AB]_0} = kt$$

$$t = \frac{\left(\frac{1}{[AB]_t} - \frac{1}{[AB]_0} \right)}{k}$$

$$t = \frac{\left(\frac{1}{0.500 \text{ M}} - \frac{1}{1.50 \text{ M}} \right)}{0.2 \text{ L/mol} \cdot \text{s}}$$

$$t = 6.6667 = 7 \text{ s}$$

- 16.33 a) The given information is the amount that has reacted in a specified amount of time. With this information, the integrated rate law must be used to find a value for the rate constant. For a first order reaction, the rate law is $\ln [A]_t = \ln [A]_0 - kt$. Using the fact that 50% has decomposed, let $[A]_0 = 1 \text{ M}$ and then $[A]_t = 1 \text{ M}/2 = 0.5 \text{ M}$:
 $\ln [A]_t = \ln [A]_0 - kt$
 $\ln [0.5] = \ln [1] - k(10.5 \text{ min})$
 $-0.693147 = 0 - k(10.5 \text{ min})$
 $0.693147 = k(10.5 \text{ min})$
 $k = 0.0660 \text{ min}^{-1}$
 Alternatively, 50.0% decomposition means that one half-life has passed. Thus, the first order half-life equation may be used:

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{10.5 \text{ min}} = 0.066014 = \mathbf{0.0660 \text{ min}^{-1}}$$

- b) Use the value for k calculated in part a. Let $[A]_0 = 1 \text{ M}$; since 75% of A has decomposed, 25% of A remains and $[A]_t = 25\% \text{ of } [A]_0 \text{ or } 0.25 [A]_0 = 0.25 [1] = 0.25 \text{ M}$

$$\ln [A]_t = \ln [A]_0 - kt$$

$$\frac{\ln [A]_t - \ln [A]_0}{-k} = t$$

$$\frac{\ln [0.25] - \ln [1]}{-0.0660 \text{ min}^{-1}} = t$$

$$t = 21.0045 = \mathbf{21.0 \text{ min}}$$

If you recognize that 75.0% decomposition means that two half-lives have passed, then $t = 2 (10.5 \text{ min}) = \mathbf{21.0 \text{ min}}$

- 16.36 The Arrhenius equation, $k = Ae^{-E_a/RT}$, can be used directly to solve for activation energy at a specified temperature if the rate constant, k , and the frequency factor, A , are known. However, the frequency factor is usually not known. To find E_a without knowing A , rearrange the Arrhenius equation to put it in the form of a linear plot: $\ln k = \ln A - E_a/RT$ where the y value is $\ln k$ and the x value is $1/T$. Measure the rate constant at a series of temperatures and plot $\ln k$ versus $1/T$. The slope equals $-E_a/R$.

- 16.38 Substitute the given values into Equation 16.9 and solve for k_2 .

$$\begin{aligned} k_1 &= 4.7 \times 10^{-3} \text{ s}^{-1} & T_1 &= 25^\circ\text{C} = (273 + 25) = 298 \text{ K} \\ k_2 &= ? & T_2 &= 75^\circ\text{C} = (273 + 75) = 348 \text{ K} \\ E_a &= 33.6 \text{ kJ/mol} = 33600 \text{ J/mol} \end{aligned}$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_2}{4.7 \times 10^{-3} \text{ s}^{-1}} = -\frac{33600 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{348 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\ln \frac{k_2}{4.7 \times 10^{-3} \text{ s}^{-1}} = 1.948515 \text{ (unrounded)} \quad \text{Raise each side to } e^x$$

$$\frac{k_2}{4.7 \times 10^{-3} \text{ s}^{-1}} = 7.0182577$$

$$k_2 = (4.7 \times 10^{-3} \text{ s}^{-1}) (7.0182577) = 0.0329858 = \mathbf{0.033 \text{ s}^{-1}}$$

- 16.42 **No**, collision frequency is not the only factor affecting reaction rate. The collision frequency is a count of the total number of collisions between reactant molecules. Only a small number of these collisions lead to a reaction. Other factors that influence the fraction of collisions that lead to reaction are the energy and orientation of the collision. A collision must occur with a minimum energy (activation energy) to be successful. In a collision, the orientation — which ends of the reactant molecules collide — must bring the reacting atoms in the molecules together in order for the collision to lead to a reaction.
- 16.45 Collision frequency is proportional to the velocity of the reactant molecules. At the same temperature, both reaction mixtures have the same average kinetic energy, but not the same velocity. Kinetic energy equals $1/2 mv^2$, where m is mass and v velocity. The methylamine ($\text{N}(\text{CH}_3)_3$) molecule has a greater mass than the ammonia molecule, so methylamine molecules will collide less often than ammonia molecules, because of their slower velocities. Collision energy thus is less for the $\text{N}(\text{CH}_3)_3(\text{g}) + \text{HCl}(\text{g})$ reaction than for the $\text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ reaction. Therefore, the **rate of the reaction between ammonia and hydrogen chloride is greater** than the rate of the reaction between methylamine and hydrogen chloride.
- The fraction of successful collisions also differs between the two reactions. In both reactions the hydrogen from HCl is bonding to the nitrogen in NH_3 or $\text{N}(\text{CH}_3)_3$. The difference between the reactions is in how easily the H can collide with the N, the correct orientation for a successful reaction. The groups (H) bonded to nitrogen in ammonia are less bulky than the groups bonded to nitrogen in trimethylamine (CH_3). So, collisions with correct orientation between HCl and NH_3 occur more frequently than between HCl and $\text{N}(\text{CH}_3)_3$ and $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ occurs at a higher rate than $\text{N}(\text{CH}_3)_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow (\text{CH}_3)_3\text{NHCl}(\text{s})$. Therefore, the **rate of the reaction between ammonia and hydrogen chloride is greater** than the rate of the reaction between methylamine and hydrogen chloride.
- 16.46 Each A particle can collide with three B particles, so $(4 \times 3) = \mathbf{12 \text{ unique collisions}}$ are possible.

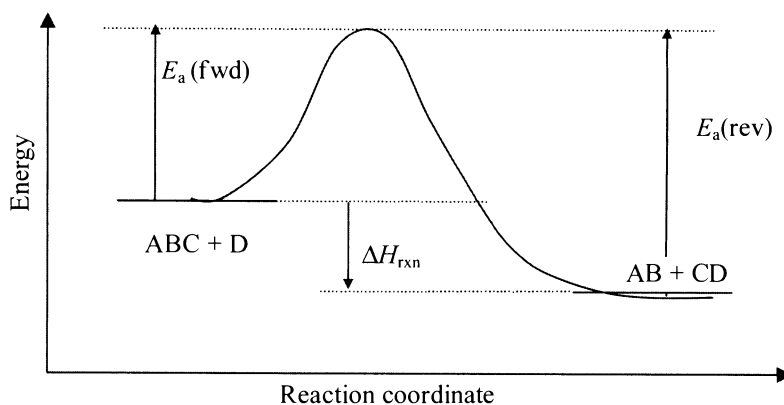
- 16.48 The fraction of collisions with a specified energy is equal to the $e^{-E_a/RT}$ term in the Arrhenius equation.

$$f = e^{-E_a/RT} \quad (25^\circ\text{C} = 273 + 25 = 298 \text{ K}) \quad -E_a / RT = -\frac{100 \text{ kJ/mol}}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

$$-E_a / RT = -40.362096$$

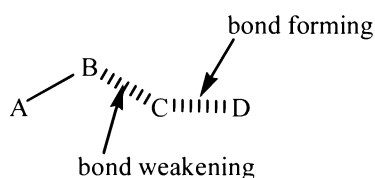
$$\text{Fraction} = e^{-E_a/RT} = e^{-40.362096} = 2.9577689 \times 10^{-18} = \mathbf{2.96 \times 10^{-18}}$$

- 16.50 a) The reaction is exothermic, so the energy of the reactants is higher than the energy of the products.

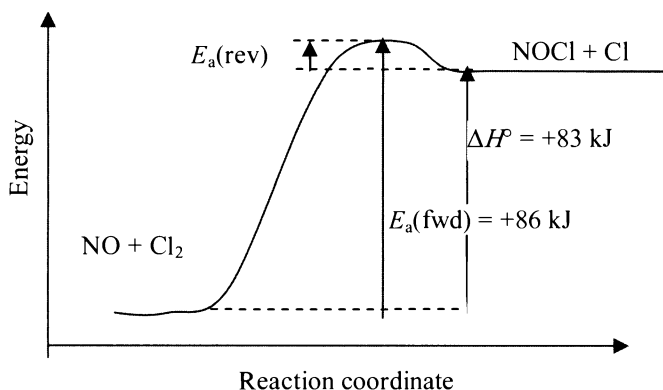


b) $E_{a(\text{rev})} = E_{a(\text{fwd})} - \Delta H_{\text{rxn}} = 215 \text{ kJ/mol} - (-55 \text{ kJ/mol}) = 2.70 \times 10^2 \text{ kJ/mol}$

c)

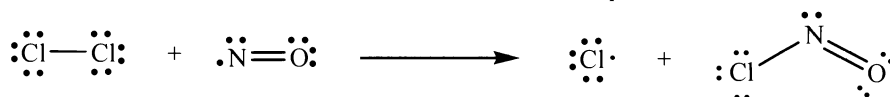


- 16.52 a) The reaction is endothermic since the enthalpy change is positive.

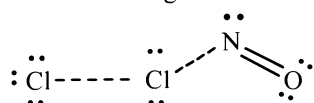


b) Activation energy for the reverse reaction: $E_{a(\text{rev})} = E_{a(\text{fwd})} - \Delta H^\circ = 86 \text{ kJ} - 83 \text{ kJ} = 3 \text{ kJ}$.

c) To draw the transition state, look at structures of reactants and products:



The collision must occur between one of the chlorines and the nitrogen. The transition state would have weak bonds between the nitrogen and chlorine and between the two chlorines.



- 16.53 The rate of an overall reaction depends on the slowest step. Each individual step's reaction rate can vary widely, so the rate of the slowest step, and hence the overall reaction, will be **slower than the average of the individual rates** because the average contains faster rates as well as the rate-determining step.

- 16.57 A bimolecular step (a collision between two particles) is more reasonable physically than a termolecular step (a collision involving three particles) because the likelihood that two reactant molecules will collide with the proper energy and orientation is much greater than the likelihood that three reactant molecules will collide simultaneously with the proper energy and orientation.
- 16.58 **No**, the overall rate law must contain reactants only (no intermediates) and is determined by the slow step. If the first step in a reaction mechanism is slow, the rate law for that step is the overall rate law.
- 16.59 a) The overall reaction can be obtained by adding the two steps together:
- $$\text{CO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$$
- $$\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- Total: $\text{CO}_2(\text{aq}) + \text{OH}^-(\text{aq}) + \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- Overall reaction: $\text{CO}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- b) Intermediates appear in the mechanism first as products, then as reactants. HCO_3^- is an intermediate.
- c)
- | <u>Step:</u> | <u>Molecularity</u> | <u>Rate law</u> |
|---|---------------------|--|
| $\text{CO}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$ | bimolecular | $\text{rate}_1 = k_1[\text{CO}_2][\text{OH}^-]$ |
| $\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ | bimolecular | $\text{rate}_2 = k_2[\text{HCO}_3^-][\text{OH}^-]$ |
- d) **Yes**, the mechanism is consistent with the actual rate law. The slow step in the mechanism is the first step with the rate law: $\text{rate} = k_1[\text{CO}_2][\text{OH}^-]$. This rate law is the same as the actual rate law.
- 16.60 a) The overall reaction can be obtained by adding the two steps together:
- $$\text{Cl}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{Cl}(\text{g}) + \text{NO}_2\text{Cl}(\text{g})$$
- $$\text{Cl}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}_2\text{Cl}(\text{g})$$
- Total: $\text{Cl}_2(\text{g}) + \text{NO}_2(\text{g}) + \text{Cl}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{Cl}(\text{g}) + \text{NO}_2\text{Cl}(\text{g}) + \text{NO}_2\text{Cl}(\text{g})$
- Overall reaction: $\text{Cl}_2(\text{g}) + 2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}_2\text{Cl}(\text{g})$
- b) Intermediates appear in the mechanism first as products, then as reactants. Cl is an intermediate.
- c)
- | <u>Step:</u> | <u>Molecularity</u> | <u>Rate law</u> |
|--|---------------------|---|
| $\text{Cl}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{Cl}(\text{g}) + \text{NO}_2\text{Cl}(\text{g})$ | bimolecular | $\text{rate}_1 = k_1[\text{Cl}_2][\text{NO}_2]$ |
| $\text{Cl}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}_2\text{Cl}(\text{g})$ | bimolecular | $\text{rate}_2 = k_2[\text{Cl}][\text{NO}_2]$ |
- d) **Yes**, the mechanism is consistent with the actual rate law. The slow step in the mechanism is the first step with the rate law: $\text{rate} = k_1[\text{Cl}_2][\text{NO}_2]$. This rate law is the same as the actual rate law.
- 16.61 a) The overall reaction can be obtained by adding the three steps together:
- $$(1) \text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{X}(\text{g}) \text{ fast}$$
- $$(2) \text{X}(\text{g}) + \text{C}(\text{g}) \rightarrow \text{Y}(\text{g}) \text{ slow}$$
- $$(3) \text{Y}(\text{g}) \rightarrow \text{D}(\text{g}) \text{ fast}$$
- Total: $\text{A}(\text{g}) + \text{B}(\text{g}) + \text{X}(\text{g}) + \text{C}(\text{g}) + \text{Y}(\text{g}) \rightarrow \text{X}(\text{g}) + \text{Y}(\text{g}) + \text{D}(\text{g})$
- $\text{A}(\text{g}) + \text{B}(\text{g}) + \text{C}(\text{g}) \rightarrow \text{D}(\text{g})$
- b) Intermediates appear in the mechanism first as products, then as reactants. Both X and Y are intermediates in the given mechanism.
- c)
- | <u>Step:</u> | <u>Molecularity</u> | <u>Rate law</u> |
|---|---------------------|---|
| $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{X}(\text{g})$ | bimolecular | $\text{rate}_1 = k_1[\text{A}][\text{B}]$ |
| $\text{X}(\text{g}) + \text{C}(\text{g}) \rightarrow \text{Y}(\text{g})$ | bimolecular | $\text{rate}_2 = k_2[\text{X}][\text{C}]$ |
| $\text{Y}(\text{g}) \rightarrow \text{D}(\text{g})$ | unimolecular | $\text{rate}_3 = k_3[\text{Y}]$ |

d) **Yes**, the mechanism is consistent with the actual rate law. The slow step in the mechanism is the second step with rate law: $\text{rate} = k_2[X][C]$. Since X is an intermediate, it must be replaced by using the first step. For an equilibrium, $\text{rate}_{\text{forward rxn}} = \text{rate}_{\text{reverse rxn}}$. For step 1 then, $k_1[A][B] = k_{-1}[X]$. Rearranging to solve for [X] gives $[X] = (k_1/k_{-1})[A][B]$. Substituting this value for [X] into the rate law for the second step gives the overall rate law as $\text{rate} = (k_2k_1/k_{-1})[A][B][C]$ which is identical to the actual rate law with $k = k_2k_1/k_{-1}$.

e) **Yes**, The one step mechanism $A(g) + B(g) + C(g) \rightarrow D(g)$ would have a rate law of $\text{rate} = k[A][B][C]$, which is the actual rate law.

- 16.63 Nitrosyl bromide is NOBr(g). The reactions sum to the equation $2 \text{NO}(g) + \text{Br}_2(g) \rightarrow 2 \text{NOBr}(g)$, so criterion 1 (elementary steps must add to overall equation) is satisfied. Both elementary steps are bimolecular and chemically reasonable, so criterion 2 (steps are physically reasonable) is met. The reaction rate is determined by the slow step; however, rate expressions do not include reaction intermediates (NOBr₂). Derive the rate law. The slow step in the mechanism is the second step with rate law: $\text{rate} = k_2[\text{NOBr}_2][\text{NO}]$. Since NOBr₂ is an intermediate, it must be replaced by using the first step. For an equilibrium like Step 1, $\text{rate}_{\text{forward rxn}} = \text{rate}_{\text{reverse rxn}}$.

- (1) Rate₁ (forward) = $k_1[\text{NO}][\text{Br}_2]$
 (2) Rate₁ (reverse) = $k_{-1}[\text{NOBr}_2]$
 (3) Rate₂ (forward) = $k_2[\text{NOBr}_2][\text{NO}]$

Solve for [NOBr₂] in Step 1:

$$\begin{aligned}\text{Rate}_1 (\text{forward}) &= \text{Rate}_1 (\text{reverse}) \\ k_1[\text{NO}][\text{Br}_2] &= k_{-1}[\text{NOBr}_2] \\ [\text{NOBr}_2] &= (k_1 / k_{-1})[\text{NO}][\text{Br}_2]\end{aligned}$$

Substitute the expression for [NOBr₂] into equation (3), the slow step:

$$\text{Rate}_2 (\text{forward}) = k_2(k_1 / k_{-1})[\text{NO}][\text{Br}_2][\text{NO}]$$

Combine the separate constants into one constant: $k = k_2(k_1 / k_{-1})$

$$\text{Rate}_2 = k[\text{NO}]^2[\text{Br}_2]$$

The derived rate law equals the known rate law, so criterion 3 is satisfied. The proposed mechanism is valid.

- 16.66 **No**, a catalyst changes the mechanism of a reaction to one with lower activation energy. Lower activation energy means a faster reaction. An increase in temperature does not influence the activation energy, but instead increases the fraction of collisions with sufficient energy to react.

- 16.69 The activation energy can be calculated using Equation 16.9. Although the rate constants, k_1 and k_2 , are not expressly stated, the relative times give an idea of the rate. The reaction rate is proportional to the rate constant. At $T_1 = 20^\circ\text{C} = (273 + 20) = 293 \text{ K}$, the rate of reaction is 1 apple/4 days while at $T_2 = 0^\circ\text{C} = (273 + 0) = 273 \text{ K}$, the rate is 1 apple/16 days. Therefore, $\text{rate}_1 = 1 \text{ apple}/4 \text{ days}$ and $\text{rate}_2 = 1 \text{ apple}/16 \text{ days}$ are substituted for k_1 and k_2 , respectively.

$$\begin{aligned}k_1 &= 1/4 & T_1 &= 293 \text{ K} \\ k_2 &= 1/16 & T_2 &= 273 \text{ K} \\ E_a &= ?\end{aligned}$$

$$\begin{aligned}\ln \frac{k_2}{k_1} &= -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ E_a &= -\frac{R \left(\ln \frac{k_2}{k_1} \right)}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)} = -\frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \left(\ln \frac{(1/16)}{(1/4)} \right)}{\left(\frac{1}{273 \text{ K}} - \frac{1}{293 \text{ K}} \right)}\end{aligned}$$

$$E_a = 4.6096266 \times 10^4 \text{ J/mol} = \mathbf{4.61 \times 10^4 \text{ J/mol}}$$

The significant figures are based on the Kelvin temperatures.

- 16.72 Use the given rate law, and enter the given values:

$$\text{rate} = k[\text{H}^+][\text{sucrose}]$$

$$[\text{H}^+]_i = 0.01 \text{ M} \quad [\text{sucrose}]_i = 1.0 \text{ M}$$

The glucose and fructose are not in the rate law, so they may be ignored.

a) The rate is first order with respect to [sucrose]. The [sucrose] is changed from 1.0 M to 2.5 M, or is increased by a factor of 2.5/1.0 or 2.5. Then the rate = $k[\text{H}^+][2.5 \times \text{sucrose}]$; the rate **increases by a factor of 2.5**.

b) The [sucrose] is changed from 1.0 M to 0.5 M, or is decreased by a factor of 0.5/1.0 or 0.5. Then the rate = $k[\text{H}^+][0.5 \times \text{sucrose}]$; the rate decreases by a factor of $\frac{1}{2}$ or **half the original rate**.

c) The rate is first order with respect to $[\text{H}^+]$. The $[\text{H}^+]$ is changed from 0.01 M to 0.0001 M, or is decreased by a factor of 0.0001/0.01 or 0.01. Then the rate = $k[0.01 \times \text{H}^+][\text{sucrose}]$; the rate **decreases by a factor of 0.01**.

Thus, the reaction will decrease to **1/100 the original**.

d) [sucrose] decreases from 1.0 M to 0.1 M, or by a factor of (0.1 M / 1.0 M) = 0.1. $[\text{H}^+]$ increases from 0.01 M to 0.1 M, or by a factor of (0.1 M / 0.01 M) = 10. Then the rate will increase by

$$k[10 \times \text{H}^+][0.1 \times \text{sucrose}] = 1.0 \text{ times as fast. Thus, there will be no change.}$$

- 16.75 First, find the rate constant, k , for the reaction by solving the first order half-life equation for k . Then use the first order integrated rate law expression to find t , the time for decay.

$$\text{Rearrange } t_{1/2} = \frac{\ln 2}{k} \text{ to } k = \frac{\ln 2}{t_{1/2}}$$

$$k = \frac{\ln 2}{12 \text{ yr}} = 5.7762 \times 10^{-2} \text{ yr}^{-1} \text{ (unrounded)}$$

Use the first-order integrated rate law:

$$\ln [A]_t = \ln [A]_0 - kt$$

$$\frac{\ln [A]_t - \ln [A]_0}{-k} = t$$

$$\frac{\ln [10. \text{ ppbm}] - \ln [275 \text{ ppbm}]}{-5.7762 \times 10^{-2} \text{ yr}^{-1}} = t$$

$$t = 57.3765798 = \mathbf{57 \text{ yr}}$$

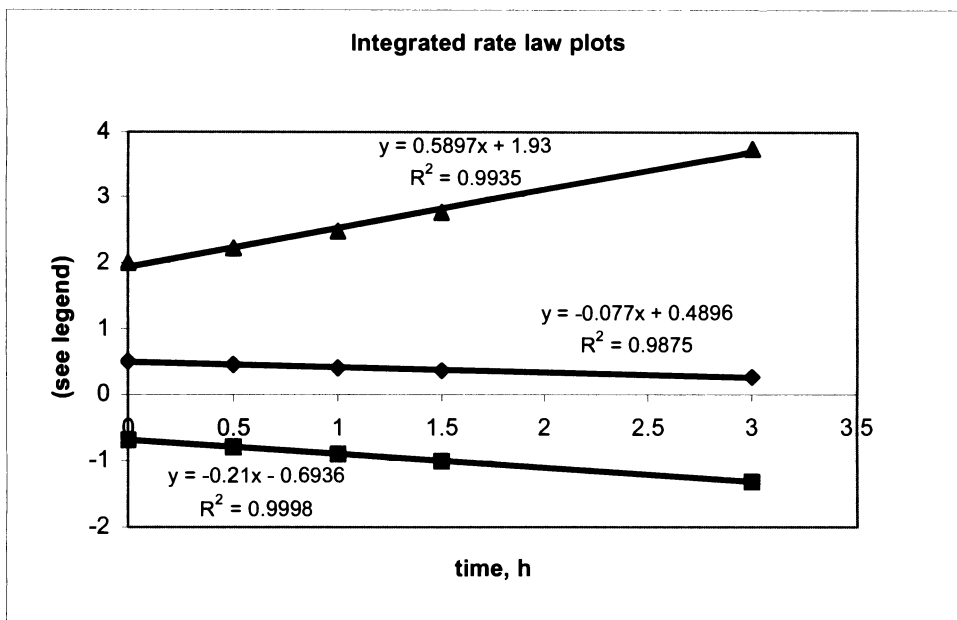
- 16.77 a) The rate constant can be determined from the slope of the integrated rate law plot. To find the correct order, the data should be plotted as 1) [sucrose] versus time – linear for zero order, 2) $\ln[\text{sucrose}]$ versus time – linear for first order, and 3) $1/[\text{sucrose}]$ versus time – linear for second order.

All three graphs are linear, so picking the correct order is difficult. One way to select the order is to compare correlation coefficients (R^2) — you may or may not have experience with this. The best correlation coefficient is the one closest to a value of 1.00. Based on this selection criterion, the plot of $\ln[\text{sucrose}]$ vs. time for the first order reaction is the best.

Another method when linearity is not obvious from the graphs is to examine the reaction and decide which order fits the reaction. For the reaction of one molecule of sucrose with one molecule of liquid water, the rate law would most likely include sucrose with an order of one and would not include water.

The plot for a first order reaction is described by the equation $\ln [A]_t = -kt + \ln [A]_0$. The slope of the plot of $\ln[\text{sucrose}]$ versus t equals $-k$. The equation for the straight line in the first order plot is $y = -0.21x - 0.6936$. So, $k = -(-0.21 \text{ h}^{-1}) = \mathbf{0.21 \text{ h}^{-1}}$.

Half-life for a first order reaction equals $\ln 2/k$, so $t_{1/2} = \ln 2 / 0.21 \text{ h}^{-1} = 3.3007 = \mathbf{3.3 \text{ h}}$.



Legend: ♦ y-axis is [sucrose]
 ■ – axis is ln[sucrose]
 ▲ – y-axis is 1/[sucrose]

b) If 75% of the sucrose has been reacted, 25% of the sucrose remains. The time to hydrolyze 75% of the sucrose can be calculated by substituting 1.0 M for $[A]_0$ and 0.25 M for $[A]_t$ in the integrated rate law equation:

$$\ln[A]_t = (-0.21 \text{ h}^{-1})t + \ln[A]_0$$

$$\ln[A]_t - \ln[A]_0 = (-0.21 \text{ h}^{-1})t$$

$$\ln[0.25] - \ln[1.0] = (-0.21 \text{ h}^{-1})t$$

$$t = 6.6014 = \mathbf{6.6 \text{ h}}$$

c) The reaction might be second order overall with first order in sucrose and first order in water. If the concentration of sucrose is relatively low, the concentration of water remains constant even with small changes in the amount of water. This gives an apparent zero-order reaction with respect to water. Thus, the reaction appears to be first order overall because the rate does not change with changes in the amount of water.

16.81 $k_1 = 1 \text{ egg} / 4.8 \text{ min}$

$$T_1 = (273.2 + 90.0) \text{ K} = 363.2 \text{ K}$$

$$k_2 = 1 \text{ egg} / 4.5 \text{ min}$$

$$T_2 = (273.2 + 100.0) \text{ K} = 373.2 \text{ K}$$

$$E_a = ?$$

The number of eggs (1) is exact, and has no bearing on the significant figures.

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$E_a = -\frac{R \left(\ln \frac{k_2}{k_1} \right)}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)} = -\frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \left(\ln \frac{(1 \text{ egg}/4.5 \text{ min})}{(1 \text{ egg}/4.8 \text{ min})} \right)}{\left(\frac{1}{373.2 \text{ K}} - \frac{1}{363.2 \text{ K}} \right)}$$

$$E_a = 7.2730 \times 10^3 \text{ J/mol} = \mathbf{7.3 \times 10^3 \text{ J/mol}}$$

- 16.82 a) Starting with the fact that rate of formation of O (rate of step 1) equals the rate of consumption of O (rate of step 2), set up an equation to solve for [O] using the given values of k_1 , k_2 , $[\text{NO}_2]$, and $[\text{O}_2]$.

$$\text{rate}_1 = \text{rate}_2$$

$$k_1[\text{NO}_2] = k_2[\text{O}][\text{O}_2]$$

$$[\text{O}] = \frac{k_1[\text{NO}_2]}{k_2[\text{O}_2]} = \frac{(6.0 \times 10^{-3} \text{ s}^{-1})[4.0 \times 10^{-9} \text{ M}]}{(1.0 \times 10^6 \text{ L/mol} \cdot \text{s})[1.0 \times 10^{-2} \text{ M}]} = \mathbf{2.4 \times 10^{-15} \text{ M}}$$

- b) Since the rate of the two steps is equal, either can be used to determine rate of formation of ozone.

$$\text{rate}_2 = k_2[\text{O}][\text{O}_2] = (1.0 \times 10^6 \text{ L/mol} \cdot \text{s})(2.4 \times 10^{-15} \text{ M})(1.0 \times 10^{-2} \text{ M}) = \mathbf{2.4 \times 10^{-11} \text{ mol/L} \cdot \text{s}}$$

Chapter 17 Equilibrium: The Extent of Chemical Reactions

FOLLOW-UP PROBLEMS

- 17.1 **Plan:** First, balance the equations and then use the coefficients to write the reaction quotient as outlined in Equation 17.4.

Solution:

a) Balanced equation: $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightleftharpoons 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

$$\text{Reaction quotient: } Q_c = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$$

b) Balanced equation: $3 \text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g})$

$$\text{Reaction quotient: } Q_c = \frac{[\text{N}_2\text{O}][\text{NO}_2]}{[\text{NO}]^3}$$

Check: Are products in numerator and reactants in denominator? Are all reactants and products expressed as concentrations by using brackets? Are all exponents equal to the coefficient of the reactant or product in the balanced equation?

- 17.2 **Plan:** K_p and K_c for a reaction are related through the ideal gas equation as shown in $K_p = K_c(\text{RT})^{\Delta n}$. Find Δn_{gas} , the change in the number of moles of gas between reactants and products (calculated as products minus reactants). Then, use the given K_c to solve for K_p .

Solution: The total number of product moles of gas is 1 (PCl_5) and the total number of reactant moles of gas is 2 ($\text{PCl}_3 + \text{Cl}_2$).

$$\Delta n = 1 - 2 = -1.$$

$$K_p = K_c(\text{RT})^{\Delta n}$$

$$K_p = 1.67[(0.08206)(500.)]^{-1}$$

$$K_p = \frac{1.67}{(0.08206)(500)}$$

$$K_p = 0.040701925 = \mathbf{4.07 \times 10^{-2}}$$

- 17.3 **Plan:** To decide whether CH_3Cl or CH_4 are forming while the reaction system moves toward equilibrium, calculate Q_p and compare it to K_p . If $Q_p > K_p$, the reaction is proceeding to the left and reactants are forming. If $Q_p < K_p$, the reaction is proceeding to the right and products are forming.

Solution:

$$Q_p = \frac{P_{\text{CH}_3\text{Cl}} P_{\text{HCl}}}{P_{\text{CH}_4} P_{\text{Cl}_2}} = \frac{(0.24 \text{ atm})(0.47 \text{ atm})}{(0.13 \text{ atm})(0.035 \text{ atm})} = 24.7912 = 25$$

K_p for this reaction is given as 1.6×10^4 . Q_p is smaller than K_p ($Q_p < K_p$) so more products will form. CH_3Cl is one of the products forming.

Check: Since number of moles of gas is proportional to pressure, a new calculation of Q_p can be done with increased pressures for products and decreased pressures for reactants. If the conclusion that formation of products moves the reaction system closer to equilibrium then the new Q_p should be closer to K_p than the 25 found for the original Q_p .

Increasing and decreasing by 0.01 atm:

$$Q_p = \frac{(0.25 \text{ atm})(0.48 \text{ atm})}{(0.12 \text{ atm})(0.025 \text{ atm})} = 40$$

40 is closer to 16,000 than 25, so the answer that CH_3Cl is forming is correct.

- 17.4 **Plan:** The information given includes the equilibrium constant, initial pressures of both reactants and equilibrium pressure for one reactant. First, set up a reaction table showing initial partial pressures for reactants and 0 for product. The change to get to equilibrium is to react some of reactants to form some product. The mole ratio between $\text{NO}:\text{O}_2:\text{NO}_2$ is 2:1:2. Use the equilibrium quantity for O_2 and the expression for O_2 at equilibrium to solve for the change. From the change find the equilibrium partial pressure for NO and NO_2 . Calculate K_p using the equilibrium values.

Solution:

Pressures (atm)	2 NO(g) +	O ₂ (g)	\rightleftharpoons	2 NO ₂ (g)	
Initial	1.000	1.000		0	
Change	-2 x	-x		+2 x	(2:1:2 mole ratio)
Equilibrium	1.000 - 2 x	1.000 - x		2 x	
At equilibrium	P _{O₂} = 0.506 atm = 1.000 - x; so x = 1.000 - 0.506 = 0.494 atm				
	P _{NO} = 1.000 - 2 x = 1.000 - 2(0.494) = 0.012 atm				
	P _{NO₂} = 2 x = 2 (0.494) = 0.988 atm				

Use the equilibrium pressures to calculate K_p .

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} = \frac{(0.988)^2}{(0.012)^2 (0.506)} = 1.339679 \times 10^4 = 1.3 \times 10^4$$

Check: One way to check is to plug the equilibrium expressions for NO and NO_2 into the equilibrium expression along with 0.506 atm for the equilibrium pressure of O_2 . Then solve for x and make sure the value of x by this calculation is the same as the 0.494 atm calculated above.

$$1.3 \times 10^4 = \frac{(2x)^2 (0.506)}{(1.000 - 2x)^2}$$

$$(1.3 \times 10^4) / 0.506 = 2.569 \times 10^4 = \frac{(2x)^2}{(1.000 - 2x)^2}$$

$$\sqrt{2.569 \times 10^4} = \frac{(2x)}{(1.000 - 2x)}$$

$$x = 0.497$$

The two values for x agree to give $K_p = 1.3 \times 10^4$.

- 17.5 **Plan:** Convert K_c to K_p for the reaction. Write the equilibrium expression for K_p and insert the atmospheric pressures for P_{N_2} and P_{O_2} as their equilibrium values. Solve for P_{NO} .

Solution: The conversion of K_c to K_p : $K_p = K_c(RT)^{\Delta n}$.

For this reaction $\Delta n = 2 - 2 = 0$ (2 mol of product gas, N_2 and O_2 and 2 mol of reactant gas, NO)

$$K_p = K_c(RT)^0 \text{ so } K_p = K_c.$$

$$K_p = \frac{P_{\text{N}_2} P_{\text{O}_2}}{P_{\text{NO}}^2} = K_c = 2.3 \times 10^{30} = \frac{(0.781)(0.209)}{x^2}$$

$$x = 2.6640 \times 10^{-16} = 2.7 \times 10^{-16} \text{ atm}$$

The equilibrium partial pressure of NO in the atmosphere is **2.7×10^{-16} atm**.

Check: Insert the pressure of NO and calculate the equilibrium constant to check the result.

$$\frac{(0.781)(0.209)}{(2.6640 \times 10^{-16})^2} = 2.300 \times 10^{30} = 2.3 \times 10^{30}$$

- 17.6 **Plan:** Set up a reaction table and use the variables to find equilibrium concentrations in the equilibrium expression.

Solution: The initial $[\text{HI}] = \frac{2.50 \text{ mol}}{10.32 \text{ L}} = 0.242248 \text{ M}$

Concentration (M)	2 HI(g)	\rightleftharpoons	H ₂ (g)	+	I ₂ (g)
Initial	0.242248		0		0
Change	-2x		+x		+x (2:1:1 mole ratio)
Equilibrium	0.242248 - 2x		x		x (unrounded values)

Set up equilibrium expression:

$$K_c = 1.26 \times 10^{-3} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{[x][x]}{[0.242248 - 2x]^2} \quad \text{Take the square root of each side}$$

$$0.035496 = \frac{[x]}{[0.242248 - 2x]}$$

$$0.0085988 - 0.070992x = x$$

$$x = 8.0288 \times 10^{-3} = 8.03 \times 10^{-3}$$

$$[\text{H}_2] = [\text{I}_2] = \mathbf{8.03 \times 10^{-3} \text{ M}}$$

Check: Plug equilibrium concentrations into the equilibrium expression and calculate K_c .

$$[\text{HI}] = 0.242 - 2(8.03 \times 10^{-3}) = 0.226 \text{ M}$$

$$(8.03 \times 10^{-3})^2 / (0.226)^2 = 1.2624 \times 10^{-3} = 1.26 \times 10^{-3}$$

- 17.7 **Plan:** First set up the reaction table, then set up the equilibrium expression. To solve for variable, x, first assume that x is negligible with respect to initial concentration of I₂. Check the assumption by calculating the % error. If the error is greater than 5%, calculate x using the quadratic equation. The next step is to use x to determine the equilibrium concentrations of I₂ and I.

Solution: $[\text{I}_2]_{\text{init}} = 0.50 \text{ mol I}_2 / 2.5 \text{ L} = 0.20 \text{ M}$

a) Equilibrium at 600 K

Concentration (M)	I ₂ (g)	\rightleftharpoons	2 I(g)
Initial	0.20		0
Change	-x		+2x
Equilibrium	0.20 - x		2x

$$\text{Equilibrium expression: } K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = 2.94 \times 10^{-10}$$

$$\frac{[2x]^2}{[0.20 - x]} = 2.94 \times 10^{-10}$$

Assume x is negligible so $0.20 - x \approx 0.20$.

$$\frac{4x^2}{0.20} = 2.94 \times 10^{-10}$$

$$x = 3.834 \times 10^{-6} = 3.8 \times 10^{-6} \text{ M}$$

Check the assumption by calculating the % error: $(3.8 \times 10^{-6} / 0.20) \times 100\% = 1.9 \times 10^{-3} \%$ which is smaller than 5%, so the assumption is valid.

$$\text{At equilibrium } [\text{I}]_{\text{eq}} = 2x = 7.668 \times 10^{-6} = \mathbf{7.7 \times 10^{-6} \text{ M}}$$

$$\text{and } [\text{I}_2]_{\text{eq}} = 0.20 - 3.834 \times 10^{-6} = 0.199996 = \mathbf{0.20 \text{ M}}$$

b) Equilibrium at 2000 K

$$\text{Equilibrium expression: } K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = 0.209$$

$$\frac{[2x]^2}{[0.20 - x]} = 0.209$$

Assume x is negligible so $0.20 - x$ is approximately 0.20 .

$$\frac{4x^2}{0.20} = 0.209$$

$$x = 0.102225 = 0.102 \text{ M}$$

Check the assumption by calculating the % error: $0.102 \div 0.20 = 51\%$ which is larger than 5% so the assumption is not valid. Solve using quadratic equation.

$$\begin{aligned} \frac{4x^2}{[0.20 - x]} &= 0.209 \\ 4x^2 + 0.209x - 0.0418 &= 0 \\ a = 4; b = 0.209; c &= -0.0418 \\ \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} &= x \\ x &= \frac{-0.209 \pm \sqrt{(0.209)^2 - 4(4)(-0.0418)}}{2(4)} = 0.0793857 \text{ or } -0.1316 \end{aligned}$$

Choose the positive value, $x = 0.079$

At equilibrium $[I]_{\text{eq}} = 2x = 0.15877 = \mathbf{0.16 \text{ M}}$ and $[I_2]_{\text{eq}} = 0.20 - x = 0.12061 = \mathbf{0.12 \text{ M}}$

Check: Calculate equilibrium constants using calculated equilibrium concentrations:

$$\text{a) } K = (7.7 \times 10^{-6})^2 / (0.20) = 2.9645 \times 10^{-10} = 3.0 \times 10^{-10}$$

$$\text{b) } K = (0.16)^2 / (0.12) = 0.21333 = 0.213$$

- 17.8 Plan: Calculate the initial concentrations of each substance. For part (a), calculate Q_c and compare to given K_c . If $Q_c > K_c$ then the reaction proceeds to the left to make reactants from products. If $Q_c < K_c$ then the reaction proceeds to right to make products from reactants. For part (b), use the result of part (a) and the given equilibrium concentration of PCl_5 to find the equilibrium concentrations of PCl_3 and Cl_2 .

Solution:

Initial concentrations: $[\text{PCl}_5] = 0.1050 \text{ mol} / 0.5000 \text{ L} = 0.2100 \text{ M}$

$[\text{PCl}_3] = [\text{Cl}_2] = 0.0450 \text{ mol} / 0.5000 \text{ L} = 0.0900 \text{ M}$

$$\text{a) } Q_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{[0.0900][0.0900]}{[0.2100]} = 0.038571 = 0.0386$$

Q_c , 0.0386 , is less than K_c , 0.042 , so the reaction will proceed to the right to make more products.

b) To reach equilibrium, concentrations will increase for the products, PCl_3 and Cl_2 , and decrease for the reactant, PCl_5 .

	PCl_5	\rightleftharpoons	PCl_3	+	Cl_2
Initial	0.2100 M		0.0900 M		0.0900 M
Change	$-x$		$+x$		$+x$
Equilibrium	$0.2100 - x$		$0.0900 + x$		$0.0900 + x$

$$[\text{PCl}_5] = 0.2065 \text{ M} = 0.2100 - x; x = 0.0035 \text{ M}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.0900 + x = 0.0900 + 0.0035 = \mathbf{0.0935 \text{ M}}$$

Check: Calculate equilibrium constants using the calculated equilibrium concentrations:

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{[0.0935][0.0935]}{[0.2065]} = 0.042335 = 0.0423$$

- 17.9 Plan: Examine each change for its impact on Q_c . Then decide how the system would respond to re-establish equilibrium.

Solution:
$$Q_c = \frac{[\text{SiF}_4][\text{H}_2\text{O}]^2}{[\text{HF}]^4}$$

- a) Decreasing $[\text{H}_2\text{O}]$ leads to $Q_c < K_c$, so the reaction would shift to make more products from reactants. Therefore, the SiF_4 concentration, as a product, would **increase**.
- b) Adding liquid water to this system at a temperature above the boiling point of water would result in an increase in the concentration of water vapor. The increase in $[\text{H}_2\text{O}]$ increases Q_c to make it greater than K_c . To re-establish equilibrium products will be converted to reactants and the $[\text{SiF}_4]$ will **decrease**.
- c) Removing the reactant HF increases Q_c , which causes the products to react to form more reactants. Thus, $[\text{SiF}_4]$ **decreases**.
- d) Removal of a solid product has no impact on the equilibrium; $[\text{SiF}_4]$ **does not change**.

Check: Look at each change and decide which direction the equilibrium would shift using Le Châtelier's principle to check the changes predicted above.

- a) Remove product, equilibrium shifts to right.
- b) Add product, equilibrium shifts to left.
- c) Remove reactant, equilibrium shifts to left.
- d) Remove solid reactant, equilibrium does not shift.

- 17.10 Plan: Changes in pressure (and volume) affect the concentration of gaseous reactants and products. A decrease in pressure, i.e., increase in volume, favors the production of more gas molecules whereas an increase in pressure favors the production of fewer gas molecules. Examine each reaction to decide whether more or fewer gas molecules will result from producing more products. If more gas molecules result, then the pressure should be increased (volume decreased) to reduce product formation. If fewer gas molecules result, then pressure should be decreased to produce more reactants.

Solution:

- a) In $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$ three molecules of gas form two molecules of gas, so there are fewer gas molecules in the product. **Decreasing pressure** (increasing volume) will favor the reaction direction that produces more moles of gas: towards the reactants and away from products will decrease the product yield.
- b) In $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightleftharpoons 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$ 9 molecules of reactant gas convert to 10 molecules of product gas. **Increasing pressure** (decreasing volume) will favor the reaction direction that produces fewer moles of gas: towards the reactants and away from products.
- c) In $\text{CaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{CaCO}_3(\text{s}) + \text{CO}(\text{g})$ there are no reactant gas molecules and one product gas molecules. **Increasing pressure** (decreasing volume) will favor the reaction direction that produces fewer moles of gas: towards the reactants and away from products.

- 17.11 Plan: A decrease in temperature favors the exothermic direction of an equilibrium reaction, the direction that produces heat. First, identify whether the forward or reverse reaction is exothermic from the given enthalpy change. $\Delta H < 0$ means the forward reaction is exothermic, and $\Delta H > 0$ means the reverse reaction is exothermic. If the forward reaction is exothermic then a decrease in temperature will shift the equilibrium to the right to make more products from reactants and increase K_p . If the reverse reaction is exothermic then a decrease in temperature will shift the equilibrium to the left to make more reactants from products and decrease K_p .

Solution:

- a) $\Delta H < 0$ so the forward reaction is exothermic. A decrease in temperature increases the partial pressure of products and decreases the partial pressures of reactants, so P_{H_2} **decreases**. With increases in product pressures and decreases in reactant pressures, K_p **increases**.
- b) $\Delta H > 0$ so the reverse reaction is exothermic. A decrease in temperature decreases the partial pressure of products and increases the partial pressures of reactants, so P_{N_2} **increases**. K_p **decreases** with decrease in product pressures and increase in reactant pressures.
- c) $\Delta H < 0$ so the forward reaction is exothermic. Decreasing temperature **increases** P_{PCl} and **increases** K_p .

Check: Solve the problem for increasing instead of decreasing temperature and make sure the answers are opposite.

- a) Increased temperature favors the reverse endothermic reaction leading to an increase in reactant pressures, so P_{H_2} increases and K_p decreases.
- b) Increased temperature favors the forward endothermic reaction leading to a decrease in reactant pressures. P_{N_2} decreases and K_p increases.
- c) Both P_{PCl} and K_p decrease with increased temperature.

17.12 Plan: Given the balanced equilibrium equation, it is possible to set up the appropriate equilibrium expression (Q_c). For the equation given $\Delta n = 0$ meaning that $K_p = K_c$. The value of K may be found for scene 1, and values for Q may be determined for the other two scenes. The reaction will shift towards the reactant side if $Q > K$, and the reaction will shift towards the product side if $Q < K$. The reaction is exothermic, thus, heat may be considered a product. Increasing the temperature adds a product and decreasing the temperature removes a product.

Solution:

a) K_p requires the equilibrium value of P for each gas. The pressure may be found from $P = nRT / V$.

$$K_p = \frac{P_{CD}^2}{P_{C_2} P_{D_2}} = \frac{\left(\frac{n_{CD}RT}{V}\right)^2}{\left(\frac{n_{C_2}RT}{V}\right)\left(\frac{n_{D_2}RT}{V}\right)}$$

This equation may be simplified because for the sample R , T , and V are constant. Using scene 1:

$$K_p = \frac{n_{CD}^2}{n_{C_2} n_{D_2}} = \frac{(4)^2}{(2)(2)} = 4$$

$$\text{b) Scene 2 } Q_p = \frac{n_{CD}^2}{n_{C_2} n_{D_2}} = \frac{(6)^2}{(1)(1)} = 36$$

$Q > K$, thus, the reaction will **shift to the left** (towards the reactants).

$$\text{Scene 3 } Q_p = \frac{n_{CD}^2}{n_{C_2} n_{D_2}} = \frac{(3)^2}{(3)(3)} = 1$$

has $Q < K$, thus, it will **shift to the right** (towards the products).

c) Increasing the temperature is equivalent to adding a product (heat) to the equilibrium. The reaction will shift to consume the added heat. The reaction will shift to the left (towards the reactants). However, since there are 2 moles of gas on each side of the equation, the shift has **no effect** on total moles of gas.

Check: a) Remember to use the coefficients as exponents, and to multiply, not add the values for the different reactants. b) The relationship between Q and K determines the direction the reaction will precede. c) Reverse the sign on ΔH (make the reaction endothermic), and see if you get the opposite result.

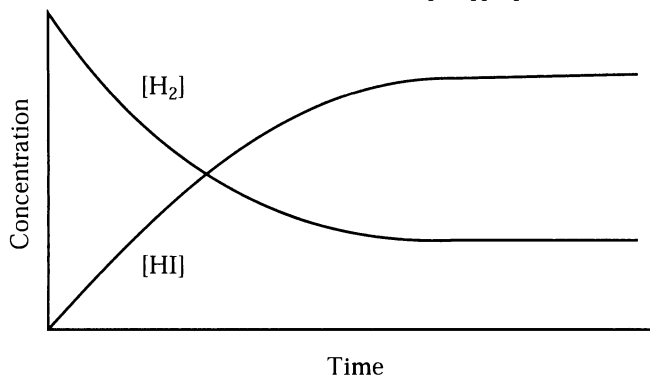
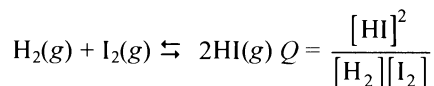
END-OF-CHAPTER PROBLEMS

17.1 If the rate of the forward reaction exceeds the rate of reverse reaction, products are formed faster than they are consumed. The change in reaction conditions results in more products and less reactants. A change in reaction conditions can result from a change in concentration or a change in temperature. If concentration changes, product concentration increases while reactant concentration decreases, but the K_c remains unchanged because the *ratio* of products and reactants remains the same. If the increase in the forward rate is due to a change in temperature, the rate of the reverse reaction also increases. The equilibrium ratio of product concentration to reactant concentration is no longer the same. Since the rate of the forward reaction increases more than the rate of the reverse reaction, K_c increases (numerator, [products], is larger and denominator, [reactants], is smaller).

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

17.6 The equilibrium constant expression is $K = [\text{O}_2]$. If the temperature remains constant, K remains constant. If the initial amount of Li_2O_2 present was sufficient to reach equilibrium, the amount of O_2 obtained will be constant, regardless of how much $\text{Li}_2\text{O}_2(\text{s})$ is present.

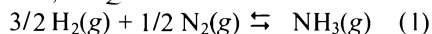
17.7 On the graph the concentration of HI increases at twice the rate that H_2 decreases because the stoichiometric ratio in the balanced equation is $1\text{H}_2 : 2\text{HI}$.
 Q for a reaction is the ratio of concentrations of products to concentrations of reactants. As the reaction progresses the concentration of reactants decrease and the concentration of products increase, which means that Q increases as a function of time.



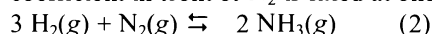
The value of Q increases as a function of time until it reaches the value of K .

b) No, Q would still increase with time because the $[\text{I}_2]$ would decrease in exactly the same way as $[\text{H}_2]$ decreases.

17.10 Yes, the Q 's for the two reactions do differ. The balanced equation for the first reaction is



The coefficient in front of NH_3 is fixed at 1 mole according to the description. In the second reaction, the coefficient in front of N_2 is fixed at one mole.

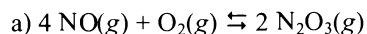


The reaction quotients for the two equations and their relationship are:

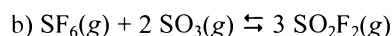
$$Q_1 = \frac{[\text{NH}_3]}{[\text{H}_2]^{3/2} [\text{N}_2]^{1/2}} \quad Q_2 = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]}$$

$$Q_2 = Q_1^2$$

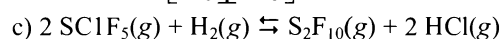
17.11 Check that correct coefficients from balanced equation are included as exponents in the mass action expression.



$$Q_c = \frac{[\text{N}_2\text{O}_3]^2}{[\text{NO}]^4 [\text{O}_2]}$$



$$Q_c = \frac{[\text{SO}_2\text{F}_2]^3}{[\text{SF}_6] [\text{SO}_3]^2}$$



$$Q_c = \frac{[\text{S}_2\text{F}_{10}] [\text{HCl}]^2}{[\text{SClF}_5]^2 [\text{H}_2]}$$

17.13 The Q for the original reaction is $Q_{\text{ref}} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$

a) The given reaction $1/2 \text{S}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$ is the reverse reaction of the original reaction multiplied by a factor of $1/2$. The equilibrium constant for the reverse reaction is the inverse of the original constant. When a reaction is multiplied by a factor, K , of the new equation is equal to the K of the original equilibrium raised to a power equal to the factor. For the reaction given in part a take $(1/K)^{1/2}$.

$$Q_a = (1 / Q_{\text{ref}})^{1/2} = \frac{[\text{H}_2\text{S}]}{[\text{S}_2]^{1/2} [\text{H}_2]}$$

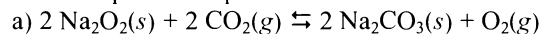
$$K = (1 / 1.6 \times 10^{-2})^{1/2} = 7.90569 = \mathbf{7.9}$$

b) The given reaction $5 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 5 \text{H}_2(\text{g}) + 5/2 \text{S}_2(\text{g})$ is the original reaction multiplied by $5/2$. Take the original K to the $5/2$ power to find K of given reaction.

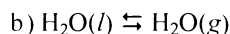
$$Q_a = (Q_{\text{ref}})^{5/2} = \frac{[\text{H}_2]^5 [\text{S}_2]^{5/2}}{[\text{H}_2\text{S}]^5}$$

$$K = (1.6 \times 10^{-2})^{5/2} = 3.23817 \times 10^{-5} = \mathbf{3.2 \times 10^{-5}}$$

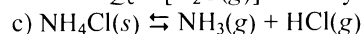
17.15 The concentration of solids and pure liquids do not change, so their concentration terms are not written in the reaction quotient expression.



$$Q_c = \frac{[\text{O}_2]}{[\text{CO}_2]^2}$$

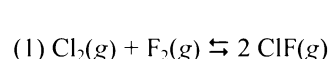


$$Q_c = [\text{H}_2\text{O}(\text{g})] \quad \text{Only the gaseous water is used. The “(g)” is for emphasis.}$$

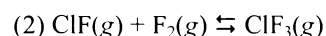


$$Q_c = [\text{NH}_3][\text{HCl}]$$

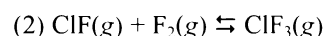
17.18 a) The balanced equations and corresponding reaction quotients are given below. Note the second equation must occur twice to get the appropriate overall equation.



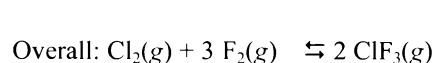
$$Q_1 = \frac{[\text{ClF}]^2}{[\text{Cl}_2][\text{F}_2]}$$



$$Q_2 = \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]}$$



$$Q_2 = \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]}$$



$$Q_{\text{overall}} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

b) The second equation occurs twice, thus it could simply be multiplied by two and its reaction quotient squared. The reaction quotient for the overall reaction, Q_{overall} , determined from the reaction is:

$$Q_{\text{overall}} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

$$Q_{\text{overall}} = Q_1 Q_2^2 = Q_1 Q_2 Q_2 = \frac{[\text{ClF}]^2}{[\text{Cl}_2][\text{F}_2]} \times \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]} \times \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

- 17.20 K_c and K_p are related by the equation $K_p = K_c(RT)^{\Delta n}$ where Δn represents the change in the number of moles of gas in the reaction (moles gaseous products – moles gaseous reactants). When Δn is zero (no change in number of moles of gas) the term $(RT)^{\Delta n}$ equals 1 and $K_c = K_p$. When Δn is not zero, meaning that there is a change in the number of moles of gas in the reaction, then $K_c \neq K_p$.
- 17.21 a) $K_p = K_c(RT)^{\Delta n}$. Since Δn = number of moles gaseous products – number of moles gaseous reactants, Δn is a positive integer. If Δn is a positive integer, then $(RT)^{\Delta n}$ is greater than 1. Thus, K_c is multiplied by a number that is greater than 1 to give K_p . **K_c is smaller than K_p .**
 b) Assuming that $RT > 1$ (which occurs when $T > 12.2\text{ K}$, because $0.0821\text{ (R)} \times 12.2 = 1$), **$K_p > K_c$** if the number of moles of gaseous products exceeds the number of moles of gaseous reactants. $K_p < K_c$ when the number of moles of gaseous reactants exceeds the number of moles of gaseous product.
- 17.22 a) Number of moles of gaseous reactants = 0; Number of moles of gaseous products = 3; $\Delta n = 3 - 0 = 3$
 b) Number of moles of gaseous reactants = 1; Number of moles of gaseous products = 0; $\Delta n = 0 - 1 = -1$
 c) Number of moles of gaseous reactants = 0; Number of moles of gaseous products = 3; $\Delta n = 3 - 0 = 3$
- 17.24 First, determine Δn for the reaction and then calculate K_c using $K_p = K_c(RT)^{\Delta n}$.
 a) Δn = Number of product gas moles – Number of reactant gas moles = $1 - 2 = -1$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{3.9 \times 10^{-2}}{[(0.0821)(1000.)]^{-1}} = 3.2019 = \mathbf{3.2}$$

 b) Δn = Number of product gas moles – Number of reactant gas moles = $1 - 1 = 0$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{28.5}{[(0.0821)(500.)]^0} = \mathbf{28.5}$$
- 17.26 When $Q < K$, the reaction proceeds to the **right** to form more products. The reaction quotient and equilibrium constant are determined by [products] / [reactants]. For Q to increase and reach the value of K , the concentration of products (numerator) must increase in relation to the concentration of reactants (denominator).
- 17.27 To decide if the reaction is at equilibrium, calculate Q_p and compare it to K_p . If $Q_p = K_p$ then the reaction is at equilibrium. If $Q_p > K_p$ then the reaction proceeds to left to produce more reactants. If $Q_p < K_p$ then the reaction proceeds to right to produce more products.

$$Q_p = \frac{P_{\text{H}_2} P_{\text{Br}_2}}{P_{\text{HBr}}^2} = \frac{(0.010)(0.010)}{(0.20)^2} = 2.5 \times 10^{-3} > K_p = 4.18 \times 10^{-9}$$

$Q_p > K_p$, thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants). Thus, the numerator will decrease in size as products are consumed and the denominator will increase in size as more reactant is produced. Q_p will decrease until $Q_p = K_p$.

- 17.31 a) The approximation applies when the change in concentration from initial to equilibrium is so small that it is insignificant. This occurs when K is small and initial concentration is large.
 b) This approximation will not work when the change in concentration is greater than 5%. This can occur when $[\text{reactant}]_{\text{initial}}$ is very small, or when $[\text{reactant}]_{\text{change}}$ is relatively large due to a large K .

- 17.32 Since all equilibrium concentrations are given in molarities and the reaction is balanced, construct an equilibrium expression and substitute the equilibrium concentrations to find K_c .

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[1.87 \times 10^{-3}]^2}{[6.50 \times 10^{-5}][1.06 \times 10^{-3}]} = 50.753 = \mathbf{50.8}$$

- 17.34 The reaction table requires that the initial $[\text{PCl}_5]$ be calculated: $[\text{PCl}_5] = 0.15 \text{ mol}/2.0 \text{ L} = 0.075 \text{ M}$
 Since there is a 1:1:1 mole ratio in this reaction:

$$x = [\text{PCl}_5] \text{ reacting } (-x), \text{ and the amount of } \text{PCl}_3 \text{ and of } \text{Cl}_2 \text{ forming } (+x).$$

Concentration (M)	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	0.075		0		0
Change	-x		+x		+x
Equilibrium	$0.075 - x$		x		x

- 17.36 Two of the three equilibrium pressures are known. Construct an equilibrium expression and solve for P_{NOCl} .

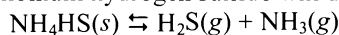
$$K_p = 6.5 \times 10^4 = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 P_{\text{Cl}_2}}$$

$$6.5 \times 10^4 = \frac{P_{\text{NOCl}}^2}{(0.35)^2 (0.10)}$$

$$P_{\text{NOCl}} = \sqrt{(6.5 \times 10^4)(0.35)^2 (0.10)} = 28.2179 = \mathbf{28 \text{ atm}}$$

A high pressure for NOCl is expected because the large value of K_p indicates that the reaction proceeds largely to the right, i.e., to the formation of products.

- 17.38 The ammonium hydrogen sulfide will decompose to produce hydrogen sulfide and ammonia gas until $K_p = 0.11$:



$x = [\text{NH}_4\text{HS}]$ reacting $(-x)$, and the amount of H_2S and of NH_3 forming $(+x)$ since there is a 1:1:1 mole ratio between the reactant and products.

(It is not necessary to calculate the molarity of NH_4HS since, as a solid, it is not included in the equilibrium expression).

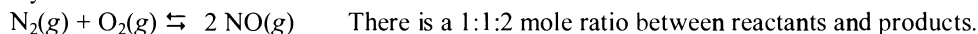
Concentration (M)	$\text{NH}_4\text{HS}(\text{s})$	\rightleftharpoons	$\text{H}_2\text{S}(\text{g})$	+	$\text{NH}_3(\text{g})$
Initial	Molarity		0		0
Change	-x		+x		+x
Equilibrium	Molarity - x		x		x

$$K_p = 0.11 = (P_{\text{H}_2\text{S}})(P_{\text{NH}_3}) \quad (\text{The solid } \text{NH}_4\text{HS} \text{ is not included})$$

$$0.11 = (x)(x)$$

$$x = P_{\text{NH}_3} = 0.33166 = \mathbf{0.33 \text{ atm}}$$

- 17.40 The initial concentrations of N_2 and O_2 are $(0.20 \text{ mol}/1.0 \text{ L}) = 0.20 \text{ M}$ and $(0.15 \text{ mol}/1.0 \text{ L}) = 0.15 \text{ M}$, respectively.



Concentration (M)	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	\rightleftharpoons	$2 \text{NO}(\text{g})$	
Initial	0.20	0.15		0	
Change	-x	-x		+ 2 x	(1:1:2 mole ratio)
Equilibrium	$0.20 - x$	$0.15 - x$		2 x	

$$K_c = 4.10 \times 10^{-4} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{[2x]^2}{[0.20 - x][0.15 - x]}$$

$$\text{Assume } 0.20 \text{ M} - x \approx 0.20 \text{ M} \quad \text{and} \quad 0.15 \text{ M} - x \approx 0.15 \text{ M}$$

$$4.10 \times 10^{-4} = \frac{4x^2}{[0.20][0.15]}$$

$$x = 1.753568 \times 10^{-3} \text{ M (unrounded)}$$

$$[\text{NO}] = 2x = 2(1.753568 \times 10^{-3} \text{ M}) = 3.507136 \times 10^{-3} = \mathbf{3.5 \times 10^{-3} \text{ M}}$$

(Since $(1.8 \times 10^{-3}) / (0.15) < 0.05$, the assumption is OK.)

- 17.42 Construct a reaction table, using $[\text{ICl}]_{\text{init}} = (0.500 \text{ mol} / 5.00 \text{ L}) = 0.100 \text{ M}$, and substitute the equilibrium concentrations into the equilibrium expression. There is a 2:1:1 mole ratio between reactant and products:

Concentration (M)	2 ICl(g)	\rightleftharpoons	I ₂ (g)	+	Cl ₂ (g)	
Initial	0.100		0		0	
Change	-2 x		+x		+x	(2:1:1 mole ratio)
Equilibrium	0.100 - 2 x		x		x	

$$K_c = 0.110 = \frac{[\text{I}_2][\text{Cl}_2]}{[\text{ICl}]^2} = \frac{[x][x]}{[0.100 - 2x]^2}$$

$$0.110 = \frac{[x]^2}{[0.100 - 2x]^2}$$

Take the square root of each side:

$$0.331662 = \frac{[x]}{[0.100 - 2x]}$$

$$x = 0.0331662 - 0.663324 x$$

$$1.663324 x = 0.0331662$$

$$x = 0.0199397$$

$$[\text{I}_2]_{\text{eq}} = [\text{Cl}_2]_{\text{eq}} = \mathbf{0.0200 \text{ M}}$$

$$[\text{ICl}]_{\text{eq}} = 0.100 - 2x = 0.601206 = \mathbf{0.060 \text{ M ICl}}$$

- 17.44 $4 \text{ NH}_3(\text{g}) + 3 \text{ O}_2(\text{g}) \rightleftharpoons 2 \text{ N}_2(\text{g}) + 6 \text{ H}_2\text{O}(\text{g})$

To find the equilibrium constant, determine the equilibrium concentrations of each reactant and product and insert into the equilibrium expression. Since $[\text{N}_2]$ increases from 0 to $1.96 \times 10^{-3} \text{ M}$, the concentration of H_2O gas will increase by 3 times as much (stoichiometric ratio is 6 H_2O : 2 N_2) and the concentration of reactants will decrease by a factor equivalent to the stoichiometric ratio (2 for NH_3 and 3/2 for O_2). Since the volume is 1.00 L, the concentrations are equal to the number of moles present.

Concentration (M)	4 NH ₃ (g)	+	3 O ₂ (g)	\rightleftharpoons	2 N ₂ (g)	+	6 H ₂ O(g)
Initial	0.0150		0.0150		0		0
Change	-4 x		-3 x		+ 2 x		+ 6 x
Equilibrium	0.0150 - 4 x		0.0150 - 3 x		+ 2 x		+ 6 x

All intermediate concentration values are unrounded.

$$[\text{N}_2]_{\text{eq}} = 2x = 1.96 \times 10^{-3} \text{ M}$$

$$[\text{H}_2\text{O}]_{\text{eq}} = (6 \text{ mol H}_2\text{O} / 2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 5.8800 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3]_{\text{eq}} = (0.0150 \text{ mol NH}_3 / 1.00 \text{ L}) - (4 \text{ mol NH}_3 / 2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 1.1080 \times 10^{-2} \text{ M}$$

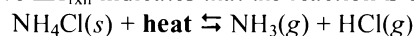
$$[\text{O}_2]_{\text{eq}} = (0.0150 \text{ mol O}_2 / 1.00 \text{ L}) - (3 \text{ mol O}_2 / 2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 1.2060 \times 10^{-2} \text{ M}$$

$$K_c = \frac{[\text{N}_2]^2 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^3} = \frac{[1.96 \times 10^{-3}]^2 [5.8800 \times 10^{-3}]^6}{[1.1080 \times 10^{-2}]^4 [1.2060 \times 10^{-2}]^3} = 6.005859 \times 10^{-6} = \mathbf{6.01 \times 10^{-6}}$$

If values for concentrations were rounded to calculate K_c , the answer is 5.90×10^{-6} .

- 17.46 Equilibrium position refers to the specific concentrations or pressures of reactants and products that exist at equilibrium, whereas equilibrium constant refers to the overall ratio of equilibrium concentrations and not to specific concentrations. Reactant concentration changes cause changes in the specific equilibrium concentrations of reactants and products (equilibrium position), but not in the equilibrium constant.

- 17.47 A positive ΔH_{rxn} indicates that the reaction is endothermic, and that heat is consumed in the reaction:



a) The addition of heat (high temperature) causes the reaction to proceed to the right to counterbalance the effect of the added heat. Therefore, more products form at a higher temperature and container **(B)** with the largest number of product molecules best represents the mixture.

b) When heat is removed (low temperature), the reaction shifts to the left to offset that disturbance. Therefore, NH_3 and HCl molecules combine to form more reactant and container (A) with the smallest number of product gas molecules best represents the mixture.

- 17.50 An endothermic reaction can be written as: reactants + heat \rightleftharpoons products. A rise in temperature (increase in heat) favors the forward direction of the reaction, i.e., the formation of products and consumption of reactants. Since $K = [\text{products}]/[\text{reactants}]$, the addition of heat increases the numerator and decreases the denominator, making K_2 larger than K_1 .
- 17.51 a) Equilibrium position shifts **toward products**. Adding a reactant (CO) causes production of more products as the system will act to reduce the increase in reactant by proceeding toward the product side, thereby consuming additional CO .
 b) Equilibrium position shifts **toward products**. Removing a product (CO_2) causes production of more products as the system acts to replace the removed product.
 c) Equilibrium position **does not shift**. The amount of a solid reactant or product does not impact the equilibrium as long as there is some solid present.
 d) Equilibrium position shifts **toward reactants**. When product is added, the system will act to reduce the increase in product by proceeding toward the reactant side, thereby consuming additional CO_2 ; dry ice is solid carbon dioxide that sublimates to carbon dioxide gas. At very low temperatures, CO_2 solid will not sublime, but since the reaction lists carbon dioxide as a gas, the assumption that sublimation takes place is reasonable.
- 17.53 An increase in container volume results in a decrease in pressure (Boyle's Law). Le Châtelier's principle states that the equilibrium will shift in the direction that forms more moles of gas to offset the decrease in pressure.
 a) **More F** forms (2 moles of gas) and **less F₂** (1 mole of gas) is present as the reaction shifts towards the right.
 b) **More C₂H₂ and H₂** form (4 moles of gas) and **less CH₄** (2 moles of gas) is present as the reaction shifts towards the right.
- 17.55 The purpose of adjusting the volume is to cause a shift in equilibrium.
 a) Because the number of reactant gaseous moles (4H_2) equals the product gaseous moles ($4\text{H}_2\text{O}$), a change in volume will have **no effect** on the yield.
 b) The moles of gaseous product (2 CO) exceed the moles of gaseous reactant (1 O_2). A decrease in pressure favors the reaction direction that forms more moles of gas, so **increase** the reaction vessel volume.
- 17.57 An increase in temperature (addition of heat) causes a shift in the equilibrium away from the side of the reaction with heat.
 a) $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)} + \text{heat}$ $\Delta H_{\text{rxn}} = -90.7 \text{ kJ}$
 A negative ΔH_{rxn} indicates an exothermic reaction. The equilibrium shifts to the left, away from heat, towards the reactants, so amount of product **decreases**.
 b) $\text{C(s)} + \text{H}_2\text{O(g)} + \text{heat} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{(g)}$ $\Delta H_{\text{rxn}} = 131 \text{ kJ}$
 A positive ΔH_{rxn} indicates an endothermic reaction. The equilibrium shifts to the right, away from heat, towards the products, so amounts of products **increase**.
 c) $2\text{NO}_2\text{(g)} + \text{heat} \rightleftharpoons 2\text{NO(g)} + \text{O}_2\text{(g)}$
 The reaction is endothermic. The equilibrium shifts to the right, away from heat, towards the product, so amounts of products **increase**.
 d) $2\text{C(s)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{CO(g)} + \text{heat}$
 The reaction is exothermic. The equilibrium shifts to the left, away from heat, towards the reactants; amount of product **decreases**.
- 17.60 a) $\text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{SO}_3\text{(g)} + \text{heat}$
 The forward reaction is exothermic (ΔH_{rxn} is negative), so it is favored by **lower temperatures**. Lower temperatures will cause a shift to the right, the heat side of the reaction. There are fewer moles of gas as products (1 SO_3) than as reactants (1 SO_2 (g) + $\frac{1}{2}\text{O}_2$), so products are favored by **higher pressure**. High pressure will cause a shift in equilibrium to the side with the fewer moles of gas.
 b) Addition of O_2 would **decrease Q** ($Q = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$) and have **no impact on K**.

c) To enhance yield of SO_3 , a low temperature is used. Reaction rates are slower at lower temperatures, so a catalyst is used **to speed up the reaction**.

- 17.65 a) You are given a value of K_c but the amounts of reactant and product is given in units of pressure. Convert K_c to K_p .

$$K_p = K_c(RT)^{\Delta n} \quad \Delta n = 1 - 2 = -1 \quad (1 \text{ mol of product, } \text{C}_2\text{H}_5\text{OH} \text{ and } 2 \text{ mol of reactants } (\text{C}_2\text{H}_4 + \text{H}_2\text{O}))$$

$$K_p = K_c(RT)^{-1} = (9 \times 10^3)[(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(600. \text{ K})]^{-1} = 1.8270 \times 10^2 \text{ (unrounded)}$$

Substitute the given values into the equilibrium expression and solve for $P_{\text{C}_2\text{H}_4}$.

$$K_p = \frac{P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{C}_2\text{H}_4} P_{\text{H}_2\text{O}}} = \frac{200.}{P_{\text{C}_2\text{H}_4} (400.)} = 1.8270 \times 10^2$$

$$P_{\text{C}_2\text{H}_4} = 2.7367 \times 10^{-3} = \mathbf{3 \times 10^{-3} \text{ atm}}$$

b) The forward direction, towards the production of ethanol, produces the least number of moles of gas and is favored by **high pressure**. A **low temperature** favors an exothermic reaction.

c) **No**, condensing the $\text{C}_2\text{H}_5\text{OH}$ would not increase the yield. Ethanol has a lower boiling point (78.5°C) than water (100°C). Decreasing the temperature to condense the ethanol would also condense the water, so moles of gas from each side of the reaction are removed. The direction of equilibrium (yield) is unaffected when there is no net change in the number of moles of gas.

- 17.68 a) You are given a value of K_c but the amounts of reactant and product is given in units of pressure. Convert K_c to K_p .

$$K_p = K_c(RT)^{\Delta n} \quad \Delta n = 2 - 3 = -1 \quad (2 \text{ mol of product, } \text{SO}_3 \text{ and } 3 \text{ mol of reactants, } 2 \text{ SO}_2 + \text{O}_2)$$

$$K_p = K_c(RT)^{-1} = (1.7 \times 10^8)[(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(600. \text{ K})]^{-1} = 3.451 \times 10^6 \text{ (unrounded)}$$

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = \frac{(300.)^2}{P_{\text{SO}_2}^2 (100.)} = 3.451 \times 10^6$$

$$P_{\text{SO}_2} = 0.016149 = \mathbf{0.016 \text{ atm}}$$

b) Create a reaction table that describes the reaction conditions. Since the volume is 1.0 L, the moles equals the molarity. Note the 2:1:2 mole ratio between SO_2 : O_2 : SO_3 .

Concentration (M)	2 $\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	2 $\text{SO}_3(\text{g})$	
Initial	0.0040		0.0028		0	
Change	-2 x		-x		+2 x	(2:1:2 mole ratio)
Equilibrium	0.0040 - 2 x		0.0028 - x		2 x = 0.0020 (given)	

x = 0.0010, therefore:

$$[\text{SO}_2] = 0.0040 - 2(0.0010) = 0.0020 \text{ M}$$

$$[\text{O}_2] = 0.0028 - 0.0010 = 0.0018 \text{ M}$$

$$[\text{SO}_3] = 2(0.0010) = 0.0020 \text{ M}$$

Substitute equilibrium concentrations into the equilibrium expression and solve for K_c .

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{[0.0020]^2}{[0.0020]^2 [0.0018]} = 555.5556 = \mathbf{5.6 \times 10^2}$$

The pressure of SO_2 is estimated using the concentration of SO_2 and the ideal gas law (although the ideal gas law is not well behaved at high pressures and temperatures).

$$P_{\text{SO}_2} = \frac{nRT}{V} = \frac{(0.0020 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1000. \text{ K})}{(1.0 \text{ L})} = 0.1642 = \mathbf{0.16 \text{ atm}}$$

- 17.69 The equilibrium constant for the reaction is $K_p = P_{\text{CO}_2} = 0.220 \text{ atm}$

The amount of calcium carbonate solid in the container at the first equilibrium equals the original amount, 0.100 mol, minus the amount reacted to form 0.220 atm of carbon dioxide. The moles of CaCO_3 reacted is equal to the number of moles of carbon dioxide produced. Use the pressure of CO_2 and the Ideal Gas Equation to calculate the moles of CaCO_3 reacted:

$$\text{Moles CaCO}_3 = \text{moles CO}_2 = n = PV / RT$$

$$n = \frac{(0.220 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(385 \text{ K})} = 0.06960 \text{ mol CaCO}_3 \text{ lost (unrounded)}$$

$$0.100 \text{ mol CaCO}_3 - 0.06960 \text{ mol CaCO}_3 = 0.0304 \text{ mol CaCO}_3 \text{ at first equilibrium}$$

As more carbon dioxide gas is added, the system returns to equilibrium by shifting to the left to convert the added carbon dioxide to calcium carbonate to maintain the partial pressure of carbon dioxide at 0.220 atm (K_p). Convert the added 0.300 atm of CO_2 to moles using the Ideal Gas Equation. The moles of CO_2 reacted equals the moles of CaCO_3 formed.

$$\text{Moles CaCO}_3 = \text{moles CO}_2 = n = PV / RT$$

$$n = \frac{(0.300 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(385 \text{ K})} = 0.09491 \text{ mol CaCO}_3 \text{ formed (unrounded)}$$

Add the moles of CaCO_3 formed in the second equilibrium to the moles of CaCO_3 at the first equilibrium position and convert to grams.

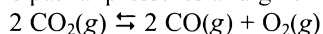
$$\text{Mass CaCO}_3 = \left(\frac{0.0304 \text{ mol} + 0.09491 \text{ mol CaCO}_3}{1 \text{ mol CaCO}_3} \right) \left(\frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \right) = 12.542 = \mathbf{12.5 \text{ g CaCO}_3}$$

- 17.73 a) Calculate the partial pressures of oxygen and carbon dioxide because volumes are proportional to moles of gas, so volume fraction equals mole fraction. Assume that the amount of carbon monoxide gas is small relative to the other gases, so the total volume of gases equals $V_{\text{CO}} + V_{\text{O}} + V_{\text{N}} = 10.0 + 1.00 + 50.0 = 61.0$.

$$P_{\text{CO}_2} = \left(\frac{10.0 \text{ mol CO}_2}{61.0 \text{ mol gas}} \right) (4.0 \text{ atm}) = 0.6557377 \text{ atm (unrounded)}$$

$$P_{\text{O}_2} = \left(\frac{1.00 \text{ mol O}_2}{61.0 \text{ mol gas}} \right) (4.0 \text{ atm}) = 0.06557377 \text{ atm (unrounded)}$$

- b) Use the partial pressures and given K_p to find P_{CO} .



$$K_p = \frac{P_{\text{CO}}^2 P_{\text{O}_2}}{P_{\text{CO}_2}^2} = \frac{P_{\text{CO}}^2 (0.06557377)}{(0.6557377)^2} = 1.4 \times 10^{-28}$$

$$P_{\text{CO}} = 3.0299 \times 10^{-14} = \mathbf{3.0 \times 10^{-14} \text{ atm}}$$

- c) Convert partial pressure to moles per liter using the ideal gas equation, and then convert moles of CO to grams.

$$n_{\text{CO}} / V = P / RT = \frac{(3.0299 \times 10^{-14} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(800 \text{ K})} = 4.6131 \times 10^{-16} \text{ mol/L (unrounded)}$$

$$\left(\frac{4.6131 \times 10^{-16} \text{ mol CO}}{\text{L}} \right) \left(\frac{28.01 \text{ g CO}}{1 \text{ mol CO}} \right) \left(\frac{1 \text{ pg}}{10^{-12} \text{ g}} \right) = 0.01292 = \mathbf{0.013 \text{ pg CO/L}}$$

- 17.76 a) Write a reaction table given that $P_{\text{CH}_4}(\text{init}) = P_{\text{CO}}(\text{init}) = 10.0 \text{ atm}$, substitute equilibrium values into the equilibrium expression, and solve for P_{H_2} .

Pressure (atm)	$\text{CH}_4(g)$	+	$\text{CO}_2(g)$	\rightleftharpoons	$2 \text{ CO}(g)$	+	$2 \text{ H}_2(g)$
Initial	10.0		10.0		0		0
Change	-x		-x		+2x		+2x
Equilibrium	10.0 - x		10.0 - x		2x		2x

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{H}_2}^2}{P_{\text{CH}_4} P_{\text{CO}_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 3.548 \times 10^6 \text{ (take square root of each side)}$$

$$\frac{(2x)^2}{(10.0 - x)} = 1.8836135 \times 10^3$$

A quadratic is necessary:

$$4x^2 + (1.8836135 \times 10^3)x - 1.8836135 \times 10^4 = 0 \text{ (unrounded)}$$

$$a = 4 \quad b = 1.8836135 \times 10^3 \quad c = -1.8836135 \times 10^4$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-1.8836135 \times 10^3 \pm \sqrt{(1.8836135 \times 10^3)^2 - 4(4)(-1.8836135 \times 10^4)}}{2(4)}$$

$$x = 9.796209 \text{ (unrounded)}$$

$$P(\text{hydrogen}) = 2x = 2(9.796209) = 19.592418 \text{ atm (unrounded)}$$

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H_2 form for each mole of CH_4 or CO_2 that reacts).

$$\text{The percent yield is } \frac{19.592418 \text{ atm}}{20.0 \text{ atm}}(100\%) = 97.96209 = \mathbf{98.0\%}.$$

b) Repeat the calculations for part (a) with the new K_p value. The reaction table is the same.

$$K_p = \frac{P_{CO}^2 P_{H_2}^2}{P_{CH_4} P_{CO_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 2.626 \times 10^7$$

$$\frac{(2x)^2}{(10.0 - x)} = 5.124451 \times 10^3$$

A quadratic is needed:

$$4x^2 + (5.124451 \times 10^3)x - 5.124451 \times 10^4 = 0 \text{ (unrounded)}$$

$$a = 4 \quad b = 5.124451 \times 10^3 \quad c = -5.124451 \times 10^4$$

$$x = \frac{-5.124451 \times 10^3 \pm \sqrt{(5.124451 \times 10^3)^2 - 4(4)(-5.124451 \times 10^4)}}{2(4)}$$

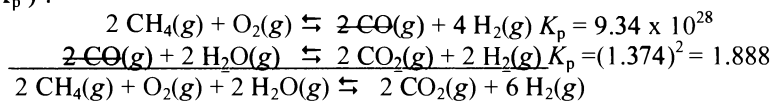
$$x = 9.923138 \text{ (unrounded)}$$

$$P(\text{hydrogen}) = 2x = 2(9.923138) = 19.846276 \text{ atm (unrounded)}$$

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H_2 form for each mole of CH_4 or CO_2 that reacts).

$$\text{The percent yield is } \frac{19.846276 \text{ atm}}{20.0 \text{ atm}}(100\%) = 99.23138 = \mathbf{99.0\%}.$$

17.77 a) Multiply the second equation by 2 to cancel the moles of CO produced in the first reaction. K_p for the second reaction is then $(K_p)^2$.



$$\text{b) } K_p = (9.34 \times 10^{28})(1.888) = 1.76339 \times 10^{29} = \mathbf{1.76 \times 10^{29}}$$

$$\text{c) } \Delta n = 8 - 5 = 3 \quad (8 \text{ moles of product gas} - 5 \text{ moles of reactant gas})$$

$$K_c = \frac{K_p}{[RT]^{\Delta n}}$$

$$K_c = \frac{1.76339 \times 10^{29}}{[(0.0821 \text{ atm}\cdot\text{L/mol}\cdot\text{K})(1000)]^3} = 3.18654 \times 10^{23} = \mathbf{3.19 \times 10^{23}}$$

d) The initial total pressure is given as 30. atm. To find the final pressure use relationship between pressure and number of moles of gas: $n_{\text{initial}}/P_{\text{initial}} = n_{\text{final}}/P_{\text{final}}$

Total mol of gas initial = 2.0 mol CH₄ + 1.0 mol O₂ + 2.0 mol H₂O = 5.0 mol

Total mol of gas final = 2.0 mol CO₂ + 6.0 mol H₂ = 8.0 mol

$$P_{\text{final}} = \frac{30. \text{ atm reactants}}{\left(\frac{8 \text{ mol products}}{5 \text{ mol reactants}} \right)} = \mathbf{48 \text{ atm}}$$

- 17.78 a) Careful reading of the problem indicates that the given K_p occurs at 1000. K and that the initial pressure of N₂ is 200. atm. $\log K_p = -43.10$; $K_p = 10^{-43.10} = 7.94328 \times 10^{-44}$

Pressure (atm)	N ₂ (g)	\rightleftharpoons	2N(g)
Initial	200.		0
Change	-x		+2x
Equilibrium	200-x		2x

$$K_p = \frac{(P_N)^2}{(P_{N_2})} = 7.94328 \times 10^{-44}$$

$$\frac{(2x)^2}{(200. - x)} = 7.94328 \times 10^{-44} \quad \text{Assume } 200. - x \cong 200.$$

$$P_N = 2x = \sqrt{(200.)(7.94328 \times 10^{-44})} = 3.985795 \times 10^{-21} = \mathbf{4.0 \times 10^{-21}}$$

- b) $\log K_p = -17.30$; $K_p = 10^{-17.30} = 5.01187 \times 10^{-18}$

Pressure (atm)	H ₂ (g)	\rightleftharpoons	2H(g)
Initial	600.		0
Change	-x		+2x
Equilibrium	600-x		2x

$$K_p = \frac{(P_H)^2}{(P_{H_2})} = 5.01187 \times 10^{-18}$$

$$\frac{(2x)^2}{(600. - x)} = 5.01187 \times 10^{-18} \quad \text{Assume } 600. - x \cong 600.$$

$$P_H = 2x = \sqrt{(600.)(5.01187 \times 10^{-18})} = 5.48372 \times 10^{-8} = \mathbf{5.5 \times 10^{-8}}$$

- c) Convert pressures to moles using the ideal gas law. $PV = nRT$. Convert moles to atoms using Avogadro's number.

$$\begin{aligned} \text{Moles N} / V = P / RT &= \frac{(3.985795 \times 10^{-21} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1000. \text{ K})} \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} \right) \\ &= 29.2356 = \mathbf{29 \text{ N atoms/L}} \end{aligned}$$

$$\begin{aligned} \text{Moles H} / V = P / RT &= \frac{(5.48372 \times 10^{-8} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1000. \text{ K})} \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} \right) \\ &= 4.022 \times 10^{14} = \mathbf{4.0 \times 10^{14} \text{ H atoms/L}} \end{aligned}$$

- d) The more reasonable step is $\text{N}_2(\text{g}) + \text{H}(\text{g}) \rightarrow \text{NH}(\text{g}) + \text{N}(\text{g})$. With only 29 N atoms in 1.0 L, the first reaction would produce virtually no NH(g) molecules. There are orders of magnitude more N₂ molecules than N atoms, so the second reaction is the more reasonable step.

17.79 a) $3 \text{ H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{ NH}_3(\text{g})$ The mole ratio $\text{H}_2:\text{N}_2 = 3:1$; if $\text{N}_2 = x$, $\text{H}_2 = 3x$ $P_{\text{NH}_3} = 50. \text{ atm}$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = 1.00 \times 10^{-4}$$

$$K_p = \frac{(50.)^2}{(x)(3x)^3} = 1.00 \times 10^{-4}$$

$$x = 31.02016 = \mathbf{31 \text{ atm N}_2}$$

$$3x = 3(31.02016) = 93.06048 = \mathbf{93 \text{ atm H}_2}$$

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (31.02016 \text{ atm}) + (93.06048 \text{ atm}) + (50. \text{ atm}) \\ = 174.08064 = \mathbf{174 \text{ atm total}}$$

$$\text{b) } K_p = \frac{(50.)^2}{(x)(6x)^3} = 1.00 \times 10^{-4} \quad \text{N}_2 = x \text{ and } \text{H}_2 = 6x$$

$$x = 18.44 = \mathbf{18 \text{ atm N}_2}$$

$$6x = 6(18.44) = 110.64 = \mathbf{111 \text{ atm H}_2}$$

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (18.44 \text{ atm}) + (110.64 \text{ atm}) + (50. \text{ atm}) \\ = 179.09 = \mathbf{179 \text{ atm total}}$$

This is not a valid argument. The total pressure in (b) is greater than in (a) to produce the same amount of NH_3 .

17.80 a) Equilibrium partial pressures for the reactants, nitrogen and oxygen, can be assumed to equal their initial partial pressures because the equilibrium constant is so small that very little nitrogen and oxygen will react to form nitrogen monoxide. After calculating the equilibrium partial pressure of nitrogen monoxide, test this assumption by comparing the partial pressure of nitrogen monoxide with that of nitrogen and oxygen.

Pressure (atm)	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	$2\text{NO}(\text{g})$
Initial	0.780		0.210		0
Change	-x		-x		+2x
Equilibrium	$0.780 - x$		$0.210 - x$		2x

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = 4.35 \times 10^{-31}$$

$$\frac{(2x)^2}{(0.780 - x)(0.210 - x)} = 4.35 \times 10^{-31} \quad \text{Assume } x \text{ is small because } K \text{ is small.}$$

$$\frac{(2x)^2}{(0.780)(0.210)} = 4.35 \times 10^{-31}$$

$$x = 1.33466 \times 10^{-16} \text{ (unrounded)}$$

Based on the small amount of nitrogen monoxide formed, the assumption that the partial pressures of nitrogen and oxygen change to an insignificant degree holds.

$$P_{\text{nitrogen}} (\text{equilibrium}) = (0.780 - 1.33466 \times 10^{-16}) \text{ atm} = \mathbf{0.780 \text{ atm N}_2}$$

$$P_{\text{oxygen}} (\text{equilibrium}) = (0.210 - 1.33466 \times 10^{-16}) \text{ atm} = \mathbf{0.210 \text{ atm O}_2}$$

$$P_{\text{NO}} (\text{equilibrium}) = 2(1.33466 \times 10^{-16}) \text{ atm} = 2.66932 \times 10^{-16} = \mathbf{2.67 \times 10^{-16} \text{ atm NO}}$$

b) The total pressure is the sum of the three partial pressures:

$$0.780 \text{ atm} + 0.210 \text{ atm} + 2.67 \times 10^{-16} \text{ atm} = \mathbf{0.990 \text{ atm}}$$

c) $K_p = K_c(RT)^{\Delta n}$ $\Delta n = 2 \text{ mol NO product} - 2 \text{ mol reactant (1 N}_2 + 1 \text{ O}_2) = 0$

$$K_p = K_c(RT)^0$$

$K_c = K_p = \mathbf{4.35 \times 10^{-31}}$ because there is no net increase or decrease in the number of moles of gas in the course of the reaction.

17.84 The reaction is: $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$

a) Set up a table with the initial CO and initial $\text{H}_2 = 0.100 \text{ mol} / 20.00 \text{ L} = 0.00500 \text{ M}$.

	CO	H ₂ O	CO ₂	H ₂
Initial	0.00500 M	0.00500 M	0	0
Change	-x	-x	+x	+x
Equilibrium	0.00500 - x	0.00500 - x	x	x

$$[\text{CO}]_{\text{equilibrium}} = 0.00500 - x = 2.24 \times 10^{-3} \text{ M} = [\text{H}_2\text{O}] \quad (\text{given in problem})$$

$$x = 0.00276 \text{ M} = [\text{CO}_2] = [\text{H}_2]$$

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.00276][0.00276]}{[0.00224][0.00224]} = 1.518176 = \mathbf{1.52}$$

$$\text{b) } M_{\text{total}} = [\text{CO}] + [\text{H}_2\text{O}] + [\text{CO}_2] + [\text{H}_2] = (0.00224 \text{ M}) + (0.00224 \text{ M}) + (0.00276 \text{ M}) + (0.00276 \text{ M}) \\ = 0.01000 \text{ M}$$

$$n_{\text{total}} = M_{\text{total}} V = (0.01000 \text{ mol/L}) (20.00 \text{ L}) = 0.2000 \text{ mol total}$$

$$P_{\text{total}} = n_{\text{total}} RT / V = \frac{(0.2000 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 900.) \text{ K})}{(20.00 \text{ L})} = 0.9625638 = \mathbf{0.9626 \text{ atm}}$$

c) Initially, an equal number of moles must be added = **0.2000 mol CO**

d) Set up a table with the initial concentrations equal to the final concentrations from part (a), and then add 0.2000 mol CO / 20.00 L = 0.01000 M to compensate for the added CO.

	CO	H ₂ O	CO ₂	H ₂
Initial	0.00224 M	0.00224 M	0.00276 M	0.00276 M
Added CO	0.01000 M			
Change	-x	-x	+x	+x
Equilibrium	0.01224 - x	0.00224 - x	0.00276 + x	0.00276 + x

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.00276 + x][0.00276 + x]}{[0.01224 - x][0.00224 - x]} = 0.9625638$$

$$\frac{[7.6176 \times 10^{-6} + 5.52 \times 10^{-3} x + x^2]}{2.74176 \times 10^{-5} - 1.448 \times 10^{-2} x + x^2} = 0.9625638$$

$$7.6176 \times 10^{-6} + 5.52 \times 10^{-3} x + x^2 = (0.9625638) (2.74176 \times 10^{-5} - 1.448 \times 10^{-2} x + x^2)$$

$$7.6176 \times 10^{-6} + 5.52 \times 10^{-3} x + x^2 = 2.6391189 \times 10^{-5} - 1.3937923 \times 10^{-2} x + 0.9625638 x^2$$

$$0.0374362 x^2 + 1.9457923 \times 10^{-2} x - 1.8773589 \times 10^{-5} = 0$$

$$a = 0.0374362 \quad b = 1.9457923 \times 10^{-2} \quad c = -1.8773589 \times 10^{-5}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(1.9457923 \times 10^{-2}) \pm \sqrt{(1.9457923 \times 10^{-2})^2 - 4(0.0374362)(-1.8773589 \times 10^{-5})}}{2(0.0374362)}$$

$$x = 9.6304567 \times 10^{-4} \text{ (unrounded)}$$

$$[\text{CO}] = 0.01224 - x = 0.01224 - (9.6304567 \times 10^{-4}) = 0.011276954 = \mathbf{0.01128 \text{ M}}$$

Chapter 18 Acid-Base Equilibria

FOLLOW-UP PROBLEMS

- 18.1 a) Chloric acid, **HClO₃**, is the stronger acid because acid strength increases as the number of O atoms in the acid increases.
 b) Hydrochloric acid, **HCl**, is one of the strong hydrohalic acids whereas acetic acid, CH₃COOH, is a weak carboxylic acid.
 c) Sodium hydroxide, **NaOH**, is a strong base because Na is a Group 1A(1) metal. Methylamine, CH₃NH₂, is an organic amine and, therefore, a weak base.

- 18.2 Plan: The product of [H₃O⁺] and [OH⁻] remains constant at 25°C because the value of K_w is constant at a given temperature. Use $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ to solve for [H₃O⁺].

Solution: Calculating [H₃O⁺]:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{6.7 \times 10^{-2}} = 1.4925 \times 10^{-13} = \mathbf{1.5 \times 10^{-13} \text{ M}}$$

Since [OH⁻] > [H₃O⁺], the solution is **basic**.

Check: The solution is neutral when either species concentration is $1 \times 10^{-7} \text{ M}$. Since the problem specifies an [OH⁻] much greater than this, the solution is basic.

- 18.3 Plan: NaOH is a strong base that dissociates completely in water. Subtract pH from 14.00 to find the pOH, and calculate inverse logs of pH and pOH to find [H₃O⁺] and [OH⁻], respectively.

Solution: pH + pOH = 14.00

$$\text{pOH} = 14.00 - 9.52 = \mathbf{4.48}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.52} = 3.01995 \times 10^{-10} = \mathbf{3.0 \times 10^{-10} \text{ M}}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.48} = 3.3113 \times 10^{-5} = \mathbf{3.3 \times 10^{-5} \text{ M}}$$

Check: At 25°C, [H₃O⁺][OH⁻] should equal 1.0×10^{-14} . $(3.0 \times 10^{-10})(3.3 \times 10^{-5}) = 9.9 \times 10^{-15} \approx 1.0 \times 10^{-14}$. The significant figures in the concentrations reflect the number of significant figures after the decimal point in the pH and pOH values.

- 18.4 Plan: Identify the conjugate pairs by first identifying the species that donates H⁺ (the acid) in either reaction direction. The other reactant accepts the H⁺ and is the base. The acid has one more H and +1 greater charge than its conjugate base.

Solution:

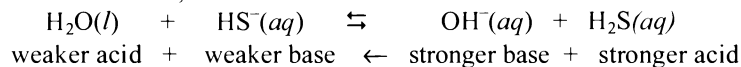
a) CH₃COOH has one more H⁺ than CH₃COO⁻. H₃O⁺ has one more H⁺ than H₂O. Therefore, CH₃COOH and H₃O⁺ are the acids, and CH₃COO⁻ and H₂O are the bases. The conjugate acid/base pairs are **CH₃COOH/CH₃COO⁻** and **H₃O⁺/H₂O**.

b) H₂O donates a H⁺ and acts as the acid. F⁻ accepts the H⁺ and acts as the base. In the reverse direction, HF acts as the acid and OH⁻ acts as the base. The conjugate acid/base pairs are **H₂O/OH⁻** and **HF/F⁻**.

- 18.5 Plan: Identify the conjugate acid-base pairs. To predict the direction, consult Figure 18.9 to see which acid and base are stronger. The reaction will proceed in the direction which forms the weaker acid and base.

Solution: $\text{H}_2\text{O}(l) + \text{HS}^-(aq) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{S}(aq)$

The conjugate pairs are H₂O/OH⁻ and H₂S/HS⁻. H₂S is higher than H₂O on the list of acids and OH⁻ is lower than HS⁻ on the list of bases. Thus, we have



The **net direction is to the left** to form the weaker acid and base. Since [reactants] will be greater than [products], $K_c < 1$.

- 18.6 **Plan:** Write a balanced equation for the dissociation of NH_4^+ in water. Using the given information, construct a table that describes the initial and equilibrium concentrations. Construct an equilibrium expression and make assumptions where possible to simplify the calculations.

Solution:

	$\text{NH}_4^+(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{NH}_3(g)$
Initial	0.2 M				0		0
Change	-x				+x		+x
Equilibrium	0.2 - x				x		x

The initial concentration of $\text{NH}_4^+ = 0.2 \text{ M}$ because each mole of NH_4Cl completely dissociates to form one mole of NH_4^+ .

$$x = [\text{H}_3\text{O}^+] = [\text{NH}_3] = 10^{-\text{pH}} = 10^{-5.0} = 1.0 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{(0.2 - x)} = \frac{(1.0 \times 10^{-5})(1.0 \times 10^{-5})}{(0.2 - 1.0 \times 10^{-5})}$$

$$= 5 \times 10^{-10}$$

Check: The small value of K_a is consistent with the value expected for a weak acid.

- 18.7 **Plan:** Write a balanced equation for the dissociation of HOCN in water. Using the given information, construct a table that describes the initial and equilibrium concentrations. Construct an equilibrium expression and solve the quadratic expression for x, the concentration of H_3O^+ .

Solution:

	$\text{HOCN}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{OCN}^-(aq)$
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium	0.10 - x				x		x

$$K_a = \frac{[\text{OCN}^-][\text{H}_3\text{O}^+]}{[\text{HOCN}]} = \frac{x^2}{(0.10 - x)} = 3.5 \times 10^{-4}$$

In this example, the dissociation of HOCN is not negligible in comparison to the initial concentration:

Therefore, $[\text{HOCN}]_{\text{eq}} = 0.10 - x$ and the equilibrium expression is solved using the quadratic formula.

$$x^2 = 3.5 \times 10^{-4} (0.10 - x)$$

$$x^2 = 3.5 \times 10^{-5} - 3.5 \times 10^{-4} x$$

$$x^2 + 3.5 \times 10^{-4} x - 3.5 \times 10^{-5} = 0 \quad (a x^2 + b x + c = 0)$$

$$a = 1 \quad b = 3.5 \times 10^{-4} \quad c = -3.5 \times 10^{-5}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-3.5 \times 10^{-4} \pm \sqrt{(3.5 \times 10^{-4})^2 - 4(1)(-3.5 \times 10^{-5})}}{2(1)}$$

$$x = 5.7436675 \times 10^{-3} = \mathbf{5.7 \times 10^{-3} \text{ M } H_3O^+}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [5.7436675 \times 10^{-3}] = 2.2408 = \mathbf{2.24}$$

- 18.8 **Plan:** Pyridine contains a nitrogen atom that accepts H^+ from water to form OH^- ions in aqueous solution. Write a balanced equation and equilibrium expression for the reaction, convert $\text{p}K_b$ to K_b , make simplifying assumptions (if valid) and solve for $[\text{OH}^-]$. Calculate $[\text{H}_3\text{O}^+]$ using $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and convert to pH.

Solution: $\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$

$$K_b = 10^{-\text{p}K_b} = 10^{-8.77} = 1.69824 \times 10^{-9}$$

$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = 1.69824 \times 10^{-9}$$

Assumptions:

1) Since $K_b \gg K_w$, disregard the $[\text{OH}^-]$ that results from the autoionization of water.

2) Since K_b is small, $[\text{C}_5\text{H}_5\text{N}] = 0.10 - x \approx 0.10$.

$$K_b = \frac{[\text{C}_5\text{N}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{N}_5\text{N}]} = \frac{x^2}{(0.10)} = 1.69824 \times 10^{-9} \text{ (unrounded)}$$

$$x = 1.303165 \times 10^{-5} = 1.3 \times 10^{-5} \text{ M} = [\text{OH}^-] = [\text{C}_5\text{H}_5\text{NH}^+]$$

Since $\frac{[\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}_5]}(100) = \frac{1.303265 \times 10^{-5}}{0.10}(100) = 0.01313$ which $< 5\%$, the assumption that the dissociation of $\text{C}_5\text{H}_5\text{N}_5$ is small is valid.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.303165 \times 10^{-5}} = 7.67362 \times 10^{-10} \text{ M (unrounded)}$$

$$\text{pH} = -\log(7.67362 \times 10^{-10}) = 9.1149995 = \mathbf{9.11}$$

Check: Since pyridine is a weak base, a $\text{pH} > 7$ is expected.

- 18.9 Plan: The hypochlorite ion, ClO^- , acts as a weak base in water. Write a balanced equation and equilibrium expression for this reaction. The K_b of ClO^- is calculated from the K_a of its conjugate acid, hypochlorous acid, HClO (from Appendix C, $K_a = 2.9 \times 10^{-8}$). Make simplifying assumptions (if valid), solve for $[\text{OH}^-]$, convert to $[\text{H}_3\text{O}^+]$ and calculate pH.

Solution:

	$\text{ClO}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HClO}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.20 M		_____		0		0
Change	-x		_____		+x		+x
Equilibrium	0.20 - x		_____		x		x

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.448276 \times 10^{-7} \text{ (unrounded)}$$

Assumptions:

1) Since $K_b \gg K_w$, the dissociation of water provides a negligible amount of $[\text{OH}^-]$.

2) Since K_b is very small, $[\text{ClO}^-]_{\text{eq}} = 0.20 - x \approx 0.2$.

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{x^2}{(0.20)} = 3.448276 \times 10^{-7}$$

$$x = 2.6261 \times 10^{-4}$$

Therefore, $[\text{HClO}] = [\text{OH}^-] = 2.6 \times 10^{-4} \text{ M}$.

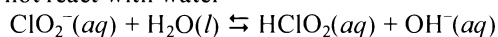
Since $\frac{[\text{OH}^-]}{[\text{ClO}^-]}(100) = \frac{2.6261 \times 10^{-4}}{0.20}(100) = 0.1313$ which $< 5\%$, the assumption that the dissociation of ClO^- is small is valid.

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{2.6261 \times 10^{-4}} = 3.8079 \times 10^{-11} \text{ M and } \text{pH} = -\log(3.8079 \times 10^{-11}) = 10.4193 = \mathbf{10.42}$$

Check: Since hypochlorite ion is a weak base, a $\text{pH} > 7$ is expected.

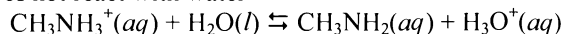
- 18.10 a) The ions are K^+ and ClO_2^- ; the K^+ is from the strong base KOH , and does **not** react with water. The ClO_2^- is from the weak acid HClO_2 , so it reacts with water to produce OH^- ions. Since the base is strong and the acid is weak, the salt derived from this combination will produce a **basic** solution.

K^+ does not react with water



b) The ions are CH_3NH_3^+ and NO_3^- ; CH_3NH_3^+ is derived from the weak base methylamine, CH_3NH_2 . Nitrate ion, NO_3^- , is derived from the strong acid HNO_3 (nitric acid). A salt derived from a weak base and strong acid produces an **acidic** solution.

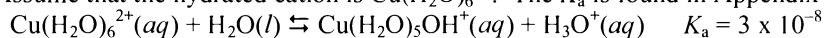
NO_3^- does not react with water



c) The ions are Cs^+ and I^- . Cesium ion is derived from cesium hydroxide, CsOH , which is a strong base because Cs is a Group 1A(1) metal. Iodide ion is derived from hydroiodic acid, HI , a strong hydrohalic acid. Since both the base and acid are strong, the salt derived from this combination will produce a **neutral** solution.

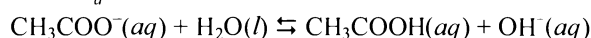
Neither Cs^+ nor I^- react with water.

- 18.11 a) The two ions that comprise this salt are cupric ion, Cu^{2+} , and acetate ion, CH_3COO^- . Metal ions are acidic in water. Assume that the hydrated cation is $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The K_a is found in Appendix C.



Acetate ion acts like a base in water. The K_b is calculated from the K_a of acetic acid (1.8×10^{-5}):

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

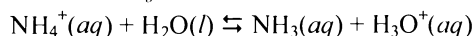


$$K_b = 5.6 \times 10^{-10}$$

$\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is a better proton donor than CH_3COO^- is a proton acceptor (i.e., $K_a > K_b$), so a solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ is **acidic**.

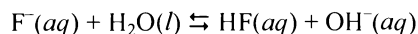
b) The two ions that comprise this salt are ammonium ion, NH_4^+ , and fluoride ion, F^- . Ammonium ion is the acid

$$\text{of NH}_3 \text{ with } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$$



$$K_a = 5.7 \times 10^{-10}$$

$$\text{Fluoride ion is the base with } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$



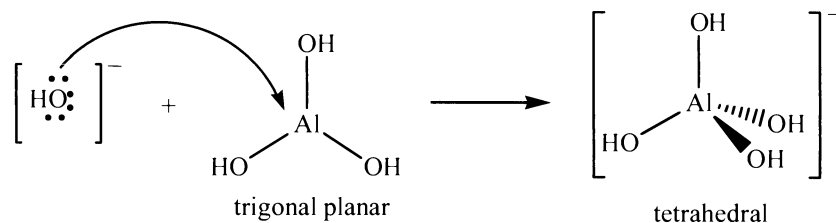
$$K_b = 1.5 \times 10^{-11}$$

Since $K_a > K_b$, a solution of (NH_4F) is **acidic**.

- 18.12 Plan: Begin by drawing Lewis dot structures for the reactants to see which molecule donates the electron pair (Lewis base) and which molecule accepts the electron pair (Lewis acid).

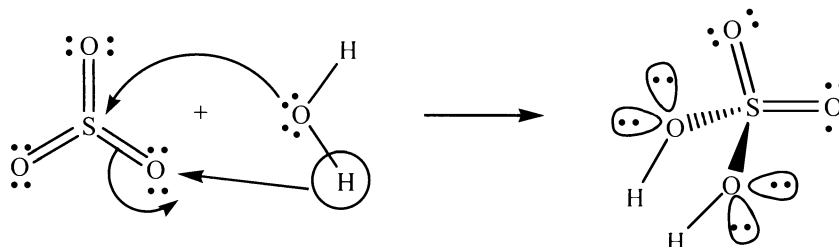
Solution:

a)



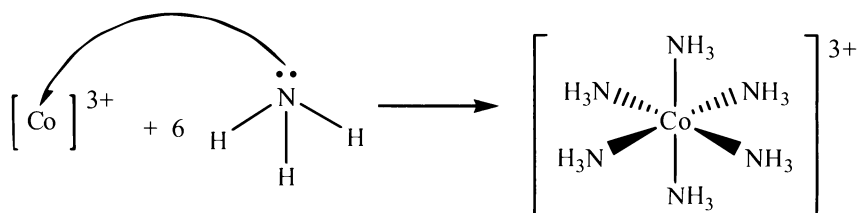
Hydroxide ion, OH^- , donates an electron pair and is the Lewis base; $\text{Al}(\text{OH})_3$ accepts the electron pair and is the Lewis acid. Note the change in geometry caused by the formation of the adduct.

b)



Sulfur trioxide accepts the electron pair and is the Lewis acid. Water donates an electron pair and is the Lewis base.

c)



Co^{3+} accepts six electron pairs and is the Lewis acid. Ammonia donates an electron pair and is the Lewis base.

END-OF-CHAPTER PROBLEMS

- 18.2 All Arrhenius acids contain hydrogen and produce hydronium ion (H_3O^+) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion (OH^-) in aqueous solution. Neutralization occurs when each H_3O^+ molecule combines with an OH^- molecule to form 2 molecules of H_2O . Chemists found that the ΔH_{rxn} was independent of the combination of strong acid with strong base. In other words, the reaction of any strong base with any strong acid always produced 56 kJ/mol ($\Delta H = -56$ kJ/mol). This was consistent with Arrhenius's hypothesis describing neutralization, because all other counter ions (those present from the dissociation of the strong acid and base) were spectators and did not participate in the overall reaction.
- 18.4 Strong acids and bases dissociate completely into their ions when dissolved in water. Weak acids only partially dissociate. The characteristic property of all weak acids is that a significant number of the acid molecules are not dissociated. For a strong acid, the concentration of hydronium ions produced by dissolving the acid is equal to the initial concentration of the undissociated acid. For a weak acid, the concentration of hydronium ions produced when the acid dissolves is less than the initial concentration of the acid.
- 18.5 a) Water, H_2O , is an **Arrhenius acid** because it produces H_3O^+ ion in aqueous solution. Water is also an Arrhenius base because it produces the OH^- ion as well.
 b) Calcium hydroxide, $\text{Ca}(\text{OH})_2$ is a base, not an acid.
 c) Phosphorous acid, H_3PO_3 , is a weak **Arrhenius acid**. It is weak because the number of O atoms equals the number of ionizable H atoms.
 d) Hydroiodic acid, HI, is a strong **Arrhenius acid**.
- 18.7 a) $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$

$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]}$$

 b) $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

 c) $\text{HBrO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{BrO}_2^-(\text{aq})$

$$K_a = \frac{[\text{BrO}_2^-][\text{H}_3\text{O}^+]}{[\text{HBrO}_2]}$$
- 18.9 Appendix C lists the K_a values. The larger the K_a value, the stronger the acid. Hydroiodic acid, HI, is not shown in Appendix C because K_a approaches infinity for strong acids and is not meaningful. Therefore, HI is the strongest acid and acetic acid, CH_3COOH , is the weakest: **$\text{CH}_3\text{COOH} < \text{HF} < \text{HIO}_3 < \text{HI}$** .
- 18.11 a) Arsenic acid, H_3AsO_4 , is a **weak acid**. The number of O atoms is 4, which exceeds the number of ionizable H atoms, 3, by one. This identifies H_3AsO_4 as a weak acid.
 b) Strontium hydroxide, $\text{Sr}(\text{OH})_2$, is a **strong base**. Soluble compounds containing OH^- ions are strong bases.
 c) HIO is a **weak acid**. The number of O atoms is 1, which is equal to the number of ionizable H atoms identifying HIO as a weak acid.

- d) Perchloric acid, HClO_4 , is a **strong acid**. HClO_4 is one example of the type of strong acid in which the number of O atoms exceeds the number of ionizable H atoms by more than 2.
- 18.15 The lower the concentration of hydronium (H_3O^+) ions, the higher the pH:
- At equal concentrations, the acid with the larger K_a will ionize to produce more hydronium ions than the acid with the smaller K_a . The solution of an **acid with the smaller $K_a = 4 \times 10^{-5}$** has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 - $\text{p}K_a$ is equal to $-\log K_a$. The smaller the K_a , the larger the $\text{p}K_a$ is. So the **acid with the larger $\text{p}K_a$, 3.5**, has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 - Lower concentration** of the same acid means lower concentration of hydronium ions produced. The 0.01 M solution has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 - At the same concentration, strong acids dissociate to produce more hydronium ions than weak acids. The 0.1 M solution of a **weak acid** has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 - Bases produce OH^- ions in solution, so the concentration of hydronium ion for a solution of a base solution is lower than that for a solution of an acid. The 0.1 M **base solution** has the higher pH.
 - pOH equals $-\log [\text{OH}^-]$. At 25°C , the equilibrium constant for water ionization, K_w , equals 1×10^{-14} so $14 = \text{pH} + \text{pOH}$. As pOH decreases, pH increases. The solution of **$\text{pOH} = 6.0$** has the higher pH.
- 18.16 a) This problem can be approached two ways. Because NaOH is a strong base, the $[\text{OH}^-]_{\text{eq}} = [\text{NaOH}]_{\text{init}}$. One method involves calculating $[\text{H}_3\text{O}^+]$ using from $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$, then calculating pH from the relationship $\text{pH} = -\log [\text{H}_3\text{O}^+]$. The other method involves calculating pOH and then using $\text{pH} + \text{pOH} = 14.00$ to calculate pH.
- First method:
- $$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0111} = 9.0090 \times 10^{-13} \text{ M (unrounded)}$$
- $$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.0090 \times 10^{-13}) = 12.04532 = \mathbf{12.05}$$
- Second method:
- $$\text{pOH} = -\log [\text{OH}^-] = -\log (0.0111) = 1.954677 \text{ (unrounded)}$$
- $$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.954677 = 12.04532 = \mathbf{12.05}$$
- With a $\text{pH} > 7$, the solution is **basic**.
- b) There are again two acceptable methods analogous to those in part a; only one will be used here.
- For a strong acid:
- $$[\text{H}_3\text{O}^+] = [\text{HCl}] = 1.23 \times 10^{-3} \text{ M}$$
- $$\text{pH} = -\log (1.23 \times 10^{-3}) = 2.91009 \text{ (unrounded)}$$
- $$\text{pOH} = 14.00 - 2.91009 = 11.08991 = \mathbf{11.09}$$
- With a $\text{pH} < 7$, the solution is **acidic**.
- 18.18 a) $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.78} = 1.659587 \times 10^{-10} = \mathbf{1.7 \times 10^{-10} \text{ M } \text{H}_3\text{O}^+}$
- $$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.78 = \mathbf{4.22}$$
- $$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.22} = 6.025596 \times 10^{-5} = \mathbf{6.0 \times 10^{-5} \text{ M } \text{OH}^-}$$
- b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 10.43 = \mathbf{3.57}$
- $$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.57} = 2.69153 \times 10^{-4} = \mathbf{2.7 \times 10^{-4} \text{ M } \text{H}_3\text{O}^+}$$
- $$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-10.43} = 3.751535 \times 10^{-11} = \mathbf{3.7 \times 10^{-11} \text{ M } \text{OH}^-}$$

- 18.20 The pH is increasing so the solution is becoming more basic. Therefore, OH^- ion is added to increase the pH. Since 1 mole of H_3O^+ reacts with 1 mole of OH^- , the difference in $[\text{H}_3\text{O}^+]$ would be equal to the $[\text{OH}^-]$ added.
- $$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.82} = 1.51356 \times 10^{-5} \text{ M } \text{H}_3\text{O}^+ \text{ (unrounded)}$$
- $$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.22} = 6.02560 \times 10^{-6} \text{ M } \text{H}_3\text{O}^+ \text{ (unrounded)}$$
- $$1.51356 \times 10^{-5} \text{ M} - 6.02560 \times 10^{-6} \text{ M} = 9.11 \times 10^{-6} \text{ M } \text{OH}^- \text{ must be added.}$$
- $$\frac{9.11 \times 10^{-6} \text{ mol}}{\text{L}} (6.5 \text{ L}) = 5.9215 \times 10^{-5} = \mathbf{6 \times 10^{-5} \text{ mol of } \text{OH}^-}$$

- 18.23 a) Heat is absorbed in an endothermic process: $2 \text{H}_2\text{O}(l) + \text{heat} \rightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$. As the temperature increases, the reaction shifts to the formation of products. Since the products are in the numerator of the K_w expression, rising temperature **increases** the value of K_w .
 b) Given that the pH is 6.80, the $[\text{H}^+]$ can be calculated. The problem specifies that the solution is neutral, meaning $[\text{H}^+] = [\text{OH}^-]$. A new K_w can then be calculated.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.80} = 1.58489 \times 10^{-7} \text{ M}$$

$$\text{H}_3\text{O}^+ = 1.6 \times 10^{-7} \text{ M} = [\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1.58489 \times 10^{-7})(1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} = 2.5 \times 10^{-14}$$
 For a neutral solution: $\text{pH} = \text{pOH} = 6.80$
- 18.24 The Brønsted-Lowry theory defines acids as proton donors and bases as proton acceptors, while the Arrhenius definition looks at acids as containing ionizable H atoms and at bases as containing hydroxide ions. In both definitions, an acid produces hydronium ions and a base produces hydroxide ions when added to water. Ammonia, NH_3 , and carbonate ion, CO_3^{2-} , are two Brønsted-Lowry bases that are not Arrhenius bases because they do not contain hydroxide ions. Brønsted-Lowry acids must contain an ionizable H atom in order to be proton donors, so a Brønsted-Lowry acid that is not an Arrhenius acid cannot be identified. (Other examples are also acceptable.)
- 18.27 An amphoteric substance can act as either an acid or a base. In the presence of a strong base (OH^-), the dihydrogen phosphate ion acts like an acid by donating hydrogen:

$$\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(aq) + \text{HPO}_4^{2-}(aq)$$

 In the presence of a strong acid (HCl), the dihydrogen phosphate ion acts like a base by accepting hydrogen:

$$\text{H}_2\text{PO}_4^-(aq) + \text{HCl}(aq) \rightarrow \text{H}_3\text{PO}_4(aq) + \text{Cl}^-(aq)$$
- 18.28 To derive the conjugate base, remove one H and decrease the charge by 1. Since each formula is neutral, the conjugate base will have a charge of -1 .
 a) Cl^- b) HCO_3^- c) OH^-
- 18.30 To derive the conjugate acid, add an H and increase the charge by 1.
 a) NH_4^+ b) NH_3 c) $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+$
- 18.32 The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid:
- a)
$$\begin{array}{ccccccc} \text{NH}_3 & + & \text{H}_3\text{PO}_4 & \rightleftharpoons & \text{NH}_4^+ & + & \text{H}_2\text{PO}_4^- \\ \text{base} & & \text{acid} & & \text{conjugate acid} & & \text{conjugate base} \end{array}$$

 Conjugate acid-base pairs: $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$; $\text{NH}_4^+/\text{NH}_3$
- b)
$$\begin{array}{ccccccc} \text{CH}_3\text{O}^- & + & \text{NH}_3 & \rightleftharpoons & \text{CH}_3\text{OH} & + & \text{NH}_2^- \\ \text{base} & & \text{acid} & & \text{conjugate acid} & & \text{conjugate base} \end{array}$$

 Conjugate acid-base pairs: $\text{NH}_3/\text{NH}_2^-$; $\text{CH}_3\text{OH}/\text{CH}_3\text{O}^-$
- c)
$$\begin{array}{ccccccc} \text{HPO}_4^{2-} & + & \text{HSO}_4^- & \rightleftharpoons & \text{H}_2\text{PO}_4^- & + & \text{SO}_4^{2-} \\ \text{base} & & \text{acid} & & \text{conjugate acid} & & \text{conjugate base} \end{array}$$

 Conjugate acid-base pairs: $\text{HSO}_4^-/\text{SO}_4^{2-}$; $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$
- 18.34 Write total ionic equations and then remove the spectator ions to write the net ionic equations. The (aq) subscript denotes that each species is soluble and dissociates in water.
- a)
$$\text{Na}^+(aq) + \text{OH}^-(aq) + \text{Na}^+(aq) + \text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}_2\text{O}(l) + 2\text{Na}^+(aq) + \text{HPO}_4^{2-}(aq)$$

 Net:
$$\text{OH}^-(aq) + \text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{HPO}_4^{2-}(aq)$$

$$\begin{array}{ccccccc} & \text{base} & & \text{acid} & & \text{conjugate acid} & & \text{conjugate base} \end{array}$$

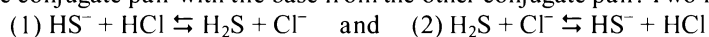
 Conjugate acid/base pairs: $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{H}_2\text{O}/\text{OH}^-$
- b)
$$\text{K}^+(aq) + \text{HSO}_4^-(aq) + 2\text{K}^+(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons 2\text{K}^+(aq) + \text{SO}_4^{2-}(aq) + \text{K}^+(aq) + \text{HCO}_3^-(aq)$$

 Net:
$$\text{HSO}_4^-(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{HCO}_3^-(aq)$$

$$\begin{array}{ccccccc} & \text{acid} & & \text{base} & & \text{conjugate base} & & \text{conjugate acid} \end{array}$$

 Conjugate acid/base pairs: $\text{HSO}_4^-/\text{SO}_4^{2-}$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$

- 18.36 The conjugate pairs are H_2S (acid)/ HS^- (base) and HCl (acid)/ Cl^- (base). The reactions involve reacting one acid from one conjugate pair with the base from the other conjugate pair. Two reactions are possible:

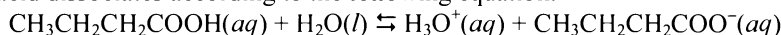


The first reaction is the reverse of the second. To decide which will have an equilibrium constant greater than 1, look for the stronger acid producing a weaker acid. HCl is a strong acid and H_2S a weak acid. The reaction that favors the products ($K_c > 1$) is the first one where the strong acid produces the weak acid. Reaction (2) with a weaker acid forming a stronger acid favors the reactants and $K_c < 1$.

- 18.38 a) $\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$
 strong acid + stronger base \rightleftharpoons weak acid + weaker base
 HCl is ranked above NH_4^+ in Figure 18.9 and is the stronger acid. NH_3 is ranked above Cl^- and is the stronger base. NH_3 is shown as a “stronger” base because it is stronger than Cl^- , but is not considered a “strong” base. The reaction proceeds towards the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $K_c > 1$. The stronger acid is more likely to donate a proton than the weaker acid.
- b) $\text{H}_2\text{SO}_3 + \text{NH}_3 \rightleftharpoons \text{HSO}_3^- + \text{NH}_4^+$
 stronger acid + stronger base \rightleftharpoons weaker base + weaker acid
 H_2SO_3 is ranked above NH_4^+ and is the stronger acid. NH_3 is a stronger base than HSO_3^- . The reaction proceeds towards the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $K_c > 1$.

- 18.40 a) The concentration of a strong acid is **very different** before and after dissociation since a strong acid exhibits 100% dissociation.. After dissociation, the concentration of the strong acid approaches 0, or $[\text{HA}] \approx 0$.
 b) A weak acid dissociates to a very small extent ($\ll 100\%$), so the acid concentration after dissociation is **nearly the same** as before dissociation.
 c) Same as (b), but the percent, or extent, of dissociation is greater than in (b).
 d) Same as (a)

- 18.43 Butanoic acid dissociates according to the following equation:



Initial: 0.15 M 0 0

Change: $-x$ $+x$ $+x$

Equilibrium: $0.15 - x$ $+x$ $+x$

According to the information given in the problem, $[\text{H}_3\text{O}^+]_{\text{eq}} = 1.51 \times 10^{-3} \text{ M} = x$

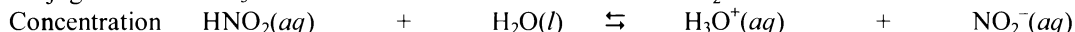
Thus, $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-] = 1.51 \times 10^{-3} \text{ M}$

$[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}] = (0.15 - x) = (0.15 - 1.51 \times 10^{-3}) \text{ M} = 0.14849 \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]}$$

$$K_a = \frac{(1.51 \times 10^{-3})(1.51 \times 10^{-3})}{(0.14849)} = 1.53552 \times 10^{-5} = \mathbf{1.5 \times 10^{-5}}$$

- 18.45 For a solution of a weak acid, the acid dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and H_3O^+ . The acid dissociation reaction for HNO_2 is:



Concentration 0.50 — 0 0

Change $-x$ $+x$ $+x$

Equilibrium $0.50 - x$ x x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 7.1 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$K_a = 7.1 \times 10^{-4} = \frac{(x)(x)}{(0.50 - x)} \quad \text{Assume } x \text{ is small compared to } 0.50: 0.50 - x = 0.50.$$

$$K_a = 7.1 \times 10^{-4} = \frac{(x)(x)}{(0.50)}$$

$$x = 0.018841 \text{ (unrounded)}$$

Check assumption: $(0.018841 / 0.50) \times 100\% = 4\%$ error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = [\text{NO}_2^-] = \mathbf{1.9 \times 10^{-2} M}$$

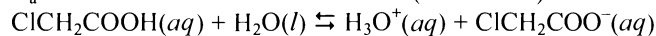
The concentration of hydroxide ion is related to concentration of hydronium ion through the equilibrium for water: $2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$ with $K_w = 1.0 \times 10^{-14}$

$$[\text{OH}^-] = 1.0 \times 10^{-14} / 0.018841 = 5.30757 \times 10^{-13} = \mathbf{5.3 \times 10^{-13} M \text{ OH}^-}$$

$$[\text{OH}^-] = 1.0 \times 10^{-14} / 0.018841 = 5.30757 \times 10^{-13} = \mathbf{5.3 \times 10^{-13} M \text{ OH}^-}$$

- 18.47 Write a balanced chemical equation and equilibrium expression for the dissociation of chloroacetic acid and convert $\text{p}K_a$ to K_a .

$$K_a = 10^{-\text{p}K} = 10^{-2.87} = 1.34896 \times 10^{-3} \text{ (unrounded)}$$



$$1.05 - x$$

$$x$$

$$x$$

$$K_a = 1.34896 \times 10^{-3} = \frac{(\text{H}_3\text{O}^+)(\text{ClCH}_2\text{COO}^-)}{(\text{ClCH}_2\text{COOH})}$$

$$K_a = 1.34896 \times 10^{-3} = \frac{(x)(x)}{(1.05 - x)} \quad \text{Assume } x \text{ is small compared to } 1.05.$$

$$K_a = 1.34896 \times 10^{-3} = \frac{(x)(x)}{(1.05)}$$

$$x = 0.037635 \text{ (unrounded)}$$

Check assumption: $(0.037635 / 1.05) \times 100\% = 4\%$. The assumption is good.

$$[\text{H}_3\text{O}^+] = [\text{ClCH}_2\text{COO}^-] = \mathbf{0.038 M}$$

$$[\text{ClCH}_2\text{COOH}] = 1.05 - 0.037635 = 1.012365 = \mathbf{1.01 M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.037635) = 1.4244 = \mathbf{1.42}$$

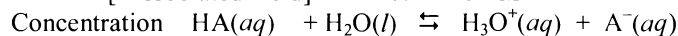
- 18.49 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.

a) The concentration of acid dissociated is equal to the equilibrium concentrations of A^- and H_3O^+ . Then pH and $[\text{OH}^-]$ are determined from $[\text{H}_3\text{O}^+]$.

$$\text{Percent HA} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \times 100\%$$

$$3.0\% = \frac{x}{0.25}(100)$$

$$[\text{Dissociated Acid}] = x = 7.5 \times 10^{-3} M$$



$$\text{Initial:} \quad 0.25 \quad 0 \quad 0$$

$$\text{Change:} \quad -x \quad +x \quad +x$$

$$\text{Equilibrium:} \quad 0.25 - x \quad x \quad x$$

$$[\text{Dissociated Acid}] = x = [\text{H}_3\text{O}^+] = \mathbf{7.5 \times 10^{-3} M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.5 \times 10^{-3}) = 2.1249 = \mathbf{2.12}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3333 \times 10^{-12} = \mathbf{1.3 \times 10^{-12} M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.3333 \times 10^{-12}) = 11.87506 = \mathbf{11.88}$$

b) In the equilibrium expression, substitute the concentrations above and calculate K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(7.5 \times 10^{-3})(7.5 \times 10^{-3})}{(0.25 - 7.5 \times 10^{-3})} = 2.319588 \times 10^{-4} = \mathbf{2.3 \times 10^{-4}}$$

18.51 a) Begin with a reaction table, then use the K_a expression as in earlier problems.

Concentration	$\text{HZ}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{Z}^-(aq)$	
Initial	0.075		—		0		0	
Change	-x				+x		+x	
Equilibrium	$0.075 - x$				x		x	

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 1.55 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{Z}^-]}{[\text{HZ}]}$$

$$K_a = 1.55 \times 10^{-4} = \frac{(x)(x)}{(0.075 - x)} \quad \text{Assume } x \text{ is small compared to } 0.075.$$

$$K_a = 1.55 \times 10^{-4} = \frac{(x)(x)}{(0.075)}$$

$$[\text{H}_3\text{O}^+] = x = 3.4095 \times 10^{-3} \text{ (unrounded)}$$

Check assumption: $(3.4095 \times 10^{-3} / 0.075) \times 100\% = 5\%$ error, so the assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.4095 \times 10^{-3}) = 2.4673 = \mathbf{2.47}$$

b) Begin this part like part a.

Concentration	$\text{HZ}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{Z}^-(aq)$	
Initial	0.045		—		0		0	
Change	-x				+x		+x	
Equilibrium	$0.045 - x$				x		x	

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 1.55 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{Z}^-]}{[\text{HZ}]}$$

$$K_a = 1.55 \times 10^{-4} = \frac{(x)(x)}{(0.045 - x)} \quad \text{Assume } x \text{ is small compared to } 0.045.$$

$$K_a = 1.55 \times 10^{-4} = \frac{(x)(x)}{(0.045)}$$

$$[\text{H}_3\text{O}^+] = x = 2.6410 \times 10^{-3} \text{ (unrounded)}$$

Check assumption: $(2.6410 \times 10^{-3} / 0.045) \times 100\% = 6\%$ error, so the assumption is not valid.

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.045, and it is necessary to use the quadratic equation.

$$x^2 = (1.55 \times 10^{-4})(0.045 - x) = 6.975 \times 10^{-6} - 1.55 \times 10^{-4}x$$

$$x^2 + 1.55 \times 10^{-4}x - 6.975 \times 10^{-6} = 0$$

$$a = 1 \quad b = 1.55 \times 10^{-4} \quad c = -6.975 \times 10^{-6}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-1.55 \times 10^{-4} \pm \sqrt{(1.55 \times 10^{-4})^2 - 4(1)(-6.975 \times 10^{-6})}}{2(1)}$$

$$x = 2.564659 \times 10^{-3} \text{ M H}_3\text{O}^+$$

$$[\text{OH}^-] = [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.564659 \times 10^{-3}} = 3.899153 \times 10^{-12} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (3.899153 \times 10^{-12}) = 11.4090 = \mathbf{11.41}$$

- 18.54 First, find the concentration of formate ion at equilibrium. Then use the initial concentration of formic acid and equilibrium concentration of formate to find % dissociation.

Concentration	$\text{HCOOH}(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	$+$	$\text{HCOO}^-(aq)$
Initial	0.50				0		0
Change	-x				+x		+x
Equilibrium	$0.50 - x$				x		x

$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$K_a = 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.50 - x)} \quad \text{Assume } x \text{ is small compared to } 0.50.$$

$$K_a = 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.50)}$$

$$x = 9.4868 \times 10^{-3} \text{ (unrounded)}$$

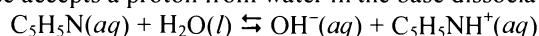
Check assumption: $(9.4868 \times 10^{-3} / 0.50) \times 100\% = 2\%$ error, so the assumption is valid.

$$\text{Percent HCOOH Dissociated} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \times 100\%$$

$$\text{Percent HCOOH Dissociated} = \frac{x}{0.50} \times 100\% = \frac{9.4868 \times 10^{-3}}{0.50} \times 100\% = 1.89736 = \mathbf{1.9\%}$$

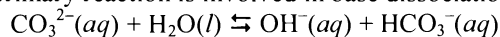
- 18.55 All Brønsted-Lowry bases contain at least one lone pair of electrons. This lone pair binds with an H^+ and allows the base to act as a proton-acceptor.

- 18.58 a) A base accepts a proton from water in the base dissociation reaction:



$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}$$

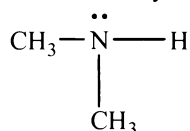
- b) The primary reaction is involved in base dissociation of carbonate ion is:



$$K_b = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

The bicarbonate can then also dissociate as a base, but this occurs to an insignificant amount in a solution of carbonate ions.

- 18.60 The formula of dimethylamine has two methyl (CH_3 -) groups attached to a nitrogen:



The nitrogen has a lone pair of electrons that will accept the proton from water in the base dissociation reaction: The value for the dissociation constant is from Appendix C.

Concentration	$(\text{CH}_3)_2\text{NH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + (\text{CH}_3)_2\text{NH}_2^+(aq)$	
Initial	0.050	0
Change	-x	+x
Equilibrium	0.050 - x	x

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = 5.9 \times 10^{-4}$$

$$K_b = \frac{[x][x]}{[0.050 - x]} = 5.9 \times 10^{-4} \quad \text{Assume } 0.050 - x = 0.050.$$

$$\frac{[x][x]}{[0.050]} = 5.9 \times 10^{-4}$$

$$x = 5.4314 \times 10^{-3} M$$

Check assumption: $(5.4314 \times 10^{-3} / 0.050) \times 100\% = 11\%$ error, so the assumption is invalid.

The problem will need to be solved as a quadratic.

$$\frac{[x][x]}{[0.050 - x]} = 5.9 \times 10^{-4}$$

$$x^2 = (5.9 \times 10^{-4})(0.050 - x) = 2.95 \times 10^{-5} - 5.9 \times 10^{-4} x$$

$$x^2 + 5.9 \times 10^{-4} x - 2.95 \times 10^{-5} = 0$$

$$a = 1 \quad b = 5.9 \times 10^{-4} \quad c = -2.95 \times 10^{-5}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-5.9 \times 10^{-4} \pm \sqrt{(5.9 \times 10^{-4})^2 - 4(1)(-2.95 \times 10^{-5})}}{2(1)}$$

$$x = 5.1443956 \times 10^{-3} M \text{ OH}^- \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.1443956 \times 10^{-3}} = 1.94386 \times 10^{-12} M \text{ H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.94386 \times 10^{-12}) = 11.71122 = \mathbf{11.71}$$

- 18.62 a) The K_a of chlorous acid, HClO_2 , is reported in Appendix C. HClO_2 is the conjugate acid of chlorite ion, ClO_2^- . The K_b for chlorite ion is related to the K_a for chlorous acid through the equation $K_w = K_a \times K_b$, and $\text{p}K_b = -\log K_b$.

$$K_b \text{ of } \text{ClO}_2^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.0909 \times 10^{-13} \text{ (unrounded)}$$

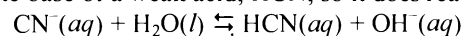
$$\text{p}K_b = -\log (9.0909 \times 10^{-13}) = 12.04139 = \mathbf{12.04}$$

- b) The K_b of dimethylamine, $(\text{CH}_3)_2\text{NH}$, is reported in Appendix C. $(\text{CH}_3)_2\text{NH}$ is the conjugate base of $(\text{CH}_3)_2\text{NH}_2^+$. The K_a for $(\text{CH}_3)_2\text{NH}_2^+$ is related to the K_b for $(\text{CH}_3)_2\text{NH}$ through the equation $K_w = K_a \times K_b$, and $\text{p}K_a = -\log K_a$.

$$K_a \text{ of } (\text{CH}_3)_2\text{NH}_2^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.694915 \times 10^{-11} \text{ (unrounded)}$$

$$\text{p}K_a = -\log (1.694915 \times 10^{-11}) = 10.77085 = \mathbf{10.77}$$

- 18.64 a) Potassium cyanide, when placed in water, dissociates into potassium ions, K^+ , and cyanide ions, CN^- . Potassium ion is the conjugate acid of a strong base, KOH , so K^+ does not react with water. Cyanide ion is the conjugate base of a weak acid, HCN , so it does react with the base dissociation reaction:



To find the pH, first set up a reaction table and use K_b for CN^- to calculate $[\text{OH}^-]$.

Concentration (M)	$\text{CN}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HCN}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.050		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.050 - x$		—		x		x

$$K_b \text{ of } \text{CN}^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.612903 \times 10^{-5} \text{ (unrounded)}$$

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = 1.612903 \times 10^{-5}$$

$$K_b = \frac{[x][x]}{[0.050 - x]} = 1.612903 \times 10^{-5} \quad \text{Assume } x \text{ is small compared to } 0.050: 0.050 - x = 0.050.$$

$$K_b = 1.612903 \times 10^{-5} = \frac{(x)(x)}{(0.050)}$$

$$x = 8.9803 \times 10^{-4} \text{ M OH}^- \text{ (unrounded)}$$

Check assumption: $(8.9803 \times 10^{-4} / 0.050) \times 100\% = 2\%$ error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{\text{OH}^-} = \frac{1.0 \times 10^{-14}}{8.9803 \times 10^{-4}} = 1.1135857 \times 10^{-11} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.1135857 \times 10^{-11}) = 10.953276 = \mathbf{10.95}$$

b) The salt triethylammonium chloride in water dissociates into two ions: $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ and Cl^- . Chloride ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Triethylammonium ion is the conjugate acid of a weak base, so the acid dissociation reaction below determines the pH of the solution.

Concentration (M)	$(\text{CH}_3\text{CH}_2)_3\text{NH}^+(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$(\text{CH}_3\text{CH}_2)_3\text{N}(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.30		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.30 - x$		—		x		x

$$K_a \text{ of } (\text{CH}_3\text{CH}_2)_3\text{NH}^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.2 \times 10^{-4}} = 1.9230769 \times 10^{-11} \text{ (unrounded)}$$

$$K_a = 1.9230769 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][(\text{CH}_3\text{CH}_2)_3\text{N}]}{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+]}$$

$$K_a = 1.9230769 \times 10^{-11} = \frac{(x)(x)}{(0.30 - x)} \quad \text{Assume } x \text{ is small compared to } 0.30: 0.30 - x = 0.30.$$

$$K_a = 1.9230769 \times 10^{-11} = \frac{(x)(x)}{(0.30)}$$

$$[\text{H}_3\text{O}^+] = x = 2.4019223 \times 10^{-6} \text{ (unrounded)}$$

Check assumption: $(2.4019223 \times 10^{-6} / 0.30) \times 100\% = 0.0008\%$ error, so the assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.4019223 \times 10^{-6}) = 5.619441 = \mathbf{5.62}$$

18.66 First, calculate the initial molarity of ClO^- . Then, set up reaction table with base dissociation of OCl^- :

$$[\text{ClO}^-] = \left(\frac{1 \text{ mL Solution}}{10^{-3} \text{ L Solution}} \right) \left(\frac{1.0 \text{ g Solution}}{1 \text{ mL Solution}} \right) \left(\frac{5.0\% \text{ NaOCl}}{100\% \text{ Solution}} \right) \left(\frac{1 \text{ mol NaOCl}}{74.44 \text{ g NaOCl}} \right) \left(\frac{1 \text{ mol OCl}^-}{1 \text{ mol NaOCl}} \right)$$

$$= 0.67168 \text{ M OCl}^- \text{ (unrounded)}$$

The sodium ion is from a strong base; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$\text{OCl}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HOCl}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.67168		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.67168 - x$		—		x		x

$$K_b \text{ of } \text{OCl}^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.448275862 \times 10^{-7}$$

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{ClO}^-]} = 3.448275862 \times 10^{-7}$$

$$K_b = \frac{[x][x]}{[0.67168 - x]} = 3.448275862 \times 10^{-7} \quad \text{Assume } x \text{ is small compared to } 0.67168.$$

$$K_b = 3.448275862 \times 10^{-7} = \frac{(x)(x)}{(0.67168)}$$

$$x = 4.812627 \times 10^{-4} = \mathbf{4.8 \times 10^{-4} \text{ M OH}^-}$$

Check assumption: $(4.812627 \times 10^{-4} / 0.67168) \times 100\% = 0.074\%$ error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{4.812627 \times 10^{-4}} = 2.077867 \times 10^{-11} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.077867 \times 10^{-11}) = 10.68238 = \mathbf{10.68}$$

- 18.68 Electronegativity increases left to right across a period. As the nonmetal becomes more electronegative, the acidity of the binary hydride increases. The electronegative nonmetal attracts the electrons more strongly in the polar bond, shifting the electron density away from H^+ and making the H^+ more easily transferred to a surrounding water molecule to make H_3O^+ .
- 18.71 The two factors that explain the greater acid strength of HClO_4 are:
 1) Chlorine is more electronegative than iodine, so chlorine more strongly attracts the electrons in the bond with oxygen. This makes the H in HClO_4 less tightly held by the oxygen than the H in HIO .
 2) Perchloric acid has more oxygen atoms than HIO , which leads to a greater shift in electron density from the hydrogen atom to the oxygens making the H in HClO_4 more susceptible to transfer to a base.
- 18.72 a) H_2Se , hydrogen selenide, is a stronger acid than H_3As , arsenic hydride, because Se is more electronegative than As.
 b) B(OH)_3 , boric acid also written as H_3BO_3 , is a stronger acid than Al(OH)_3 , aluminum hydroxide, because boron is more electronegative than aluminum.
 c) HBrO_2 , bromous acid, is a stronger acid than HBrO , hypobromous acid, because there are more oxygen atoms in HBrO_2 than in HBrO .
- 18.74 Acidity increases as the value of K_a increases. Determine the ion formed from each salt and compare the corresponding K_a values from Appendix C.
 a) Copper(II) sulfate, CuSO_4 , contains Cu^{2+} ion with $K_a = 3 \times 10^{-8}$. Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, contains Al^{3+} ion with $K_a = 1 \times 10^{-5}$. The concentrations of Cu^{2+} and Al^{3+} are equal, but the K_a of $\text{Al}_2(\text{SO}_4)_3$ is almost three orders of magnitude greater. Therefore, $\mathbf{0.05 \text{ M Al}_2(\text{SO}_4)_3}$ is the stronger acid.
 b) Zinc chloride, ZnCl_2 , contains the Zn^{2+} ion with $K_a = 1 \times 10^{-9}$. Lead chloride, PbCl_2 , contains the Pb^{2+} ion with $K_a = 3 \times 10^{-8}$. Since both solutions have the same concentration, and $K_a(\text{Pb}^{2+}) > K_a(\text{Zn}^{2+})$, $\mathbf{0.1 \text{ M PbCl}_2}$ is the stronger acid.
- 18.77 Sodium fluoride, NaF , contains the cation of a strong base, NaOH , and anion of a weak acid, HF . This combination yields a salt that is basic in aqueous solution as the F^- ion acts as a base:

$$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$$

 Sodium chloride, NaCl , is the salt of a strong base, NaOH , and strong acid, HCl . This combination yields a salt that is neutral in aqueous solution as neither Na^+ or Cl^- react in water to change the $[\text{H}^+]$.

- 18.79 For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.
- a) $\text{KBr}(s) + \text{H}_2\text{O}(l) \rightarrow \text{K}^+(aq) + \text{Br}^-(aq)$
 K^+ is the conjugate acid of a strong base, so it does not influence pH.
 Br^- is the conjugate base of a strong acid, so it does not influence pH.
 Since neither ion influences the pH of the solution, it will remain at the pH of pure water with a **neutral** pH.
- b) $\text{NH}_4\text{I}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4^+(aq) + \text{I}^-(aq)$
 NH_4^+ is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce H_3O^+ as represented by the acid dissociation reaction:

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$$
 I^- is the conjugate base of a strong acid, so it will not influence the pH.
 The production of H_3O^+ from the ammonium ion makes the solution of NH_4I **acidic**.
- c) $\text{KCN}(s) + \text{H}_2\text{O}(l) \rightarrow \text{K}^+(aq) + \text{CN}^-(aq)$
 K^+ is the conjugate acid of a strong base, so it does not influence pH.
 CN^- is the conjugate base of a weak acid, so it will act as a weak base in solution and impact pH by the base dissociation reaction:

$$\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$$
 Hydroxide ions are produced in this equilibrium so solution will be **basic**.
- 18.81 a) Order of increasing pH: **$\text{KNO}_3 < \text{K}_2\text{SO}_3 < \text{K}_2\text{S}$** (assuming concentrations equivalent)
 Potassium nitrate, KNO_3 , is a neutral solution because potassium ion is the conjugate acid of a strong base and nitrate ion is the conjugate base of a strong acid, so neither influences solution pH.
 Potassium sulfite, K_2SO_3 , and potassium sulfide, K_2S , are similar in that the potassium ion does not influence solution pH but the anions do because they are conjugate bases of weak acids. K_a for HSO_3^- is 6.5×10^{-8} from Table 18.5, so K_b for SO_3^{2-} is 1.5×10^{-7} , which indicates that sulfite ion is a weak base. K_a for HS^- is 1×10^{-17} from Table 18.5, so sulfide ion has a K_b equal to 1×10^3 . Sulfide ion is thus, a strong base. The solution of a strong base will have a greater concentration of hydroxide ions (and higher pH) than a solution of a weak base of equivalent concentrations.
- b) In order of increasing pH: **$\text{NaHSO}_4 < \text{NH}_4\text{NO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3$**
 In solutions of ammonium nitrate, only the ammonium will influence pH by dissociating as a weak acid:

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$$
 with $K_a = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$
 Therefore, the solution of ammonium nitrate is acidic.
 In solutions of sodium hydrogen sulfate, only HSO_4^- will influence pH. The hydrogen sulfate ion is amphoteric so both the acid and base dissociations must be evaluated for influence on pH. As a base, HSO_4^- is the conjugate base of a strong acid, so it will not influence pH. As an acid, HSO_4^- is the conjugate acid of a weak base, so the acid dissociation applies

$$\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a2} = 1.2 \times 10^{-2}$$
 In solutions of sodium hydrogen carbonate, only the HCO_3^- will influence pH and it, like HSO_4^- , is amphoteric:
 As an acid: $\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq)$
 $K_a = 4.7 \times 10^{-11}$, the second K_a for carbonic acid from Table 18.5
 As a base: $\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$
 $K_b = 1.0 \times 10^{-14} / 4.5 \times 10^{-7} = 2.2 \times 10^{-8}$
 Since $K_b > K_a$, a solution of sodium hydrogen carbonate is basic.
 In a solution of sodium carbonate, only CO_3^{2-} will influence pH by acting as a weak base:

$$\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$$
 $K_b = 1.0 \times 10^{-14} / 4.7 \times 10^{-11} = 2.1 \times 10^{-4}$
 Therefore, the solution of sodium carbonate is basic.

Two of the solutions are acidic. Since the K_a of HSO_4^- is greater than that of NH_4^+ , the solution of sodium hydrogen sulfate has a lower pH than the solution of ammonium nitrate, assuming the concentrations are relatively close.

Two of the solutions are basic. Since the K_b of CO_3^{2-} is greater than that of HCO_3^- , the solution of sodium carbonate has a higher pH than the solution of sodium hydrogen carbonate, assuming concentrations are not extremely different.

- 18.84 A Lewis acid is defined as an electron pair acceptor, while a Brønsted-Lowry acid is a proton donor. If only the proton in a Brønsted-Lowry acid is considered, then every Brønsted-Lowry acid fits the definition of a Lewis acid since the proton is accepting an electron pair when it bonds with a base. There are Lewis acids that do not include a proton, so all Lewis acids are not Brønsted-Lowry acids.
A Lewis base is defined as an electron pair donor and a Brønsted-Lowry base is a proton acceptor. In this case, the two definitions are essentially the same except that for a Brønsted-Lowry base the acceptor is a proton.
- 18.85 a) **No**, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, water molecules solvate metal ions very well:

$$\text{Zn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Zn}(\text{H}_2\text{O})_6^{2+}(\text{aq})$$
Water is a very weak Brønsted-Lowry base, but forms the Zn complex fairly well and is a reasonably strong Lewis base.
b) The **cyanide ion** has a lone pair to donate from either the C or the N, and donates an electron pair to the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex. It is the Lewis base for the forward direction of this reaction. In the reverse direction, **water** donates one of the electron pairs on the oxygen to the $\text{Cu}(\text{CN})_4^{2-}$ and is the Lewis base.
c) Because $K_c > 1$, the reaction proceeds in the direction written (left to right) and is driven by the stronger Lewis base, the **cyanide ion**.
- 18.88 a) Cu^{2+} is a **Lewis acid** because it accepts electron pairs from molecules such as water.
b) Cl^- is a **Lewis base** because it has lone pairs of electrons it can donate to a Lewis acid.
c) Tin(II) chloride, SnCl_2 , is a compound with a structure similar to carbon dioxide so it will act as a **Lewis acid** to form an additional bond to the tin.
d) Oxygen difluoride, OF_2 , is a **Lewis base** with a structure similar to water, where the oxygen has lone pairs of electrons that it can donate to a Lewis acid.
- 18.90 a) Sodium ion is the Lewis acid because it is accepting electron pairs from water, the Lewis base.

$$\begin{array}{ccccccc} \text{Na}^+ & + & 6 \text{H}_2\text{O} & \rightleftharpoons & \text{Na}(\text{H}_2\text{O})_6^+ \\ \text{Lewis acid} & & \text{Lewis base} & & \text{adduct} \end{array}$$
b) The oxygen from water donates a lone pair to the carbon in carbon dioxide. Water is the Lewis base and carbon dioxide the Lewis acid.

$$\begin{array}{ccccccc} \text{CO}_2 & + & \text{H}_2\text{O} & \rightleftharpoons & \text{H}_2\text{CO}_3 \\ \text{Lewis acid} & & \text{Lewis base} & & \text{adduct} \end{array}$$
c) Fluoride ion donates an electron pair to form a bond with boron in BF_4^- . The fluoride ion is the Lewis base and the boron trifluoride is the Lewis acid.

$$\begin{array}{ccccccc} \text{F}^- & + & \text{BF}_3 & \rightleftharpoons & \text{BF}_4^- \\ \text{Lewis base} & & \text{Lewis acid} & & \text{adduct} \end{array}$$
- 18.92 a) Since neither H^+ nor OH^- is involved, this is not an Arrhenius acid-base reaction. Since there is no exchange of protons, this is not a Brønsted-Lowry reaction. This reaction is only classified as **Lewis acid-base reaction**, where Ag^+ is the acid and NH_3 is the base.
b) Again, no OH^- is involved, so this is not an Arrhenius acid-base reaction. This is an exchange of a proton, from H_2SO_4 to NH_3 , so it is a **Brønsted-Lowry acid-base reaction**. Since the Lewis definition is most inclusive, anything that is classified as a Brønsted-Lowry (or Arrhenius) reaction is automatically classified as a **Lewis acid-base reaction**.
c) This is not an acid-base reaction.
d) For the same reasons listed in (a), this reaction is only classified as **Lewis acid-base reaction**, where AlCl_3 is the acid and Cl^- is the base.

- 18.94 Calculate the $[\text{H}_3\text{O}^+]$ using the pH values given. Determine the value of K_w from the $\text{p}K_w$ given. The $[\text{H}_3\text{O}^+]$ is combined with the K_w value at 37°C to find $[\text{OH}^-]$ using $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$.

$$K_w = 10^{-\text{p}K_w} = 10^{-13.63} = 2.3442 \times 10^{-14} \text{ (unrounded)}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.3442 \times 10^{-14} \text{ at } 37^\circ\text{C}$$

$[\text{H}_3\text{O}^+]$ range

$$\text{High value (low pH)} = 10^{-\text{pH}} = 10^{-7.35} = 4.4668 \times 10^{-8} = 4.5 \times 10^{-8} \text{ M } \text{H}_3\text{O}^+$$

$$\text{Low value (high pH)} = 10^{-\text{pH}} = 10^{-7.45} = 3.5481 \times 10^{-8} = 3.5 \times 10^{-8} \text{ M } \text{H}_3\text{O}^+$$

$$\text{Range: } 3.5 \times 10^{-8} \text{ to } 4.5 \times 10^{-8} \text{ M } \text{H}_3\text{O}^+$$

$[\text{OH}^-]$ range

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.3442 \times 10^{-14} \text{ at } 37^\circ\text{C}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

$$\text{High value (high pH)} = \frac{2.3442 \times 10^{-14}}{3.5481 \times 10^{-8}} = 6.6069 \times 10^{-7} = 6.6 \times 10^{-7} \text{ M } \text{OH}^-$$

$$\text{Low value (low pH)} = \frac{2.3442 \times 10^{-14}}{4.4668 \times 10^{-8}} = 5.24805 \times 10^{-7} = 5.2 \times 10^{-7} \text{ M } \text{OH}^-$$

$$\text{Range: } 5.2 \times 10^{-7} \text{ to } 6.6 \times 10^{-7} \text{ M } \text{OH}^-$$

- 18.97 a) SnCl_4 is the Lewis acid accepting an electron pair from $(\text{CH}_3)_3\text{N}$, the Lewis base.
b) Tin is the element in the Lewis acid accepting the electron pair. The electron configuration of tin is $[\text{Kr}]5s^2 4d^{10} 5p^2$. The four bonds to tin are formed by sp^3 hybrid orbitals, which completely fill the $5s$ and $5p$ orbitals. The $5d$ orbitals are empty and available for the bond with trimethylamine.

- 18.98 Hydrochloric acid is a strong acid that almost completely dissociates in water. Therefore, the concentration of H_3O^+ is the same as the starting acid concentration: $[\text{H}_3\text{O}^+] = [\text{HCl}]$. The original solution pH:

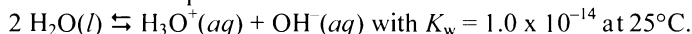
$$\text{pH} = -\log(1.0 \times 10^{-5}) = \mathbf{5.00 = \text{pH.}}$$

A 1:10 dilution means that the chemist takes 1 mL of the $1.0 \times 10^{-5} \text{ M}$ solution and dilutes it to 10 mL (or dilute 10 mL to 100 mL). The chemist then dilutes the diluted solution in a 1:10 ratio, and repeats this process for the next two successive dilutions. $M_1V_1 = M_2V_2$ can be used to find the molarity after each dilution:

Dilution 1: $M_1V_1 = M_2V_2$
 $(1.0 \times 10^{-5} \text{ M})(1.0 \text{ mL}) = (x)(10. \text{ mL})$
 $[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-6} \text{ M } \text{H}_3\text{O}^+$
 $\text{pH} = -\log(1.0 \times 10^{-6}) = \mathbf{6.00.}$

Dilution 2:
 $(1.0 \times 10^{-6} \text{ M})(1.0 \text{ mL}) = (x)(10. \text{ mL})$
 $[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-7} \text{ M } \text{H}_3\text{O}^+$

Once the concentration of strong acid is close to the concentration of H_3O^+ from water autoionization, the $[\text{H}_3\text{O}^+]$ in the solution does not equal the initial concentration of the strong acid. The calculation of $[\text{H}_3\text{O}^+]$ must be based on the water ionization equilibrium:



The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-7} \text{ M}$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2 \text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	—		1×10^{-7}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-7} + x$		x

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

Set up as a quadratic equation: $x^2 + 1.0 \times 10^{-7}x - 1.0 \times 10^{-14} = 0$

$$a = 1 \quad b = 1.0 \times 10^{-7} \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-7} \pm \sqrt{(1.0 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 6.1803 \times 10^{-8} \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-7} + x) M = (1.0 \times 10^{-7} + 6.1803 \times 10^{-8}) M = 1.61803 \times 10^{-7} M \text{H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.61803 \times 10^{-7}) = 6.79101 = \mathbf{6.79}$$

Dilution 3:

$$(1.0 \times 10^{-7} M) (1.0 \text{ mL}) = (x)(10. \text{ mL})$$

$$[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-8} M \text{H}_3\text{O}^+$$

The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-8} M$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2 \text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	—		1×10^{-8}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-8} + x$		x

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = (1 \times 10^{-8} + x) (x) = 1.0 \times 10^{-14}$$

$$\text{Set up as a quadratic equation: } x^2 + 1.0 \times 10^{-8} x - 1.0 \times 10^{-14} = 0$$

$$a = 1 \quad b = 1.0 \times 10^{-8} \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{(1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.51249 \times 10^{-8} \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-8} + x) M = (1.0 \times 10^{-8} + 9.51249 \times 10^{-8}) M = 1.051249 \times 10^{-7} M \text{H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.051249 \times 10^{-7}) = 6.97829 = \mathbf{6.98}$$

Dilution 4:

$$(1.0 \times 10^{-8} M) (1.0 \text{ mL}) = (x)(10. \text{ mL})$$

$$[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-9} M \text{H}_3\text{O}^+$$

The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-9} M$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2 \text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	—		1×10^{-9}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-9} + x$		x

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = (1 \times 10^{-9} + x) (x) = 1.0 \times 10^{-14}$$

$$\text{Set up as a quadratic equation: } x^2 + 1.0 \times 10^{-9} x - 1.0 \times 10^{-14} = 0$$

$$a = 1 \quad b = 1.0 \times 10^{-9} \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-9} \pm \sqrt{(1.0 \times 10^{-9})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.95012 \times 10^{-8} \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-9} + x) M = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8}) M = 1.00512 \times 10^{-7} M \text{H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.00512 \times 10^{-7}) = 6.99778 = \mathbf{7.00}$$

As the HCl solution is diluted, the pH of the solution becomes closer to 7.0. Continued dilutions will not significantly change the pH from 7.0. Thus, a solution with a basic pH cannot be made by adding acid to water.

18.99 Compare the contribution of each acid by calculating the concentration of H_3O^+ produced by each.

For 3% hydrogen peroxide, first find initial molarity of H_2O_2 , assuming the density is 1.00 g/mL (the density of water).

$$M \text{H}_2\text{O}_2 = \left(\frac{1.00 \text{ g}}{\text{mL}} \right) \left(\frac{3\% \text{H}_2\text{O}_2}{100\%} \right) \left(\frac{1 \text{ mol H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.881834 M \text{H}_2\text{O}_2 \text{ (unrounded)}$$

$$\text{Find } K_a \text{ from } \text{p}K_a: K_a = 10^{-\text{p}K_a} = 10^{-11.75} = 1.778279 \times 10^{-12} \text{ (unrounded)}$$

	H_2O_2	+	H_2O	\rightleftharpoons	H_2O_2^+	+	OH^-
\rightleftharpoons initial	0.881834		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.881834 - x$		—		x		x

$$K_a = 1.778279 \times 10^{-12} = \frac{[\text{H}_3\text{O}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]}$$

$$K_a = 1.778279 \times 10^{-12} = \frac{(x)(x)}{(0.881834 - x)} \quad \text{Assume } x \text{ is small compared to } 0.881834.$$

$$K_a = 1.778279 \times 10^{-12} = \frac{(x)(x)}{(0.881834)}$$

$$[\text{H}_3\text{O}^+] = x = 1.2522567 \times 10^{-6} \text{ (unrounded)}$$

Check assumption: $(1.2522567 \times 10^{-6} / 0.881834) \times 100\% = 0.0001\%$ error, so the assumption is valid.

$$M \text{H}_3\text{PO}_4 = \left(\frac{1.00 \text{ g}}{\text{mL}} \right) \left(\frac{0.001\% \text{H}_3\text{PO}_4}{100\%} \right) \left(\frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g H}_3\text{PO}_4} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 1.0205 \times 10^{-4} M \text{H}_3\text{PO}_4 \text{ (unrounded)}$$

From Appendix C, K_a for phosphoric acid is 7.2×10^{-3} . The subsequent K_a values may be ignored. In this calculation x is not negligible since the initial concentration of acid is less than the K_a .

	H_3PO_4	+	H_2O	\rightleftharpoons	H_2PO_4^-	+	H_3O^+
\Rightarrow initial	1.0205×10^{-4}		—		0		0
Change	— x		—		$+x$		$+x$
Equilibrium	$1.0205 \times 10^{-4} - x$		—		x		x

$$K_a = 7.2 \times 10^{-3} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$K_a = 7.2 \times 10^{-3} = \frac{[x][x]}{[1.0205 \times 10^{-4} - x]}$$

The problem will need to be solved as a quadratic.

$$x^2 = (7.2 \times 10^{-3})(1.0205 \times 10^{-4} - x) = 7.3476 \times 10^{-7} - 7.2 \times 10^{-3} x$$

$$x^2 + 7.2 \times 10^{-3} x - 7.3476 \times 10^{-7} = 0$$

$$a = 1 \quad b = 7.2 \times 10^{-3} \quad c = -7.3476 \times 10^{-7}$$

$$x = \frac{-7.2 \times 10^{-3} \pm \sqrt{(7.2 \times 10^{-3})^2 - 4(1)(-7.3476 \times 10^{-7})}}{2(1)}$$

$$x = 1.00643 \times 10^{-4} M \text{H}_3\text{O}^+ \text{ (unrounded)}$$

The concentration of hydronium ion produced by the phosphoric acid, $1 \times 10^{-4} M$, is greater than the concentration produced by the hydrogen peroxide, $1 \times 10^{-6} M$. Therefore, the **phosphoric acid** contributes more H_3O^+ to the solution.

18.104 The freezing point depression equation is required to determine the molality of the solution.

$$\Delta T = [0.00 - (-1.93^\circ\text{C})] = 1.93^\circ\text{C} = iK_f m$$

Temporarily assume $i = 1$.

$$m = \frac{\Delta T}{iK_f} = \frac{1.93^\circ\text{C}}{(1)(1.86^\circ\text{C/m})} = 1.037634 \text{ m} = 1.037634 M \text{ (unrounded)}$$

This molality is the total molality of all species in the solution, and is equal to their molarity.

From the equilibrium:

	$\text{ClCH}_2\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{ClCH}_2\text{COO}^-(aq)$
Initial	1.000 M		—		x		x
Change	— x		—		$+x$		$+x$
Equilibrium	$1.000 - x$		—		x		x

The total concentration of all species is:

$$[\text{ClCH}_2\text{COOH}] + [\text{H}_3\text{O}^+] + [\text{ClCH}_2\text{COO}^-] = 1.037634 M$$

$$[1.000 - x] + [x] + [x] = 1.000 + x = 1.037634 M$$

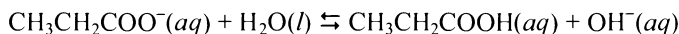
$$x = 0.037634 M \text{ (unrounded)}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

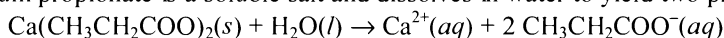
$$K_a = \frac{(0.037634)(0.037634)}{(1.000 - 0.037634)} = 0.0014717 = \mathbf{0.00147}$$

- 18.105 a) The two ions that comprise this salt are Ca^{2+} (derived from the strong base $\text{Ca}(\text{OH})_2$) and $\text{CH}_3\text{CH}_2\text{COO}^-$ (derived from the weak acid, propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$). A salt derived from a strong base and weak acid produces a **basic** solution.

Ca^{2+} does not react with water.



- b) Calcium propionate is a soluble salt and dissolves in water to yield two propionate ions:



The molarity of the solution is

$$\text{Molarity} = \left(\frac{7.05 \text{ g Ca}(\text{CH}_3\text{CH}_2\text{COO})_2}{0.500 \text{ L}} \right) \left(\frac{1 \text{ mol Ca}(\text{CH}_3\text{CH}_2\text{COO})_2}{186.22 \text{ g Ca}(\text{CH}_3\text{CH}_2\text{COO})_2} \right) \left(\frac{2 \text{ mol CH}_3\text{CH}_2\text{COO}^-}{1 \text{ mol Ca}(\text{CH}_3\text{CH}_2\text{COO})_2} \right)$$

$$= 0.151433788 \text{ M CH}_3\text{CH}_2\text{COO}^- \text{ (unrounded)}$$

	$\text{CH}_3\text{CH}_2\text{COO}^-$	+	H_2O	\rightleftharpoons		$\text{CH}_3\text{CH}_2\text{COOH}$	+	OH^-
Initial	0.151433788 M				0	0		
Change	-x				+x	+x		
Equilibrium	0.151433788 - x				x	x		

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.3 \times 10^{-5}) = 7.6923 \times 10^{-10} \text{ (unrounded)}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{[\text{CH}_3\text{CH}_2\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{COO}^-]}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.151433788 - x)} \quad \text{Assume } x \text{ is small compared to } 0.151433788.$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.151433788)}$$

$$x = 1.079293 \times 10^{-5} = [\text{OH}^-] \text{ (unrounded)}$$

Check assumption: $[1.079293 \times 10^{-5} / 0.151433788] \times 100\% = 0.007\%$, therefore, the assumption is good.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.079293 \times 10^{-5}} = 9.26532 \times 10^{-10} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.26532 \times 10^{-10}) = 9.0331 = \mathbf{9.03}$$

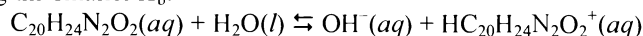
- 18.111 a) The concentration of oxygen is higher in the lungs so the equilibrium shifts to the right.
 b) In an oxygen deficient environment, the equilibrium would shift to the left to release oxygen.
 c) A decrease in the $[\text{H}_3\text{O}^+]$ concentration would shift the equilibrium to the right. More oxygen is absorbed, but it will be more difficult to remove the O_2 .
 d) An increase in the $[\text{H}_3\text{O}^+]$ concentration would shift the equilibrium to the left. Less oxygen is absorbed, but it will be easier to remove the O_2 .

- 18.113 Note that both $\text{p}K_b$ values only have one significant figure. This will limit the final answers.

$$K_b \text{ (tertiary amine N)} = 10^{-\text{p}K_b} = 10^{-5.1} = 7.94328 \times 10^{-6} \text{ (unrounded)}$$

$$K_b \text{ (aromatic ring N)} = 10^{-\text{p}K_b} = 10^{-9.7} = 1.995262 \times 10^{-10} \text{ (unrounded)}$$

- a) Ignoring the smaller K_b :



Initial	$1.6 \times 10^{-3} \text{ M}$	0	0
Change	-x	+x	+x
Equilibrium	$1.6 \times 10^{-3} - x$	x	x

$$K_b = \frac{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+][\text{OH}^-]}{[\text{H}_2\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]} = 7.94328 \times 10^{-6}$$

$$K_b = \frac{[x][x]}{[1.6 \times 10^{-3} - x]} = 7.94328 \times 10^{-6}$$

The problem will need to be solved as a quadratic.

$$x^2 = (7.94328 \times 10^{-6})(1.6 \times 10^{-3} - x) = 1.27092 \times 10^{-8} - 7.94328 \times 10^{-6}x$$

$$x^2 + 7.94328 \times 10^{-6}x - 1.27092 \times 10^{-8} = 0$$

$$a = 1 \quad b = 7.94328 \times 10^{-6} \quad c = -1.27092 \times 10^{-8}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

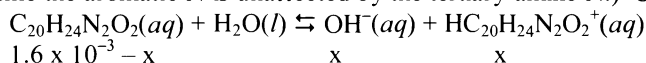
$$x = \frac{-7.94328 \times 10^{-6} \pm \sqrt{(7.94328 \times 10^{-6})^2 - 4(1)(-1.27092 \times 10^{-8})}}{2(1)}$$

$$x = 1.08833 \times 10^{-4} M \text{OH}^- \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.08833 \times 10^{-4}} = 9.18838955 \times 10^{-11} M \text{H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.18838955 \times 10^{-11}) = 10.03676 = \mathbf{10.0}$$

b) (Assume the aromatic N is unaffected by the tertiary amine N.) Use the K_b value for the aromatic nitrogen.



$$1.6 \times 10^{-3} - x \quad x \quad x$$

$$K_b = \frac{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+][\text{OH}^-]}{[\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]} = 1.995262 \times 10^{-10}$$

$$K_b = \frac{[x][x]}{[1.6 \times 10^{-3} - x]} = 1.995262 \times 10^{-10} \quad \text{Assume } x \text{ is small compared to } 1.6 \times 10^{-3}.$$

$$K_b = \frac{[x][x]}{[1.6 \times 10^{-3}]} = 1.995262 \times 10^{-10}$$

$$x = 5.6501 \times 10^{-7} M \text{OH}^- \text{ (unrounded)}$$

The hydroxide ion from the smaller K_b is much smaller than the hydroxide ion from the larger K_b (compare the powers of ten in the concentration).

c) $\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7.94328 \times 10^{-6}} = 1.2589 \times 10^{-9} \text{ (unrounded)}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+]}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.53 - x)} \quad \text{Assume } x \text{ is small compared to } 0.53.$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.53)}$$

$$[\text{H}_3\text{O}^+] = x = 2.58305 \times 10^{-5} \text{ (unrounded)}$$

Check assumption: $(2.58305 \times 10^{-5} / 0.53) \times 100\% = 0.005\%$. The assumption is good.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.58305 \times 10^{-5}) = 4.58779 = \mathbf{4.6}$$

d) Quinine hydrochloride will be indicated as QHCl.

$$M = \left(\frac{1.5\%}{100\%} \right) \left(\frac{1.0 \text{ g}}{\text{mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol QHCl}}{360.87 \text{ QHCl}} \right) = 0.041566 \text{ M (unrounded)}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+]}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.041566 - x)} \quad \text{Assume } x \text{ is small compared to } 0.041566.$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.041566)}$$

$$[\text{H}_3\text{O}^+] = x = 7.23377 \times 10^{-6} \text{ (unrounded)}$$

Check assumption: $(7.23377 \times 10^{-6} / 0.041566) \times 100\% = 0.02\%$. The assumption is good.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.23377 \times 10^{-6}) = 5.1406 = \mathbf{5.1}$$

Chapter 19 Ionic Equilibria in Aqueous Systems

FOLLOW-UP PROBLEMS

- 19.1 Plan: The problems are both equilibria with the initial concentration of reactant and product given. For part (a), set up a reaction table for the dissociation of HF. Set up an equilibrium expression and solve for $[H_3O^+]$, assuming that the change in $[HF]$ and $[F^-]$ is negligible. Check this assumption after finding $[H_3O^+]$. Convert $[H_3O^+]$ to pH. For part (b), first find the concentration of OH^- added. Then, use the neutralization reaction to find the change in initial $[HF]$ and $[F^-]$. Repeat the solution in part (a) to find pH.

a) Solution:

Concentration (M)	HF(aq)	+	H ₂ O(l)	\rightleftharpoons	F ⁻ (aq)	+	H ₃ O ⁺ (aq)
Initial	0.50		—		0.45		0
Change	-x		—		+x		+x
Equilibrium	0.50 - x		—		0.45 + x		x

Assumptions: 1) initial $[H_3O^+]$, from water, at $1.0 \times 10^{-7} M$, can be assumed to be zero and 2) x is negligible with respect to 0.50 M and 0.45 M.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$[H_3O^+] = K_a \frac{[HF]}{[F^-]} = (6.8 \times 10^{-4}) \frac{[0.50]}{[0.45]} = 7.5556 \times 10^{-4} = 7.6 \times 10^{-4}$$

Check assumptions:

1) $1.0 \times 10^{-7} \ll 7.6 \times 10^{-4}$ Thus, the assumption to set the initial concentration of H_3O^+ to zero is valid.

2) Percent error in assuming x is negligible: $(7.5556 \times 10^{-4} / 0.45) \times 100 = 0.17\%$. The error is less than 5%, so the assumption is valid.

Solve for pH:

$$pH = -\log(7.5556 \times 10^{-4}) = 3.12173 = \mathbf{3.12}$$

The other method to calculate the pH of a buffer is to use the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$pH = pK_a + \log \frac{[F^-]}{[HF]} \quad pK_a = -\log K_a = -\log(6.8 \times 10^{-4}) = 3.16749$$

$$pH = 3.16749 + \log \frac{[0.45]}{[0.50]}$$

$$pH = 3.12173 = \mathbf{3.12}$$

Check: Since $[HF]$ and $[F^-]$ are similar, the pH should be close to pK_a , which equals $\log(6.8 \times 10^{-4}) = 3.17$. The pH should be slightly less (more acidic) than pK_a because $[HF] > [F^-]$. The calculated pH of 3.12 is slightly less than pK_a of 3.17.

b) Solution: What is the initial molarity of the OH^- ion?

$$\left(\frac{0.40 \text{ g NaOH}}{L} \right) \left(\frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \right) \left(\frac{1 \text{ mol } OH^-}{1 \text{ mol NaOH}} \right) = 0.010 M OH^-$$

Set up reaction table for neutralization of $0.010 M OH^-$ (note the quantity of water is irrelevant).

Concentration (M)	HF(aq)	+	OH ⁻ (aq)	\rightarrow	F ⁻ (aq)	+	H ₂ O(l)
Before addition	0.50		—		0.45		—
Addition	—		0.010		—		—
Change	-0.010		-0.010		+0.010		—
After addition	0.49		0		0.46		—

Following the same solution path with the same assumptions as part (a):

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HF}]}{[\text{F}^-]} = (6.8 \times 10^{-4}) \frac{[0.49]}{[0.46]} = 7.2434782 \times 10^{-4} = 7.2 \times 10^{-4} M$$

Check assumptions:

1) $7.2 \times 10^{-4} \gg 1.0 \times 10^{-7}$, the assumption is valid.

2) $(7.2 \times 10^{-4}/0.46)100 = 0.16\%$, which is less than the 5% maximum \rightarrow assumption acceptable.

Solve for pH:

$$\text{pH} = -\log(7.2434782 \times 10^{-4}) = 3.14005 = \mathbf{3.14}$$

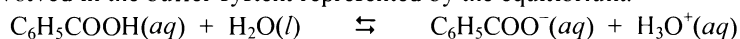
or using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.16749 + \log \frac{[0.46]}{[0.49]}$$

$$\text{pH} = 3.14005 = \mathbf{3.14}$$

Check: With addition of base, the pH should increase and it does, from 3.12 to 3.14. However, the pH should still be slightly less than $\text{p}K_a$: 3.14 is still less than 3.17.

- 19.2 Plan: Sodium benzoate is a salt so it dissolves in water to form Na^+ ions and $\text{C}_6\text{H}_5\text{COO}^-$ ions. Only the benzoate ion is involved in the buffer system represented by the equilibrium:



Given in the problem are the volume and pH of the buffer and the concentration of the base, benzoate ion. The question asks for the mass of benzoic acid to add to the sodium benzoate solution. First, find the concentration of $\text{C}_6\text{H}_5\text{COOH}$ needed to make a buffer with a pH of 4.25. Multiply the volume by the concentration to find moles of $\text{C}_6\text{H}_5\text{COOH}$ and use the molar mass to find grams of benzoic acid.

Solution: From the given pH, calculate $[\text{H}_3\text{O}^+]$:

$$[\text{H}_3\text{O}^+] = 10^{-4.25} = 5.62341 \times 10^{-5} M \text{ (unrounded)}$$

The concentration of benzoic acid is calculated from the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\text{p}K_a = -\log K_a = -\log 6.3 \times 10^{-5} = 4.20066$$

$$4.25 = 4.20066 + \log \frac{[0.050]}{[x]}$$

$$0.04934 = \log \frac{[0.050]}{[x]} \quad \text{Raise each side to } 10^x.$$

$$1.1203146 = \frac{[0.050]}{[x]}$$

$$x = 4.46303 \times 10^{-2} M$$

The number of moles of benzoic acid is determined from the concentration and volume:

$$(4.46303 \times 10^{-2} M \text{ C}_6\text{H}_5\text{COOH}) \times (5.0 \text{ L}) = 0.22315 \text{ mol C}_6\text{H}_5\text{COOH} \text{ (unrounded)}$$

Mass of $\text{C}_6\text{H}_5\text{COOH}$:

$$(0.22315 \text{ mol C}_6\text{H}_5\text{COOH}) \left(\frac{1 \text{ mol C}_6\text{H}_5\text{COOH}}{122.12 \text{ g C}_6\text{H}_5\text{COOH}} \right) = 27.2511 = \mathbf{27 \text{ g C}_6\text{H}_5\text{COOH}}$$

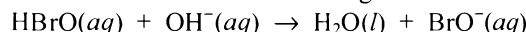
Prepare a benzoic acid/benzoate buffer by dissolving 27 g of $\text{C}_6\text{H}_5\text{COOH}$ into 5.0 L of 0.050 M $\text{C}_6\text{H}_5\text{COONa}$.

Using a pH meter, adjust the pH to 4.25 with strong acid or base.

Check: $\text{p}K_a$ for benzoic acid is 4.20. The buffer pH is slightly greater than the $\text{p}K_a$, so the concentration of the acid should be slightly less than the concentration of the base. The calculation confirms this with $[\text{C}_6\text{H}_5\text{COOH}]$ at 0.045 M, which is slightly less than $[\text{C}_6\text{H}_5\text{COO}^-]$ at 0.050 M.

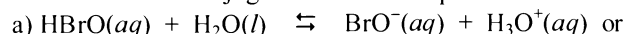
19.3 Plan: The titration is of a weak acid, HBrO, with a strong base, NaOH. The reactions involved are:

1) Neutralization of weak acid with strong base:



Note that the reaction goes to completion and produces the conjugate base, BrO^- .

2) The weak acid and its conjugate base are in equilibrium based on the acid dissociation reaction:



b) the base dissociation reaction:



The pH of the solution is controlled by the relative concentrations of HBrO and BrO^- .

For each step in the titration, first think about what is present initially in the solution. Then use the two reactions to determine solution pH.

It is useful in a titration problem to first determine at what volume of titrant the equivalence point occurs.

e) Use the pH values from (a) – (d) to plot the titration curve.

Solution:

a) Before any base is added, the solution contains only HBrO and water. Equilibrium reaction 2a applies and pH can be found in the same way as for a weak acid solution:

Concentration (M)	HBrO(aq)	+	H ₂ O(aq)	\rightleftharpoons	BrO ⁻ (aq)	+	H ₃ O ⁺ (aq)
Initial	0.2000		—		0		0
Change	-x		—		+x		+x
Equilibrium	0.2000 - x		—		x		x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{BrO}^-]}{[\text{HBrO}]} = 2.3 \times 10^{-9} = \frac{[x][x]}{[0.2000 - x]}$$

Assume $0.2000 - x = 0.2000 \text{ M}$

$$2.3 \times 10^{-9} = \frac{[x][x]}{[0.2000]}$$

$$x = [\text{H}_3\text{O}^+] = 2.144761 \times 10^{-5} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.144761 \times 10^{-5}) = 4.66862 = \mathbf{4.67}$$

Check the assumption by calculating the percent error in $[\text{HBrO}]_{\text{eq}}$.

Percent error = $(2.144761 \times 10^{-5} / 0.2000)100 = 0.01\%$, this is well below the 5% maximum.

b) When $[\text{HBrO}] = [\text{BrO}^-]$, the solution contains significant concentrations of both the weak acid and its conjugate base. For the concentrations to be equal, half of the equivalence point volume has to have been added. Calculate the concentration of the acid and base and use the equilibrium expression for reaction 2a to find pH.

Since $[\text{HBrO}] = [\text{BrO}^-]$ their ratio equals 1.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{BrO}^-]}{[\text{HBrO}]}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HBrO}]}{[\text{BrO}^-]} = (2.3 \times 10^{-9}) \frac{[1]}{[1]} = 2.3 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.3 \times 10^{-9}) = 8.63827 = \mathbf{8.64}$$

Note that when $[\text{HBrO}] = [\text{BrO}^-]$, the titration is at the midpoint (half the volume to the equivalence point) and $\text{pH} = \text{p}K_a$.

c) At the equivalence point, the total number of moles of HBrO present initially in solution equals the number of moles of base added. Therefore, reaction 1 goes to completion to produce that number of moles of BrO^- . The solution consists of BrO^- and water. Calculate the concentration of BrO^- , and then find the pH using the base dissociation equilibrium, reaction 2b.

First, find equivalence point volume of NaOH.

$$\left(\frac{0.2000 \text{ mol HBrO}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (20.00 \text{ mL}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol HBrO}} \right) \left(\frac{1 \text{ L}}{0.1000 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 40.00 \text{ mL NaOH added}$$

All of the HBrO present at the beginning of the titration is neutralized and converted to BrO⁻ at the equivalence point. Calculate the concentration of BrO⁻.

Initial moles of HBrO: (0.2000 M)(0.02000 L) = 0.004000 mol

Moles of added NaOH: (0.1000 M)(0.04000 L) = 0.004000 mol

Amount (mol)	HBrO(aq)	+	OH ⁻ (aq)	→	H ₂ O(l)	+	BrO ⁻ (aq)
Before addition	0.004000 mol		—		—		0
Addition	—		0.004000 mol		—		—
Change	-0.004000 mol		-0.004000 mol		—		+0.004000 mol
After addition	0		0		—		0.004000 mol

At the equivalence point, 40.00 mL of NaOH solution has been added (see calculation above) to make the total volume of the solution (20.00 + 40.00) mL = 60.00 mL.

$$[\text{BrO}^-] = \left(\frac{0.004000 \text{ mol BrO}^-}{60.00 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.06666667 \text{ M (unrounded)}$$

Set up reaction table with reaction 2b, since only BrO⁻ and water are present initially:

Concentration (M)	BrO ⁻ (aq)	+	H ₂ O(l)	↔	HBrO(aq)	+	OH ⁻ (aq)
Initial	0.06666667		—		0		0
Change	-x		—		+x		+x
Equilibrium	0.06666667 - x		—		x		x

$$K_b = K_w/K_a = (1.0 \times 10^{-14} / 2.3 \times 10^{-9}) = 4.347826 \times 10^{-6} \text{ (unrounded)}$$

$$K_b = \frac{[\text{OH}^-][\text{HBrO}]}{[\text{BrO}^-]} = \frac{[x][x]}{[0.06666667 - x]} = 4.347826 \times 10^{-6}$$

Assume that x is negligible, since [BrO⁻] >> K_b.

$$4.347826 \times 10^{-6} = \frac{[x][x]}{[0.06666667]}$$

$$x = [\text{OH}^-] = 5.3838191 \times 10^{-4} = 5.4 \times 10^{-4} \text{ M}$$

Check the assumption by calculating the percent error in [BrO⁻]_{eq}.

percent error = (5.3838191 × 10⁻⁴ / 0.06666667)100 = 0.8%, which is well below the 5% maximum.

$$\text{pOH} = -\log(5.3838191 \times 10^{-4}) = 3.26891$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.26891 = 10.73109 = \mathbf{10.73}$$

d) After the equivalence point, the concentration of excess strong base determines the pH. Find the concentration of excess base and use it to calculate the pH.

Initial moles of HBrO: (0.2000 M)(0.02000 L) = 0.004000 mol

Moles of added NaOH: 2 × 0.004000 mol = 0.008000 mol NaOH

Amount (mol)	HBrO(aq)	+	OH ⁻ (aq)	→	H ₂ O(l)	+	BrO ⁻ (aq)
Before addition	0.004000 mol		—		—		0
Addition	—		0.008000 mol		—		—
Change	-0.004000 mol		-0.004000 mol		—		+0.004000 mol
After addition	0		0.004000 mol		—		0.004000 mol

Excess NaOH: 0.004000 mol

$$\text{Volume of added NaOH: } (0.0080000 \text{ mol NaOH}) \left(\frac{1 \text{ L}}{0.1000 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 80.00 \text{ mL}$$

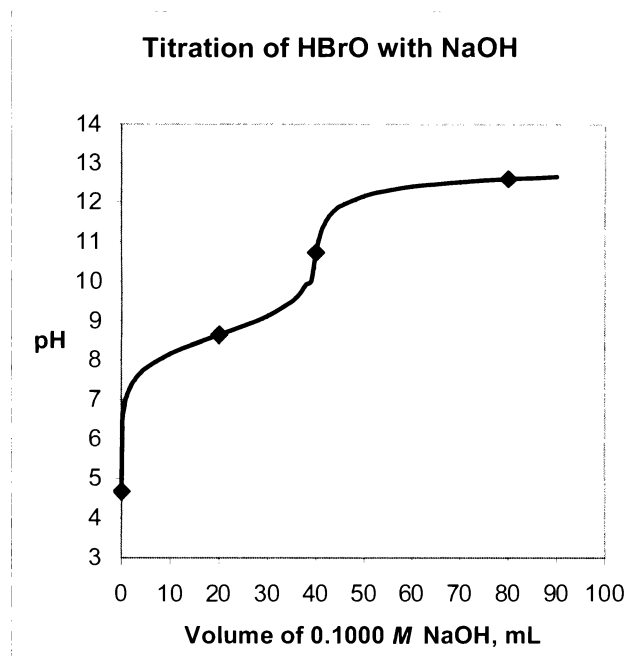
Total volume: 20.00 mL + 80.00 mL = 100.0 mL

$$[\text{NaOH}] = 0.004000 \text{ mol NaOH} / 0.1000 \text{ L} = 0.0400 \text{ M}$$

$$\text{pOH} = -\log(0.0400) = 1.3979$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.3979 = \mathbf{12.60}$$

e) Plot the pH values calculated in the preceding parts of this problem as a function of the volume of titrant.

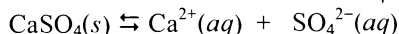


Check: The plot and pH values follow the pattern for a weak acid vs. strong base titration. The pH at the midpoint of the titration does equal pK_a . The equivalence point should be, and is, greater than 7.

19.4 Plan: Write the formula of the salt and the reaction showing the equilibrium of a saturated solution. The ion-product expression can be written from the stoichiometry of the solution reaction.

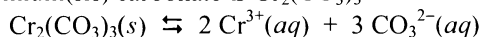
Solution:

a) The formula of calcium sulfate is CaSO_4 . The equilibrium reaction is



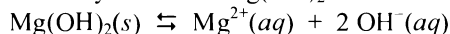
$$\text{Ion-product expression: } K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

b) Chromium(III) carbonate is $\text{Cr}_2(\text{CO}_3)_3$



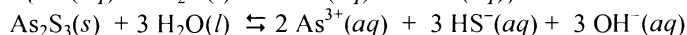
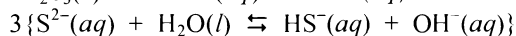
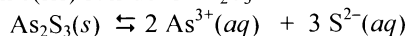
$$\text{Ion-product expression: } K_{sp} = [\text{Cr}^{3+}]^2[\text{CO}_3^{2-}]^3$$

c) Magnesium hydroxide is $\text{Mg}(\text{OH})_2$



$$\text{Ion-product expression: } K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$

d) Arsenic(III) sulfide is As_2S_3 .



The second equilibrium must be considered in this case because its equilibrium constant is large, so essentially all the sulfide ion is converted to HS^{-} and OH^{-} .

$$\text{Ion-product expression: } K_{sp} = [\text{As}^{3+}]^2[\text{HS}^{-}]^3[\text{OH}^{-}]^3$$

Check: All equilibria agree with the formulas of salts.

19.5 Plan: Calculate the solubility of CaF_2 as molarity and use molar ratios to find the molarity of Ca^{2+} and F^{-} dissolved in solution. Calculate K_{sp} from $[\text{Ca}^{2+}]$ and $[\text{F}^{-}]$ using the ion-product expression.

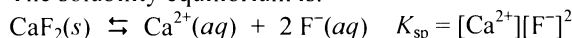
Solution: Convert the solubility to molar solubility:

$$\left(\frac{1.5 \times 10^{-4} \text{ g CaF}_2}{10.0 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol CaF}_2}{78.08 \text{ g CaF}_2} \right) = 1.9211 \times 10^{-4} \text{ M CaF}_2 \text{ (unrounded)}$$

$[\text{Ca}^{2+}] = [\text{CaF}_2] = 1.9211 \times 10^{-4} \text{ M}$ because there is 1 mol of calcium ions in each mol of CaF_2 .

$[\text{F}^-] = 2[\text{CaF}_2] = 3.8422 \times 10^{-4} \text{ M}$ because there are 2 mol of fluoride ions in each mol of CaF_2 .

The solubility equilibrium is:



Calculate K_{sp} using the solubility product expression from above and the saturated concentrations of calcium and fluoride ions.

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = (1.9211 \times 10^{-4}) (3.8422 \times 10^{-4})^2 = 2.836024 \times 10^{-11} = \mathbf{2.8 \times 10^{-11}}$$

The K_{sp} for CaF_2 is 2.8×10^{-11} at 18°C .

Check: Appendix C reports a K_{sp} value at 25°C for CaF_2 of 3.2×10^{-11} . The calculated value at 18°C is very close to this literature value.

- 19.6 Plan: Write the solubility reaction for $\text{Mg}(\text{OH})_2$ and set up a reaction table, where S is the unknown molar solubility of the Mg^{2+} ion. Use the ion-product expression to solve for the concentration of $\text{Mg}(\text{OH})_2$ in a saturated solution (also called the solubility of $\text{Mg}(\text{OH})_2$).

Solution:

Concentration (M)	$\text{Mg}(\text{OH})_2(s)$	\rightleftharpoons	$\text{Mg}^{2+}(aq)$	+	$2 \text{OH}^-(aq)$
Initial	—		0		0
Change	—		+ S		+ 2 S
Equilibrium	—		S		2 S

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (S)(2S)^2 = 4S^3 = 6.3 \times 10^{-10}$$

$$S = 5.4004114 \times 10^{-4} = 5.4 \times 10^{-4} \text{ M } \text{Mg}(\text{OH})_2$$

The solubility of $\text{Mg}(\text{OH})_2$ is equal to S, the concentration of magnesium ions at equilibrium, so the molar solubility of magnesium hydroxide in pure water is $\mathbf{5.4 \times 10^{-4} \text{ M}}$.

Check: To check the calculation, work it backwards (also a good technique when using problems as study tools).

From the calculated solubility, find K_{sp} .

$$[\text{Mg}^{2+}] = 5.4 \times 10^{-4} \text{ M} \text{ and } [\text{OH}^-] = 2(5.4 \times 10^{-4} \text{ M}) = 1.08 \times 10^{-4} \text{ M}$$

$$K_{\text{sp}} = (5.4 \times 10^{-4})(1.08 \times 10^{-4})^2 = 6.5 \times 10^{-10}$$

The backwards calculation gives back given K_{sp} .

- 19.7 Plan: Write the solubility reaction of BaSO_4 . For part (a) set up a reaction table in which $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = S$, which also equals the solubility of BaSO_4 . Then, solve for S using the ion-product expression. For part (b), there is an initial concentration of sulfate, so set up the reaction table including this initial $[\text{SO}_4^{2-}]$. Solve for the solubility, S, which equals $[\text{Ba}^{2+}]$ at equilibrium.

Solution:

a) Set up reaction table.

Concentration (M)	$\text{BaSO}_4(s)$	\rightleftharpoons	$\text{Ba}^{2+}(aq)$	+	$\text{SO}_4^{2-}(aq)$
Initial	—		0		0
Change	—		+ S		+ S
Equilibrium	—		S		S

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = S^2 = 1.1 \times 10^{-10}$$

$$S = 1.0488 \times 10^{-5} = \mathbf{1.0 \times 10^{-5} \text{ M}}$$

The molar solubility of BaSO_4 in pure water is $1.0 \times 10^{-5} \text{ M}$.

b) Set up another reaction table with initial $[\text{SO}_4^{2-}] = 0.10 \text{ M}$.

Concentration (M)	$\text{BaSO}_4(s)$	\rightleftharpoons	$\text{Ba}^{2+}(aq)$	+	$\text{SO}_4^{2-}(aq)$
Initial	—		0		0.10
Change	—		+ S		+ S
Equilibrium	—		S		0.10 + S

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = S(0.10 + S) = 1.1 \times 10^{-10}$$

Assume that $0.10 + S$ is approximately equal to 0.10, which appears to be a good assumption based on the fact that $0.10 \gg 1 \times 10^{-10}$, K_{sp} .

$$K_{\text{sp}} = S(0.10) = 1.1 \times 10^{-10}$$

$$S = 1.1 \times 10^{-9} \text{ M}$$

Molar solubility of BaSO_4 in $0.10 \text{ M } \text{Na}_2\text{SO}_4$ is $1.1 \times 10^{-9} \text{ M}$.

Check: The solubility of BaSO_4 decreases when sulfate ions are already present in the solution. The calculated decrease is from 10^{-5} M to 10^{-9} M , for a 10,000-fold decrease. This decrease is expected to be large because of the high concentration of sulfate ions.

19.8 Plan: First, write the solubility reaction for the salt. Then, check the ions produced when the salt dissolves to see if they will react with acid. Three cases are possible:

1) If OH^- is produced, then addition of acid will neutralize the hydroxide ions and shift the solubility equilibrium toward the products. This causes more salt to dissolve. Write the solubility and neutralization reactions.

2) If the anion from the salt is the conjugate base of a weak acid, it will react with the added acid in a neutralization reaction. Solubility of the salt increases as the anion is neutralized. Write the solubility and neutralization reactions.

3) If the anion from the salt is the conjugate base of a strong acid, it does not react with a strong acid. The solubility of the salt is unchanged by the addition of acid. Write the solubility reaction.

Solution:

a) Calcium fluoride, CaF_2

Solubility reaction: $\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^-(aq)$

Fluoride ion is the conjugate base of HF, a weak acid. Thus, it will react with H_3O^+ from the strong acid, HNO_3 .

Neutralization reaction: $\text{F}^-(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{HF}(aq) + \text{H}_2\text{O}(l)$

The neutralization reaction decreases the concentration of fluoride ions, which causes the solubility equilibrium to shift to the right and more CaF_2 dissolves. The solubility of CaF_2 increases with the addition of HNO_3 .

b) Zinc sulfide, ZnS

Solubility reaction: $\text{ZnS}(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$

Two anions are formed because the sulfide ion from ZnS reacts almost completely with water to form HS^- and OH^- .

The hydroxide ion reacts with the added acid:

Neutralization reaction: $\text{OH}^-(aq) + \text{H}_3\text{O}^+(aq) \rightarrow 2 \text{H}_2\text{O}(l)$

In addition, the hydrogen sulfide ion, the conjugate base of the weak acid H_2S , reacts with the added acid:

Neutralization reaction: $\text{HS}^-(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{H}_2\text{S}(aq) + \text{H}_2\text{O}(l)$

Both neutralization reactions decrease the concentration of products in the solubility equilibrium, which causes a shift to the right, and more ZnS dissolves. The addition of HNO_3 will increase the solubility of ZnS .

c) Silver iodide, AgI

Solubility reaction: $\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$

The iodide ion is the conjugate base of a strong acid, HI. So, I^- will not react with added acid. The solubility of AgI will not change with added HNO_3 .

19.9 Plan: First, write the solubility equilibrium equation and ion-product expression. Use the given concentrations of calcium and phosphate ions to calculate Q_{sp} . Compare Q_{sp} to K_{sp} .

If $K_{\text{sp}} < Q_{\text{sp}}$, precipitation occurs. If $K_{\text{sp}} \geq Q_{\text{sp}}$ then, precipitation will not occur.

Solution:

Write the solubility equation:

$\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3 \text{Ca}^{2+}(aq) + 2 \text{PO}_4^{3-}(aq)$

and ion-product expression: $Q_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$

$$[\text{Ca}^{2+}] = [\text{PO}_4^{3-}] = 1.0 \times 10^{-9} \text{ M}$$

$$Q_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (1.0 \times 10^{-9})^3(1.0 \times 10^{-9})^2 = 1.0 \times 10^{-45}$$

$$\text{Compare } K_{\text{sp}} \text{ and } Q_{\text{sp}}. \quad K_{\text{sp}} = 1.2 \times 10^{-29} > 1.0 \times 10^{-45} = Q_{\text{sp}}$$

Precipitation will not occur because concentrations are below the level of a saturated solution as shown by the value of Q_{sp} .

Check: The concentrations of calcium and phosphate ions are quite low, but K_{sp} is also small so it is difficult to predict whether precipitation will occur by just looking at the numbers. One way to check is with an estimate of the concentrations of ions in a saturated solution.

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3 \text{ S})^3(2 \text{ S})^2 = 108 \text{ S}^5 = 1 \times 10^{-29}$$

$$\text{S} = 6.213 \times 10^{-7} \text{ M (unrounded)}$$

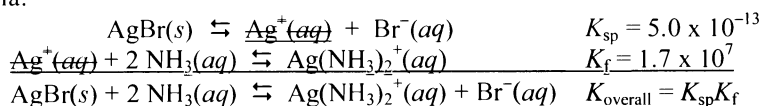
In a saturated solution

$$[\text{Ca}^{2+}] = 3(6.213 \times 10^{-7} \text{ M}) = 1.86 \times 10^{-6} \text{ M} \text{ and } [\text{PO}_4^{3-}] = 2(6.213 \times 10^{-7}) = 1.24 \times 10^{-6} \text{ M}$$

Both of these concentrations are much greater than the actual concentrations of $1 \times 10^{-9} \text{ M}$ for both ions, so the solution is unsaturated and no $\text{Ca}_3(\text{PO}_4)_2$ will precipitate.

- 19.10 **Plan:** Write equations for the solubility equilibrium and formation of the silver-ammonia complex ion. Add the two equations to get the overall reaction. Set up a reaction table for the overall reaction with the given value for initial $[\text{NH}_3]$. Write equilibrium expressions from the overall balanced reaction and calculate K_{overall} from K_f and K_{sp} values. Insert the equilibrium concentration values from the reaction table into the equilibrium expression and calculate solubility.

Solution: Equilibria:



Set up reaction table:

Concentration (M)	AgBr(s)	+	2 NH ₃ (aq)	\rightleftharpoons	Ag(NH ₃) ₂ ⁺ (aq)	+	Br ⁻ (aq)
Initial	—		1.0		0		0
Change	—		- 2 S		+ S		+ S
Equilibrium	—		1.0 - 2 S		S		S

$$K_{\text{overall}} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Br}^-]}{[\text{NH}_3]^2} = K_{\text{sp}}K_f = (5.0 \times 10^{-13})(1.7 \times 10^7) = 8.5 \times 10^{-6}$$

Calculate the solubility of AgBr:

$$K_{\text{overall}} = \frac{[\text{S}][\text{S}]}{[1.0 - 2\text{S}]^2} = 8.5 \times 10^{-6}$$

Assume that $1.0 - 2\text{S}$ is approximately equal to 1.0, which appears to be a good assumption based on the fact that $1.0 \gg 8.5 \times 10^{-6}$, K_{overall} .

$$\frac{[\text{S}][\text{S}]}{[1.0]^2} = 8.5 \times 10^{-6}$$

$$\text{S} = 2.9154759 \times 10^{-3} = 2.9 \times 10^{-3} \text{ M}$$

The solubility of AgBr in ammonia is **less** than its solubility in hypo (sodium thiosulfate).

Check: Since the formation constant for $\text{Ag}(\text{NH}_3)_2^+$ is less than the formation constant of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, the addition of ammonia will increase the solubility of AgBr less than the addition of thiosulfate ion increases its solubility.

END-OF-CHAPTER PROBLEMS

- 19.2 The weak acid component of a buffer neutralizes added base and the weak base component neutralizes added acid so that the pH of the buffer solution remains relatively constant. The components of a buffer do not neutralize one another when they are a conjugate acid/base pair.
- 19.4 A buffer is a mixture of a weak acid and its conjugate base (or weak base and its conjugate acid). The pH of a buffer changes only slightly with added H_3O^+ because the added H_3O^+ reacts with the base of the buffer. The net result is that the concentration of H_3O^+ does not change much from the original concentration, keeping the pH nearly constant.
- 19.7 The buffer component ratio refers to the ratio of concentrations of the acid and base that make up the buffer. When this ratio is equal to 1, the buffer resists changes in pH with added acid to the same extent that it resists changes in pH with added base. The buffer range extends equally in both the acidic and basic direction. When the ratio shifts with higher [base] than [acid], the buffer is more effective at neutralizing added acid than base so the range extends further in the acidic than basic direction. The opposite is true for a buffer where [acid] > [base]. Buffers with a ratio equal to 1 have the greatest buffer range. The more the buffer component ratio deviates from 1, the smaller the buffer range.

- 19.9 The buffer components are propanoic acid and propanoate ion. The sodium ions are spectator ions and are ignored because they are not involved in the buffer. The reaction table that describes this buffer is:

Concentration (<i>M</i>)	$\text{HC}_3\text{H}_5\text{O}_2(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{C}_3\text{H}_5\text{O}_2^-(aq)$	$+$	$\text{H}_3\text{O}^+(aq)$
Initial	0.15		—		0.25		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.15 - x$		—		$0.25 + x$		x

Assume that x is negligible with respect to both 0.15 and 0.25 since both concentrations are much larger than K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{[x][0.25 + x]}{[0.15 - x]} = \frac{[x][0.25]}{[0.15]} = 1.3 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HC}_3\text{H}_5\text{O}_2]}{[\text{C}_3\text{H}_5\text{O}_2^-]} = (1.3 \times 10^{-5}) \left(\frac{0.15}{0.25} \right) = 7.8 \times 10^{-6} M$$

Check assumption: percent error = $(7.8 \times 10^{-6} / 0.15)100\% = 0.0052\%$. The assumption is valid.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.8 \times 10^{-6}) = 5.107905 = \mathbf{5.11}$$

Another solution path to find pH is using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{p}K_a = -\log(1.3 \times 10^{-5}) = 4.89$$

$$\text{pH} = 4.89 + \log \left(\frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} \right) = 4.89 + \log \left(\frac{[0.25]}{[0.15]} \right)$$

$$\mathbf{\text{pH} = 5.11}$$

- 19.11 The buffer components are phenol, $\text{C}_6\text{H}_5\text{OH}$, and phenolate ion, $\text{C}_6\text{H}_5\text{O}^-$. The sodium ions are ignored because they are not involved in the buffer. Calculate K_a from $\text{p}K_a$ and set up the problem with a reaction table.

$$K_a = 10^{-\text{p}K_a} = 10^{-10.00} = 1.0 \times 10^{-10}$$

Concentration (<i>M</i>)	$\text{C}_6\text{H}_5\text{OH}(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{C}_6\text{H}_5\text{O}^-(aq)$	$+$	$\text{H}_3\text{O}^+(aq)$
Initial	1.2		—		1.0		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$1.2 - x$		—		$1.0 + x$		x

Assume that x is negligible with respect to both 1.0 and 1.2 because both concentrations are much larger than K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} = \frac{[x][1.0 + x]}{[1.2 - x]} = \frac{[x][1.0]}{[1.2]} = 1.0 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{C}_6\text{H}_5\text{OH}]}{[\text{C}_6\text{H}_5\text{O}^-]} = (1.0 \times 10^{-10}) \left(\frac{1.2}{1.0} \right) = 1.2 \times 10^{-10} M$$

Check assumption: percent error = $(1.2 \times 10^{-10} / 1.0)100\% = 1.2 \times 10^{-8}\%$. The assumption is valid.

$$\text{pH} = -\log (1.2 \times 10^{-10}) = 9.9208 = \mathbf{9.92}$$

Verify the pH using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$\text{pH} = 10.00 + \log \left(\frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} \right) = 10.00 + \log \left(\frac{[1.0]}{[1.2]} \right)$$

$$\mathbf{\text{pH} = 9.92}$$

- 19.13 The buffer components are phenol, NH_3 , and ammonium ion, NH_4^+ . The chloride ions are ignored because they are not involved in the buffer. Calculate K_b from $\text{p}K_b$ and set up the problem with a reaction table.

$$K_b = 10^{-\text{p}K_b} = 10^{-4.75} = 1.7782794 \times 10^{-5} \text{ (unrounded)}$$

Concentration (<i>M</i>)	$\text{NH}_3(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NH}_4^+(aq)$	$+$	$\text{OH}^-(aq)$
Initial	0.20		—		0.10		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.20 - x$		—		$0.10 + x$		x

Assume that x is negligible with respect to both 0.20 and 0.10 because both concentrations are much larger than K_b .

$$K_b = 10^{-pK_b} = 10^{-4.75} = 1.7782794 \times 10^{-5} \text{ (unrounded)}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[0.10 + x][\text{OH}^-]}{[0.20 - x]} = \frac{[0.10][\text{OH}^-]}{[0.20]} = 1.7782794 \times 10^{-5} \text{ (unrounded)}$$

$$[\text{OH}^-] = K_b \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = (1.7782794 \times 10^{-5}) \left(\frac{0.20}{0.10} \right) = 3.5565588 \times 10^{-5} \text{ M (unrounded)}$$

Check assumption: percent error = $(3.5565588 \times 10^{-5} / 0.10)100\% = 0.036\%$. The assumption is valid.

$$\text{pOH} = -\log [\text{OH}^-] = -\log (3.5565588 \times 10^{-5}) = 4.448970 \text{ (unrounded)}$$

$$14.00 = \text{pH} + \text{pOH}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.448970 = 9.551030 = \mathbf{9.55}$$

Verify the pH using the Henderson-Hasselbalch equation. To do this, you must find the pK_a of the acid NH_4^+ :

$$14 = \text{pK}_a + \text{pK}_b$$

$$\text{pK}_a = 14 - \text{pK}_b = 14 - 4.75 = 9.25$$

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$\text{pH} = 9.25 + \log \left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right) = 9.25 + \log \left(\frac{[0.20]}{[0.10]} \right)$$

$$\mathbf{\text{pH} = 9.55}$$

- 19.15 Given the pH and K_a of an acid, the buffer-component ratio can be calculated from the Henderson-Hasselbalch equation.

$$\text{pK}_a = -\log K_a = -\log (1.3 \times 10^{-5}) = 4.8860566 \text{ (unrounded)}$$

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$5.11 = 4.8860566 + \log \left(\frac{[\text{Pr}^-]}{[\text{HPr}]} \right)$$

$$0.2239434 = \log \left(\frac{[\text{Pr}^-]}{[\text{HPr}]} \right) \quad \text{Raise each side to } 10^x$$

$$\frac{[\text{Pr}^-]}{[\text{HPr}]} = 1.674724 = \mathbf{1.7}$$

- 19.17 Determine the pK_a of the acid from the concentrations of the conjugate acid and base, and the pH of the solution. This requires the Henderson-Hasselbalch equation.

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$3.35 = \text{pK}_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) = \text{pK}_a + \log \left(\frac{[0.1500]}{[0.2000]} \right)$$

$$3.35 = \text{pK}_a - 0.1249387$$

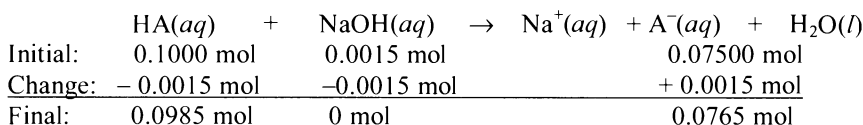
$$\text{pK}_a = 3.474939 = \mathbf{3.47}$$

Determine the moles of conjugate acid (HA) and conjugate base (A^-) using $(\text{M})(\text{V}) = \text{moles}$

$$\text{Moles HA} = (0.5000 \text{ L}) (0.2000 \text{ mol HA} / \text{L}) = 0.1000 \text{ mol HA}$$

$$\text{Moles A}^- = (0.5000 \text{ L}) (0.1500 \text{ mol A}^- / \text{L}) = 0.07500 \text{ mol A}^-$$

The reaction is:



NaOH is the limiting reagent. The addition of 0.0015 mol NaOH produces an additional 0.0015 mol A^- and consumes 0.0015 mol of HA.

Then

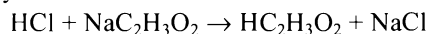
$$[\text{A}^-] = \frac{0.0765 \text{ mol A}^-}{0.5000 \text{ L}} = 0.153 \text{ M A}^-$$

$$[\text{HA}] = \frac{0.0985 \text{ mol HA}}{0.5000 \text{ L}} = 0.197 \text{ M HA}$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\text{pH} = 3.474938737 + \log\left(\frac{[0.153]}{[0.197]}\right) = 3.365163942 = \mathbf{3.37}$$

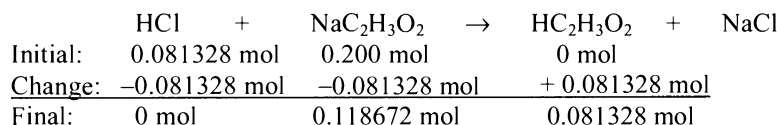
- 19.19 a) The hydrochloric acid will react with the sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, to form acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$:



Calculate the number of moles of HCl and $\text{NaC}_2\text{H}_3\text{O}_2$. All of the HCl will be consumed to form $\text{HC}_2\text{H}_3\text{O}_2$, and the number of moles of $\text{C}_2\text{H}_3\text{O}_2^-$ will decrease.

$$\text{Initial moles HCl} = \left(\frac{0.442 \text{ mol HCl}}{\text{L}}\right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(184 \text{ mL}) = 0.081328 \text{ mol HCl (unrounded)}$$

$$\text{Initial moles NaC}_2\text{H}_3\text{O}_2 = \left(\frac{0.400 \text{ mol NaC}_2\text{H}_3\text{O}_2}{\text{L}}\right)(0.500 \text{ L}) = 0.200 \text{ mol NaC}_2\text{H}_3\text{O}_2$$



$$\text{Total volume} = 0.500 \text{ L} + (184 \text{ mL})(10^{-3} \text{ L} / 1 \text{ mL}) = 0.684 \text{ L}$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.081328 \text{ mol}}{0.684 \text{ L}} = 0.118900584 \text{ M (unrounded)}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.118672 \text{ mol}}{0.684 \text{ L}} = 0.173497076 \text{ M (unrounded)}$$

$$\text{pK}_a = -\log K_a = -\log (1.8 \times 10^{-5}) = 4.744727495$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)$$

$$\text{pH} = 4.744727495 + \log\left(\frac{[0.173497076]}{[0.118900584]}\right) = 4.9088 = \mathbf{4.91}$$

- b) The addition of base would increase the pH, so the new pH is $(4.91 + 0.15) = 5.06$.

The new $[\text{C}_2\text{H}_3\text{O}_2^-] / [\text{HC}_2\text{H}_3\text{O}_2]$ ratio is calculated using the Henderson-Hasselbalch equation.

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)$$

$$5.06 = 4.744727495 + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)$$

$$0.315272505 = \log \left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 2.06676519 \text{ (unrounded)}$$

From part (a), we know that $[\text{HC}_2\text{H}_3\text{O}_2] + [\text{C}_2\text{H}_3\text{O}_2^-] = (0.118900584 \text{ M} + 0.173497076 \text{ M}) = 0.29239766 \text{ M}$. Although the *ratio* of $[\text{C}_2\text{H}_3\text{O}_2^-]$ to $[\text{HC}_2\text{H}_3\text{O}_2]$ can change when acid or base is added, the *absolute amount* does not change unless acetic acid or an acetate salt is added.

Given that $[\text{C}_2\text{H}_3\text{O}_2^-] / [\text{HC}_2\text{H}_3\text{O}_2] = 2.06676519$ and $[\text{HC}_2\text{H}_3\text{O}_2] + [\text{C}_2\text{H}_3\text{O}_2^-] = 0.29239766 \text{ M}$, solve for $[\text{C}_2\text{H}_3\text{O}_2^-]$ and substitute into the second equation.

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 2.06676519 [\text{HC}_2\text{H}_3\text{O}_2] \text{ and } [\text{HC}_2\text{H}_3\text{O}_2] + 2.06676519 [\text{HC}_2\text{H}_3\text{O}_2] = 0.29239766 \text{ M}$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.095343999 \text{ M and } [\text{C}_2\text{H}_3\text{O}_2^-] = 0.19705366 \text{ M}$$

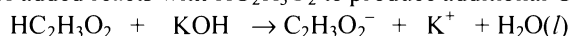
$$\text{Moles of } \text{C}_2\text{H}_3\text{O}_2^- \text{ needed} = (0.19705366 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^- / \text{L}) (0.500 \text{ L}) = 0.09852683 \text{ mol (unrounded)}$$

$$\text{Moles of } \text{C}_2\text{H}_3\text{O}_2^- \text{ initially} = (0.173497076 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^- / \text{L}) (0.500 \text{ L}) = 0.086748538 \text{ mol (unrounded)}$$

$$\text{This would require the addition of } (0.09852683 \text{ mol} - 0.086748538 \text{ mol})$$

$$= 0.011778292 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^- \text{ (unrounded)}$$

The KOH added reacts with $\text{HC}_2\text{H}_3\text{O}_2$ to produce additional $\text{C}_2\text{H}_3\text{O}_2^-$:



To produce $0.011778292 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-$ would require the addition of $0.011778292 \text{ mol KOH}$.

$$\text{Mass KOH} = (0.011778292 \text{ mol KOH}) \left(\frac{56.11 \text{ g KOH}}{1 \text{ mol KOH}} \right) = 0.660879964 = \mathbf{0.66 \text{ g KOH}}$$

19.21 Select conjugate pairs with K_a values close to the desired $[\text{H}_3\text{O}^+]$.

a) For $\text{pH} \approx 4.0$, $[\text{H}_3\text{O}^+] = 10^{-4.0} = 1.0 \times 10^{-4} \text{ M}$. The best selection is the $\text{HCOOH} / \text{HCOO}^-$ conjugate pair with K_a equal to 1.8×10^{-4} . From the base list, the $\text{C}_6\text{H}_5\text{NH}_2 / \text{C}_6\text{H}_5\text{NH}_3^+$ conjugate pair comes close with $K_a = 1.0 \times 10^{-14} / 4.0 \times 10^{-10} = 2.5 \times 10^{-5}$.

b) For $\text{pH} \approx 7.0$, $[\text{H}_3\text{O}^+] = 10^{-7.0} = 1.0 \times 10^{-7} \text{ M}$. Two choices are the $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ conjugate pair with K_a of 6.3×10^{-8} and the $\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$ conjugate pair with K_a of 1.1×10^{-7} .

19.24 The value of the K_a from the appendix: $K_a = 6.3 \times 10^{-8}$ (We are using K_{a2} since we are dealing with the equilibrium in which the second hydrogen ion is being lost).

Determine the $\text{p}K_a$ using $\text{p}K_a = -\log 6.3 \times 10^{-8} = 7.200659451$ (unrounded)

Use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$7.40 = 7.200659451 + \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

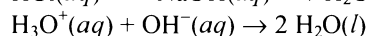
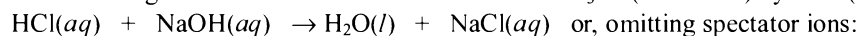
$$0.19934055 = \log \left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \right)$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 1.582486 = \mathbf{1.6}$$

19.26 To see a distinct color in a mixture of two colors, you need one color to be about 10 times the intensity of the other. For this to take place, the concentration ratio $[\text{HIn}] / [\text{In}^-]$ needs to be greater than 10:1 or less than 1:10. This will occur when $\text{pH} = \text{p}K_a - 1$ or $\text{pH} = \text{p}K_a + 1$, respectively, giving a transition range of about two units.

- 19.28 The equivalence point in a titration is the point at which the number of moles of OH^- equals the number of moles of H_3O^+ (be sure to account for stoichiometric ratios, e.g., 1 mol of $\text{Ca}(\text{OH})_2$ produces 2 moles of OH^-). The endpoint is the point at which the added indicator changes color. If an appropriate indicator is selected, the endpoint is close to the equivalence point, but not normally the same. Using an indicator that changes color at a pH after the equivalence point means the equivalence point is reached first. However, if an indicator is selected that changes color at a pH before the equivalence point, then the endpoint is reached first.
- 19.30 a) The initial pH is lowest for flask solution of the strong acid, followed by the weak acid and then the weak base. In other words, *strong acid* - strong base < *weak acid* - strong base < strong acid - *weak base*.
 b) At the equivalence point, the moles of H_3O^+ equal the moles of OH^- , regardless of the type of titration. However, the strong acid - strong base equivalence point occurs at pH = 7.00 because the resulting cation-anion combination does not react with water. An example is the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$. Neither Na^+ nor Cl^- ions dissociate in water.
 The weak acid - strong base equivalence point occurs at pH > 7, because the anion of the weak acid is weakly basic, whereas the cation of the strong base does not react with water. An example is the reaction $\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOO}^- + \text{H}_2\text{O} + \text{Na}^+$. The conjugate base, HCOO^- , reacts with water according to this reaction: $\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{OH}^-$.
 The strong acid - weak base equivalence point occurs at pH < 7, because the anion of the strong acid does not react with water, whereas the cation of the weak base is weakly acidic. An example is the reaction $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-$. The conjugate acid, NH_4^+ , dissociates slightly in water: $\text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{H}_3\text{O}^+$.
 In rank order of pH of equivalence point, strong acid - *weak base* < *strong acid* - strong base < *weak acid* - strong base.
- 19.32 At the very center of the buffer region of a weak acid-strong base titration, the concentration of the weak acid and its conjugate base are equal, which means that at this point the pH of the solution equals the pK_a of the weak acid.
- 19.33 Indicators have a pH range that is approximated by $\text{pK}_a \pm 1$. The pK_a of cresol red is $-\log(5.0 \times 10^{-9}) = 8.3$, so the indicator changes color over an approximate range of **7.3 to 9.3**.
- 19.35 Choose an indicator that changes color at a pH close to the pH of the equivalence point.
 a) The equivalence point for a strong acid-strong base titration occurs at pH = 7.0. **Bromthymol blue** is an indicator that changes color around pH 7.
 b) The equivalence point for a weak acid-strong base is above pH 7. Estimate the pH at equivalence point from equilibrium calculations.
 At the equivalence point, all of the HCOOH and NaOH have been consumed; the solution is 0.050 M HCOO^- . (The volume doubles because equal volumes of base and acid are required to reach the equivalence point. When the volume doubles, the concentration is halved.) The weak base HCOO^- undergoes a base reaction:
- | | | | | | | | |
|-------------------------|---------------------|-----|-------------------------|----------------------|--------------------|-----|-------------------|
| Concentration, <i>M</i> | $\text{COOH}^-(aq)$ | $+$ | $\text{H}_2\text{O}(l)$ | \rightleftharpoons | $\text{HCOOH}(aq)$ | $+$ | $\text{OH}^-(aq)$ |
| Initial: | 0.050 M | | — | | 0 | | 0 |
| Change: | — x | | | | +x | | +x |
| Equilibrium: | 0.050 — x | | | | x | | x |
- The K_a for HCOOH is 1.8×10^{-4} , so $K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-4} = 5.5556 \times 10^{-11}$ (unrounded)
- $$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{[x][x]}{[0.050 - x]} = \frac{[x][x]}{[0.050]} = 5.5556 \times 10^{-11}$$
- $$[\text{OH}^-] = x = 1.666673 \times 10^{-6} \text{ M}$$
- $$\text{pOH} = -\log(1.666673 \times 10^{-6}) = 5.7781496 \text{ (unrounded)}$$
- $$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.7781496 = 8.2218504 = 8.22$$
- Choose **thymol blue** or **phenolphthalein**.

19.37 The reaction occurring in the titration is the neutralization of H_3O^+ (from HCl) by OH^- (from NaOH):



For the titration of a strong acid with a strong base, the pH before the equivalence point depends on the excess concentration of acid and the pH after the equivalence point depends on the excess concentration of base. At the equivalence point, there is not an excess of either acid or base so the pH is 7.0. The equivalence point occurs when 50.00 mL of base has been added. Use (M)(V) to determine the number of moles.

The initial number of moles of HCl = $(0.1000 \text{ mol HCl} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (50.00 \text{ mL}) = 5.000 \times 10^{-3} \text{ mol HCl}$

a) At 0 mL of base added, the concentration of hydronium ion equals the original concentration of HCl.

$$\text{pH} = -\log (0.1000 \text{ M}) = \mathbf{1.0000}$$

b) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.00 \text{ mL}) = 2.500 \times 10^{-3} \text{ mol NaOH}$$

	$\text{HCl}(aq)$	+	$\text{NaOH}(aq)$	\rightarrow	$\text{H}_2\text{O}(l)$	+	$\text{NaCl}(aq)$
Initial:	$5.000 \times 10^{-3} \text{ mol}$		$2.500 \times 10^{-3} \text{ mol}$		–		0
Change:	$- 2.500 \times 10^{-3} \text{ mol}$		$-2.500 \times 10^{-3} \text{ mol}$		–		$+ 2.500 \times 10^{-3} \text{ mol}$
Final:	$2.500 \times 10^{-3} \text{ mol}$		0				$2.500 \times 10^{-3} \text{ mol}$

The volume of the solution at this point is $[(50.00 + 25.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.07500 \text{ L}$

The molarity of the excess HCl is $(2.500 \times 10^{-3} \text{ mol HCl}) / (0.07500 \text{ L}) = 0.03333 \text{ M}$ (unrounded)

$$\text{pH} = -\log (0.03333) = \mathbf{1.4772}$$

(Note that the NaCl product is a neutral salt that does not affect the pH).

c) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (49.00 \text{ mL}) = 4.900 \times 10^{-3} \text{ mol NaOH}$$

	$\text{HCl}(aq)$	+	$\text{NaOH}(aq)$	\rightarrow	$\text{H}_2\text{O}(l)$	+	$\text{NaCl}(aq)$
Initial:	$5.000 \times 10^{-3} \text{ mol}$		$4.900 \times 10^{-3} \text{ mol}$		–		0
Change:	$- 4.900 \times 10^{-3} \text{ mol}$		$-4.900 \times 10^{-3} \text{ mol}$		–		$+ 4.900 \times 10^{-3} \text{ mol}$
Final:	$1.000 \times 10^{-4} \text{ mol}$		0				$4.900 \times 10^{-3} \text{ mol}$

The volume of the solution at this point is $[(50.00 + 49.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.09900 \text{ L}$

The molarity of the excess HCl is $(1.00 \times 10^{-4} \text{ mol HCl}) / (0.09900 \text{ L}) = 0.00101 \text{ M}$ (unrounded)

$$\text{pH} = -\log (0.00101) = \mathbf{2.996}$$

d) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (49.90 \text{ mL}) = 4.990 \times 10^{-3} \text{ mol NaOH}$$

	$\text{HCl}(aq)$	+	$\text{NaOH}(aq)$	\rightarrow	$\text{H}_2\text{O}(l)$	+	$\text{NaCl}(aq)$
Initial:	$5.000 \times 10^{-3} \text{ mol}$		$4.990 \times 10^{-3} \text{ mol}$		–		0
Change:	$- 4.990 \times 10^{-3} \text{ mol}$		$-4.990 \times 10^{-3} \text{ mol}$		–		$+ 4.990 \times 10^{-3} \text{ mol}$
Final:	$1.000 \times 10^{-5} \text{ mol}$		0				$4.900 \times 10^{-3} \text{ mol}$

The volume of the solution at this point is $[(50.00 + 49.90) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.09990 \text{ L}$

The molarity of the excess HCl is $(1.0 \times 10^{-5} \text{ mol HCl}) / (0.09990 \text{ L}) = 0.0001001 \text{ M}$ (unrounded)

$$\text{pH} = -\log (0.0001001) = \mathbf{4.0000}$$

e) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (50.00 \text{ mL}) = 5.000 \times 10^{-3} \text{ mol NaOH}$$

	$\text{HCl}(aq)$	+	$\text{NaOH}(aq)$	\rightarrow	$\text{H}_2\text{O}(l)$	+	$\text{NaCl}(aq)$
Initial:	$5.000 \times 10^{-3} \text{ mol}$		$5.000 \times 10^{-3} \text{ mol}$		–		0
Change:	$- 5.000 \times 10^{-3} \text{ mol}$		$-5.000 \times 10^{-3} \text{ mol}$		–		$+ 5.000 \times 10^{-3} \text{ mol}$
Final:	0		0				$5.000 \times 10^{-3} \text{ mol}$

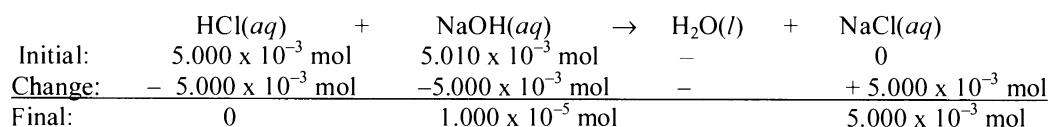
The NaOH will react with an equal amount of the acid and 0.0 mol HCl will remain. This is the equivalence point of a strong acid-strong base titration, thus, the pH is **7.00**. Only the neutral salt NaCl is in solution at the equivalence point.

f) The NaOH is now in excess. It will be necessary to calculate the excess base after reacting with the HCl. The excess strong base will give the pOH, which can be converted to the pH.

Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (50.10 \text{ mL}) = 5.010 \times 10^{-3} \text{ mol NaOH}$$

The HCl will react with an equal amount of the base, and $1.0 \times 10^{-5} \text{ mol NaOH}$ will remain.



The volume of the solution at this point is [(50.00 + 50.10) mL] (10⁻³ L / 1 mL) = 0.1010 L

The molarity of the excess NaOH is (1.0 x 10⁻⁵ mol NaOH) / (0.1010 L) = 0.00009901 M (unrounded)

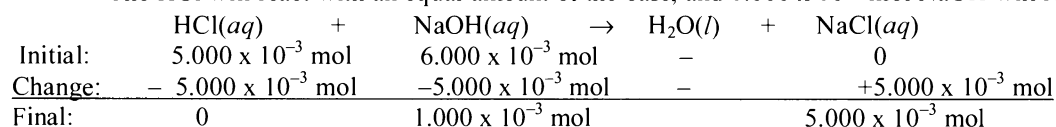
$$\text{pOH} = -\log(0.00009901) = 4.0043 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.0043 = 9.9957 = \mathbf{10.00}$$

g) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (60.00 \text{ mL}) = 6.000 \times 10^{-3} \text{ mol NaOH}$$

The HCl will react with an equal amount of the base, and 1.000 x 10⁻³ mol NaOH will remain.



The volume of the solution at this point is [(50.00 + 60.00) mL] (10⁻³ L / 1 mL) = 0.1100 L

The molarity of the excess NaOH is (1.000 x 10⁻³ mol NaOH) / (0.1100 L) = 0.0090909 M (unrounded)

$$\text{pOH} = -\log(0.0090909) = 2.041393 \text{ (unrounded)}$$

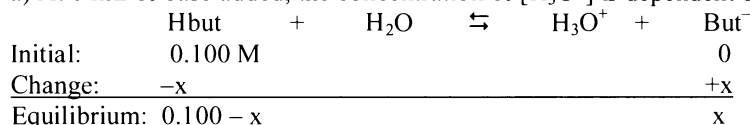
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.041393 = 11.958607 = \mathbf{11.96}$$

19.39 This is a titration between a weak acid and a strong base. The pH before addition of the base is dependent on the K_a of the acid (labeled HBut). Prior to reaching the equivalence point, the added base reacts with the acid to form butanoate ion (labeled But⁻). The equivalence point occurs when 20.00 mL of base is added to the acid because at this point, moles acid = moles base. Addition of base beyond the equivalence point is simply the addition of excess OH⁻.

The initial number of moles of HBut = (M)(V) =

$$(0.1000 \text{ mol HBut} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (20.00 \text{ mL}) = 2.000 \times 10^{-3} \text{ mol HBut}$$

a) At 0 mL of base added, the concentration of [H₃O⁺] is dependent on the dissociation of butanoic acid:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x^2}{0.1000 - x} = \frac{x^2}{0.1000} = 1.54 \times 10^{-5}$$

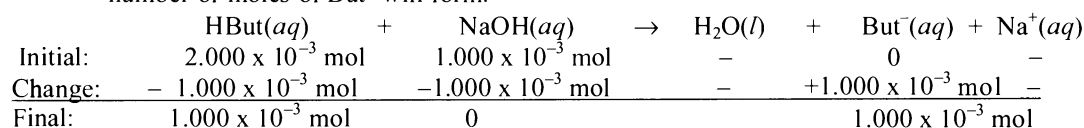
$$x = [\text{H}_3\text{O}^+] = 1.2409673 \times 10^{-3} \text{ M (unrounded)}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.2409673 \times 10^{-3}) = 2.9062 = \mathbf{2.91}$$

b) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (10.00 \text{ mL}) = 1.000 \times 10^{-3} \text{ mol NaOH}$$

The NaOH will react with an equal amount of the acid, and 1.000 x 10⁻³ mol HBut will remain. An equal number of moles of But⁻ will form.

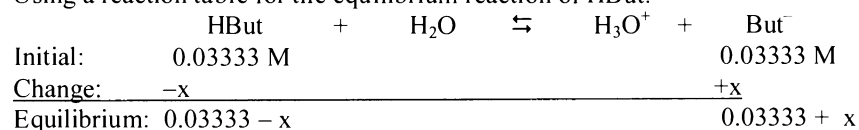


The volume of the solution at this point is [(20.00 + 10.00) mL] (10⁻³ L / 1 mL) = 0.03000 L

The molarity of the excess HBut is (1.000 x 10⁻³ mol HBut) / (0.03000 L) = 0.03333 M (unrounded)

The molarity of the But⁻ formed is (1.000 x 10⁻³ mol But⁻) / (0.03000 L) = 0.03333 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0333 + x)}{0.0333 - x} = \frac{x(0.0333)}{0.0333} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 1.54 \times 10^{-5} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.54 \times 10^{-5}) = 4.812479 = \mathbf{4.81}$$

c) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH / L}) (10^{-3} \text{ L / 1 mL}) (15.00 \text{ mL}) = 1.500 \times 10^{-3} \text{ mol NaOH}$$

The NaOH will react with an equal amount of the acid, and 5.00×10^{-4} mol HBut will remain, and 1.500×10^{-3} moles of But^- will form.

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial:	2.000 × 10 ⁻³ mol		1.500 × 10 ⁻³ mol		–		0		–
Change:	– 1.500 × 10 ⁻³ mol		– 1.500 × 10 ⁻³ mol		–		+ 1.500 × 10 ⁻³ mol		–
Final:	5.000 × 10 ⁻⁴ mol		0				1.500 × 10 ⁻³ mol		

The volume of the solution at this point is [(20.00 + 15.00) mL] (10⁻³ L / 1 mL) = 0.03500 L

The molarity of the excess HBut is (5.00×10^{-4} mol HBut) / (0.03500 L) = 0.0142857 M (unrounded)

The molarity of the But^- formed is (1.500×10^{-3} mol But^-) / (0.03500 L) = 0.0428571 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial:	0.0142857 M						0.0428571 M
Change:	–x						+x
Equilibrium:	0.0142857 – x						0.0428571 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0428571 + x)}{0.0142857 - x} = \frac{x(0.0428571)}{0.0142857} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 5.1333 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.1333 \times 10^{-6}) = 5.2896 = \mathbf{5.29}$$

d) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH / L}) (10^{-3} \text{ L / 1 mL}) (19.00 \text{ mL}) = 1.900 \times 10^{-3} \text{ mol NaOH}$$

The NaOH will react with an equal amount of the acid, and 1.00×10^{-4} mol HBut will remain, and 1.900×10^{-3} moles of But^- will form.

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial:	2.000 × 10 ⁻³ mol		1.900 × 10 ⁻³ mol		–		0		–
Change:	– 1.900 × 10 ⁻³ mol		– 1.900 × 10 ⁻³ mol		–		+ 1.900 × 10 ⁻³ mol		–
Final:	1.000 × 10 ⁻⁴ mol		0				1.900 × 10 ⁻³ mol		

The volume of the solution at this point is [(20.00 + 19.00) mL] (10⁻³ L / 1 mL) = 0.03900 L

The molarity of the excess HBut is (1.00×10^{-4} mol HBut) / (0.03900 L) = 0.0025641 M (unrounded)

The molarity of the But^- formed is (1.900×10^{-3} mol But^-) / (0.03900 L) = 0.0487179 M (unrounded)

Using a reaction table for the equilibrium reaction of HBut:

	HBut	+	H ₂ O	⇌	H ₃ O ⁺	+	But ⁻
Initial:	0.0025641 M						0.0487179 M
Change:	–x						+x
Equilibrium:	0.0025641 – x						0.0487179 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0487179 + x)}{0.0025641 - x} = \frac{x(0.0487179)}{0.0025641} = 1.54 \times 10^{-5}$$

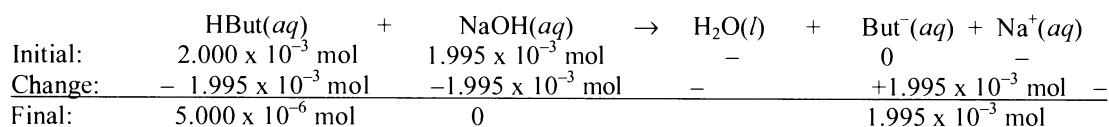
$$x = [\text{H}_3\text{O}^+] = 8.1052631 \times 10^{-7} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.1052631 \times 10^{-7}) = 6.09123 = \mathbf{6.09}$$

e) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH / L}) (10^{-3} \text{ L / 1 mL}) (19.95 \text{ mL}) = 1.995 \times 10^{-3} \text{ mol NaOH}$$

The NaOH will react with an equal amount of the acid, and 5×10^{-6} mol HBut will remain, and 1.995×10^{-3} moles of But^- will form.

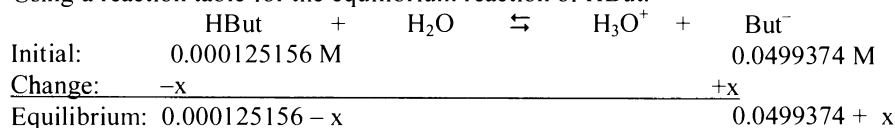


The volume of the solution at this point is $[(20.00 + 19.95) \text{ mL}](10^{-3} \text{ L} / 1 \text{ mL}) = 0.03995 \text{ L}$

The molarity of the excess HBut is $(5 \times 10^{-6} \text{ mol HBut}) / (0.03995 \text{ L}) = 0.000125156 \text{ M}$ (unrounded)

The molarity of the But^- formed is $(1.995 \times 10^{-3} \text{ mol But}^-) / (0.03995 \text{ L}) = 0.0499374 \text{ M}$ (unrounded)

Using a reaction table for the equilibrium reaction of HBut:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{But}^-]}{[\text{HBut}]} = \frac{x(0.0499374 + x)}{0.000125156 - x} = \frac{x(0.0499374)}{0.000125156} = 1.54 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 3.859637 \times 10^{-8} \text{ M (unrounded)}$$

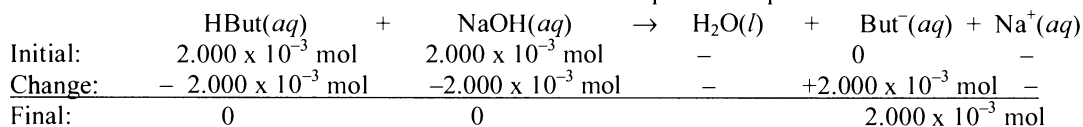
$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.859637 \times 10^{-8}) = 7.41345 = \mathbf{7.41}$$

f) Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L})(10^{-3} \text{ L} / 1 \text{ mL})(20.00 \text{ mL}) = 2.000 \times 10^{-3} \text{ mol NaOH}$

The NaOH will react with an equal amount of the acid, and 0 mol HBut will remain, and

2.000×10^{-3} moles of But^- will form. This is the equivalence point.



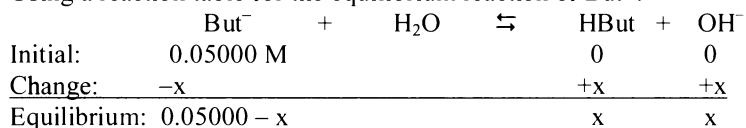
The K_b of But^- is now important.

The volume of the solution at this point is $[(20.00 + 20.00) \text{ mL}](10^{-3} \text{ L} / 1 \text{ mL}) = 0.04000 \text{ L}$

The molarity of the But^- formed is $(2.000 \times 10^{-3} \text{ mol But}^-) / (0.04000 \text{ L}) = 0.05000 \text{ M}$ (unrounded)

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.54 \times 10^{-5}) = 6.4935 \times 10^{-10} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of But^- :



$$K_b = \frac{[\text{HBut}][\text{OH}^-]}{[\text{But}^-]} = \frac{[x][x]}{[0.05000 - x]} = \frac{[x][x]}{[0.05000]} = 6.4935 \times 10^{-10}$$

$$[\text{OH}^-] = x = 5.6980259 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log (5.6980259 \times 10^{-6}) = 5.244275575 \text{ (unrounded)}$$

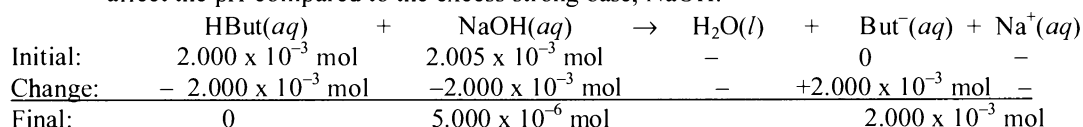
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.244275575 = 8.755724425 = \mathbf{8.76}$$

g) After the equivalence point, the excess strong base is the primary factor influencing the pH.

Determine the moles of NaOH added:

Moles of NaOH = $(0.1000 \text{ mol NaOH} / \text{L})(10^{-3} \text{ L} / 1 \text{ mL})(20.05 \text{ mL}) = 2.005 \times 10^{-3} \text{ mol NaOH}$

The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and 5×10^{-6} moles of NaOH will be in excess. There will be $2.000 \times 10^{-3} \text{ mol}$ of But^- produced, but this weak base will not affect the pH compared to the excess strong base, NaOH.



The volume of the solution at this point is $[(20.00 + 20.05) \text{ mL}](10^{-3} \text{ L} / 1 \text{ mL}) = 0.04005 \text{ L}$

The molarity of the excess OH^- is $(5 \times 10^{-6} \text{ mol OH}^-) / (0.04005 \text{ L}) = 1.2484 \times 10^{-4} \text{ M}$ (unrounded)

$$\text{pOH} = -\log (1.2484 \times 10^{-4}) = 3.9036 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.9036 = 10.0964 = \mathbf{10.10}$$

h) Determine the moles of NaOH added:

$$\text{Moles of NaOH} = (0.1000 \text{ mol NaOH} / \text{L}) (10^{-3} \text{ L} / 1 \text{ mL}) (25.00 \text{ mL}) = 2.500 \times 10^{-3} \text{ mol NaOH}$$

The NaOH will react with an equal amount of the acid, 0 mol HBut will remain, and

5.00×10^{-4} moles of NaOH will be in excess.

	HBut(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	But ⁻ (aq)	+	Na ⁺ (aq)
Initial:	$2.000 \times 10^{-3} \text{ mol}$		$2.500 \times 10^{-3} \text{ mol}$		-		0		-
Change:	$- 2.000 \times 10^{-3} \text{ mol}$		$-2.000 \times 10^{-3} \text{ mol}$		-		$+2.000 \times 10^{-3} \text{ mol}$		-
Final:	0		$5.000 \times 10^{-4} \text{ mol}$				$2.000 \times 10^{-3} \text{ mol}$		

The volume of the solution at this point is $[(20.00 + 25.00) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.04500 \text{ L}$

The molarity of the excess OH⁻ is $(5.00 \times 10^{-4} \text{ mol OH}^-) / (0.04500 \text{ L}) = 1.1111 \times 10^{-2} \text{ M (unrounded)}$

$$\text{pOH} = -\log (1.1111 \times 10^{-2}) = 1.9542 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.9542 = 12.0458 = \mathbf{12.05}$$

19.41 a) The balanced chemical equation is:



The sodium ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of NaOH needed:

Volume =

$$\left(\frac{0.0520 \text{ mol CH}_3\text{COOH}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (42.2 \text{ mL}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol CH}_3\text{COOH}} \right) \left(\frac{\text{L}}{0.0372 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 58.989247 = \mathbf{59.0 \text{ mL NaOH}}$$

Determine the moles of CH₃COOH present:

$$\text{Moles} = \left(\frac{0.0520 \text{ mol CH}_3\text{COOH}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (42.2 \text{ mL})$$

$$= 0.0021944 \text{ mol CH}_3\text{COOH (unrounded)}$$

At the equivalence point, 0.0021944 mol NaOH will be added so the moles acid = moles base.

The NaOH will react with an equal amount of the acid, 0 mol CH₃COOH will remain, and 0.0021944 moles of CH₃COO⁻ will be formed.

	CH ₃ COOH(aq)	+	NaOH(aq)	→	H ₂ O(l)	+	CH ₃ COO ⁻ (aq)	+	Na ⁺ (aq)
Initial:	0.0021944 mol		0.0021944 mol		-		0		-
Change:	$- 0.0021944 \text{ mol}$		-0.0021944 mol		-		$+0.0021944 \text{ mol}$		-
Final:	0		0				0.0021944 mol		

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(42.0 + 58.989247) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.100989 \text{ L (unrounded)}$$

Concentration of CH₃COO⁻ at equivalence point:

$$\text{Molarity} = (0.0021944 \text{ mol CH}_3\text{COO}^-) / (0.100989 \text{ L}) = 0.021729 \text{ M (unrounded)}$$

Calculate K_b for CH₃COO⁻: $K_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5}$

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.556 \times 10^{-10} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of CH₃COO⁻:

	CH ₃ COO ⁻	+	H ₂ O	⇌	CH ₃ COOH	+	OH ⁻
Initial:	0.021729 M				0		0
Change:	-x				+x		+x
Equilibrium:	$0.021729 - x$				x		x

Determine the hydroxide ion concentration from the K_b , and then determine the pH from the pOH.

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{[x][x]}{[0.021729 - x]} = \frac{[x][x]}{[0.021729]} = 5.556 \times 10^{-10}$$

$$[\text{OH}^-] = x = 3.4745693 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pOH} = -\log (3.4745693 \times 10^{-6}) = 5.459099012 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.459099012 = 8.54090 = \mathbf{8.54}$$

b) The balanced chemical equation is:



The sodium ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of NaOH needed:

Volume =

$$\left(\frac{0.0390 \text{ mol HNO}_2}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (23.4 \text{ mL}) \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol HNO}_2} \right) \left(\frac{\text{L}}{0.0372 \text{ mol NaOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 24.532 = \mathbf{24.5 \text{ mL NaOH}}$$

Determine the moles of HNO₂ present:

$$\text{Moles} = \left(\frac{0.0390 \text{ mol HNO}_2}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (23.4 \text{ mL})$$

$$= 0.0009126 \text{ mol HNO}_2$$

At the equivalence point, 0.0009126 mol NaOH will be added so the moles acid = moles base.

The NaOH will react with an equal amount of the acid, 0 mol HNO₂ will remain, and 0.0009126 moles of NO₂⁻ will be formed.

	HNO ₂ (aq)	+	NaOH(aq)	→	H ₂ O(l)	+	NO ₂ ⁻ (aq)	+	Na ⁺ (aq)
Initial:	0.0009126 mol		0.0009126 mol		–		0		–
Change:	– 0.0009126 mol		– 0.0009126 mol		–		+ 0.0009126 mol		–
Final:	0		0				0.0009126 mol		

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(23.4 + 24.532) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.047932 \text{ L (unrounded)}$$

Concentration of NO₂⁻ at equivalence point:

$$\text{Molarity} = (0.0009126 \text{ mol NO}_2^-) / (0.047932 \text{ L}) = 0.0190395 \text{ M (unrounded)}$$

Calculate K_b for NO₂⁻:

$$K_a \text{ HNO}_2 = 7.1 \times 10^{-4}$$

$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (7.1 \times 10^{-4}) = 1.40845 \times 10^{-11} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of NO₂⁻:

	NO ₂ ⁻	+	H ₂ O	⇌	HNO ₂	+	OH ⁻
Initial:	0.0190395 M				0		0
Change:	– x				+ x		+ x
Equilibrium:	0.0190395 – x				x		x

Determine the hydroxide ion concentration from the K_b, and then determine the pH from the pOH.

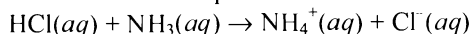
$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{[x][x]}{[0.0190395 - x]} = \frac{[x][x]}{[0.0190395]} = 1.40845 \times 10^{-11}$$

$$[\text{OH}^-] = x = 5.178431 \times 10^{-7} \text{ M (unrounded)}$$

$$\text{pOH} = -\log(5.178431 \times 10^{-7}) = 6.285802 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 6.285802 = 7.714198 = \mathbf{7.71}$$

19.42 a) The balanced chemical equation is:



The chloride ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of HCl needed:

Volume =

$$\left(\frac{0.234 \text{ mol NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (55.5 \text{ mL}) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol NH}_3} \right) \left(\frac{\text{L}}{0.135 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= \mathbf{96.2 \text{ mL HCl}}$$

Determine the moles of NH₃ present:

$$\text{Moles} = \left(\frac{0.234 \text{ mol NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (55.5 \text{ mL})$$

$$= 0.012987 \text{ mol NH}_3 \text{ (unrounded)}$$

At the equivalence point, 0.012987 mol HCl will be added so the moles acid = moles base. The HCl will react with an equal amount of the base, 0 mol NH₃ will remain, and 0.012987 moles of NH₄⁺ will be formed.

	HCl(aq)	+	NH ₃ (aq)	→	NH ₄ ⁺ (aq)	+	Cl ⁻ (aq)
Initial:	0.012987 mol		0.012987 mol		0		-
Change:	- 0.012987 mol		-0.012987 mol		+0.012987 mol		-
Final:	0		0		0.012987 mol		

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(55.5 + 96.2) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1517 \text{ L}$$

Concentration of NH₄⁺ at equivalence point:

$$\text{Molarity} = (0.012987 \text{ mol NH}_4^+) / (0.1517 \text{ L}) = 0.0856098 \text{ M (unrounded)}$$

Calculate K_a for NH₄⁺:

$$K_b \text{ NH}_3 = 1.76 \times 10^{-5}$$

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (1.76 \times 10^{-5}) = 5.6818 \times 10^{-10} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of NH₄⁺:

	NH ₄ ⁺	+	H ₂ O	⇌	NH ₃	+	H ₃ O ⁺
Initial:	0.0856098 M				0		0
Change:	-x				+x		+x
Equilibrium:	0.0856098 - x				x		x

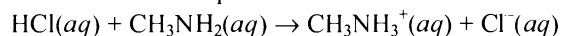
Determine the hydrogen ion concentration from the K_a , and then determine the pH.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{[x][x]}{[0.0856098 - x]} = \frac{[x][x]}{[0.0856098]} = 5.6818 \times 10^{-10}$$

$$x = [\text{H}_3\text{O}^+] = 6.974366 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.974366 \times 10^{-6}) = 5.1565 = \mathbf{5.16}$$

b) The balanced chemical equation is:



The chloride ions on the product side are written as separate species because they have no effect on the pH of the solution. Calculate the volume of HCl needed:

Volume =

$$\left(\frac{1.11 \text{ mol CH}_3\text{NH}_2}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (17.8 \text{ mL}) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol CH}_3\text{NH}_2} \right) \left(\frac{\text{L}}{0.135 \text{ mol HCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 146.3556 = \mathbf{146 \text{ mL HCl}}$$

Determine the moles of CH₃NH₂ present:

$$\text{Moles} = \left(\frac{1.11 \text{ mol CH}_3\text{NH}_2}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (17.8 \text{ mL})$$

$$= 0.019758 \text{ mol CH}_3\text{NH}_2 \text{ (unrounded)}$$

At the equivalence point, 0.019758 mol HCl will be added so the moles acid = moles base.

The HCl will react with an equal amount of the base, 0 mol CH₃NH₂ will remain, and 0.019758 moles of CH₃NH₃⁺ will be formed.

	HCl(aq)	+	CH ₃ NH ₂ (aq)	→	CH ₃ NH ₃ ⁺ (aq)	+	Cl ⁻ (aq)
Initial:	0.019758 mol		0.019758 mol		0		-
Change:	- 0.019758 mol		-0.019758 mol		+0.019758 mol		-
Final:	0		0		0.019758 mol		

Determine the liters of solution present at the equivalence point:

$$\text{Volume} = [(17.8 + 146.3556) \text{ mL}] (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1641556 \text{ L (unrounded)}$$

Concentration of CH₃NH₃⁺ at equivalence point:

$$\text{Molarity} = (0.019758 \text{ mol CH}_3\text{NH}_3^+) / (0.1641556 \text{ L}) = 0.122298 \text{ M (unrounded)}$$

Calculate K_a for CH₃NH₃⁺:

$$K_b \text{ CH}_3\text{NH}_2 = 4.4 \times 10^{-4}$$

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (4.4 \times 10^{-4}) = 2.2727 \times 10^{-11} \text{ (unrounded)}$$

Using a reaction table for the equilibrium reaction of CH₃NH₃⁺:

	CH_3NH_3^+	+	H_2O	\rightleftharpoons	CH_3NH_2	+	H_3O^+
Initial:	0.122298 M				0		0
Change:	-x				+x		+x
Equilibrium:	0.122298 - x				x		x

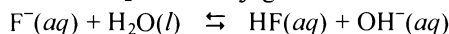
Determine the hydrogen ion concentration from the K_a , and then determine the pH.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = \frac{[x][x]}{[0.122298 - x]} = \frac{[x][x]}{[0.122298]} = 2.2727 \times 10^{-11}$$

$$x = [\text{H}_3\text{O}^+] = 1.66717 \times 10^{-6} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.66717 \times 10^{-6}) = 5.778019 = \mathbf{5.78}$$

- 19.44 Fluoride ion in CaF_2 is the conjugate base of the weak acid HF. The base hydrolysis reaction of fluoride ion

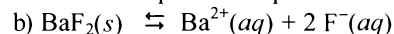


therefore is influenced by the pH of the solution. As the pH increases, $[\text{OH}^-]$ increases and the equilibrium shifts to the left to decrease $[\text{OH}^-]$ and increase the $[\text{F}^-]$. As the pH decreases, $[\text{OH}^-]$ decreases and the equilibrium shifts to the right to increase $[\text{OH}^-]$ and decrease $[\text{F}^-]$. The changes in $[\text{F}^-]$ influence the solubility of CaF_2 . Chloride ion is the conjugate base of a strong acid so it does not react with water. Thus, its concentration is not influenced by pH, and solubility of CaCl_2 does not change with pH.

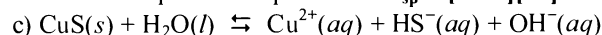
- 19.45 Consider the reaction $\text{AB}(s) \rightleftharpoons \text{A}^+(aq) + \text{B}^-(aq)$, where $Q_{sp} = [\text{A}^+][\text{B}^-]$. If $Q_{sp} > K_{sp}$, then there are more ions dissolved than expected at equilibrium, and the equilibrium shifts to the left and the compound AB precipitates. The excess ions precipitate as solid from the solution.

- 19.46 a) $\text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CO}_3^{2-}(aq)$

$$\text{Ion-product expression: } K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$



$$\text{Ion-product expression: } K_{sp} = [\text{Ba}^{2+}][\text{F}^-]^2$$



$$\text{Ion-product expression: } K_{sp} = [\text{Cu}^{2+}][\text{HS}^-][\text{OH}^-]$$

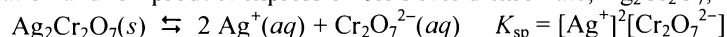
- 19.48 Write a reaction table, where S is the molar solubility of Ag_2CO_3 :

Concentration (M)	$\text{Ag}_2\text{CO}_3(s)$	\rightleftharpoons	$2 \text{Ag}^+(aq)$	+	$\text{CO}_3^{2-}(aq)$
Initial	—		0		0
Change	—		+ 2 S		+ S
Equilibrium	—		2 S		S

$$S = [\text{Ag}_2\text{CO}_3] = 0.032 \text{ M so } [\text{Ag}^+] = 2 S = 0.064 \text{ M and } [\text{CO}_3^{2-}] = S = 0.032 \text{ M}$$

$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (0.064)^2(0.032) = 1.31072 \times 10^{-4} = \mathbf{1.3 \times 10^{-4}}$$

- 19.50 The equation and ion-product expression for silver dichromate, $\text{Ag}_2\text{Cr}_2\text{O}_7$, is:



The solubility of $\text{Ag}_2\text{Cr}_2\text{O}_7$, converted from g/100 mL to M is:

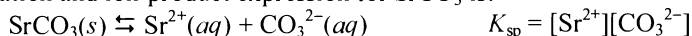
$$\text{Molar solubility} = S = \left(\frac{8.3 \times 10^{-3} \text{ g Ag}_2\text{Cr}_2\text{O}_7}{100 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol Ag}_2\text{Cr}_2\text{O}_7}{431.8 \text{ g Ag}_2\text{Cr}_2\text{O}_7} \right) = 0.00019221861 \text{ M (unrounded)}$$

Since 1 mol of $\text{Ag}_2\text{Cr}_2\text{O}_7$ dissociates to form 2 moles of Ag^+ , the concentration of Ag^+ is 2 S

$= 2(0.00019221861 \text{ M}) = 0.00038443723 \text{ M (unrounded)}$. The concentration of $\text{Cr}_2\text{O}_7^{2-}$ is $S = 0.00019221861 \text{ M}$ because 1 mol of $\text{Ag}_2\text{Cr}_2\text{O}_7$ dissociates to form 1 mol of $\text{Cr}_2\text{O}_7^{2-}$.

$$K_{sp} = [\text{Ag}^+]^2[\text{Cr}_2\text{O}_7^{2-}] = (2 S)^2(S) = (0.00038443723)^2(0.00019221861) = 2.8408 \times 10^{-11} = \mathbf{2.8 \times 10^{-11}}$$

- 19.52 The equation and ion-product expression for SrCO_3 is:



a) The solubility, S , in pure water equals $[\text{Sr}^{2+}]$ and $[\text{CO}_3^{2-}]$

Write a reaction table, where S is the molar solubility of SrCO_3 :

Concentration (M)	$\text{SrCO}_3(s)$	\rightleftharpoons	$\text{Sr}^{2+}(aq)$	+	$\text{CO}_3^{2-}(aq)$
Initial	—		0		0
Change	—		+ S		+ S
Equilibrium	—		S		S

$$K_{\text{sp}} = 5.4 \times 10^{-10} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = [S][S] = S^2$$

$$S = 2.32379 \times 10^{-5} = \mathbf{2.3 \times 10^{-5} M}$$

b) In $0.13 M \text{Sr}(\text{NO}_3)_2$, the initial concentration of Sr^{2+} is $0.13 M$.

Equilibrium $[\text{Sr}^{2+}] = 0.13 + S$ and equilibrium $[\text{CO}_3^{2-}] = S$ where S is the solubility of SrCO_3 .

Concentration (M)	$\text{SrCO}_3(s)$	\rightleftharpoons	$\text{Sr}^{2+}(aq)$	+	$\text{CO}_3^{2-}(aq)$
Initial	—		0.13		0
Change	—		+ S		+ S
Equilibrium	—		$0.13 + S$		S

$$K_{\text{sp}} = 5.4 \times 10^{-10} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = (0.13 + S)S$$

This calculation may be simplified by assuming S is small and setting $(0.13 + S) = (0.13)$.

$$K_{\text{sp}} = 5.4 \times 10^{-10} = (0.13)S$$

$$S = 4.1538 \times 10^{-9} = \mathbf{4.2 \times 10^{-9} M}$$

- 19.54 The equilibrium is: $\text{Ca}(\text{IO}_3)_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{IO}_3^-(aq)$. From the Appendix, $K_{\text{sp}}(\text{Ca}(\text{IO}_3)_2) = 7.1 \times 10^{-7}$.

a) Write a reaction table that reflects an initial concentration of $\text{Ca}^{2+} = 0.060 M$. In this case, Ca^{2+} is the common ion.

Concentration (M)	$\text{Ca}(\text{IO}_3)_2(s)$	\rightleftharpoons	$\text{Ca}^{2+}(aq)$	+	$2 \text{IO}_3^-(aq)$
Initial	—		0.060		0
Change	—		+ S		+ $2 S$
Equilibrium	—		$0.060 + S$		$2 S$

Assume that $0.060 + S \approx 0.060$ because the amount of compound that dissolves will be negligible in comparison to $0.060 M$.

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^-]^2 = (0.060)(2 S)^2 = 7.1 \times 10^{-7}$$

$$S = 1.71998 \times 10^{-3} = 1.7 \times 10^{-3} M$$

Check assumption: $(1.71998 \times 10^{-3} M) / (0.060 M) \times 100\% = 2.9\% < 5\%$, so the assumption is good.

S represents both the molar solubility of Ca^{2+} and $\text{Ca}(\text{IO}_3)_2$, so the molar solubility of $\text{Ca}(\text{IO}_3)_2$ is $\mathbf{1.7 \times 10^{-3} M}$.

b) In this case,

Concentration (M)	$\text{Ca}(\text{IO}_3)_2(s)$	\rightleftharpoons	$\text{Ca}^{2+}(aq)$	+	$2 \text{IO}_3^-(aq)$
Initial	—		0		0.060
Change	—		+ S		+ $2 S$
Equilibrium	—		S		$0.060 + 2 S$

The equilibrium concentration of Ca^{2+} is S , and the IO_3^- concentration is $0.060 + 2 S$. The iodate ion is the common ion in this problem.

Assume that $0.060 + 2 S \approx 0.060$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^-]^2 = (S)(0.060)^2 = 7.1 \times 10^{-7}$$

$$S = 1.97222 \times 10^{-4} = 2.0 \times 10^{-4} M$$

Check assumption: $(1.97222 \times 10^{-4} M) / (0.060 M) \times 100\% = 0.3\% < 5\%$, so the assumption is good.

S represents both the molar solubility of Ca^{2+} and $\text{Ca}(\text{IO}_3)_2$, so the molar solubility of $\text{Ca}(\text{IO}_3)_2$ is $\mathbf{2.0 \times 10^{-4} M}$.

- 19.56 The larger the K_{sp} , the larger the molar solubility if the number of ions are equal.

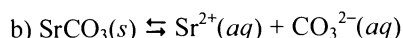
a) $\text{Mg}(\text{OH})_2$ with $K_{\text{sp}} = 6.3 \times 10^{-10}$ has higher molar solubility than $\text{Ni}(\text{OH})_2$ with $K_{\text{sp}} = 6 \times 10^{-16}$.

b) PbS with $K_{\text{sp}} = 3 \times 10^{-25}$ has higher molar solubility than CuS with $K_{\text{sp}} = 8 \times 10^{-34}$.

c) Ag_2SO_4 with $K_{\text{sp}} = 1.5 \times 10^{-5}$ has higher molar solubility than MgF_2 with $K_{\text{sp}} = 7.4 \times 10^{-9}$.

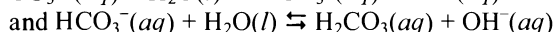
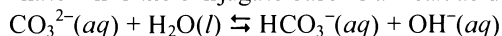
- 19.58 a) $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$

The chloride ion is the anion of a strong acid, so it does not react with H_3O^+ . The solubility is not affected by pH.



The strontium ion is the cation of a strong base, so pH will not affect its solubility.

The carbonate ion is the conjugate base of a weak acid and will act as a base:



The H_2CO_3 will decompose to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. The gas will escape and further shift the equilibrium. Changes in pH will change the $[\text{CO}_3^{2-}]$, so the solubility of SrCO_3 will increase with decreasing pH. **Solubility increases with addition of H_3O^+ (decreasing pH).**

- 19.60 The ion-product expression for $\text{Cu}(\text{OH})_2$ is $K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2$ and, from the Appendix, K_{sp} equals 2.2×10^{-20} . To decide if a precipitate will form, calculate Q_{sp} with the given quantities and compare it to K_{sp} .

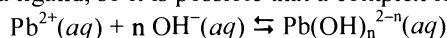
$$[\text{Cu}^{2+}] = \left(\frac{1.0 \times 10^{-3} \text{ mol Cu}(\text{NO}_3)_2}{L} \right) \left(\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu}(\text{NO}_3)_2} \right) = 1.0 \times 10^{-3} M \text{ Cu}^{2+}$$

$$[\text{OH}^-] = \left(\frac{0.075 \text{ g KOH}}{1.0 L} \right) \left(\frac{1 \text{ mol KOH}}{56.11 \text{ g KOH}} \right) \left(\frac{1 \text{ mol OH}^-}{1 \text{ mol KOH}} \right) = 1.33666 \times 10^{-3} M \text{ OH}^- \text{ (unrounded)}$$

$$Q_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (1.0 \times 10^{-3})(1.33666 \times 10^{-3})^2 = 1.7866599 \times 10^{-9} \text{ (unrounded)}$$

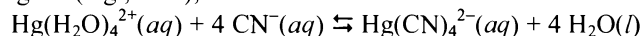
Q_{sp} is greater than K_{sp} ($1.8 \times 10^{-9} > 2.2 \times 10^{-20}$), so **$\text{Cu}(\text{OH})_2$ will precipitate.**

- 19.65 In the context of this equilibrium only, the increased solubility with added OH^- appears to be a violation of Le Châtelier's Principle. Adding OH^- should cause the equilibrium to shift towards the left, decreasing the solubility of PbS . Before accepting this conclusion, other possible equilibria must be considered. Lead is a metal ion and hydroxide ion is a ligand, so it is possible that a complex ion forms between the lead ion and hydroxide ion:



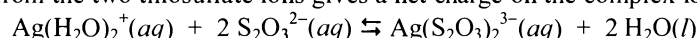
This decreases the concentration of Pb^{2+} , shifting the solubility equilibrium to the right to dissolve more PbS .

- 19.66 In many cases, a hydrated metal complex (e.g., $\text{Hg}(\text{H}_2\text{O})_4^{2+}$) will exchange ligands when placed in a solution of another ligand (e.g., CN^-),



Note that both sides of the equation have the same "overall" charge of -2 . The mercury complex changes from $+2$ to -2 because water is a neutral *molecular* ligand, whereas cyanide is an *ionic* ligand.

- 19.68 The two water ligands are replaced by two thiosulfate ion ligands. The $+1$ charge from the silver ion plus -4 charge from the two thiosulfate ions gives a net charge on the complex ion of -3 .



- 19.70 Write the ion-product equilibrium reaction and the complex-ion equilibrium reaction. Sum the two reactions to yield an overall reaction; multiply the two constants to obtain K_{overall} . Write a reaction table where

$S = [\text{AgI}]_{\text{dissolved}} = [\text{Ag}(\text{NH}_3)_2^+]$.

Solubility-product: $\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$

Complex-ion: $\text{Ag}^+(aq) + 2 \text{ NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$

Overall: $\text{AgI}(s) + 2 \text{ NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq) + \text{I}^-(aq)$

$$K_{\text{overall}} = K_{sp} \times K_f = (8.3 \times 10^{-17})(1.7 \times 10^7) = 1.411 \times 10^{-9} \text{ (unrounded)}$$

Reaction table:

Concentration (M)	$\text{AgI}(s)$	+	$2 \text{ NH}_3(aq)$	\rightleftharpoons	$\text{Ag}(\text{NH}_3)_2^+(aq)$	+	$\text{I}^-(aq)$
Initial	—		2.5		0		0
Change	—		$-2S$		$+S$		$+S$
Equilibrium	—		$2.5 - 2S$		S		S

Assume that $2.5 - 2S \approx 2.5$ because K_{overall} is so small.

$$K_{\text{overall}} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{I}^-]}{[\text{NH}_3]^2} = \frac{[S][S]}{[2.5 - S]^2} = \frac{[S][S]}{[2.5]^2} = 1.411 \times 10^{-9}$$

$$S = 9.3908 \times 10^{-5} = \mathbf{9.4 \times 10^{-5} M}$$

- 19.74 The minimum urate ion concentration necessary to cause a deposit of sodium urate is determined by the K_{sp} for the salt. Convert solubility in g/100. mL to molar solubility and calculate K_{sp} . Substituting $[Na^+]$ and K_{sp} into the ion-product expression allows one to find $[Ur^-]$.

Molar solubility of NaUr:

$$[NaUr] = \left(\frac{0.085 \text{ g NaUr}}{100. \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol NaUr}}{190.10 \text{ mol NaUr}} \right) = 4.47133 \times 10^{-3} \text{ M NaUr (unrounded)}$$

$$4.47133 \times 10^{-3} \text{ M NaUr} = [Na^+] = [Ur^-]$$

$$K_{sp} = [Na^+][Ur^-] = (4.47133 \times 10^{-3})(4.47133 \times 10^{-3}) = 1.999279 \times 10^{-5} \text{ M (unrounded)}$$

When $[Na^+] = 0.15 \text{ M}$:

$$K_{sp} = 1.999279 \times 10^{-5} \text{ M} = [0.15][Ur^-]$$

$$[Ur^-] = 1.33285 \times 10^{-4} \text{ (unrounded)}$$

The minimum urate ion concentration that will cause precipitation of sodium urate is **$1.3 \times 10^{-4} \text{ M}$** .

- 19.76 a) The solubility equilibrium for KCl is: $KCl(s) \rightleftharpoons K^+(aq) + Cl^-(aq)$

$$K_{sp} = [K^+][Cl^-] = (3.7)(3.7) = 13.69 = \mathbf{14}$$

- b) Determine the total concentration of chloride ion in each beaker after the HCl has been added. This requires the moles originally present and the moles added.

Original moles from the KCl:

$$\text{Moles } K^+ = \text{Moles } Cl^- = \left(\frac{3.7 \text{ mol KCl}}{1 \text{ L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100. \text{ mL}) \left(\frac{1 \text{ mol } Cl^- \text{ ion}}{1 \text{ mol KCl}} \right) = 0.37 \text{ mol } Cl^-$$

Original moles from the 6.0 M HCl:

$$\text{Moles } Cl^- = \left(\frac{6.0 \text{ mol HCl}}{1 \text{ L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100. \text{ mL}) \left(\frac{1 \text{ mol } Cl^-}{1 \text{ mol HCl}} \right) = 0.60 \text{ mol } Cl^-$$

This results in $(0.37 + 0.60) \text{ mol} = 0.97 \text{ mol } Cl^-$

Original moles from the 12 M HCl:

$$\text{Moles } Cl^- = \left(\frac{12 \text{ mol HCl}}{1 \text{ L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100. \text{ mL}) \left(\frac{1 \text{ mol } Cl^-}{1 \text{ mol HCl}} \right) = 1.2 \text{ mol } Cl^-$$

This results in $(0.37 + 1.2) \text{ mol} = 1.57 \text{ mol } Cl^-$ (unrounded)

Volume of mixed solutions = $(100. \text{ mL} + 100. \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.200 \text{ L}$

After the mixing:

$$[K^+] = (0.37 \text{ mol } K^+) / (0.200 \text{ L}) = 1.85 \text{ M } K^+ \text{ (unrounded)}$$

From 6.0 M HCl:

$$[Cl^-] = (0.97 \text{ mol } Cl^-) / (0.200 \text{ L}) = 4.85 \text{ M } Cl^- \text{ (unrounded)}$$

From 12 M HCl:

$$[Cl^-] = (1.57 \text{ mol } Cl^-) / (0.200 \text{ L}) = 7.85 \text{ M } Cl^- \text{ (unrounded)}$$

Determine a Q_{sp} value to see if K_{sp} is exceeded. If $Q < K_{sp}$, nothing will precipitate.

From 6.0 M HCl

$$Q_{sp} = [K^+][Cl^-] = (1.85)(4.85) = 8.9725 = 9.0 < 14, \text{ so no KCl will precipitate.}$$

From 12 M HCl

$$Q_{sp} = [K^+][Cl^-] = (1.85)(7.85) = 14.5225 = 15 > 14, \text{ so KCl will precipitate.}$$

The mass of KCl that will precipitate when 12 M HCl is added:

Equal amounts of K and Cl will precipitate. Let x be the molarity change.

$$K_{sp} = [K^+][Cl^-] = (1.85 - x)(7.85 - x) = 13.69$$

$$x = 0.088697657 = 0.09$$

This is the change in the molarity of each of the ions.

$$\text{Mass KCl} = \left(\frac{0.088697657 \text{ mol } K^+}{1 \text{ L}} \right) (0.200 \text{ L}) \left(\frac{1 \text{ mol KCl}}{1 \text{ mol } K^+} \right) \left(\frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} \right) = 1.32248 = \mathbf{1 \text{ g KCl}}$$

- 19.78 a) Use the Henderson-Hasselbalch equation. $K_{a1} = 4.5 \times 10^{-7}$ (From Appendix C)
 $pK_a = -\log K_a = -\log(4.5 \times 10^{-7}) = 6.34679$ (unrounded)

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.40 = 6.34679 + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$1.05321 = \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 11.3034235 \text{ (unrounded)}$$

$$\frac{[H_2CO_3]}{[HCO_3^-]} = 0.0884688 = \mathbf{0.088}$$

- b) Use the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.20 = 6.34679 + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$0.85321 = \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 7.131978 \text{ (unrounded)}$$

$$\frac{[H_2CO_3]}{[HCO_3^-]} = 0.14021 = \mathbf{0.14}$$

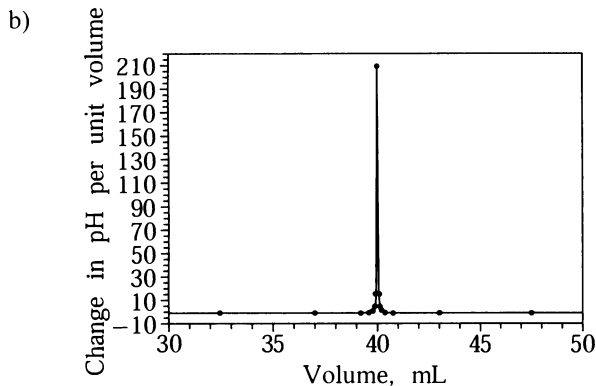
- 19.80 An indicator changes color when the buffer component ratio of the two forms of the indicator changes from a value greater than 1 to a value less than 1. The pH at which the ratio equals 1 is equal to pK_a . The midpoint in the pH range of the indicator is a good estimate of the pK_a of the indicator.

$$pK_a = (3.4 + 4.8)/2 = 4.1 \quad K_a = 10^{-4.1} = 7.943 \times 10^{-5} = \mathbf{8 \times 10^{-5}}$$

- 19.81 a) A spreadsheet will help you to quickly calculate $\Delta pH/\Delta V$ and average volume for each data point. At the equivalence point, the pH changes drastically when only a small amount of base is added, therefore, $\Delta pH/\Delta V$ is at a maximum at the equivalence point.

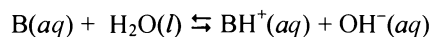
V(mL)	pH	$\frac{\Delta pH}{\Delta V}$	$V_{\text{average}}(\text{mL})$
0.00	1.00		
10.00	1.22	0.022	5.00
20.00	1.48	0.026	15.00
30.00	1.85	0.037	25.00
35.00	2.18	0.066	32.50
39.00	2.89	0.18	37.00
39.50	3.20	0.62	39.25
39.75	3.50	1.2	39.63
39.90	3.90	2.67	39.83
39.95	4.20	6	39.93
39.99	4.90	18	39.97
40.00	7.00	200	40.00
40.01	9.40	200	40.01

40.05	9.80	10	40.03
40.10	10.40	10	40.08
40.25	10.50	0.67	40.18
40.50	10.79	1.2	40.38
41.00	11.09	0.60	40.75
45.00	11.76	0.17	43.00
50.00	12.05	0.058	47.50
60.00	12.30	0.025	55.00
70.00	12.43	0.013	65.00
80.00	12.52	0.009	75.00



Maximum slope (equivalence point) is at $V = 40.00$ mL

19.84 The equation that describes the behavior of a weak base in water is:



$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

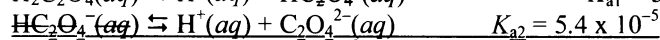
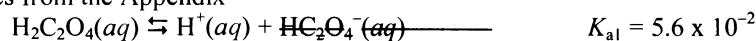
$$-\log K_b = -\log \frac{[BH^+][OH^-]}{[B]}$$

$$-\log K_b = -\log \frac{[BH^+]}{[B]} - \log [OH^-]$$

$$pK_b = -\log \frac{[BH^+]}{[B]} + pOH$$

$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

19.89 K values from the Appendix



$$K = \frac{[H^+]^2 [C_2O_4^{2-}]}{[H_2C_2O_4]} \quad [C_2O_4^{2-}] = K[H_2C_2O_4] / [H^+]^2$$

a) At pH = 5.5 $[H^+] = 10^{-5.5} = 3.162 \times 10^{-6} M$ (unrounded)

$$[C_2O_4^{2-}] = K[H_2C_2O_4] / [H^+]^2 = (3.024 \times 10^{-6}) (3.0 \times 10^{-3}) / (3.162 \times 10^{-6})^2$$

$$[C_2O_4^{2-}] = 9.07359 \times 10^{-8} M \text{ (unrounded)}$$

$$Q = [Ca^{2+}][C_2O_4^{2-}]$$

$$Q = (2.6 \times 10^{-3}) (9.07359 \times 10^{-8}) = 2.3591 \times 10^{-10} = 2.4 \times 10^{-10} < K_{sp} = \text{No precipitate}$$

b) At pH = 7.0 $[H^+] = 10^{-7.0} = 1 \times 10^{-7} M$

$$[C_2O_4^{2-}] = K[H_2C_2O_4] / [H^+]^2 = (3.024 \times 10^{-6}) (3.0 \times 10^{-3}) / (1 \times 10^{-7})^2$$

$$[C_2O_4^{2-}] = 9.072 \times 10^{-5} M \text{ (unrounded)}$$

$$Q = (2.6 \times 10^{-3}) (9.072 \times 10^{-5}) = 2.35872 \times 10^{-7} = 2.4 \times 10^{-7} > K_{sp} = \text{Precipitate forms}$$

c) The higher pH would favor precipitation.

- 19.92 To find the volume of rain, first convert the inches to yards and find the volume in yd^3 . Then convert units to cm^3 and on to L.

$$(10.0 \text{ acres}) \left(\frac{4.840 \times 10^3 \text{ yd}^2}{1 \text{ acre}} \right) \left(\frac{36 \text{ in}}{1 \text{ yd}} \right)^2 (1.00 \text{ in}) \left(\frac{2.54 \text{ cm}}{1 \text{ in}} \right)^3 \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 1.0279015 \times 10^6 \text{ L (unrounded)}$$

- a) At $\text{pH} = 4.20$, $[\text{H}_3\text{O}^+] = 10^{-4.20} = 6.3095734 \times 10^{-5} \text{ M (unrounded)}$

$$\text{Mol H}_3\text{O}^+ = (6.3095734 \times 10^{-5} \text{ M}) (1.0279015 \times 10^6 \text{ L}) = 64.8562 = \mathbf{65 \text{ mol}}$$

b) Volume = $(10.0 \text{ acres}) \left(\frac{4.840 \times 10^3 \text{ yd}^2}{1 \text{ acre}} \right) \left(\frac{36 \text{ in}}{1 \text{ yd}} \right)^2 (10.0 \text{ ft}) \left(\frac{12 \text{ in}}{1 \text{ ft}} \right) \left(\frac{2.54 \text{ cm}}{1 \text{ in}} \right)^3 \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right)$

$$= 1.23348 \times 10^8 \text{ L (unrounded)}$$

$$\text{Total volume of lake after rain} = 1.23348 \times 10^8 \text{ L} + 1.0279015 \times 10^6 \text{ L} = 1.243759 \times 10^8 \text{ L (unrounded)}$$

$$[\text{H}_3\text{O}^+] = 64.8562 \text{ mol H}_3\text{O}^+ / 1.243759 \times 10^8 \text{ L} = 5.214531 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(5.214531 \times 10^{-7}) = 6.2827847 = \mathbf{6.28}$$

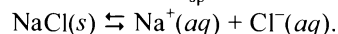
- c) Each mol of H_3O^+ requires one mole of HCO_3^- for neutralization.

$$\text{Mass} = (64.8562 \text{ mol H}_3\text{O}^+) \left(\frac{1 \text{ mol HCO}_3^-}{1 \text{ mol H}_3\text{O}^+} \right) \left(\frac{61.02 \text{ g HCO}_3^-}{1 \text{ mol HCO}_3^-} \right) = 3.97575 \times 10^3 = \mathbf{4.0 \times 10^3 \text{ g HCO}_3^-}$$

- 19.93 The molarity of a saturated NaCl solution must be found.

$$M \text{ NaCl} = \left(\frac{317 \text{ g NaCl}}{\text{L}} \right) \left(\frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) = 5.42436687 \text{ M NaCl (unrounded)}$$

Determine the K_{sp} from the molarity just calculated.



$$K_{\text{sp}} = [\text{Na}^+][\text{Cl}^-] = S^2 = (5.42436687)^2 = 29.42375594 = 29.4$$

$$\text{Moles of Cl}^- \text{ initially} = \left(\frac{5.4236687 \text{ mol NaCl}}{\text{L}} \right) (0.100 \text{ L}) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} \right) = 0.54236687 \text{ mol Cl}^- \text{ (unrounded)}$$

This is the same as the moles of Na^+ in the solution.

$$\text{Moles of Cl}^- \text{ added} = \left(\frac{7.85 \text{ mol HCl}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (25.5 \text{ mL}) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol HCl}} \right) = 0.200175 \text{ mol Cl}^- \text{ (unrounded)}$$

0.100 L of saturated solution contains 0.542 mol each Na^+ and Cl^- , to which you are adding 0.2 mol of additional Cl^- from HCl.

$$\text{Volume of mixed solutions} = 0.100 \text{ L} + (25.5 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL}) = 0.1255 \text{ L (unrounded)}$$

$$\text{Molarity of Cl}^- \text{ in mixture} = [(0.54236687 + 0.200175) \text{ mol Cl}^-] / (0.1255 \text{ L}) = 5.916668 \text{ M Cl}^- \text{ (unrounded)}$$

$$\text{Molarity of Na}^+ \text{ in mixture} = (0.54236687 \text{ mol Na}^+) / (0.1255 \text{ L}) = 4.321648 \text{ M Na}^+ \text{ (unrounded)}$$

Determine a Q value and compare this value to the K_{sp} to determine if precipitation will occur.

$$Q_{\text{sp}} = [\text{Na}^+][\text{Cl}^-] = (4.321648) (5.916668) = 25.569756 = 25.6$$

Since $Q_{\text{sp}} < K_{\text{sp}}$, no NaCl will precipitate.

- 19.95 a) For the solution to be a buffer, both HA and A^- must be present in the solution. This situation occurs in **A** and **D**.

- b) Box A

The amounts of HA and A^- are equal.

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}} \right) \quad \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) = 1 \text{ when the amounts of HA and } \text{A}^- \text{ are equal}$$

$$\text{pH} = \text{pK}_a + \log 1$$

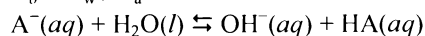
$$\text{pH} = \text{pK}_a = -\log(4.5 \times 10^{-5}) = 4.346787 = \mathbf{4.35}$$

Box B

Only A^- is present at a concentration of 0.10 M.

The K_b for A^- is needed.

$$K_b = K_w / K_a = 1.0 \times 10^{-14} / 4.5 \times 10^{-5} = 2.222 \times 10^{-10} \text{ (unrounded)}$$



Initial:	0.10 M	0	0
Change:	-x	-x	-x
Equilibrium:	0.10 - x	x	x

$$K_b = \frac{[HA][OH^-]}{[A^-]} = 2.222 \times 10^{-10}$$

$$K_b = \frac{[x][x]}{[0.10 - x]} = 2.222 \times 10^{-10} \quad \text{Assume that } x \text{ is small compared to } 0.10.$$

$$K_b = 2.222 \times 10^{-10} = \frac{(x)(x)}{(0.10)}$$

$$x = 4.7138095 \times 10^{-6} \text{ M } OH^- \text{ (unrounded)}$$

Check assumption: $(4.7138095 \times 10^{-6} / 0.10) \times 100\% = 0.005\%$ error, so the assumption is valid.

$$[H_3O^+] = K_w / [OH^-] = (1.0 \times 10^{-14}) / (4.7138095 \times 10^{-6})$$

$$= 2.1214264 \times 10^{-9} \text{ M } H_3O^+ \text{ (unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (2.1214264 \times 10^{-9}) = 8.67337 = \mathbf{8.67}$$

Box C

This is a 0.10 M HA solution. The hydrogen ion, and hence the pH, can be determined from the K_a .

Concentration	HA(aq)	+	H ₂ O(l)	\rightleftharpoons	H ₃ O ⁺ (aq)	+ A ⁻ (aq)
Initial	0.10		—		0	0
Change	-x				+x	+x
Equilibrium	0.10 - x				x	x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 4.5 \times 10^{-5} = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = 4.5 \times 10^{-5} = \frac{(x)(x)}{(0.10 - x)} \quad \text{Assume that } x \text{ is small compared to } 0.10.$$

$$K_a = 4.5 \times 10^{-5} = \frac{(x)(x)}{(0.10)}$$

$$[H_3O^+] = x = 2.12132 \times 10^{-3} \text{ (unrounded)}$$

Check assumption: $(2.12132 \times 10^{-3} / 0.10) \times 100\% = 2\%$ error, so the assumption is valid.

$$pH = -\log [H_3O^+] = -\log (2.12132 \times 10^{-3}) = 2.67339 = \mathbf{2.67}$$

Box D

This is a buffer with a ratio of $[A^-] / [HA] = 5 / 3$.

Use the Henderson-Hasselbalch equation for this buffer.

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

$$pH = -\log (4.5 \times 10^{-5}) + \log \left[\frac{5}{3} \right] = 4.568636 = \mathbf{4.57}$$

c) The initial stage in the titration would only have HA present. The amount of HA will decrease, and the amount of A^- will increase until only A^- remains. The sequence will be: **C, A, D, and B**.

d) At the equivalence point, all the HA will have reacted with the added base. This occurs in scene **B**.

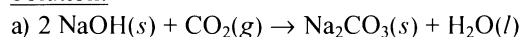
Chapter 20 Thermodynamics: Entropy, Free Energy, and the Direction of Chemical Reactions

FOLLOW-UP PROBLEMS

- 20.1 a) $\text{PCl}_5(\text{g})$. For substances with the same type of atoms and in the same physical state, entropy increases with increasing number of atoms per molecule because more types of molecular motion are available.
 b) $\text{BaCl}_2(\text{s})$. Entropy increases with increasing atomic size. The Ba^{2+} ion and Cl^- ion are larger than the Ca^{2+} ion and F^- ion, respectively.
 c) $\text{Br}_2(\text{g})$. Entropy increases from solid \rightarrow liquid \rightarrow gas.

- 20.2 Plan: Predict the sign of $\Delta S_{\text{sys}}^\circ$ by comparing the randomness of the products with the randomness of the reactants. Calculate $\Delta S_{\text{sys}}^\circ$ using Appendix B values.

Solution:



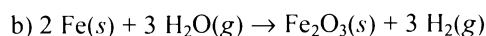
The $\Delta S_{\text{sys}}^\circ$ is predicted to decrease ($\Delta S_{\text{sys}}^\circ < 0$) because the more random, gaseous reactant is transformed into a more ordered, liquid product.

$$\Delta S_{\text{sys}}^\circ = \Sigma(m \Delta S_{\text{products}}^\circ) - \Sigma(n \Delta S_{\text{reactants}}^\circ)$$

$$\Delta S_{\text{sys}}^\circ = [(1 \text{ mol Na}_2\text{CO}_3) (S_{\text{Na}_2\text{CO}_3(\text{s})}^\circ) + 1 \text{ mol H}_2\text{O}) (S_{\text{H}_2\text{O}(\text{l})}^\circ)] - [(2 \text{ mol NaOH}) (S_{\text{NaOH}(\text{s})}^\circ) + 1 \text{ mol CO}_2) (S_{\text{CO}_2(\text{g})}^\circ)]$$

$$\Delta S_{\text{sys}}^\circ = [(1 \text{ mol Na}_2\text{CO}_3) (139 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol H}_2\text{O}) (69.940 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol NaOH}) (64.454 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol CO}_2) (213.7 \text{ J/mol}\cdot\text{K})] = -133.668 = -134 \text{ J/K}$$

$\Delta S_{\text{sys}}^\circ < 0$ as predicted.



The change in gaseous moles is zero, so the sign of $\Delta S_{\text{sys}}^\circ$ is difficult to predict. Iron(III) oxide has greater entropy than Fe because it is more complex, but this is offset by the greater molecular complexity of H_2O versus H_2 .

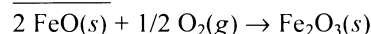
$$\Delta S_{\text{sys}}^\circ = [(1 \text{ mol Fe}_2\text{O}_3) (S_{\text{Fe}_2\text{O}_3}^\circ) + (3 \text{ mol H}_2) (S_{\text{H}_2}^\circ)] - [(2 \text{ mol Fe}) (S_{\text{Fe}}^\circ) + (3 \text{ mol H}_2\text{O}) (S_{\text{H}_2\text{O}}^\circ)]$$

$$\Delta S_{\text{sys}}^\circ = [(1 \text{ mol Fe}_2\text{O}_3) (87.400 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol Fe}) (27.3 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol H}_2\text{O}) (188.72 \text{ J/mol}\cdot\text{K})] = -141.56 = -141.6 \text{ J/K}$$

The negative $\Delta S_{\text{sys}}^\circ$ for equation (b) reflects that greater entropy of H_2O versus H_2 does outweigh the greater entropy of Fe_2O_3 versus Fe.

- 20.3 Plan: Write the balanced equation for the reaction and calculate the $\Delta S_{\text{sys}}^\circ$ using Appendix B. Determine the $\Delta S_{\text{surr}}^\circ$ by first finding $\Delta H_{\text{rxn}}^\circ$. Add $\Delta S_{\text{surr}}^\circ$ to $\Delta S_{\text{sys}}^\circ$ to verify that $\Delta S_{\text{univ}}^\circ$ is positive.

Solution:



$$\Delta S_{\text{sys}}^\circ = [(1 \text{ mol Fe}_2\text{O}_3) (S_{\text{Fe}_2\text{O}_3}^\circ)] - [(2 \text{ mol FeO}) (S_{\text{FeO}}^\circ) + (1/2 \text{ mol O}_2) (S_{\text{O}_2}^\circ)]$$

$$\Delta S_{\text{sys}}^\circ = [(1 \text{ mol Fe}_2\text{O}_3) (87.400 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol FeO}) (60.75 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{sys}}^\circ = -136.6 \text{ J/K (entropy change is expected to be negative because gaseous reactant is converted to solid product)}$$

$$\Delta H_{\text{sys}}^{\circ} = [(1 \text{ mol Fe}_2\text{O}_3) (\Delta H_f^{\circ} \text{Fe}_2\text{O}_3)] - [(2 \text{ mol FeO}) (\Delta H_f^{\circ} \text{FeO}) + (1/2 \text{ mol O}_2) (\Delta H_f^{\circ} \text{O}_2)]$$

$$\Delta H_{\text{sys}}^{\circ} = [(1 \text{ mol Fe}_2\text{O}_3) (-825.5 \text{ kJ/mol})] - [(2 \text{ mol FeO}) (-272.0 \text{ kJ/mol}) + (1/2 \text{ mol O}_2) (0)]$$

$$\Delta H_{\text{sys}}^{\circ} = -281.5 \text{ kJ}$$

$$\Delta S_{\text{surr}}^{\circ} = -\frac{\Delta H_{\text{sys}}^{\circ}}{T} = -\frac{-281.5 \text{ kJ}}{298 \text{ K}} = 0.94463 \text{ kJ/K}(10^3 \text{ J/1 kJ}) = 944.63 \text{ J/K (unrounded)}$$

$$\Delta S_{\text{univ}}^{\circ} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}}^{\circ} = (-136.6 \text{ J/K}) + (944.63 \text{ J/K}) = 808.03 = \mathbf{808 \text{ J/K}}$$

Because $\Delta S_{\text{univ}}^{\circ}$ is positive, the reaction is spontaneous at 298 K.

Check: This process is also known as rusting. Common sense tells us that rusting occurs spontaneously.

Although the entropy change of the system is negative, the increase in entropy of the surroundings is large enough to offset $\Delta S_{\text{sys}}^{\circ}$.

- 20.4 Plan: Calculate the $\Delta H_{\text{rxn}}^{\circ}$ using ΔH_f° values from Appendix B. Calculate $\Delta S_{\text{rxn}}^{\circ}$ from tabulated S° values and then use the relationship $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$.

Solution:

$$\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol NO}_2) (\Delta H_f^{\circ} (\text{NO}_2))] - [(2 \text{ mol NO}) (\Delta H_f^{\circ} (\text{NO})) + (1 \text{ mol O}_2) (\Delta H_f^{\circ} (\text{O}_2))]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol NO}_2) (33.2 \text{ kJ/mol})] - [(2 \text{ mol NO}) (90.29 \text{ kJ/mol}) + (1 \text{ mol O}_2) (0)]$$

$$\Delta H_{\text{rxn}}^{\circ} = -114.18 = -114.2 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol NO}_2) (S^{\circ} (\text{NO}_2))] - [(2 \text{ mol NO}) (S^{\circ} (\text{NO})) + (1 \text{ mol O}_2) (S^{\circ} (\text{O}_2))]$$

$$\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol NO}_2) (239.9 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol NO}) (210.65 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^{\circ} = -146.5 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -114.2 \text{ kJ} - [(298 \text{ K}) (-146.5 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = -70.543 = \mathbf{-70.5 \text{ kJ}}$$

- 20.5 Plan: Use ΔG_f° values from Appendix B to calculate $\Delta G_{\text{rxn}}^{\circ}$. $\Delta G_{\text{sys}}^{\circ} = \Sigma(m \Delta G_f^{\circ}(\text{products})) - \Sigma(n \Delta G_f^{\circ}(\text{reactants}))$

Solution:

$$\text{a) } \Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol NO}_2) (\Delta G_f^{\circ} (\text{NO}_2))] - [(2 \text{ mol NO}) (\Delta G_f^{\circ} (\text{NO})) + (1 \text{ mol O}_2) (\Delta G_f^{\circ} (\text{O}_2))]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol NO}_2) (51 \text{ kJ/mol})] - [(2 \text{ mol NO}) (86.60 \text{ kJ/mol}) + (1 \text{ mol O}_2) (0)]$$

$$\Delta G_{\text{rxn}}^{\circ} = -71.2 = \mathbf{-71 \text{ kJ}} \text{ (result agrees with answer in 20.4)}$$

$$\text{b) } \Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol CO}) (\Delta G_f^{\circ} (\text{CO}))] - [(2 \text{ mol C}) (\Delta G_f^{\circ} (\text{C})) + (1 \text{ mol O}_2) (\Delta G_f^{\circ} (\text{O}_2))]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol CO}) (-137.2 \text{ kJ/mol})] - [(2 \text{ mol C}) (0) + (1 \text{ mol O}_2) (0)]$$

$$\Delta G_{\text{rxn}}^{\circ} = \mathbf{-274.4 \text{ kJ}}$$

- 20.6 Plan: Examine the equation $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ and determine which combination of enthalpy and entropy will describe the given reaction.

Solution: Two choices can already be eliminated:

1) When $\Delta H > 0$ (endothermic reaction) and $\Delta S < 0$ (entropy decreases), the reaction is always nonspontaneous, regardless of temperature, so this combination does not describe the reaction.

2) When $\Delta H < 0$ (exothermic reaction) and $\Delta S > 0$ (entropy increases), the reaction is always spontaneous, regardless of temperature, so this combination does not describe the reaction.

Two combinations remain: 3) $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$, or 4) $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} < 0$. If the reaction becomes spontaneous at -40°C , this means that ΔG° becomes negative at lower temperatures. Case 3) becomes spontaneous at higher temperatures, when the $-T \Delta S^{\circ}$ term is larger than the positive enthalpy term. By process of elimination, Case 4) describes the reaction.

Check: At a lower temperature, the negative ΔH° becomes larger than the positive ($-T \Delta S^{\circ}$) value, so ΔG° becomes negative.

- 20.7 **Plan:** Write a balanced equation for the dissociation of hypobromous acid in water. The free energy of the reaction at standard state (part (a)) is calculated using $\Delta G^\circ = -RT \ln K$. The free energy of the reaction under non-standard state conditions is calculated using $\Delta G = \Delta G^\circ + RT \ln Q$.

Solution: $\text{HBrO}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{BrO}^-(aq) + \text{H}_3\text{O}^+(aq)$

a) $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K}) (298) \ln (2.3 \times 10^{-9}) = 4.927979 \times 10^4 = \mathbf{4.9 \times 10^4 \text{ J/mol}}$

b) $Q = \frac{[\text{H}_3\text{O}^+][\text{BrO}^-]}{[\text{HBrO}]} = \frac{[6.0 \times 10^{-4}][0.10]}{[0.20]}$

$$\Delta G = \Delta G^\circ + RT \ln Q = (4.927979 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/mol}\cdot\text{K}) (298 \text{ K}) \ln \frac{[6.0 \times 10^{-4}][0.10]}{[0.20]}$$

$$= 2.9182399 \times 10^4 = \mathbf{2.9 \times 10^4 \text{ J/mol}}$$

Check: The value of K_a is very small, so it makes sense that ΔG° is a positive number. The natural log of a negative exponent gives a negative number ($\ln 3.0 \times 10^{-4}$), so the value of ΔG decreases with concentrations lower than the standard state 1 M values.

END-OF-CHAPTER PROBLEMS

- 20.2 A spontaneous process occurs by itself (possibly requiring an initial input of energy) whereas a nonspontaneous process requires a continuous supply of energy to make it happen. It is possible to cause a nonspontaneous process to occur, but the process stops once the energy source is removed. A reaction that is found to be nonspontaneous under one set of conditions may be spontaneous under a different set of conditions (different temperature, different concentrations).
- 20.5 Vaporization is the change of a liquid substance to a gas so $\Delta S_{\text{vaporization}} = S_{\text{gas}} - S_{\text{liquid}}$. Fusion is the change of a solid substance into a liquid so $\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}}$. Vaporization involves a greater change in volume than fusion. Thus, the transition from liquid to gas involves a greater entropy change than the transition from solid to liquid.
- 20.6 In an exothermic process, the *system* releases heat to its *surroundings*. The entropy of the surroundings increases because the temperature of the surroundings increases ($\Delta S_{\text{surr}} > 0$). In an endothermic process, the system absorbs heat from the surroundings and the surroundings become cooler. Thus, the entropy of the surroundings decreases ($\Delta S_{\text{surr}} < 0$). A chemical cold pack for injuries is an example of a spontaneous, endothermic chemical reaction as is the melting of ice cream at room temperature.
- 20.8 a) **Spontaneous.** Evaporation occurs because a few of the liquid molecules have enough energy to break away from the intermolecular forces of the other liquid molecules and move spontaneously into the gas phase.
b) **Spontaneous.** A lion spontaneously chases an antelope without added force. This assumes that the lion has not just eaten.
c) **Spontaneous.** An unstable substance decays spontaneously to a more stable substance.
- 20.10 a) ΔS_{sys} **positive**, melting is the change in state from solid to liquid. The solid state of a particular substance always has lower entropy than the same substance in the liquid state. Entropy increases during melting.
b) ΔS_{sys} **negative**, the entropy of most salt solutions is greater than the entropy of the solvent and solute separately, so entropy decreases as a salt precipitates.
c) ΔS_{sys} **negative**, dew forms by the condensation of water vapor to liquid. Entropy of a substance in the gaseous state is greater than its entropy in the liquid state. Entropy decreases during condensation.
- 20.12 a) ΔS_{sys} **negative**, reaction involves a gaseous reactant and no gaseous products, so entropy decreases. The number of particles also decreases, indicating a decrease in entropy.
b) ΔS_{sys} **negative**, gaseous reactants form solid product and number of particles decreases, so entropy decreases.
c) ΔS_{sys} **positive**, when salts dissolve in water, entropy generally increases.

- 20.14 a) ΔS_{sys} **positive**, the reaction produces gaseous CO_2 molecules that have greater entropy than the physical states of the reactants.
 b) ΔS_{sys} **negative**, the reaction produces a net decrease in the number of gaseous molecules, so the system's entropy decreases.
 c) ΔS_{sys} **positive**, the reaction produces a gas from a solid.
- 20.16 a) ΔS_{sys} **positive**, decreasing the pressure increases the volume available to the gas molecules, so entropy of the system increases.
 b) ΔS_{sys} **negative**, gaseous nitrogen molecules have greater entropy (more possible states) than dissolved nitrogen molecules.
 c) ΔS_{sys} **positive**, dissolved oxygen molecules have lower entropy than gaseous oxygen molecules.
- 20.18 a) **Butane** has the greater molar entropy because it has two additional C–H bonds that can vibrate and has greater rotational freedom around its bond. The presence of the double bond in 2-butene restricts rotation.
 b) **Xe(g)** has the greater molar entropy because entropy increases with atomic size.
 c) **CH₄(g)** has the greater molar entropy because gases in general have greater entropy than liquids.
- 20.20 a) **Diamond < graphite < charcoal**. Diamond has an ordered, 3-dimensional crystalline shape, followed by graphite with an ordered 2-dimensional structure, followed by the amorphous (disordered) structure of charcoal.
 b) **Ice < liquid water < water vapor**. Entropy increases as a substance changes from solid to liquid to gas.
 c) **O atoms < O₂ < O₃**. Entropy increases with molecular complexity because there are more modes of movement (e.g., bond vibration) available to the complex molecules.
- 20.22 a) **ClO₄[–](aq) > ClO₃[–](aq) > ClO₂[–](aq)**. The decreasing order of molar entropy follows the order of decreasing molecular complexity.
 b) **NO₂(g) > NO(g) > N₂(g)**. N₂ has lower molar entropy than NO because N₂ consists of two of the same atoms while NO consists of two different atoms. NO₂ has greater molar entropy than NO because NO₂ consists of three atoms while NO consists of only two.
 c) **Fe₃O₄(s) > Fe₂O₃(s) > Al₂O₃(s)**. Fe₃O₄ has greater molar entropy than Fe₂O₃ because Fe₃O₄ is more complex and more massive. Fe₂O₃ and Al₂O₃ contain the same number of atoms but Fe₂O₃ has greater molar entropy because iron atoms are more massive than aluminum atoms.
- 20.25 A system at equilibrium does not spontaneously produce more products or more reactants. For either reaction direction, the entropy change of the system is exactly offset by the entropy change of the surroundings. Therefore, for system at equilibrium, $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$. However, for a system moving to equilibrium, $\Delta S_{\text{univ}} > 0$, because the Second Law states that for any spontaneous process, the entropy of the universe increases.
- 20.26 Since entropy is a state function, the entropy changes can be found by summing the entropies of the products and subtracting the sum of the entropies of the reactants.
 For the given reaction $\Delta S_{\text{rxn}}^{\circ} = 2 S^{\circ}_{\text{HClO(g)}} - (S^{\circ}_{\text{H}_2\text{O(g)}} + S^{\circ}_{\text{Cl}_2\text{O(g)}})$. Rearranging this expression to solve for $S^{\circ}_{\text{Cl}_2\text{O(g)}}$ gives
- $$S^{\circ}_{\text{Cl}_2\text{O(g)}} = 2 S^{\circ}_{\text{HClO(g)}} - S^{\circ}_{\text{H}_2\text{O(g)}} - \Delta S_{\text{rxn}}^{\circ}$$
- 20.27 a) Prediction: ΔS° **negative** because number of moles of (Δn) gas decreases.
 $\Delta S^{\circ} = [(1 \text{ mol N}_2\text{O(g)}) (S^{\circ} \text{ of N}_2\text{O}) + (1 \text{ mol NO}_2\text{(g)}) (S^{\circ} \text{ of NO}_2)]$
 $\quad - [(3 \text{ mol NO(g)}) (S^{\circ} \text{ of NO})]$
 $\Delta S^{\circ} = [(1 \text{ mol N}_2\text{O(g)}) (219.7 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol NO}_2\text{(g)}) (239.9 \text{ J/mol}\cdot\text{K})]$
 $\quad - [(3 \text{ mol NO(g)}) (210.65 \text{ J/mol}\cdot\text{K})]$
 $\Delta S^{\circ} = -172.35 = \mathbf{-172.4 \text{ J/K}}$

b) Prediction: Sign difficult to predict because $\Delta n = 0$, but **possibly ΔS° positive** because water vapor has greater complexity than H_2 gas.

$$\begin{aligned}\Delta S^\circ &= [(2 \text{ mol Fe}(s)) (S^\circ \text{ of Fe}) + (3 \text{ mol H}_2\text{O}(g)) (S^\circ \text{ of H}_2\text{O})] \\ &\quad - [(3 \text{ mol H}_2(g)) (S^\circ \text{ of H}_2) + (1 \text{ mol Fe}_2\text{O}_3(s)) (S^\circ \text{ of Fe}_2\text{O}_3)] \\ \Delta S^\circ &= [(2 \text{ mol Fe}(s)) (27.3 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol H}_2\text{O}(g)) (188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(3 \text{ mol H}_2(g)) (130.6 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol Fe}_2\text{O}_3(s)) (87.400 \text{ J/mol}\cdot\text{K})] \\ \Delta S^\circ &= 141.56 = \mathbf{141.6 \text{ J/K}}\end{aligned}$$

c) Prediction: $\Delta S^\circ_{\text{sys}}$ **negative** because a gaseous reactant forms a solid product and also because the number of moles of gas (Δn) decreases.

$$\begin{aligned}\Delta S^\circ &= [(1 \text{ mol P}_4\text{O}_{10}(s)) (S^\circ \text{ of P}_4\text{O}_{10})] - [(1 \text{ mol P}_4(s)) (S^\circ \text{ of P}_4) + (5 \text{ mol O}_2(g)) (S^\circ \text{ of O}_2)] \\ \Delta S^\circ &= [(1 \text{ mol P}_4\text{O}_{10}(s)) (229 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol P}_4(s)) (41.1 \text{ J/mol}\cdot\text{K}) + (5 \text{ mol O}_2(g)) (205.0 \text{ J/mol}\cdot\text{K})] \\ \Delta S^\circ &= -837.1 = \mathbf{-837 \text{ J/K}}\end{aligned}$$

20.29 The balanced combustion reaction is

$$\begin{aligned}2 \text{ C}_2\text{H}_6(g) + 7 \text{ O}_2(g) &\rightarrow 4 \text{ CO}_2(g) + 6 \text{ H}_2\text{O}(g) \\ \Delta S^\circ_{\text{rxn}} &= [4 \text{ mol } (S^\circ(\text{CO}_2)) + 6 \text{ mol } (S^\circ(\text{H}_2\text{O}))] - [2 \text{ mol } (S^\circ(\text{C}_2\text{H}_6)) + 7 \text{ mol } (S^\circ(\text{O}_2))] \\ &= [4 \text{ mol } (213.7 \text{ J/mol}\cdot\text{K}) + 6 \text{ mol } (188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [2 \text{ mol } (229.5 \text{ J/mol}\cdot\text{K}) + 7 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] = 93.12 = \mathbf{93.1 \text{ J/K}}\end{aligned}$$

The entropy value is not per mole of C_2H_6 but per 2 moles. Divide the calculated value by 2 to obtain entropy per mole of C_2H_6 .

Yes, the positive sign of ΔS is expected because there is a net increase in the number of gas molecules from 9 moles as reactants to 10 moles as products.

20.31 The reaction for forming Cu_2O from copper metal and oxygen gas is

$$\begin{aligned}2 \text{ Cu}(s) + 1/2 \text{ O}_2(g) &\rightarrow \text{Cu}_2\text{O}(s) \\ \Delta S^\circ_{\text{rxn}} &= [1 \text{ mol } (S^\circ(\text{Cu}_2\text{O}))] - [2 \text{ mol } (S^\circ(\text{Cu})) + 1/2 \text{ mol } (S^\circ(\text{O}_2))] \\ &= [1 \text{ mol } (93.1 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol } (33.1 \text{ J/mol}\cdot\text{K}) + 1/2 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] \\ &= \mathbf{-75.6 \text{ J/K}}\end{aligned}$$

20.34 Complete combustion of a hydrocarbon includes oxygen as a reactant and carbon dioxide and water as the products.

$$\begin{aligned}\text{C}_2\text{H}_2(g) + 5/2 \text{ O}_2(g) &\rightarrow 2 \text{ CO}_2(g) + \text{H}_2\text{O}(g) \\ \Delta S^\circ_{\text{rxn}} &= [2 \text{ mol } (S^\circ(\text{CO}_2)) + 1 \text{ mol } (S^\circ(\text{H}_2\text{O}))] - [1 \text{ mol } (S^\circ(\text{C}_2\text{H}_2)) + 5/2 \text{ mol } (S^\circ(\text{O}_2))] \\ &= [2 \text{ mol } (213.7 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol } (188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [1 \text{ mol } (200.85 \text{ J/mol}\cdot\text{K}) + 5/2 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] = -97.23 = \mathbf{-97.2 \text{ J/K}}\end{aligned}$$

20.36 A spontaneous process has $\Delta S_{\text{univ}} > 0$. Since the Kelvin temperature is always positive, ΔG_{sys} must be negative ($\Delta G_{\text{sys}} < 0$) for a spontaneous process.

20.38 $\Delta H^\circ_{\text{rxn}}$ **positive** and $\Delta S^\circ_{\text{sys}}$ **positive**. The reaction is endothermic ($\Delta H^\circ_{\text{rxn}} > 0$) and requires a lot of heat from its surroundings to be spontaneous. The removal of heat from the surroundings results in $\Delta S^\circ_{\text{surr}} < 0$. The only way an endothermic reaction can proceed spontaneously is if $\Delta S^\circ_{\text{sys}} \gg 0$, effectively offsetting the decrease in surroundings entropy. In summary, the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{sys}}$ are both positive for this reaction. Melting is an example.

20.39 The $\Delta G^\circ_{\text{rxn}}$ can be calculated from the individual ΔG°_f 's of the reactants and products found in Appendix B.

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \Sigma[m \Delta G^\circ_f(\text{products})] - \Sigma[n \Delta G^\circ_f(\text{reactants})] \\ \text{a) } \Delta G^\circ_{\text{rxn}} &= [(2 \text{ mol MgO}) (\Delta G^\circ_f \text{ MgO})] - [(2 \text{ mol Mg}) (\Delta G^\circ_f \text{ Mg}) + (1 \text{ mol O}_2) (\Delta G^\circ_f \text{ O}_2)] \\ \Delta G^\circ_{\text{rxn}} &= [(2 \text{ mol MgO}) (-569.0 \text{ kJ/mol})] - [(2 \text{ mol Mg}) (0) + (1 \text{ mol O}_2) (0)] = \mathbf{-1138.0 \text{ kJ}}\end{aligned}$$

$$\begin{aligned}
 \text{b) } \Delta G_{\text{rxn}}^{\circ} &= [(2 \text{ mol CO}_2) (\Delta G_f^{\circ} \text{ CO}_2) + (4 \text{ mol H}_2\text{O}) (\Delta G_f^{\circ} \text{ H}_2\text{O})] \\
 &\quad - [(2 \text{ mol CH}_3\text{OH}) (\Delta G_f^{\circ} \text{ CH}_3\text{OH}) + (3 \text{ mol O}_2) (\Delta G_f^{\circ} \text{ O}_2)] \\
 \Delta G_{\text{rxn}}^{\circ} &= [(2 \text{ mol CO}_2) (-394.4 \text{ kJ/mol}) + (4 \text{ mol H}_2\text{O}) (-228.60 \text{ kJ/mol})] \\
 &\quad - [(2 \text{ mol CH}_3\text{OH}) (-161.9 \text{ kJ/mol}) + (3 \text{ mol O}_2) (0)] \\
 \Delta G_{\text{rxn}}^{\circ} &= \mathbf{-1379.4 \text{ kJ}} \\
 \text{c) } \Delta G_{\text{rxn}}^{\circ} &= [(1 \text{ mol BaCO}_3) (\Delta G_f^{\circ} \text{ BaCO}_3)] - [(1 \text{ mol BaO}) (\Delta G_f^{\circ} \text{ BaO}) + (1 \text{ mol CO}_2) (\Delta G_f^{\circ} \text{ CO}_2)] \\
 \Delta G_{\text{rxn}}^{\circ} &= [(1 \text{ mol BaCO}_3) (-1139 \text{ kJ/mol})] - [(1 \text{ mol BaO}) (-520.4 \text{ kJ/mol}) + (1 \text{ mol CO}_2) (-394.4 \text{ kJ/mol})] \\
 \Delta G_{\text{rxn}}^{\circ} &= -224.2 = \mathbf{-224 \text{ kJ}}
 \end{aligned}$$

20.41 The $\Delta H_{\text{rxn}}^{\circ}$ can be calculated from the individual ΔH_f° 's of the reactants and products found in Appendix B.

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma[m \Delta H_f^{\circ} (\text{products})] - \Sigma[n \Delta H_f^{\circ} (\text{reactants})]$$

The S_{rxn}° can be calculated from the individual S° 's of the reactants and products found in Appendix B.

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma[m \Delta H_f^{\circ} (\text{products})] - \Sigma[n \Delta H_f^{\circ} (\text{reactants})]$$

$$\Delta G_{\text{rxn}}^{\circ} \text{ can be calculated using } \Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\begin{aligned}
 \text{a) } \Delta H_{\text{rxn}}^{\circ} &= [2 \text{ mol } (\Delta H_f^{\circ} (\text{MgO}))] - [2 \text{ mol } (\Delta H_f^{\circ} (\text{Mg})) + 1 \text{ mol } (\Delta H_f^{\circ} (\text{O}_2))] \\
 &= [2 \text{ mol } (-601.2 \text{ kJ/mol})] - [2 \text{ mol } (0) + 1 \text{ mol } (0)] \\
 &= -1202.4 \text{ kJ} \\
 \Delta S_{\text{rxn}}^{\circ} &= [2 \text{ mol } (S^{\circ} (\text{MgO}))] - [2 \text{ mol } (S^{\circ} (\text{Mg})) + 1 \text{ mol } (S^{\circ} (\text{O}_2))] \\
 &= [2 \text{ mol } (26.9 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol } (32.69 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] \\
 &= -216.58 \text{ J/K (unrounded)} \\
 \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -1202.4 \text{ kJ} - [(298 \text{ K}) (-216.58 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -1137.859 = \mathbf{-1138 \text{ kJ}} \\
 \text{b) } \Delta H_{\text{rxn}}^{\circ} &= [2 \text{ mol } (\Delta H_f^{\circ} (\text{CO}_2)) + 4 \text{ mol } (\Delta H_f^{\circ} (\text{H}_2\text{O(g)}))] - [2 \text{ mol } (\Delta H_f^{\circ} (\text{CH}_3\text{OH})) + 3 \text{ mol } (\Delta H_f^{\circ} (\text{O}_2))] \\
 &= [2 \text{ mol } (-393.5 \text{ kJ/mol}) + 4 \text{ mol } (-241.826 \text{ kJ/mol})] - [2 \text{ mol } (-201.2 \text{ kJ/mol}) + 3 \text{ mol } (0)] \\
 &= -1351.904 \text{ kJ (unrounded)} \\
 \Delta S_{\text{rxn}}^{\circ} &= [2 \text{ mol } (S^{\circ} (\text{CO}_2)) + 4 \text{ mol } (S^{\circ} (\text{H}_2\text{O(g)}))] - [2 \text{ mol } (S^{\circ} (\text{CH}_3\text{OH})) + 3 \text{ mol } (S^{\circ} (\text{O}_2))] \\
 &= [2 \text{ mol } (213.7 \text{ J/mol}\cdot\text{K}) + 4 \text{ mol } (188.72 \text{ J/mol}\cdot\text{K})] \\
 &\quad - [2 \text{ mol } (238 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] \\
 &= 91.28 \text{ J/K (unrounded)} \\
 \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -1351.904 \text{ kJ} - [(298 \text{ K}) (91.28 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -1379.105 = \mathbf{-1379 \text{ kJ}} \\
 \text{c) } \Delta H_{\text{rxn}}^{\circ} &= [1 \text{ mol } (\Delta H_f^{\circ} (\text{BaCO}_3(s)))] - [1 \text{ mol } (\Delta H_f^{\circ} (\text{BaO})) + 1 \text{ mol } (\Delta H_f^{\circ} (\text{CO}_2))] \\
 &= [1 \text{ mol } (-1219 \text{ kJ/mol})] - [1 \text{ mol } (-548.1 \text{ kJ/mol}) + 1 \text{ mol } (-393.5 \text{ kJ/mol})] \\
 &= -277.4 \text{ kJ (unrounded)} \\
 \Delta S_{\text{rxn}}^{\circ} &= [1 \text{ mol } (S^{\circ} (\text{BaCO}_3(s)))] - [1 \text{ mol } (S^{\circ} (\text{BaO})) + 1 \text{ mol } (S^{\circ} (\text{CO}_2))] \\
 &= [1 \text{ mol } (112 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol } (72.07 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol } (213.7 \text{ J/mol}\cdot\text{K})] \\
 &= -173.77 \text{ J/K (unrounded)} \\
 \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -277.4 \text{ kJ} - [(298 \text{ K}) (-173.77 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -225.6265 = \mathbf{-226 \text{ kJ}}
 \end{aligned}$$

20.43 a) Entropy decreases (ΔS° **negative**) because the number of moles of gas decreases from reactants (1 ½ mol) to products (1 mole). The oxidation (combustion) of CO requires initial energy input to start the reaction, but then releases energy (exothermic, ΔH° **negative**) which is typical of all combustion reactions.

b) Method 1: Calculate $\Delta G_{\text{rxn}}^{\circ}$ from ΔG_f° 's of products and reactants.

$$\Delta G_{\text{rxn}}^{\circ} = \Sigma[m \Delta G_f^{\circ} (\text{products})] - \Sigma[n \Delta G_f^{\circ} (\text{reactants})]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (\Delta G_f^{\circ} (\text{CO}_2))] - [(1 \text{ mol CO}) (\Delta G_f^{\circ} (\text{CO})) + (1/2 \text{ mol}) (\Delta G_f^{\circ} (\text{O}_2))]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (-394.4 \text{ kJ/mol})] - [(1 \text{ mol CO}) (-137.2 \text{ kJ/mol}) + (1/2 \text{ mol O}_2) (0)] = \mathbf{-257.2 \text{ kJ}}$$

Method 2: Calculate ΔG_{rxn}° from ΔH° and ΔS° at 298 K (the degree superscript indicates a reaction at standard state, given in the Appendix at 25°C).

$$\Delta H_{rxn}^\circ = \Sigma[m \Delta H_f^\circ (\text{products})] - \Sigma[n \Delta H_f^\circ (\text{reactants})]$$

$$\Delta H_{rxn}^\circ = [(1 \text{ mol CO}_2) (\Delta H_f^\circ (\text{CO}_2))] - [(1 \text{ mol CO}) (\Delta H_f^\circ (\text{CO})) + (1/2 \text{ mol}) (\Delta H_f^\circ (\text{O}_2))]$$

$$\Delta H_{rxn}^\circ = [(1 \text{ mol CO}_2) (-393.5 \text{ kJ/mol})] - [(1 \text{ mol CO}) (-110.5 \text{ kJ/mol}) + (1/2 \text{ mol O}_2) (0)] = -283.0 \text{ kJ}$$

$$S_{rxn}^\circ = \Sigma[m S^\circ (\text{products})] - \Sigma[n S^\circ (\text{reactants})]$$

$$\Delta S_{rxn}^\circ = [(1 \text{ mol CO}_2) (213.7 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol CO}) (197.5 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})] = -86.3 \text{ J/K}$$

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ = (-283.0 \text{ kJ}) - [(298 \text{ K}) (-86.3 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -257.2826 = \mathbf{-257.3 \text{ kJ}}$$

20.45 a) $\Delta H_{rxn}^\circ = [(1 \text{ mol CO}) (\Delta H_f^\circ (\text{CO})) + (2 \text{ mol H}_2) (\Delta H_f^\circ (\text{H}_2))] - [(1 \text{ mol CH}_3\text{OH}) (\Delta H_f^\circ (\text{CH}_3\text{OH}))]$

$$\Delta H_{rxn}^\circ = [(1 \text{ mol CO}) (-110.5 \text{ kJ/mol}) + (2 \text{ mol H}_2) (0)] - [(1 \text{ mol CH}_3\text{OH}) (-201.2 \text{ kJ/mol})]$$

$$\Delta H_{rxn}^\circ = \mathbf{90.7 \text{ kJ}}$$

$$\Delta S_{rxn}^\circ = [(1 \text{ mol CO}) (S_f^\circ (\text{CO})) + (2 \text{ mol H}_2) (S_f^\circ (\text{H}_2))] - [(1 \text{ mol CH}_3\text{OH}) (S_f^\circ (\text{CH}_3\text{OH}))]$$

$$\Delta S_{rxn}^\circ = [(1 \text{ mol CO}) (197.5 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol CH}_3\text{OH}) (238 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{rxn}^\circ = 220.7 = \mathbf{221 \text{ J/K}}$$

b) $T_1 = 38 + 273 = 311 \text{ K} \quad \Delta G^\circ = 90.7 \text{ kJ} - [(311 \text{ K}) (220.7 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = 22.0623 = \mathbf{22.1 \text{ kJ}}$

$$T_2 = 138 + 273 = 411 \text{ K} \quad \Delta G^\circ = 90.7 \text{ kJ} - [(411 \text{ K}) (220.7 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -0.0077 = \mathbf{0.0 \text{ kJ}}$$

$$T_3 = 238 + 273 = 511 \text{ K} \quad \Delta G^\circ = 90.7 \text{ kJ} - [(511 \text{ K}) (220.7 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -22.0777 = \mathbf{-22.1 \text{ kJ}}$$

c) For the substances in their standard states, the reaction is nonspontaneous at 38°C, near equilibrium at 138°C and spontaneous at 238°C. Reactions with positive values of ΔH_{rxn}° and ΔS_{rxn}° become spontaneous at high temperatures.

20.47 At the normal boiling point, defined as the temperature at which the vapor pressure of the liquid equals 1 atm, the phase change from liquid to gas is at equilibrium. For a system at equilibrium, the change in Gibbs free energy is zero. Since the gas is at 1 atm and the liquid assumed to be pure, the system is at standard state and $\Delta G^\circ = 0$. The temperature at which this occurs can be found from $\Delta G_{rxn}^\circ = 0 = \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ$.

$$\Delta H_{rxn}^\circ = T \Delta S_{rxn}^\circ$$

$$T_{\text{bpt}} = \Delta H^\circ / \Delta S^\circ$$

$$\Delta H^\circ = [1 \text{ mol} (\Delta H_f^\circ (\text{Br}_2(\text{g}))) - [1 \text{ mol} (\Delta H_f^\circ (\text{Br}_2(\text{l})))]$$

$$\Delta H^\circ = [1 \text{ mol}(30.91 \text{ kJ/mol})] - [1 \text{ mol} (\Delta H_f^\circ (0))] = \mathbf{30.91 \text{ kJ} = 30910 \text{ J}}$$

$$\Delta S^\circ = [1 \text{ mol} (S^\circ (\text{Br}_2(\text{g}))) - [1 \text{ mol} (S^\circ (\text{Br}_2(\text{l})))]$$

$$\Delta S^\circ = [1 \text{ mol} (S^\circ (245.38 \text{ J/K}\cdot\text{mol})) - [1 \text{ mol} (S^\circ (152.23 \text{ J/K}\cdot\text{mol}))] = \mathbf{93.15 \text{ J/K}}$$

$$T_{\text{bpt}} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{30910 \text{ J}}{93.15 \text{ J/K}} = 331.830 = \mathbf{331.8 \text{ K}}$$

20.49 a) The reaction for this process is $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$. The coefficients are written this way (instead of $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$) because the problem specifies thermodynamic values “per (1) mol H_2 ,” not per 2 mol H_2 .

$$\Delta H_{rxn}^\circ = [(1 \text{ mol H}_2\text{O}) (\Delta H_f^\circ (\text{H}_2\text{O}))] - [(1 \text{ mol H}_2) (\Delta H_f^\circ (\text{H}_2)) + (1/2 \text{ mol O}_2) (\Delta H_f^\circ (\text{O}_2))]$$

$$\Delta H_{rxn}^\circ = [(1 \text{ mol H}_2\text{O}) (-241.826 \text{ kJ/mol})] - [(1 \text{ mol H}_2) (0) + (1/2 \text{ mol O}_2) (0)]$$

$$\Delta H_{rxn}^\circ = \mathbf{-241.826 \text{ kJ}}$$

$$\begin{aligned}\Delta S_{rxn}^{\circ} &= [(1 \text{ mol H}_2\text{O}) (S_f^{\circ}(\text{H}_2\text{O}))] - [(1 \text{ mol H}_2) (S_f^{\circ}(\text{H}_2)) + (1/2 \text{ mol O}_2) (S_f^{\circ}(\text{O}_2))] \\ \Delta S_{rxn}^{\circ} &= [(1 \text{ mol H}_2\text{O}) (188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(1 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{rxn}^{\circ} &= -44.38 = \mathbf{-44.4 \text{ J/K}} \\ \Delta G_{rxn}^{\circ} &= [(1 \text{ mol H}_2\text{O}) (\Delta G_f^{\circ}(\text{H}_2\text{O}))] - [(1 \text{ mol H}_2) (\Delta G_f^{\circ}(\text{H}_2)) + (1/2 \text{ mol O}_2) (\Delta G_f^{\circ}(\text{O}_2))] \\ \Delta G_{rxn}^{\circ} &= [(1 \text{ mol H}_2\text{O}) (-228.60 \text{ kJ/mol})] - [(1 \text{ mol H}_2) (0) + (1/2 \text{ mol O}_2) (0)] \\ \Delta G_{rxn}^{\circ} &= \mathbf{-228.60 \text{ kJ}}\end{aligned}$$

b) Because $\Delta H < 0$ and $\Delta S < 0$, the reaction will become nonspontaneous at higher temperatures because the positive ($-T\Delta S$) term becomes larger than the negative ΔH term.

c) The reaction becomes spontaneous below the temperature where $\Delta G_{rxn}^{\circ} = 0$

$$\begin{aligned}\Delta G_{rxn}^{\circ} = 0 &= \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ} \\ \Delta H_{rxn}^{\circ} &= T \Delta S_{rxn}^{\circ} \\ T &= \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{-241.826 \text{ kJ}}{-44.38 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 5448.986 = \mathbf{5.45 \times 10^3 \text{ K}}\end{aligned}$$

- 20.51 a) An equilibrium constant that is much less than 1 indicates that very little product is made to reach equilibrium. The reaction, thus, is not spontaneous in the forward direction and ΔG° is a relatively large positive value.
b) A large negative ΔG° indicates that the reaction is quite spontaneous and goes almost to completion. At equilibrium, much more product is present than reactant so $K > 1$. Q depends on initial conditions, not equilibrium conditions, so its value cannot be predicted from ΔG° .

- 20.53 The standard free energy change, ΔG° , occurs when all components of the system are in their standard states (do not confuse this with ΔG_f° , the standard free energy of formation). Standard state is defined as 1 atm for gases, 1 M for solutes, and pure solids and liquids. Standard state does not specify a temperature because standard state can occur at any temperature. $\Delta G^{\circ} = \Delta G$ when all concentrations equal 1 M and all partial pressures equal 1 atm. This occurs because the value of $Q = 1$ and $\ln Q = 0$ in the equation $\Delta G = \Delta G^{\circ} + RT \ln Q$.

- 20.54 For each reaction, first find ΔG° , then calculate K from $\Delta G^{\circ} = -RT \ln K$. Calculate ΔG_{rxn}° using the ΔG_f° values from Appendix B.

$$\begin{aligned}\text{a) } \Delta G^{\circ} &= [1 \text{ mol } (\Delta G_f^{\circ}(\text{NO}_2(\text{g}))) - [1 \text{ mol } (\Delta G_f^{\circ}(\text{NO}(\text{g}))) + 1/2 \text{ mol } (\Delta G_f^{\circ}(\text{O}_2(\text{g})))] \\ &= [1 \text{ mol } (51 \text{ kJ})] - [1 \text{ mol } (86.60 \text{ kJ}) + 1/2 \text{ mol } (0 \text{ kJ})] = -35.6 \text{ kJ (unrounded)} \\ \ln K &= \frac{\Delta G^{\circ}}{-RT} = \left(\frac{-35.6 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 14.3689 \text{ (unrounded)} \\ K &= e^{14.3689} = 1.7391377 \times 10^6 = \mathbf{1.7 \times 10^6}\end{aligned}$$

$$\begin{aligned}\text{b) } \Delta G^{\circ} &= [1 \text{ mol } (\Delta G_f^{\circ}(\text{H}_2(\text{g}))) + 1 \text{ mol } (\Delta G_f^{\circ}(\text{Cl}_2(\text{g}))) - [2 \text{ mol } (\Delta G_f^{\circ}(\text{HCl}(\text{g})))]] \\ &= [1 \text{ mol } (0) + 1 \text{ mol } (0) \text{ kJ}] - [2 \text{ mol } (-95.30 \text{ kJ/mol})] = 190.60 \text{ kJ} \\ \ln K &= \frac{\Delta G^{\circ}}{-RT} = \left(\frac{190.60 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -76.930 \text{ (unrounded)} \\ K &= e^{-76.930} = 3.88799 \times 10^{-34} = \mathbf{3.89 \times 10^{-34}}\end{aligned}$$

$$\begin{aligned}\text{c) } \Delta G^{\circ} &= [2 \text{ mol } (\Delta G_f^{\circ}(\text{CO}(\text{g}))) - [2 \text{ mol } (\Delta G_f^{\circ}(\text{C}(\text{graphite}))) + 1 \text{ mol } (\Delta G_f^{\circ}(\text{O}_2(\text{g})))]] \\ &= [2 \text{ mol } (-137.2 \text{ kJ/mol})] - [2 \text{ mol } (0) + 1 \text{ mol } (0) \text{ kJ}] = -274.4 \text{ kJ} \\ \ln K &= \frac{\Delta G^{\circ}}{-RT} = \left(\frac{-274.4 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 110.75359 \text{ (unrounded)} \\ K &= e^{110.75359} = 1.2579778 \times 10^{48} = \mathbf{1.26 \times 10^{48}}\end{aligned}$$

Note: You may get a different answer depending on how you rounded in earlier calculations.

- 20.56 The solubility reaction for Ag₂S is

$$\begin{aligned}\text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(l) &\rightleftharpoons 2 \text{Ag}^+(aq) + \text{HS}^-(aq) + \text{OH}^-(aq) \\ \Delta G^\circ &= [2 \text{ mol } (\Delta G_f^\circ \text{Ag}^+(aq)) + 1 \text{ mol } (\Delta G_f^\circ \text{HS}^-(aq)) + 1 \text{ mol } (\Delta G_f^\circ \text{OH}^-(aq))] \\ &\quad - [1 \text{ mol } (\Delta G_f^\circ \text{Ag}_2\text{S}(s)) + 1 \text{ mol } (\Delta G_f^\circ \text{H}_2\text{O}(l))] \\ &= [(2 \text{ mol}) (77.111 \text{ kJ/mol}) + (1 \text{ mol}) (12.6 \text{ kJ/mol}) + (1 \text{ mol}) (-157.30 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol}) (-40.3 \text{ kJ/mol}) + (1 \text{ mol}) (-237.192 \text{ kJ/mol})] \\ &= 287.014 \text{ kJ (unrounded)} \\ \ln K &= \frac{\Delta G^\circ}{-RT} = \left(\frac{287.014 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -115.8448675 \text{ (unrounded)} \\ K &= e^{-115.8448675} = 4.8889241 \times 10^{-51} = \mathbf{4.89 \times 10^{-51}}\end{aligned}$$

- 20.58 Calculate ΔG_{rxn}° , recognizing that I₂(s), not I₂(g), is the standard state for iodine.

Solve for K_p using the equation $\Delta G^\circ = -RT \ln K$.

$$\begin{aligned}\Delta G_{rxn}^\circ &= [(2 \text{ mol}) (\Delta G_f^\circ (\text{ICl}))] - [(1 \text{ mol}) (\Delta G_f^\circ (\text{I}_2)) + (1 \text{ mol}) (\Delta G_f^\circ (\text{Cl}_2))] \\ \Delta G_{rxn}^\circ &= [(2 \text{ mol}) (-6.075 \text{ kJ/mol})] - [(1 \text{ mol}) (19.38 \text{ kJ/mol}) + (1 \text{ mol}) (0)] \\ \Delta G_{rxn}^\circ &= -31.53 \text{ kJ} \\ \ln K_p &= \Delta G^\circ / -RT = \left(\frac{-31.53 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 12.726169 \text{ (unrounded)} \\ K_p &= e^{12.726169} = 3.3643794 \times 10^5 = \mathbf{3.36 \times 10^5}\end{aligned}$$

- 20.60 $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol} \cdot \text{K}) (298 \text{ K}) \ln (1.7 \times 10^{-5}) = 2.72094 \times 10^4 \text{ J/mol} = \mathbf{2.7 \times 10^4 \text{ J/mol}}$

The large positive ΔG° indicates that it would not be possible to prepare a solution with the concentrations of lead and chloride ions at the standard state concentration of 1 *M*. A *Q* calculation using 1 *M* solutions will confirm this:

$$\begin{aligned}\text{PbCl}_2(s) &\rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{Cl}^-(aq) \\ Q &= [\text{Pb}^{2+}][\text{Cl}^-]^2 \\ &= (1 \text{ M})(1 \text{ M})^2 \\ &= 1\end{aligned}$$

Since $Q > K_{sp}$, it is impossible to prepare a standard state solution of PbCl₂.

- 20.62 a) The equilibrium constant, K , is related to ΔG° through the equation $\Delta G^\circ = -RT \ln K$.

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol} \cdot \text{K}) (298 \text{ K}) \ln (9.1 \times 10^{-6}) = 2.875776 \times 10^4 = \mathbf{2.9 \times 10^4 \text{ J/mol}}$$

b) Since ΔG_{rxn}° is positive, the reaction direction as written is nonspontaneous. The reverse direction, formation of reactants, is spontaneous, so the reaction proceeds to the left.

c) Calculate the value for Q and then use to find ΔG .

$$\begin{aligned}Q &= \frac{[\text{Fe}^{2+}]^2 [\text{Hg}_2^{2+}]}{[\text{Fe}^{3+}]^2 [\text{Hg}_2^{2+}]} = \frac{[0.010]^2 [0.025]}{[0.20]^2 [0.010]} = 1.5625 \times 10^{-4} \text{ (unrounded)} \\ \Delta G &= \Delta G^\circ + RT \ln Q = 2.875776 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol} \cdot \text{K}) (298) \ln (1.5625 \times 10^{-4}) \\ &= 7.044187 \times 10^3 = \mathbf{7.0 \times 10^3 \text{ J/mol}} \\ \text{Because } \Delta G_{298} > 0 \text{ and } Q > K, \text{ the reaction proceeds to the left to reach equilibrium.}\end{aligned}$$

- 20.64 Formation of O₃ from O₂: $3 \text{O}_2(g) \rightleftharpoons 2 \text{O}_3(g)$ or per mole of ozone: $3/2 \text{O}_2(g) \rightleftharpoons \text{O}_3(g)$

a) To decide when production of ozone is favored, both the signs of ΔH_f° and ΔS_f° for ozone are needed. From

Appendix B, the values of ΔH_f° and S° can be used:

$$\begin{aligned}\Delta H_f^\circ &= [1 \text{ mol O}_3 (\Delta H_f^\circ \text{O}_3)] - [3/2 \text{ mol } (\Delta H_f^\circ \text{O}_2)] \\ \Delta H_f^\circ &= [1 \text{ mol}(143 \text{ kJ/mol})] - [3/2 \text{ mol}(0)] = 143 \text{ kJ/mol} \\ \Delta S_f^\circ &= [1 \text{ mol O}_3 (S^\circ \text{O}_3)] - [3/2 \text{ mol O}_2 (S^\circ \text{O}_2)]\end{aligned}$$

$$\Delta S_f^\circ = [1 \text{ mol } (238.82 \text{ J/mol}\cdot\text{K})] - [3/2 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] = -68.68 \text{ J/mol}\cdot\text{K} \text{ (unrounded).}$$

The positive sign for ΔH_f° and the negative sign for ΔS_f° indicates the formation of ozone is favored at **no temperature**. The reaction is nonspontaneous at all temperatures.

b) At 298 K, ΔG° can be most easily calculated from ΔG_f° values for the reaction $3/2 \text{ O}_2(\text{g}) \rightleftharpoons \text{O}_3(\text{g})$.

$$\text{From } \Delta G_f^\circ: \Delta G^\circ = [1 \text{ mol O}_3 (\Delta G_f^\circ \text{ O}_3)] - [3/2 \text{ mol } (\Delta G_f^\circ \text{ O}_2)]$$

$$\Delta G^\circ = [1 \text{ mol } (163 \text{ kJ/mol O}_3)] - [3/2 \text{ mol } (0)] = \mathbf{163 \text{ kJ}}$$
 for the formation of one mole of O_3 .

c) Calculate the value for Q and then use to find ΔG .

$$Q = \frac{[\text{O}_3]}{[\text{O}_2]^{3/2}} = \frac{[5 \times 10^{-7} \text{ atm}]}{[0.21 \text{ atm}]^{3/2}} = 5.195664 \times 10^{-6} \text{ (unrounded)}$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q = 163 \text{ kJ/mol} + (8.314 \text{ J/mol}\cdot\text{K}) (298) (1 \text{ kJ} / 10^3 \text{ J}) \ln (5.195664 \times 10^{-6}) \\ &= 132.85368 = \mathbf{1 \times 10^2 \text{ kJ/mol}} \end{aligned}$$

20.67

	ΔS_{rxn}	ΔH_{rxn}	ΔG_{rxn}	Comment
(a)	+	–	–	Spontaneous
(b)	(+)	0	–	Spontaneous
(c)	–	+	(+)	Not spontaneous
(d)	0	(–)	–	Spontaneous
(e)	(–)	0	+	Not spontaneous
(f)	+	+	(–)	$T\Delta S > \Delta H$

a) The reaction is always spontaneous when $\Delta G_{\text{rxn}} < 0$, so there is no need to look at the other values other than to check the answer.

b) Because $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = -T\Delta S$, ΔS must be positive for ΔG_{rxn} to be negative.

c) The reaction is always nonspontaneous when $\Delta G_{\text{rxn}} > 0$, so there is no need to look at the other values other than to check the answer.

d) Because $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = \Delta H$, ΔH must be negative for ΔG_{rxn} to be negative.

e) Because $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = -T\Delta S$, ΔS must be negative for ΔG_{rxn} to be positive.

f) Because $T\Delta S > \Delta H$, the subtraction of a larger positive term causes ΔG_{rxn} to be negative.

20.69 a) For the reaction, $K = \frac{[\text{Hb} \cdot \text{CO}][\text{O}_2]}{[\text{Hb} \cdot \text{O}_2][\text{CO}]}$ since the problem states that $[\text{O}_2] = [\text{CO}]$; the K expression simplifies to:

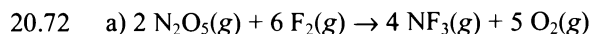
$$K = \frac{[\text{Hb} \cdot \text{CO}]}{[\text{Hb} \cdot \text{O}_2]}$$

The equilibrium constant, K , is related to ΔG° through the equation $\Delta G^\circ = -RT \ln K$.

$$\ln K = \frac{\Delta G^\circ}{RT} = \left(\frac{-14 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(273 + 37)\text{K}} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 5.431956979 \text{ (unrounded)}$$

$$K = e^{5.431956979} = 228.596 = \mathbf{2.3 \times 10^2} = \frac{[\text{Hb} \cdot \text{CO}]}{[\text{Hb} \cdot \text{O}_2]}$$

b) By increasing the concentration of oxygen, the equilibrium can be shifted in the direction of $\text{Hb} \cdot \text{O}_2$. Administer oxygen-rich air to counteract the CO poisoning.



b) Use the values from Appendix B to determine the value of ΔG° .

$$\Delta G_{\text{rxn}}^\circ = [(4 \text{ mol}) (\Delta G_f^\circ (\text{NF}_3)) + (5 \text{ mol}) (\Delta G_f^\circ (\text{O}_2))] - [(2 \text{ mol}) (\Delta G_f^\circ (\text{N}_2\text{O}_5)) + (6 \text{ mol}) (\Delta G_f^\circ (\text{F}_2))]$$

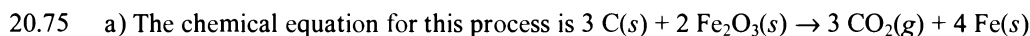
$$\Delta G_{\text{rxn}}^\circ = [(4 \text{ mol}) (-83.3 \text{ kJ/mol}) + (5 \text{ mol}) (0 \text{ kJ/mol})] - [(2 \text{ mol}) (118 \text{ kJ/mol}) + (6 \text{ mol}) (0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^\circ = -569.2 = \mathbf{-569 \text{ kJ}}$$

c) Calculate the value for Q and then use to find ΔG .

$$Q = \frac{[\text{NF}_3]^4 [\text{O}_2]^5}{[\text{N}_2\text{O}_5]^2 [\text{F}_2]^6} = \frac{[0.25 \text{ atm}]^4 [0.50 \text{ atm}]^5}{[0.20 \text{ atm}]^2 [0.20 \text{ atm}]^6} = 47.6837 \text{ (unrounded)}$$

$$\Delta G = \Delta G^\circ + RT \ln Q = -569.2 \text{ kJ/mol} + (1 \text{ kJ} / 10^3 \text{ J}) (8.314 \text{ J/mol}\cdot\text{K}) (298) \ln (47.6837) \\ = -559.625 = \mathbf{-5.60 \times 10^2 \text{ kJ/mol}}$$



$$\Delta H_{\text{rxn}}^\circ = [(3 \text{ mol}) (\Delta H_f^\circ (\text{CO}_2)) + (4 \text{ mol}) (\Delta H_f^\circ (\text{Fe}))] - [(3 \text{ mol}) (\Delta H_f^\circ (\text{C})) + (2 \text{ mol}) (\Delta H_f^\circ (\text{Fe}_2\text{O}_3))]$$

$$\Delta H_{\text{rxn}}^\circ = [(3 \text{ mol}) (-393.5 \text{ kJ/mol}) + (4 \text{ mol}) (0)] - [(3 \text{ mol}) (0) + (2 \text{ mol}) (-825.5 \text{ kJ/mol})] = \mathbf{470.5 \text{ kJ}}$$

$$\Delta S_{\text{rxn}}^\circ = [(3 \text{ mol}) (S_f^\circ (\text{CO}_2)) + (4 \text{ mol}) (S_f^\circ (\text{Fe}))] - [(3 \text{ mol}) (S_f^\circ (\text{C})) + (2 \text{ mol}) (S_f^\circ (\text{Fe}_2\text{O}_3))]$$

$$\Delta S_{\text{rxn}}^\circ = [(3 \text{ mol}) (213.7 \text{ J/mol}\cdot\text{K}) + (4 \text{ mol}) (27.3 \text{ J/mol}\cdot\text{K})] - [(3 \text{ mol}) (5.686 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol}) (87.400 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^\circ = 558.442 = \mathbf{558.4 \text{ J/K}}$$

b) The reaction will be spontaneous at higher temperatures, where the $-T\Delta S$ term will be larger in magnitude than ΔH .

$$\text{c) } \Delta G_{298}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = 470.5 \text{ kJ} - [(298 \text{ K}) (558.442 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = 304.084 = \mathbf{304.1 \text{ kJ}}$$

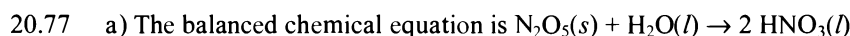
Because ΔG is positive, the reaction is **not spontaneous**.

d) The temperature at which the reaction becomes spontaneous is found by calculating

$$\Delta G_{\text{rxn}}^\circ = 0 = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$$

$$\Delta H_{\text{rxn}}^\circ = T \Delta S_{\text{rxn}}^\circ$$

$$T = \frac{\Delta H_{\text{rxn}}^\circ}{\Delta S_{\text{rxn}}^\circ} = \frac{470.5 \text{ kJ}}{558.442 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 842.5225896 = \mathbf{842.5 \text{ K}}$$



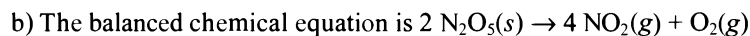
Calculate $\Delta G_{\text{rxn}}^\circ$ for the reaction and see if the value is positive or negative.

$$\Delta G_{\text{rxn}}^\circ = [(2 \text{ mol}) (\Delta G_f^\circ (\text{HNO}_3))] - [(1 \text{ mol}) (\Delta G_f^\circ (\text{N}_2\text{O}_5)) + (1 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{O}))]$$

$$\Delta G_{\text{rxn}}^\circ = [(2 \text{ mol}) (-79.914 \text{ kJ/mol})] - [(1 \text{ mol}) (114 \text{ kJ/mol}) + (1 \text{ mol}) (-237.192 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^\circ = -36.636 = \mathbf{-37 \text{ kJ}}$$

Yes, the reaction is spontaneous because the value of $\Delta G_{\text{rxn}}^\circ$ is negative.



The value of $\Delta G_{\text{rxn}}^\circ$ indicates the spontaneity of the reaction, and the individual $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ values are necessary to determine the temperature.

$$\Delta G_{\text{rxn}}^\circ = [(4 \text{ mol}) (\Delta G_f^\circ (\text{NO}_2)) + (1 \text{ mol}) (\Delta G_f^\circ (\text{O}_2))] - [(2 \text{ mol}) (\Delta G_f^\circ (\text{N}_2\text{O}_5))]$$

$$\Delta G_{\text{rxn}}^\circ = [(4 \text{ mol}) (51 \text{ kJ/mol}) + (1 \text{ mol}) (0)] - [(2 \text{ mol}) (114 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^\circ = -24 \text{ kJ}$$

Yes, the reaction is spontaneous because the value of $\Delta G_{\text{rxn}}^\circ$ is negative.

$$\begin{aligned}\Delta H_{rxn}^{\circ} &= [(4 \text{ mol}) (\Delta H_f^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (\Delta H_f^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (\Delta H_f^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta H_{rxn}^{\circ} &= [(4 \text{ mol}) (33.2 \text{ kJ/mol}) + (1 \text{ mol}) (0)] - [(2 \text{ mol}) (-43.1 \text{ kJ/mol})] \\ \Delta H_{rxn}^{\circ} &= 219.0 \text{ kJ} \\ \Delta S_{rxn}^{\circ} &= [(4 \text{ mol}) (S^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (S^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (S^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta S_{rxn}^{\circ} &= [(4 \text{ mol}) (239.9 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol}) (205 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol}) (178 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{rxn}^{\circ} &= 808.6 \text{ J/K} \\ \Delta G_{rxn}^{\circ} = 0 &= \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ} \\ \Delta H_{rxn}^{\circ} &= T \Delta S_{rxn}^{\circ} \\ T &= \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{219.0 \text{ kJ}}{808.6 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 270.838 = \mathbf{270.8 \text{ K}}\end{aligned}$$

c) The balanced chemical equation is $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

$$\begin{aligned}\Delta H_{rxn}^{\circ} &= [(4 \text{ mol}) (\Delta H_f^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (\Delta H_f^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (\Delta H_f^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta H_{rxn}^{\circ} &= [(4 \text{ mol}) (33.2 \text{ kJ/mol}) + (1 \text{ mol}) (0)] - [(2 \text{ mol}) (11 \text{ kJ/mol})] \\ \Delta H_{rxn}^{\circ} &= 110.8 = 111 \text{ kJ} \\ \Delta S_{rxn}^{\circ} &= [(4 \text{ mol}) (S^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (S^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (S^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta S_{rxn}^{\circ} &= [(4 \text{ mol}) (239.9 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol}) (205 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol}) (346 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{rxn}^{\circ} &= 472.6 = 473 \text{ J/K} \\ \Delta G_{rxn}^{\circ} = 0 &= \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ} \\ \Delta H_{rxn}^{\circ} &= T \Delta S_{rxn}^{\circ} \\ T &= \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{110.8 \text{ kJ}}{472.6 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 234.4477 = \mathbf{234 \text{ K}}\end{aligned}$$

The temperature is different because the values for N_2O_5 vary with physical state.

20.81 a) $K_p = 1.00$ when $\Delta G = 0$; combine this with $\Delta G = \Delta H - T\Delta S$. First, calculate ΔH and ΔS , using values in the Appendix.

$$\begin{aligned}\Delta H^{\circ} &= [(2 \text{ mol NH}_3) (\Delta H_f^{\circ} \text{NH}_3)] - [(1 \text{ mol N}_2) (\Delta H_f^{\circ} \text{N}_2) + (3 \text{ mol H}_2) (\Delta H_f^{\circ} \text{H}_2)] \\ &= [(2 \text{ mol NH}_3) (-45.9 \text{ kJ/mol})] - [(1 \text{ mol N}_2) (0) + (3 \text{ mol H}_2) (0)] = -91.8 \text{ kJ} \\ \Delta S^{\circ} &= [(2 \text{ mol NH}_3) (S^{\circ} \text{NH}_3)] - [(1 \text{ mol N}_2) (S^{\circ} \text{N}_2) + (3 \text{ mol H}_2) (S^{\circ} \text{H}_2)] \\ &= [(2 \text{ mol NH}_3) (193 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol N}_2) (191.50 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K})] \\ &= -197.3 \text{ J/K (unrounded)} \\ \Delta G &= 0 \text{ (at equilibrium)} \\ \Delta G = 0 &= \Delta H - T\Delta S \\ \Delta H &= T\Delta S \\ T &= \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{-91.8 \text{ kJ}}{-197.3 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 465.281 = \mathbf{465 \text{ K}}\end{aligned}$$

b) Use the relationships: $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -RT \ln K$ with $T = (273 + 400.) \text{ K} = 673 \text{ K}$

$$\begin{aligned}\Delta G = \Delta H - T\Delta S &= (-91.8 \text{ kJ}) (10^3 \text{ J} / 1 \text{ kJ}) - (673 \text{ K}) (-197.3 \text{ J/K}) \\ \Delta G &= 4.09829 \times 10^4 \text{ J (unrounded)} \\ \Delta G^{\circ} &= -RT \ln K\end{aligned}$$

$$\begin{aligned}\ln K = \Delta G^{\circ} / -RT &= \left(\frac{4.09829 \times 10^4 \text{ J/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(673 \text{ K})} \right) = -7.32449 \text{ (unrounded)} \\ K &= e^{-7.32449} = 6.591934 \times 10^{-4} = \mathbf{6.59 \times 10^{-4}}\end{aligned}$$

c) The reaction rate is higher at the higher temperature. The time required (kinetics) overshadows the lower yield (thermodynamics).

Chapter 21 Electrochemistry: Chemical Change and Electrical Work

FOLLOW-UP PROBLEMS

21.1 Plan: Follow the steps for balancing a redox reaction in acidic solution:

1. Divide into half-reactions
2. For each half-reaction balance
 - a) Atoms other than O and H,
 - b) O atoms with H_2O ,
 - c) H atoms with H^+ and
 - d) Charge with e^- .
3. Multiply each half-reaction by an integer that will make the number of electrons lost equal to the number of electrons gained.
4. Add the half-reactions and cancel substances appearing as both reactants and products. Then, add another step for basic solution:
5. Add hydroxide ions to neutralize H^+ . Cancel water.

Solution:

1. Divide into half-reactions: group the reactants and products with similar atoms.

$$\text{MnO}_4^-(aq) \rightarrow \text{MnO}_4^{2-}(aq)$$

$$\text{I}^-(aq) \rightarrow \text{IO}_3^-(aq)$$
2. For each half-reaction balance
 - a) Atoms other than O and H
Mn and I are balanced so no changes needed
 - b) O atoms with H_2O ,
 $\text{MnO}_4^-(aq) \rightarrow \text{MnO}_4^{2-}(aq)$ O already balanced
 $\text{I}^-(aq) + 3 \text{H}_2\text{O}(l) \rightarrow \text{IO}_3^-(aq)$ Add 3 H_2O to balance oxygen
 - c) H atoms with H^+
 $\text{MnO}_4^-(aq) \rightarrow \text{MnO}_4^{2-}(aq)$ H already balanced
 $\text{I}^-(aq) + 3 \text{H}_2\text{O}(l) \rightarrow \text{IO}_3^-(aq) + 6 \text{H}^+(aq)$ Add 6 H^+ to balance hydrogen
 - d) Charge with e^-
 $\text{MnO}_4^-(aq) + \text{e}^- \rightarrow \text{MnO}_4^{2-}(aq)$ Total charge of reactants is -1 and of products is -2 ,
 so add 1 e^- to reactants to balance charge:
 $\text{I}^-(aq) + 3 \text{H}_2\text{O}(l) \rightarrow \text{IO}_3^-(aq) + 6 \text{H}^+(aq) + 6 \text{e}^-$ Total charge is -1 for reactants and $+5$ for
 products, so add 6 e^- as product:
3. Multiply each half-reaction by an integer that will make the number of electrons lost equal to the number of electrons gained. One electron is gained and 6 are lost so reduction must be multiplied by 6 for the number of electrons to be equal.

$$6 \{ \text{MnO}_4^-(aq) + \text{e}^- \rightarrow \text{MnO}_4^{2-}(aq) \}$$

$$\text{I}^-(aq) + 3 \text{H}_2\text{O}(l) \rightarrow \text{IO}_3^-(aq) + 6 \text{H}^+(aq) + 6 \text{e}^-$$
4. Add half-reactions and cancel substances appearing as both reactants and products.

$$6 \text{MnO}_4^-(aq) + \cancel{6 \text{e}^-} \rightarrow 6 \text{MnO}_4^{2-}(aq)$$

$$\text{I}^-(aq) + 3 \text{H}_2\text{O}(l) \rightarrow \text{IO}_3^-(aq) + 6 \text{H}^+(aq) + \cancel{6 \text{e}^-}$$

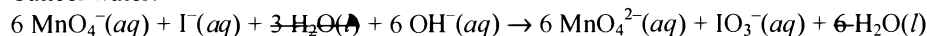
Overall: $6 \text{MnO}_4^-(aq) + \text{I}^-(aq) + 3 \text{H}_2\text{O}(l) \rightarrow 6 \text{MnO}_4^{2-}(aq) + \text{IO}_3^-(aq) + 6 \text{H}^+(aq)$
5. Add hydroxide ions to neutralize H^+ . Cancel water. The 6 H^+ are neutralized by adding 6 OH^- . The same number of hydroxide ions must be added to the reactants to keep the balance of O and H atoms on both sides of the reaction.

$$6 \text{MnO}_4^-(aq) + \text{I}^-(aq) + 3 \text{H}_2\text{O}(l) + 6 \text{OH}^-(aq) \rightarrow 6 \text{MnO}_4^{2-}(aq) + \text{IO}_3^-(aq) + 6 \text{H}^+(aq) + 6 \text{OH}^-(aq)$$

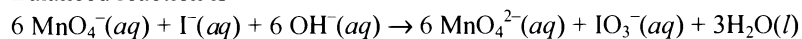
The neutralization reaction produces water: $6 \{ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \}$.

$$6 \text{MnO}_4^-(aq) + \text{I}^-(aq) + 3 \text{H}_2\text{O}(l) + 6 \text{OH}^-(aq) \rightarrow 6 \text{MnO}_4^{2-}(aq) + \text{IO}_3^-(aq) + 6 \text{H}_2\text{O}(l)$$

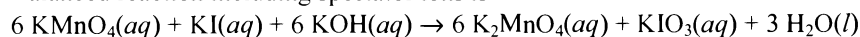
Cancel water:



Balanced reaction is



Balanced reaction including spectator ions is



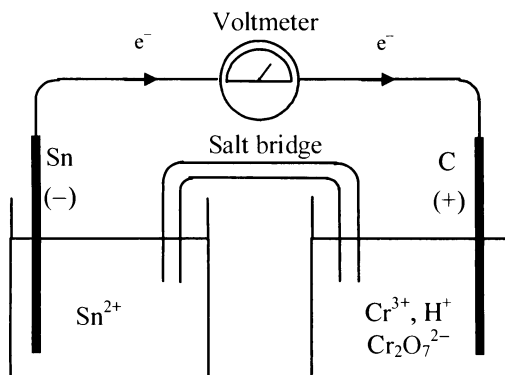
Check: Check balance of atoms and charge:

Reactants:	Products:
6 Mn atoms	6 Mn atoms
1 I atom	1 I atom
30 O atoms	30 O atoms
6 H atoms	6 atoms
-13 charge	-13 charge

- 21.2 Plan: Given the solution and electrode compositions, the two half cells involve the transfer of electrons 1) between chromium in $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{3+} and 2) between Sn and Sn^{2+} . The negative electrode is the anode so the tin half-cell is where oxidation occurs. The graphite electrode with the chromium ion/chromate solution is where reduction occurs.

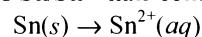
In the cell diagram, show the electrodes and the solutes involved in the half-reactions. Include the salt bridge and wire connection between electrodes. Set up the two half-reactions and balance. (Note that the $\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$ half-cell is in acidic solution.) Write the cell notation placing the anode half-cell first, then the salt bridge, then the cathode half-cell.

Solution: Cell diagram:

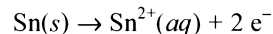


Balanced equations:

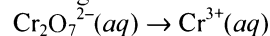
Anode is Sn/Sn^{2+} half-cell. Oxidation of Sn produces Sn^{2+} :



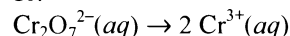
All that needs to be balanced is charge:



Cathode is the $\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$ half-cell. Check the oxidation number of chromium in each substance to determine which is reduced. Cr^{3+} oxidation number is +3 and chromium in $\text{Cr}_2\text{O}_7^{2-}$ has oxidation number +6. Going from +6 to +3 involves gain of electrons so $\text{Cr}_2\text{O}_7^{2-}$ is reduced.



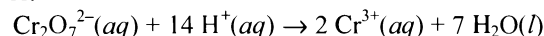
Balance Cr:



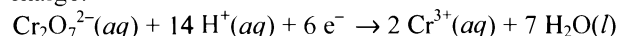
Balance O:



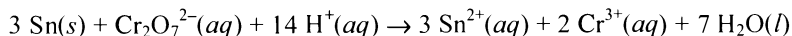
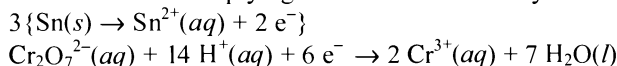
Balance H:



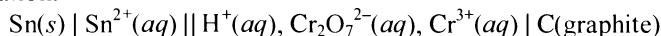
Balance charge:



Add two half-reactions multiplying the tin half-reaction by 3 to equalize the number of electrons transferred.



Cell notation:

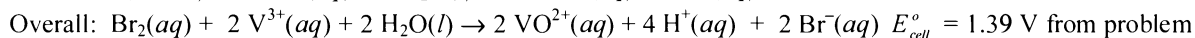
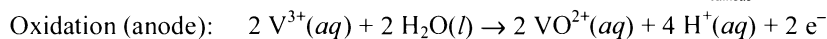
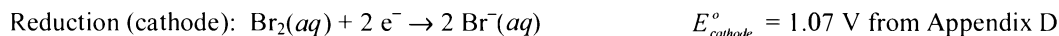


- 21.3 Plan: Divide the reaction into half-reactions showing that Br_2 is reduced and V^{3+} is oxidized. Use the equation

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \text{ to solve for } E_{\text{anode}}^{\circ}.$$

Solution:

Half-reactions:

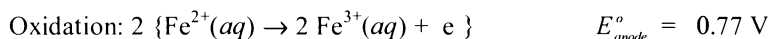
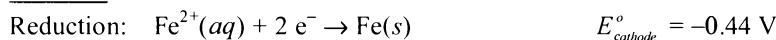


$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{anode}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{cell}}^{\circ} = 1.07 \text{ V} - 1.39 \text{ V} = -0.32 \text{ V}$$

- 21.4 Plan: To determine if the reaction is spontaneous, divide into half-reactions and calculate E_{cell}° . If E_{cell}° is negative, the reaction is not spontaneous, so reverse the reaction to obtain the spontaneous reaction. Reducing strength increases with decreasing E° .

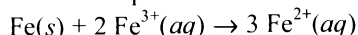
Solution: Divide into half-reactions and balance:



The first half-reaction is reduction, so it is the cathode half-cell. The second half-reaction is oxidation, so it is the anode half-cell. Find the half-reactions in Appendix D.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.44 \text{ V} - 0.77 \text{ V} = -1.21 \text{ V}$$

The reaction is not spontaneous as written, so reverse the reaction:



E_{cell}° is now +1.21 V, so the reversed reaction is spontaneous under standard state conditions.

When a substance acts as a reducing agent, it is oxidized. Both Fe and Fe^{2+} can be oxidized, so they can act as reducing agents. Since Fe^{3+} cannot lose more electrons, it cannot act as a reducing agent. The stronger reducing agent between Fe and Fe^{2+} is the one with the smaller standard reduction potential. E° for Fe is -0.44, which is less than E° for Fe^{2+} , +0.77. Therefore, Fe is a stronger reducing agent than Fe^{2+} . Ranking all three in order of decreasing reducing strength gives **Fe** > **Fe^{2+}** > **Fe^{3+}** .

- 21.5 Plan: Reaction is $\text{Cd}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Cd}^{2+}(aq) + \text{Cu}(s)$.

Given ΔG° , both K and E_{cell}° can be calculated using the relationships

$$\Delta G^{\circ} = -RT \ln K \text{ and } \Delta G^{\circ} = -nF E_{\text{cell}}^{\circ}.$$

Solution:

$$\ln K = -\frac{\Delta G^{\circ}}{RT} = -\left(\frac{-143 \text{ kJ}}{(8.314 \text{ J/mol} \cdot \text{K})(273 + 25) \text{ K}}\right)\left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right) = 57.71779791 \text{ (unrounded)}$$

$$K = 1.1655237 \times 10^{25} = \mathbf{1.17 \times 10^{25}}$$

$$\Delta G^{\circ} = -nF E_{\text{cell}}^{\circ} \quad n = 2 \text{ mol } e^{-} \text{ for this reaction}$$

$$E_{\text{cell}}^{\circ} = -\frac{\Delta G^{\circ}}{nF} = -\left(\frac{-143 \text{ kJ}}{(2 \text{ mol})(96485 \text{ C/mol})}\right)\left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right)\left(\frac{\text{C}}{\text{J/V}}\right) = 0.7410478 = \mathbf{0.741 \text{ V}}$$

Note that an alternative way to calculate E_{cell}° is as equal to $(RT/nF) \ln K$.

Check: Reverse the calculation of K :

$$\Delta G^\circ = -RT \ln K = -[(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln (1.1655237 \times 10^{25})] (1 \text{ kJ} / 10^3 \text{ J}) = 143 \text{ kJ}$$

The potential can easily be checked against the value calculated from Appendix D.

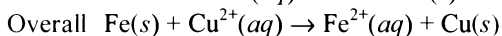
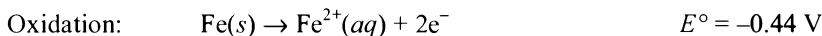
$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = (0.34 \text{ V}) - (-0.40 \text{ V}) = 0.74 \text{ V}$$

The potential value agrees with this literature value.

21.6 Plan: The problem is asking for the concentration of iron ions when $E_{\text{cell}} = E_{\text{cell}}^\circ + 0.25 \text{ V}$.

Use the Nernst equation, $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$ to find $[\text{Fe}^{2+}]$.

Solution: Determining the cell reaction and E_{cell}° :



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.34 \text{ V} - (-0.44 \text{ V}) = 0.78 \text{ V}$$

For the reaction $Q = [\text{Fe}^{2+}]/[\text{Cu}^{2+}]$, so Nernst equation is

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \text{ or}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ -$$

Substituting in values from the problem:

$$E_{\text{cell}} = E_{\text{cell}}^\circ + 0.25 \text{ V} = 0.78 \text{ V} + 0.25 \text{ V} = 1.03 \text{ V}$$

$$1.03 \text{ V} = 0.78 \text{ V} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$

$$0.25 \text{ V} = -\frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]}{[0.30]}$$

$$-8.44595 = \log \frac{[\text{Fe}^{2+}]}{[0.30]}$$

$$3.58141 \times 10^{-9} = \frac{[\text{Fe}^{2+}]}{[0.30]}$$

$$[\text{Fe}^{2+}] = 1.074423 \times 10^{-9} = \mathbf{1.1 \times 10^{-9} M}$$

Check: When $[\text{Fe}^{2+}] = [\text{Cu}^{2+}]$, the log of $[\text{Fe}^{2+}]/[\text{Cu}^{2+}]$ equals 0 and $E_{\text{cell}} = E_{\text{cell}}^\circ$. A change to $[\text{Fe}^{2+}] = (0.1)[\text{Cu}^{2+}]$ gives $\log ([\text{Fe}^{2+}]/[\text{Cu}^{2+}]) = -1$, and the potential changes by $-(-1)(0.03 \text{ V}) = 0.03 \text{ V}$. Use this to estimate the potential change that should occur if $[\text{Fe}^{2+}] = 1 \times 10^{-9} M$ and $[\text{Cu}^{2+}] = 0.1 M$. Estimating the ratio $[\text{Fe}^{2+}]/[\text{Cu}^{2+}] = 1 \times 10^{-9}/0.1 = 1 \times 10^{-8}$ gives log of the ratio equal to -8 to give a potential change of $-(-8)(0.06 \text{ V}/2) = 0.24 \text{ V}$, which is almost the given difference in potential.

21.7 Plan: Half-cell B contains a higher concentration of gold ions, so the ions will be reduced to decrease the concentration while in half-cell A, with a lower $[\text{Au}^{3+}]$, gold metal will be oxidized to increase the concentration of gold ions. In the overall cell reaction, the lower $[\text{Au}^{3+}]$ appears as a product and the higher $[\text{Au}^{3+}]$ appears as a reactant. This means that $Q = [\text{Au}^{3+}]_{\text{lower}}/[\text{Au}^{3+}]_{\text{higher}}$. Use the Nernst equation with $E_{\text{cell}}^\circ = 0$ to find E_{cell} . Oxidation of gold metal occurs at the anode, half-cell A, which is negative.

Solution:

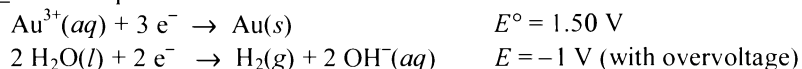
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Au}^{3+}]_{\text{lower}}}{[\text{Au}^{3+}]_{\text{higher}}} \quad n = 3 \text{ mol } e^- \text{ for the reduction of } \text{Au}^{3+} \text{ to Au}$$

$$E_{\text{cell}} = 0 - \frac{0.0592}{3} \log \frac{[7.0 \times 10^{-4}]}{[2.5 \times 10^{-2}]} = 0.0306427 = \mathbf{0.031 \text{ V}}$$

Check: The potential of the cell can be estimated by realizing that each tenfold difference in concentration between the two half cells gives a 20 mV change in potential. The difference is more than tenfold but less than 100 times, so potential should fall between 20 and 40 mV.

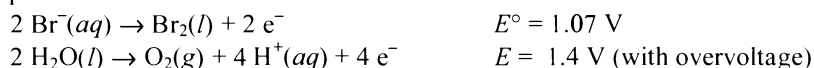
- 21.8 Plan: In aqueous AuBr_3 , the species present are $\text{Au}^{3+}(\text{aq})$, $\text{Br}^{-}(\text{aq})$, H_2O , and very small amounts of H^{+} and OH^{-} . The possible half-reactions are reduction of either Au^{3+} or H_2O and oxidation of either Br^{-} or H_2O . Whichever reduction and oxidation half-reactions are more spontaneous will take place, with consideration of the overvoltage.

Solution: The two possible reductions are



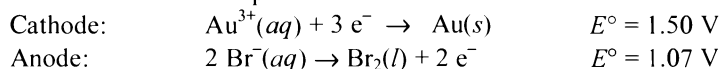
The reduction of gold ions occurs because it has a higher reduction potential (more spontaneous) than reduction of water.

The two possible oxidations are



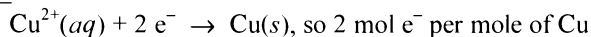
The oxidation with the less positive reduction potential is the more spontaneous oxidation so bromide ions are oxidized at the anode.

The two half-reactions that are predicted are



- 21.9 Plan: Current is charge per time, so to find the time, divide the charge by the current. To find the charge transferred, first write the balanced half-reaction, then calculate the charge from the grams of copper and moles of electrons transferred per molar mass of copper.

Solution:

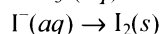
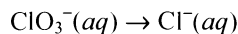


$$(1.50 \text{ g Cu}) \left(\frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \right) \left(\frac{2 \text{ mol e}^{-}}{1 \text{ mol Cu}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^{-}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1}{4.75 \text{ A}} \right) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) = 15.9816 = \mathbf{16.0 \text{ min}}$$

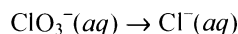
END-OF-CHAPTER PROBLEMS

- 21.1 Oxidation is the loss of electrons (resulting in a higher oxidation number), while reduction is the gain of electrons (resulting in a lower oxidation number). In an oxidation-reduction reaction, electrons transfer from the oxidized substance to the reduced substance. The oxidation number of the reactant being oxidized increases while the oxidation number of the reactant being reduced decreases.
- 21.2 **No**, one half-reaction cannot take place independently of the other because there is always a transfer of electrons from one substance to another. If one substance loses electrons (oxidation half-reaction), another substance must gain those electrons (reduction half-reaction).
- 21.3 Spontaneous reactions, $\Delta G_{\text{sys}} < 0$, take place in voltaic cells, which are also called galvanic cells. Nonspontaneous reactions take place in electrolytic cells and result in an increase in the free energy of the cell ($\Delta G_{\text{sys}} > 0$).
- 21.5 a) To decide which reactant is oxidized, look at oxidation numbers. Cl^{-} is oxidized because its oxidation number increases from -1 in Cl^{-} to 0 in Cl_2 .
b) MnO_4^{-} is reduced because the oxidation number of Mn decreases from $+7$ in MnO_4^{-} to $+2$ in Mn^{2+} .
c) The oxidizing agent is the substance that causes the oxidation by accepting electrons. The oxidizing agent is the substance reduced in the reaction, so MnO_4^{-} is the oxidizing agent.
d) Cl^{-} is the reducing agent because it loses the electrons that are gained in the reduction.
e) **From** Cl^{-} , which is losing electrons, **to** MnO_4^{-} , which is gaining electrons.
f) $8 \text{H}_2\text{SO}_4(\text{aq}) + 2 \text{KMnO}_4(\text{aq}) + 10 \text{KCl}(\text{aq}) \rightarrow 2 \text{MnSO}_4(\text{aq}) + 5 \text{Cl}_2(\text{g}) + 8 \text{H}_2\text{O}(\text{l}) + 6 \text{K}_2\text{SO}_4(\text{aq})$

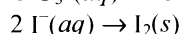
21.7 a) Divide into half-reactions:



Balance elements other than O and H

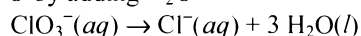


chlorine is balanced

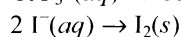


iodine now balanced

Balance O by adding H_2O

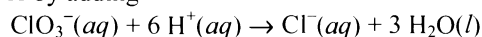


add 3 waters to add 3 O's to product

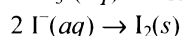


no change

Balance H by adding H^+

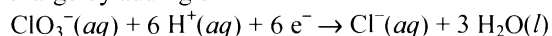


add 6 H^+ to reactants

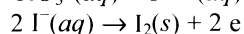


no change

Balance charge by adding e^-

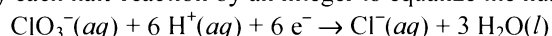


add 6 e^- to reactants for a -1 charge on each side

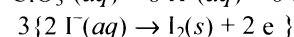


add 2 e^- to products for a -2 charge on each side

Multiply each half-reaction by an integer to equalize the number of electrons

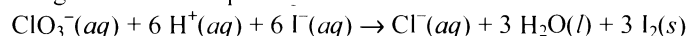


multiply by 1 to give 6 e^-



multiply by 3 to give 6 e^-

Add half-reactions to give balanced equation in acidic solution.

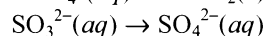
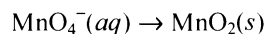


Check balancing:

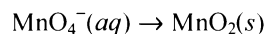
Reactants:	1 Cl	Products:	1 Cl
	3 O		3 O
	6 H		6 H
	6 I		6 I
	-1 charge		-1 charge

Oxidizing agent is ClO_3^- and reducing agent is I^- .

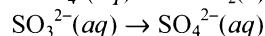
b) Divide into half-reactions:



Balance elements other than O and H



Mn is balanced

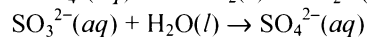


S is balanced

Balance O by adding H_2O

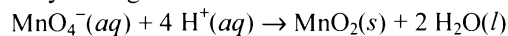


add 2 H_2O to products

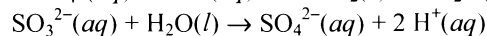


add 1 H_2O to reactants

Balance H by adding H^+

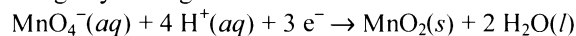


add 4 H^+ to reactants



add 2 H^+ to products

Balance charge by adding e^-

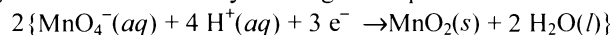


add 3 e^- to reactants for a 0 charge on each side



add 2 e^- to products for a -2 charge on each side

Multiply each half-reaction by an integer to equalize the number of electrons

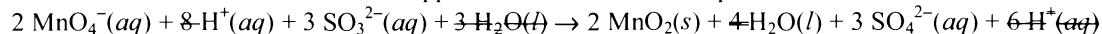


multiply by 2 to give 6 e^-

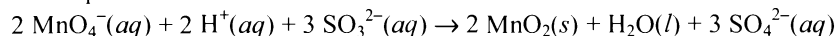


multiply by 3 to give 6 e^-

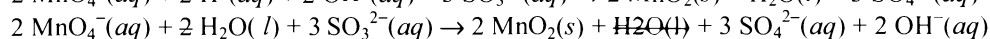
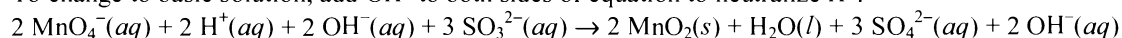
Add half-reactions and cancel substances that appear as both reactants and products



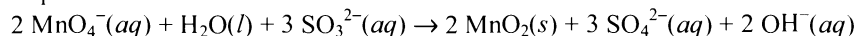
The balanced equation in acidic solution is:



To change to basic solution, add OH^- to both sides of equation to neutralize H^+ .



Balanced equation in basic solution:

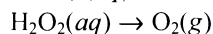
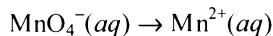


Check balancing:

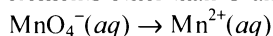
Reactants:	2 Mn	Products:	2 Mn
	18 O		18 O
	2 H		2 H
	3 S		3 S
	-8 charge		-8 charge

Oxidizing agent is MnO_4^- and reducing agent is SO_3^{2-} .

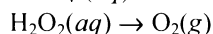
c) Divide into half-reactions:



Balance elements other than O and H

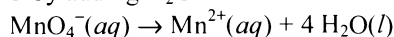


Mn is balanced

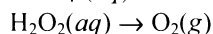


No other elements to balance

Balance O by adding H_2O

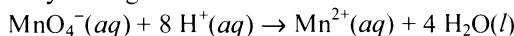


add 4 H_2O to products

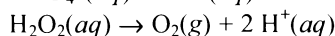


O is balanced

Balance H by adding H^+

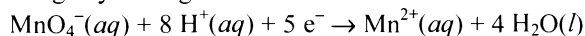


add 8 H^+ to reactants

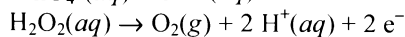


add 2 H^+ to products

Balance charge by adding e^-

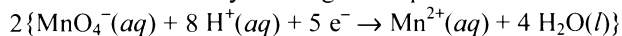


add 5 e^- to reactants for +2 on each side

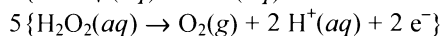


add 2 e^- to products for 0 charge on each side

Multiply each half-reaction by an integer to equalize the number of electrons

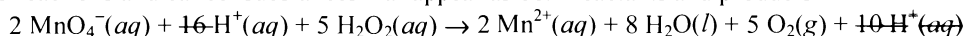


multiply by 2 to give 10 e^-

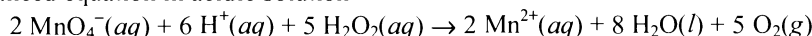


multiply by 5 to give 10 e^-

Add half-reactions and cancel substances that appear as both reactants and products



The balanced equation in acidic solution



Check balancing:

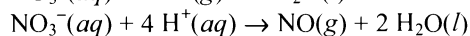
Reactants:	2 Mn	Products:	2 Mn
	18 O		18 O
	16 H		16 H
	+4 charge		+4 charge

Oxidizing agent is MnO_4^- and reducing agent is H_2O_2 .

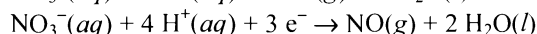
21.10 a) Balance the reduction half-reaction:



balance O

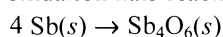


balance H

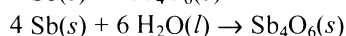


balance charge

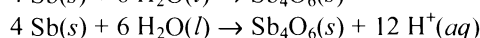
Balance oxidation half-reaction:



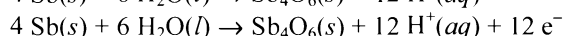
balance Sb



balance O

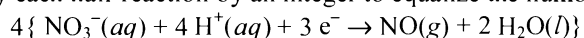


balance H

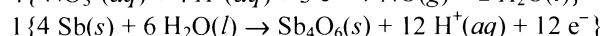


balance charge

Multiply each half-reaction by an integer to equalize the number of electrons

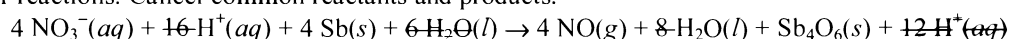


Multiply by 4 to give 12 e^-

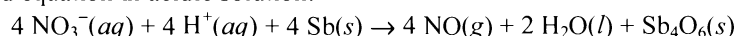


Multiply by 1 to give 12 e^-

Add half-reactions. Cancel common reactants and products.

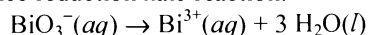


Balanced equation in acidic solution:

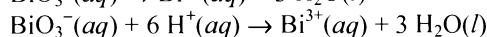


Oxidizing agent is NO_3^- and reducing agent is Sb.

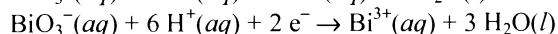
b) Balance reduction half-reaction:



balance O

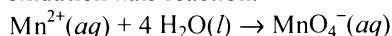


balance H

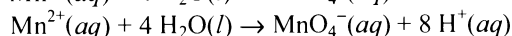


balance charge to give +3 on each side

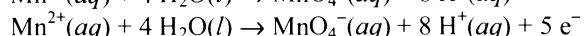
Balance oxidation half-reaction:



balance O

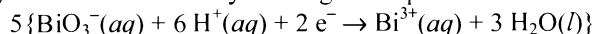


balance H

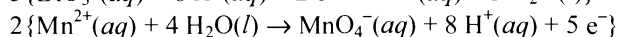


balance charge to give +2 on each side

Multiply each half-reaction by an integer to equalize the number of electrons

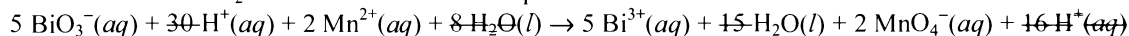


Multiply by 5 to give 10 e⁻

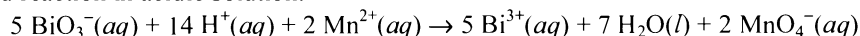


Multiply by 2 to give 10 e⁻

Add half-reactions. Cancel H₂O and H⁺ in reactants and products.

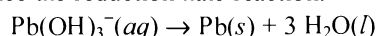


Balanced reaction in acidic solution:

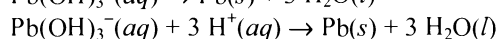


BiO₃⁻ is the oxidizing agent and Mn²⁺ is the reducing agent.

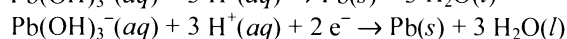
c) Balance the reduction half-reaction:



balance O

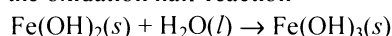


balance H

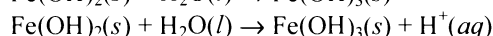


balance charge to give 0 on each side

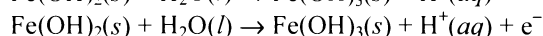
Balance the oxidation half-reaction



balance O

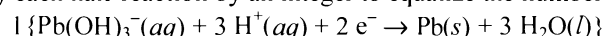


balance H

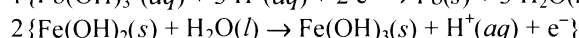


balance charge to give 0 on each side

Multiply each half-reaction by an integer to equalize the number of electrons

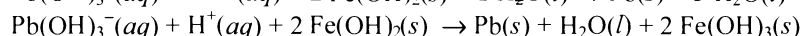
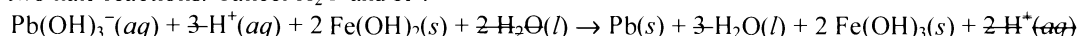


Multiply by 1 to give 2 e⁻

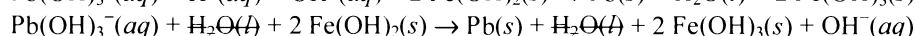
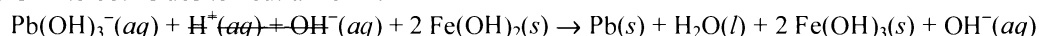


Multiply by 2 to give 2 e⁻

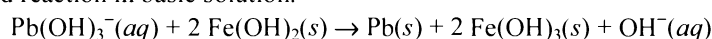
Add the two half-reactions. Cancel H₂O and H⁺.



Add one OH⁻ to both sides to neutralize H⁺.



Balanced reaction in basic solution:

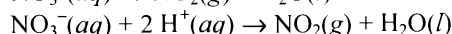


Pb(OH)₃⁻ is the oxidizing agent and Fe(OH)₂ is the reducing agent.

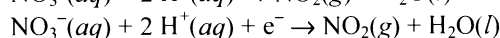
21.12 a) Balance reduction half-reaction:



balance O

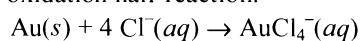


balance H

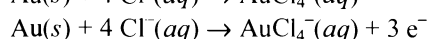


balance charge to give 0 on each side

Balance oxidation half-reaction:

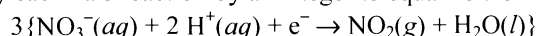


balance Cl

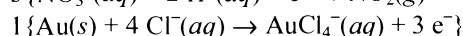


balance charge to -4 on each side

Multiply each half-reaction by an integer to equalize the number of electrons

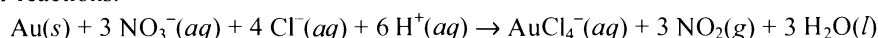


Multiply by 3 to give 3 e⁻



Multiply by 1 to give 3 e⁻

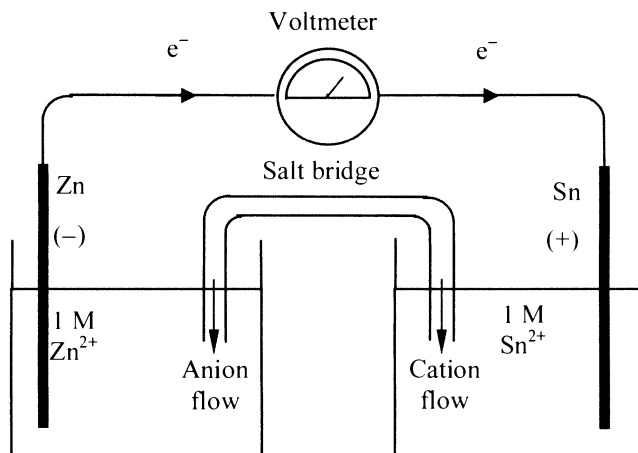
Add half-reactions.



b) Oxidizing agent is **NO₃⁻** and reducing agent is **Au**.

c) The HCl provides chloride ions that combine with the unstable gold ion to form the stable ion, AuCl₄⁻.

- 21.13 a) **A** is the anode because by convention the anode is shown on the left.
 b) **E** is the cathode because by convention the cathode is shown on the right.
 c) **C** is the salt bridge providing electrical connection between the two solutions.
 d) **A** is the anode, so oxidation takes place there. Oxidation is the loss of electrons, meaning that electrons are leaving the anode.
 e) **E** is assigned a positive charge because it is the cathode.
 f) **E** gains mass because the reduction of the metal ion produced the metal.
- 21.16 An active electrode is a reactant or product in the cell reaction, whereas an inactive electrode is neither a reactant nor a product. An inactive electrode is present only to conduct electricity when the half-cell reaction does not include a metal. Platinum and graphite are commonly used as inactive electrodes.
- 21.17 a) The metal **A** is being oxidized to form the metal cation. To form positive ions an atom must always lose electrons, so this half-reaction is always an oxidation.
 b) The metal ion **B** is gaining electrons to form the metal B, so it is displaced.
 c) The anode is the electrode at which oxidation takes place, so metal **A** is used as the anode.
 d) Acid oxidizes metal B and metal B oxidizes metal A, so acid will oxidize metal A and **bubbles will form** when metal A is placed in acid. The same answer results if strength of reducing agents is considered. The fact that metal A is a better reducing agent than metal B indicates that if metal B reduces acid then metal A will also reduce acid.
- 21.18 a) Oxidation: $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^{-}$ (oxidation takes place at the negative electrode)
 Reduction: $\text{Sn}^{2+}(aq) + 2e^{-} \rightarrow \text{Sn}(s)$
 Overall reaction: $\text{Zn}(s) + \text{Sn}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Sn}(s)$
 b)

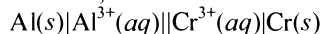


- 21.20 a) Electrons flow from the anode to the cathode, so **from the iron half-cell to the nickel half-cell**, left to right in the figure. By convention, the anode appears on the left and the cathode on the right.
 b) Oxidation occurs at the anode, which is the electrode in the **iron** half-cell.
 c) Electrons enter the reduction half-cell, the **nickel** half-cell in this example.
 d) Electrons are consumed in the reduction half-reaction. Reduction takes place at the cathode, **nickel** electrode.
 e) The anode is assigned a negative charge, so the **iron** electrode is negatively charged.
 f) Metal is oxidized in the oxidation half-cell, so the **iron** electrode will decrease in mass.
 g) The solution must contain nickel ions, so any nickel salt can be added. **1 M NiSO₄** is one choice.
 h) KNO₃ is commonly used in salt bridges, the ions being **K⁺ and NO₃⁻**. Other salts are also acceptable answers.
 i) **Neither** because an inactive electrode could not replace either electrode since both the oxidation and the reduction half-reactions include the metal as either a reactant or a product.
 j) Anions will move toward the half-cell in which positive ions are being produced. The oxidation half-cell produces Fe²⁺, so salt bridge anions move **from right (nickel half-cell) to left (iron half-cell)**.
 k) Oxidation half-reaction: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^{-}$
 Reduction half-reaction: $\text{Ni}^{2+}(aq) + 2e^{-} \rightarrow \text{Ni}(s)$
 Overall cell reaction: $\text{Fe}(s) + \text{Ni}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Ni}(s)$

- 21.22 In cell notation, the oxidation components of the anode compartment are written on the left of the salt bridge and the reduction components of the cathode compartment are written to the right of the salt bridge. A double vertical line separates the anode from the cathode and represents the salt bridge. A single vertical line separates species of different phases.

Anode || Cathode

- a) Al is oxidized, so it is the anode and appears first in the cell notation:



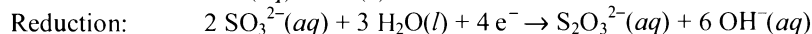
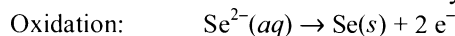
- b) Cu^{2+} is reduced, so Cu is the cathode and appears last in the cell notation. The oxidation of SO_2 does not include a metal, so an inactive electrode must be present. Hydrogen ion must be included in the oxidation half-cell.



- 21.25 A negative E_{cell}° indicates that the cell reaction is not spontaneous, $\Delta G^{\circ} > 0$. The reverse reaction is spontaneous with $E_{\text{cell}}^{\circ} > 0$.

- 21.26 Similar to other state functions, the sign of E° changes when a reaction is reversed. Unlike ΔG° , ΔH° and S° , E° is an intensive property, the ratio of energy to charge. When the coefficients in a reaction are multiplied by a factor, the values of ΔG° , ΔH° and S° are multiplied by the same factor. However, E° does not change because both the energy and charge are multiplied by the factor and their ratio remains unchanged.

- 21.27 a) Divide the balanced equation into reduction and oxidation half-reactions and add electrons. Add water and hydroxide ion to the half-reaction that includes oxygen.

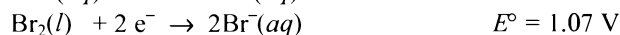
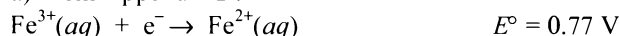


$$b) E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{anode}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{cell}}^{\circ} = -0.57 \text{ V} - 0.35 \text{ V} = -0.92 \text{ V}$$

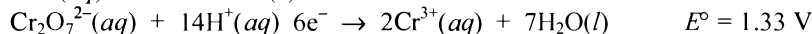
- 21.29 The greater (more positive) the reduction potential, the greater the strength as an oxidizing agent.

- a) From Appendix D:



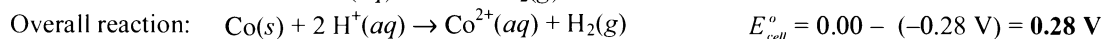
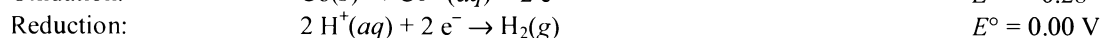
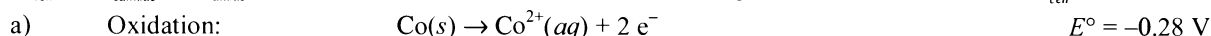
When placed in order of decreasing strength as oxidizing agents: $\text{Br}_2 > \text{Fe}^{3+} > \text{Cu}^{2+}$.

- b) From Appendix D:

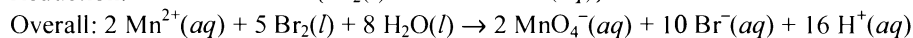
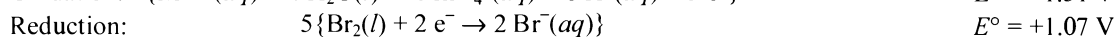
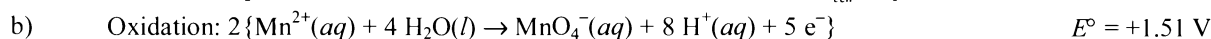


When placed in order of increasing strength as oxidizing agents: $\text{Ca}^{2+} < \text{Ag}^{+} < \text{Cr}_2\text{O}_7^{2-}$.

- 21.31 $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ E° values are found in Appendix D. Spontaneous reactions have $E_{\text{cell}}^{\circ} > 0$.

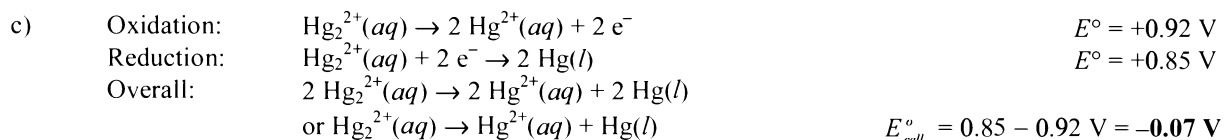


Reaction is **spontaneous** under standard state conditions because E_{cell}° is positive.



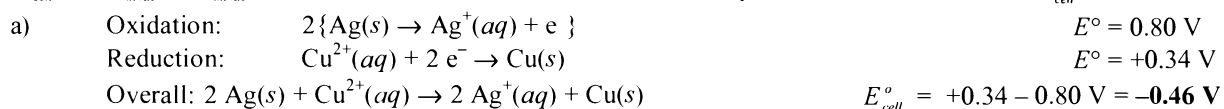
$$E_{\text{cell}}^{\circ} = 1.07 - 1.51 \text{ V} = -0.44 \text{ V}$$

Reaction is **not spontaneous** under standard state conditions with $E_{\text{cell}}^{\circ} < 0$.

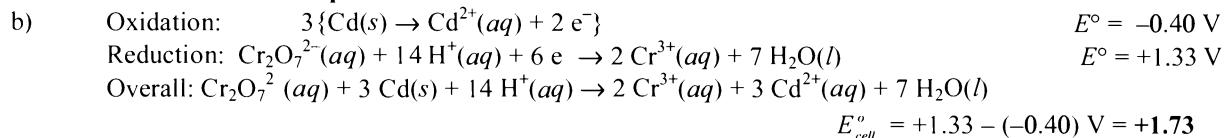


Negative E_{cell}° indicates reaction is **not spontaneous** under standard state conditions.

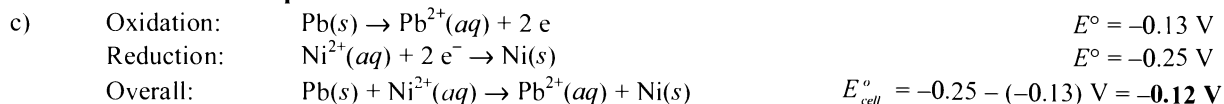
21.33 $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$ E° values are found in Appendix D. Spontaneous reactions have $E_{\text{cell}}^\circ > 0$.



The reaction is **not spontaneous**.

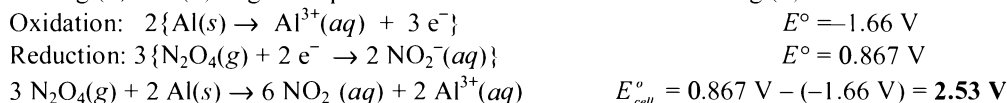


The reaction is **spontaneous**.

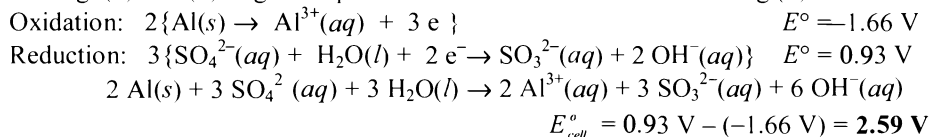


21.35 Spontaneous reactions have $E_{\text{cell}}^\circ > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of E_{cell}° .

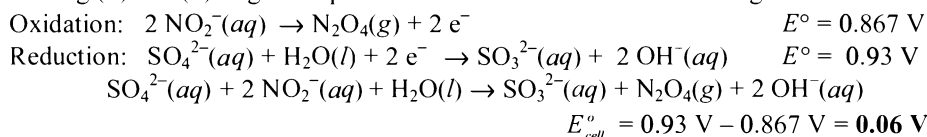
Adding (1) and (2) to give a spontaneous reaction involves converting (1) to oxidation:



Adding (1) and (3) to give a spontaneous reaction involves converting (1) to oxidation:

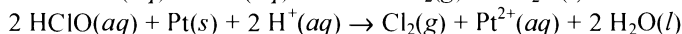
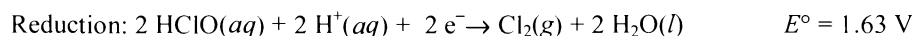


Adding (2) and (3) to give a spontaneous reaction involves converting (2) to oxidation:



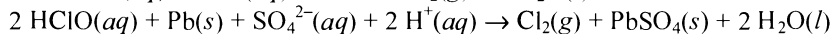
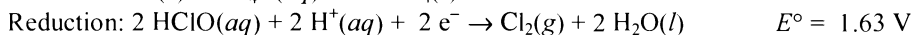
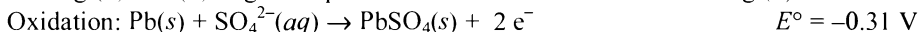
21.37 Spontaneous reactions have $E_{\text{cell}}^\circ > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of E_{cell}° .

Adding (1) and (2) to give a spontaneous reaction involves converting (2) to oxidation:



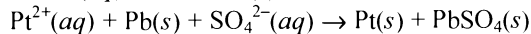
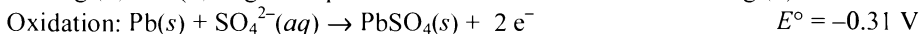
$E_{\text{cell}}^\circ = 1.63 \text{ V} - 1.20 \text{ V} = \mathbf{0.43 \text{ V}}$

Adding (1) and (3) to give a spontaneous reaction involves converting (3) to oxidation:



$$E_{\text{cell}}^\circ = 1.63 \text{ V} - (-0.31 \text{ V}) = \mathbf{1.94 \text{ V}}$$

Adding (2) and (3) to give a spontaneous reaction involves converting (3) to oxidation:



$$E_{\text{cell}}^\circ = 1.20 \text{ V} - (-0.31 \text{ V}) = \mathbf{1.51 \text{ V}}$$

- 21.39 Metal A + Metal B salt \rightarrow solid colored product on metal A

Conclusion: Product is solid metal B. B is undergoing reduction and plating out on A. A is better reducing agent than B.

Metal B + acid \rightarrow gas bubbles

Conclusion: Product is H_2 gas produced as result of reduction of H^+ . B is better reducing agent than acid.

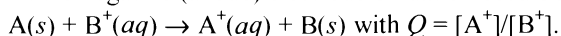
Metal A + Metal C salt \rightarrow no reaction

Conclusion: C is not undergoing reduction. C must be a better reducing agent than A.

Since C is a better reducing agent than A, which is a better reducing agent than B and B reduces acid, then **C would also reduce acid to form H_2 bubbles.**

The order of strength of reducing agents is: **C > A > B.**

- 21.42 At the negative (anode) electrode oxidation occurs so the overall cell reaction is



a) The reaction proceeds to the right because with $E_{\text{cell}} > 0$ (voltaic cell) the spontaneous reaction occurs. As the cell operates **$[\text{A}^+]$ increases and $[\text{B}^+]$ decreases.**

b) E_{cell} **decreases** because the cell reaction takes place to approach equilibrium, $E_{\text{cell}} = 0$.

c) E_{cell} and E_{cell}° are related by the Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^\circ - (RT/nF)\ln([\text{A}^+]/[\text{B}^+])$.

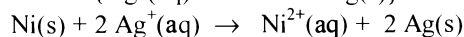
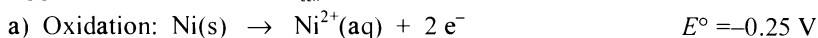
$E_{\text{cell}} = E_{\text{cell}}^\circ$ when $(RT/nF)\ln([\text{A}^+]/[\text{B}^+]) = 0$. This occurs when $\ln([\text{A}^+]/[\text{B}^+]) = 0$. Recall that $e^0 = 1$, so **$[\text{A}^+]$ must equal $[\text{B}^+]$ for E_{cell} to equal E_{cell}° .**

d) **Yes.** It is possible for E_{cell} to be less than E_{cell}° when **$[\text{A}^+] > [\text{B}^+]$.**

- 21.44 In a concentration cell, the overall reaction takes place to decrease the concentration of the more concentrated electrolyte. The more concentrated electrolyte is reduced, so it is in the **cathode** compartment.

- 21.45 The equilibrium constant can be found by using $\ln K = \frac{nFE^\circ}{RT}$ or $\log K = \frac{nE^\circ}{0.0592}$. Use E° values from

Appendix D to calculate E_{cell}° and then calculate K.



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.80 \text{ V} - (-0.25 \text{ V}) = 1.05 \text{ V}; 2 \text{ electrons are transferred.}$$

$$\log K = \frac{nE^\circ}{0.0592} = \frac{2(1.05 \text{ V})}{0.0592 \text{ V}} = 35.47297 \text{ (unrounded)}$$

$$K = 2.97146 \times 10^{35} = \mathbf{3 \times 10^{35}}$$

b) Oxidation: $3\{\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-}\}$ $E^{\circ} = -0.44\text{ V}$
 Reduction: $2\{\text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-} \rightarrow \text{Cr(s)}\}$ $E^{\circ} = -0.74\text{ V}$
 $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.74\text{ V} - (-0.44\text{ V}) = -0.30\text{ V}$; 6 electrons are transferred.

$$\log K = \frac{nE^{\circ}}{0.0592} = \frac{6(-0.30\text{ V})}{0.0592\text{ V}} = -30.4054 \text{ (unrounded)}$$

$$K = 3.9318 \times 10^{-31} = 4 \times 10^{-31}$$

21.47 Substitute J/C for V.

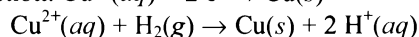
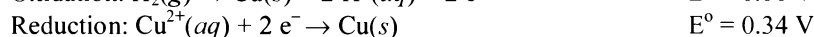
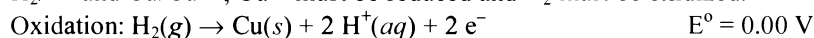
a) $\Delta G^{\circ} = -nFE^{\circ} = -(2\text{ mol e}^{-})(96485\text{ C/mol e}^{-})(1.05\text{ J/C}) = -2.026185 \times 10^5 = -2.03 \times 10^5\text{ J}$
 b) $\Delta G^{\circ} = -nFE^{\circ} = -(6\text{ mol e}^{-})(96485\text{ C/mol e}^{-})(-0.30\text{ J/C}) = 1.73673 \times 10^5 = 1.73 \times 10^5\text{ J}$

21.49 Find ΔG° from the fact that $\Delta G^{\circ} = -RT \ln K$. Then use ΔG° value to find E°_{cell} from $\Delta G^{\circ} = -nFE^{\circ}$.

$T = (273 + 25)\text{K} = 298\text{ K}$
 $\Delta G^{\circ} = -RT \ln K = -(8.314\text{ J/mol}\cdot\text{K})(298\text{ K}) \ln (5.0 \times 10^3) = -2.1101959 \times 10^4 = -2.1 \times 10^4\text{ J}$

$$E^{\circ} = -\frac{\Delta G}{nF} = -\frac{-2.1101959 \times 10^4\text{ J}}{(1\text{ mol e}^{-})(96485\text{ C/mol e}^{-})\left(\frac{1\text{ V}}{1\text{ J/C}}\right)} = 0.218707 = 0.22\text{ V}$$

21.51 Since this is a voltaic cell, a spontaneous reaction is occurring. For a spontaneous reaction between H_2/H^{+} and Cu/Cu^{2+} , Cu^{2+} must be reduced and H_2 must be oxidized:



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= 0.34\text{ V} - 0.00\text{ V} \\ &= 0.34\text{ V} \end{aligned}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log \frac{[\text{H}^{+}]^2}{[\text{Cu}^{2+}][\text{H}_2]}$$

For a standard hydrogen electrode $[\text{H}^{+}] = 1.0\text{ M}$ and $[\text{H}_2] = 1.0\text{ atm}$

$$0.25\text{ V} = 0.34\text{ V} - \frac{0.0592}{2} \log \frac{1.0}{[\text{Cu}^{2+}]1.0}$$

$$0.25\text{ V} - 0.34\text{ V} = -\frac{0.0592}{2} \log \frac{1.0}{[\text{Cu}^{2+}]1.0}$$

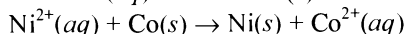
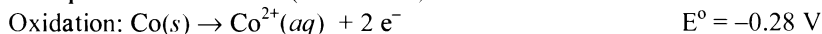
$$-0.090\text{ V} = -\frac{0.0592}{2} \log \frac{1.0}{[\text{Cu}^{2+}]1.0}$$

$$-3.04054 = \log \frac{1.0}{[\text{Cu}^{2+}]1.0} \quad \text{Raise each side to } 10^x$$

$$9.10876 \times 10^{-4} = \frac{1}{[\text{Cu}^{2+}]}$$

$$[\text{Cu}^{2+}] = 9.10876 \times 10^{-4} = 9 \times 10^{-4}\text{ M}$$

21.53 The spontaneous reaction (voltaic cell) involves the oxidation of Co and the reduction of Ni^{2+} .



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = -0.25 \text{ V} - (-0.28 \text{ V}) = 0.03 \text{ V}$$

a) Use the Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log \frac{[\text{Co}^{2+}]}{[\text{Ni}^{2+}]}$ $n = 2 e^-$

$$E_{\text{cell}} = 0.03 \text{ V} - \frac{0.0592}{2} \log \frac{[0.20]}{[0.80]}$$

$$= 0.047820975 \text{ V} = \mathbf{0.05 \text{ V}}$$

b) From part (a), notice that an increase in $[\text{Co}^{2+}]$ leads to a decrease in cell potential. Therefore, the concentration of cobalt ion must increase further to bring the potential down to 0.03 V. Thus, the new concentrations will be

$[\text{Co}^{2+}] = 0.20 \text{ M} + x$ and $[\text{Ni}^{2+}] = 0.80 \text{ M} - x$ (There is a 1:1 mole ratio)

$$0.03 \text{ V} = 0.03 \text{ V} - \frac{0.0592}{2} \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$0 = - \frac{0.0592}{2} \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$0 = \log \frac{[0.20 + x]}{[0.80 - x]} \quad \text{Raise each side to } 10^x$$

$$1 = \frac{[0.20 + x]}{[0.80 - x]}$$

$$0.20 + x = 0.80 - x$$

$$x = 0.30 \text{ M}$$

$$[\text{Ni}^{2+}] = 0.80 - 0.30 = \mathbf{0.50 \text{ M}}$$

c) At equilibrium $E_{\text{cell}} = 0.00$, to decrease the cell potential to 0.00, $[\text{Co}^{2+}]$ increases and $[\text{Ni}^{2+}]$ decreases.

$$0.00 \text{ V} = 0.03 \text{ V} - \frac{0.0592}{2} \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$-0.03 \text{ V} = -0.0296 \log \frac{[0.20 + x]}{[0.80 - x]}$$

$$1.0135135 = \log \frac{[0.20 + x]}{[0.80 - x]}$$

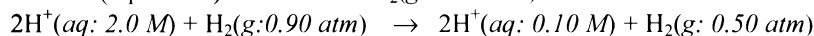
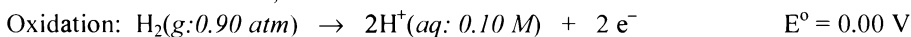
$$10.316052 = \frac{[0.20 + x]}{[0.80 - x]}$$

$$x = 0.7116332 \text{ (unrounded)}$$

$$[\text{Co}^{2+}] = 0.20 + 0.7116332 = 0.9116332 = \mathbf{0.91 \text{ M}}$$

$$[\text{Ni}^{2+}] = 0.80 - 0.7116332 = 0.08837 = \mathbf{0.09 \text{ M}}$$

21.55 The overall cell reaction proceeds to increase the 0.10 M H^+ concentration and decrease the 2.0 M H^+ concentration. Therefore, half-cell **A is the anode** because it has the lower concentration.



$$E_{\text{cell}}^\circ = 0.00 \text{ V} \quad n = 2 e^-$$

$$Q \text{ for the cell equals } \frac{[\text{H}^+]_{\text{anode}}^2 P_{\text{H(cathode)}}}{[\text{H}^+]_{\text{cathode}}^2 P_{\text{H(anode)}}} = \frac{(0.10)^2 (0.50)}{(2.0)^2 (0.90)} = 0.001388889 \text{ (unrounded)}$$

$$E_{\text{cell}} = 0.00 \text{ V} - \frac{0.0592}{2} \log (0.001388889) = 0.084577 = \mathbf{0.085 \text{ V}}$$

- 21.57 Electrons flow from the anode, where oxidation occurs, to the cathode, where reduction occurs. The electrons always flow from the anode to the cathode no matter what type of cell.
- 21.58 A D-sized battery is much larger than an AAA-sized battery, so the D-sized battery contains a greater amount of the cell components. The potential, however, is an intensive property and does not depend on the amount of the cell components. (Note that amount is different from concentration.) The total amount of charge a battery can produce does depend on the amount of cell components, so the D-sized battery produces more charge than the AAA-sized battery.
- 21.60 The Teflon spacers keep the two metals separated so the copper cannot conduct electrons that would promote the corrosion of the iron skeleton. Oxidation of the iron by oxygen causes rust to form and the metal to corrode.
- 21.62 Sacrificial anodes are metals with E° less than that for iron, -0.44 V , so they are more easily oxidized than iron.
- $E^\circ(\text{aluminum}) = -1.66$. Yes, except aluminum resists corrosion because once a coating of its oxide covers it, no more aluminum corrodes. Therefore, it would not be a good choice.
 - $E^\circ(\text{magnesium}) = -2.37 \text{ V}$. Yes, magnesium is appropriate to act as a sacrificial anode.
 - $E^\circ(\text{sodium}) = -2.71 \text{ V}$. Yes, except sodium reacts with water, so it would not be a good choice.
 - $E^\circ(\text{lead}) = -0.13 \text{ V}$. No, lead is not appropriate to act as a sacrificial anode because its value is too high.
 - $E^\circ(\text{nickel}) = -0.25 \text{ V}$. No, nickel is inappropriate as a sacrificial anode because its value is too high.
 - $E^\circ(\text{zinc}) = -0.76 \text{ V}$. Yes, zinc is appropriate to act as a sacrificial anode.
 - $E^\circ(\text{chromium}) = -0.74 \text{ V}$. Yes, chromium is appropriate to act as a sacrificial anode.
- 21.64 $3 \text{ Cd}^{2+}(\text{aq}) + 2 \text{ Cr}(\text{s}) \rightarrow 3 \text{ Cd}(\text{s}) + 2 \text{ Cr}^{3+}(\text{aq})$
 $E_{\text{cell}}^\circ = -0.40 \text{ V} - (-0.74 \text{ V}) = 0.34 \text{ V}$
 To reverse the reaction requires 0.34 V with the cell in its standard state. A 1.5 V supplies more than enough potential, so the cadmium metal oxidizes to Cd^{2+} and chromium plates out.
- 21.66 The oxidation number of nitrogen in the nitrate ion, NO_3^- , is +5 and cannot be oxidized further since nitrogen has only five electrons in its outer level. In the nitrite ion, NO_2^- , on the other hand, the oxidation number of nitrogen is +3, so it can be oxidized to the +5 state.
- 21.68 Iron and nickel are more easily oxidized than copper, so they are separated from the copper in the roasting step and conversion to slag. In the electrolyrefining process, all three metals are oxidized into solution, but only Cu^{2+} ions are reduced at the cathode to form $\text{Cu}(\text{s})$.
- 21.70 a) At the anode, bromide ions are oxidized to form bromine (**Br**₂).
 b) At the cathode, sodium ions are reduced to form sodium metal (**Na**).
- 21.72 Possible reductions:
- | | |
|--|-------------------------------------|
| $\text{Cu}^{2+}(\text{aq}) + 2 \text{ e}^- \rightarrow \text{Cu}(\text{s})$ | $E^\circ = +0.34 \text{ V}$ |
| $\text{Ba}^{2+}(\text{aq}) + 2 \text{ e}^- \rightarrow \text{Ba}(\text{s})$ | $E^\circ = -2.90 \text{ V}$ |
| $\text{Al}^{3+}(\text{aq}) + 3 \text{ e}^- \rightarrow \text{Al}(\text{s})$ | $E^\circ = -1.66 \text{ V}$ |
| $2 \text{ H}_2\text{O}(\text{l}) + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{ OH}^-(\text{aq})$ | $E = -1 \text{ V}$ with overvoltage |
- Copper** can be prepared by electrolysis of its aqueous salt since its reduction half-cell potential is more positive than the potential for the reduction of water. The reduction of copper is more spontaneous than the reduction of water. Since the reduction potentials of Ba^{2+} and Al^{3+} are more negative and therefore less spontaneous than the reduction of water, these ions cannot be reduced in the presence of water since the water is reduced instead.

Possible oxidations:



Bromine can be prepared by electrolysis of its aqueous salt because its reduction half-cell potential is more negative than the potential for the oxidation of water with overvoltage. The more negative reduction potential for Br^- indicates that its oxidation is more spontaneous than the oxidation of water.

21.74 a) Possible oxidations:



Since the reduction potential of water is more negative than the reduction potential for F^- , the oxidation of water is more spontaneous than that of F^- . The oxidation of water produces oxygen gas (O_2), and hydronium ions (H_3O^+) at the anode.

Possible reductions:



Since the reduction potential of water is more positive than that of Li^+ , the reduction of water is more spontaneous than the reduction of Li^+ . The reduction of water produces H_2 gas and OH^- at the cathode.

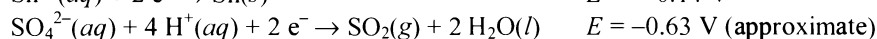
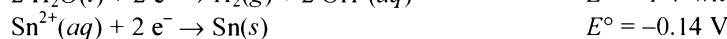
b) Possible oxidations:



The oxidation of water produces oxygen gas (O_2), and hydronium ions (H_3O^+) at the anode.

The SO_4^{2-} ion cannot oxidize as S is already in its highest oxidation state in SO_4^{2-} .

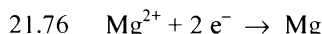
Possible reductions:



The potential for sulfate reduction is estimated from the Nernst equation using standard state concentrations and pressures for all reactants and products except H^+ , which in pure water is $1 \times 10^{-7} \text{ M}$.

$$E = 0.20 \text{ V} - (0.0592 / 2) \log [1 / (1 \times 10^{-7})^4] = -0.6288 = -0.63 \text{ V}$$

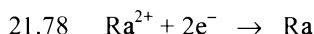
The most easily reduced ion is Sn^{2+} with the most positive reduction potential, so **tin metal** forms at the cathode.



$$\text{a) } (35.6 \text{ g Mg}) \left(\frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \right) = 2.92883587 = \mathbf{2.93 \text{ mol e}^-}$$

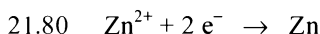
$$\text{b) } (2.92883587 \text{ mol e}^-) \left(\frac{96485 \text{ C}}{\text{mol e}^-} \right) = 2.8258872 \times 10^5 = \mathbf{2.83 \times 10^5 \text{ coulombs}}$$

$$\text{c) } \left(\frac{2.8258872 \times 10^5 \text{ C}}{2.50 \text{ h}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) = 31.3987 = \mathbf{31.4 \text{ A}}$$



In the reduction of radium ions, Ra^{2+} , to radium metal, the transfer of two electrons occurs.

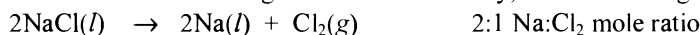
$$(215 \text{ C}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Ra}}{2 \text{ mol e}^-} \right) \left(\frac{226 \text{ g Ra}}{1 \text{ mol Ra}} \right) = 0.25180 = \mathbf{0.282 \text{ g Ra}}$$



$$\text{Time} = (85.5 \text{ g Zn}) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Zn}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1}{23.0 \text{ A}} \right) \left(\frac{1 \text{ A}}{\text{C/s}} \right) = 1.0966901 \times 10^4 = \mathbf{1.10 \times 10^4 \text{ seconds}}$$

- 21.82 a) The sodium sulfate makes the water conductive, so the current will flow through the water to complete the circuit, increasing the rate of electrolysis. Pure water, which contains very low ($10^{-7} M$) concentrations of H^+ and OH^- , conducts electricity very poorly.
 b) The reduction of H_2O has a more positive half-potential ($-1 V$) than the reduction of Na^+ ($-2.71 V$); the more spontaneous reduction of water will occur instead of the less spontaneous reduction of sodium ion. The oxidation of H_2O is the only oxidation possible because SO_4^{2-} cannot be oxidized under these conditions. In other words, it is easier to reduce H_2O than Na^+ and easier to oxidize H_2O than SO_4^{2-} .

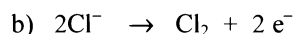
- 21.83 a) Calculate amount of chlorine gas from stoichiometry, then use ideal gas law to find volume of chlorine gas.



$$\text{Moles } Cl_2 = (30.0 \text{ kg Na}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \right) \left(\frac{1 \text{ mol } Cl_2}{2 \text{ mol Na}} \right) = 652.45759 \text{ mol } Cl_2 \text{ (unrounded)}$$

$$V = \frac{nRT}{P} = \frac{(652.45759 \text{ mol } Cl_2) \left(0.0821 \frac{L \cdot atm}{mol \cdot K} \right) ((273 + 580.) K)}{(1.0 \text{ atm})}$$

$$= 4.5692 \times 10^4 = \mathbf{4.6 \times 10^4 L}$$



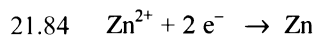
Two moles of electrons are passed through the cell for each mole of Cl_2 produced.

$$\text{Coulombs} = (652.45759 \text{ mol } Cl_2) \left(\frac{2 \text{ mol } e^-}{1 \text{ mol } Cl_2} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol } e^-} \right)$$

$$= 1.259047 \times 10^8 = \mathbf{1.26 \times 10^8 \text{ Coulombs}}$$

- c) Current is charge per time with the amp unit equal to C / s .

$$(125904741 \text{ C}) \left(\frac{1 \text{ s}}{75 \text{ C}} \right) = 1.6787 \times 10^6 = \mathbf{1.68 \times 10^6 \text{ seconds}}$$



$$\text{Mass} = (0.755 \text{ A}) \left(\frac{C/s}{A} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \left(\frac{24 \text{ h}}{1 \text{ day}} \right) (2.00 \text{ day}) \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Zn}}{2 \text{ mol } e^-} \right) \left(\frac{65.41 \text{ g Zn}}{1 \text{ mol Zn}} \right)$$

$$= 44.222678 = \mathbf{44.2 \text{ g Zn}}$$

- 21.87 From the current 70.0% of the moles of product will be copper and 30.0% zinc. Assume a current of exactly 100 coulombs. The amount of current used to generate copper would be $(70.0\% / 100\%) (100 \text{ C}) = 70.0 \text{ C}$, and the amount of current used to generate zinc would be $(30.0\% / 100\%) (100 \text{ C}) = 30.0 \text{ C}$.

The half-reactions are: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ and $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$.

$$\text{Mass copper} = (70.0 \text{ C}) \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \right) \left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 0.023052806 \text{ g Cu (unrounded)}$$

$$\text{Mass zinc} = (30.0 \text{ C}) \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Zn}}{2 \text{ mol } e^-} \right) \left(\frac{65.41 \text{ g Zn}}{1 \text{ mol Zn}} \right) = 0.010168938 \text{ g Zn (unrounded)}$$

$$\text{Mass\% copper} = \left(\frac{0.023052806 \text{ g Cu}}{(0.023052806 + 0.010168938) \text{ g Sample}} \right) \times 100\% = 69.3907 = \mathbf{69.4\% Cu}$$

- 21.89 The reaction is: $\text{Au}^{3+}(\text{aq}) + 3 \text{e}^{-} \rightarrow \text{Au}(\text{s})$
 a) Find the volume of gold needed to plate the earring and then use density to find the mass and moles of gold needed. The volume of the gold is the volume of a cylinder (see the inside back cover of the text)

$$V = \pi r^2 h$$

$$V = \pi \left(\frac{5.00 \text{ cm}}{2} \right)^2 (0.20 \text{ mm}) \left(\frac{10^{-3} \text{ m}}{1 \text{ mm}} \right) \left(\frac{1 \text{ cm}}{10^{-2} \text{ m}} \right) = 0.39269908 \text{ cm}^3$$

$$(0.39269908 \text{ cm}^3) \left(\frac{19.3 \text{ g Au}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol Au}}{197.0 \text{ g Au}} \right) = 0.03847255 \text{ mol Au (unrounded)}$$

$$\begin{aligned} \text{Time} &= (0.03847255 \text{ mol Au}) \left(\frac{3 \text{ mol e}^{-}}{1 \text{ mol Au}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^{-}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1}{0.010 \text{ A}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right) \\ &= 12.88897 = \mathbf{13 \text{ days}} \end{aligned}$$

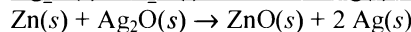
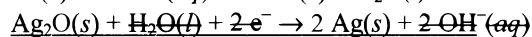
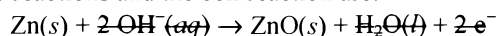
- b) The time required doubles once for the second earring of the pair and doubles again for the second side, thus it will take four times as long as one side of one earring.

$$\text{Time} = (4) (12.88897 \text{ days}) = 51.555887 = \mathbf{5.2 \times 10^1 \text{ days}}$$

- c) Start by multiplying the moles of gold from part (a) by four to get the moles for the earrings. Convert this moles to grams, then to troy ounces, and finally to dollars.

$$\text{Cost} = (4) (0.03847255 \text{ mol Au}) \left(\frac{197.0 \text{ g Au}}{1 \text{ mol Au}} \right) \left(\frac{1 \text{ Troy Ounce}}{31.10 \text{ g}} \right) \left(\frac{\$320}{\text{Troy Ounce}} \right) = 311.936917 = \mathbf{\$310}$$

- 21.91 The half-reactions and the cell reaction are:



The key is the moles of zinc. From the moles of zinc, the moles of electrons and the moles of Ag_2O may be found. Only 80% of the initial amount of zinc reacts:

$$\text{Moles Zn} = (16.0 \text{ g Zn}) \left(\frac{80\%}{100\%} \right) \left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}} \right) = 0.195688732 \text{ mol Zn (unrounded)}$$

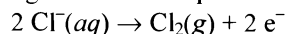
The 80% is assumed to have two significant figures.

$$\begin{aligned} \text{a) Time} &= (0.195688732 \text{ mol Zn}) \left(\frac{2 \text{ mol e}^{-}}{1 \text{ mol Zn}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^{-}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1 \text{ mA}}{10^{-3} \text{ A}} \right) \left(\frac{1}{4.8 \text{ mA}} \right) \left(\frac{1 \text{ h}}{3600 \text{ s}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right) \\ &= 91.054337 = \mathbf{91 \text{ days}} \end{aligned}$$

$$\begin{aligned} \text{b) Mass Ag} &= (0.1956887326 \text{ mol Zn}) \left(\frac{1 \text{ mol Ag}_2\text{O}}{1 \text{ mol Zn}} \right) \left(\frac{100\%}{95\%} \right) \left(\frac{2 \text{ mol Ag}}{1 \text{ mol Ag}_2\text{O}} \right) \left(\frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} \right) \\ &= 44.45224 = \mathbf{44 \text{ g Ag}} \end{aligned}$$

$$\text{c) Cost} = (44.45224 \text{ g Ag}) \left(\frac{95\%}{100\%} \right) \left(\frac{1 \text{ troy oz}}{31.10 \text{ g Ag}} \right) \left(\frac{\$5.50}{\text{troy oz}} \right) \left(\frac{1}{91.054337 \text{ days}} \right) = 0.0820198 = \mathbf{\$0.08/\text{day}}$$

- 21.92 This problem deals with the stoichiometry of electrolysis. The balanced oxidation half-reaction for the chlor-alkali process is given in the chapter:



Use the Faraday constant, F , ($1 F = 96485 \text{ C/mol e}^{-}$) and the fact that 1 mol of Cl_2 produces 2 mol e^{-} or $2 F$, to convert coulombs to moles of Cl_2 .

$$\begin{aligned} \text{Mass Cl}_2 &= (3 \times 10^4 \text{ A}) \left(\frac{\text{C/s}}{\text{A}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) (8 \text{ h}) \left(\frac{1 \text{ mol e}^{-}}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^{-}} \right) \left(\frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{2.205 \text{ lb}}{1 \text{ kg}} \right) \\ &= 699.9689 = \mathbf{7 \times 10^2 \text{ pounds Cl}_2} \end{aligned}$$

- 21.94 a) Aluminum half-reaction: $\text{Al}^{3+}(\text{aq}) + 3 \text{e}^{-} \rightarrow \text{Al}(\text{s})$, so $n = 3$. Remember that $1 \text{ A} = 1 \text{ C/s}$.

$$\text{Time} = (1000 \text{ kg Al}) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{3 \text{ mol e}^{-}}{1 \text{ mol Al}} \right) \left(\frac{96485 \text{ C}}{1 \text{ mol e}^{-}} \right) \left(\frac{\text{A}}{\text{C/s}} \right) \left(\frac{1}{100,000 \text{ A}} \right)$$

$$= 1.0728502 \times 10^5 = \mathbf{1.073 \times 10^5 \text{ s}}$$

The molar mass of aluminum limits the significant figures.

- b) Multiply the time by the current and voltage, remembering that $1 \text{ A} = 1 \text{ C/s}$ (thus $100,000 \text{ A}$ is $100,000 \text{ C/s}$) and $1 \text{ V} = 1 \text{ J/C}$ (thus, $5.0 \text{ V} = 5.0 \text{ J/C}$). Change units of J to $\text{kW}\cdot\text{h}$.

$$(1.0728502 \times 10^5 \text{ s}) \left(\frac{100,000 \text{ C}}{\text{s}} \right) \left(\frac{5.0 \text{ J}}{\text{C}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left(\frac{1 \text{ kW}\cdot\text{h}}{3.6 \times 10^3 \text{ kJ}} \right) = 1.4900698 \times 10^4 = \mathbf{1.5 \times 10^4 \text{ kW}\cdot\text{h}}$$

- c) From part (b), the $1.5 \times 10^4 \text{ kW}\cdot\text{h}$ calculated is per 1000 kg of aluminum. Use the ratio of $\text{kW}\cdot\text{h}$ to mass to find $\text{kW}\cdot\text{h/lb}$ and then use efficiency and cost per $\text{kW}\cdot\text{h}$ to find cost per pound.

$$\text{Cost} = \left(\frac{1.4900698 \times 10^4 \text{ kW}\cdot\text{h}}{1000 \text{ kg Al}} \right) \left(\frac{1 \text{ kg}}{2.205 \text{ lb}} \right) \left(\frac{0.90 \text{ cents}}{1 \text{ kW}\cdot\text{h}} \right) \left(\frac{100\%}{90\%} \right) = 6.757686 = \mathbf{6.8\text{¢ / lb Al}}$$

- 21.96 Statement: metal D + hot water \rightarrow reaction Conclusion: D reduces water.

Statement: D + E salt \rightarrow no reaction. Conclusion: D does not reduce E salt, so E reduces D salt. E is better reducing agent than D.

Statement: D + F salt \rightarrow reaction Conclusion: D reduces F salt. D is better reducing agent than F.

If E metal and F salt are mixed, the salt would be reduced producing F metal because E has the greatest reducing strength of the three metals (E is stronger than D and D is stronger than F). The ranking of increasing reducing strength is $\mathbf{F < D < E}$.

- 21.97 Substitute J/C for V.

a) Cell I: Oxidation number (O.N.) of H from 0 to +1, so 1 electron lost from each of 4 hydrogens for a total of 4 electrons. Oxygen O.N. goes from 0 to -2 indicating that 2 electrons are gained by each of the two oxygens for a total of 4 electrons. There is a transfer of **four electrons** in the reaction. The potential given in the problem allows the calculation of ΔG° :

$$\Delta G^\circ = -nFE^\circ = -(4 \text{ mol e}^{-}) (96485 \text{ C/mol e}^{-}) (1.23 \text{ J/C}) = -4.747062 \times 10^5 = \mathbf{-4.75 \times 10^5 \text{ J}}$$

Cell II: In $\text{Pb}(\text{s}) \rightarrow \text{PbSO}_4$, O.N. of Pb goes from 0 to +2 and in $\text{PbO}_2 \rightarrow \text{PbSO}_4$, O.N. goes from +4 to +2. There is a transfer of **two electrons** in the reaction.

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol e}^{-}) (96485 \text{ C/mol e}^{-}) (2.04 \text{ J/C}) = -3.936588 \times 10^5 = \mathbf{-3.94 \times 10^5 \text{ J}}$$

Cell III: O.N. of each of two Na atoms changes from 0 to +1 and O.N. of Fe changes from +2 to 0. There is a transfer of **two electrons** in the reaction.

$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol e}^{-}) (96485 \text{ C/mol e}^{-}) (2.35 \text{ J/C}) = -4.534795 \times 10^5 = \mathbf{-4.53 \times 10^5 \text{ J}}$$

- b) Cell I: Mass of reactants = $(2 \text{ mol H}_2) \left(\frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} \right) + (1 \text{ mol O}_2) \left(\frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \right) = 36.032 \text{ g}$ (unrounded)

$$\frac{w_{\text{max}}}{\text{Reactant Mass}} = \left(\frac{-4.747062 \times 10^5 \text{ J}}{36.032 \text{ g}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = -13.17457 = \mathbf{-13.2 \text{ kJ/g}}$$

Cell II: Mass of reactants =

$$(1 \text{ mol Pb}) \left(\frac{207.2 \text{ g Pb}}{1 \text{ mol Pb}} \right) + (1 \text{ mol PbO}_2) \left(\frac{239.2 \text{ g PbO}_2}{1 \text{ mol PbO}_2} \right) + (2 \text{ mol H}_2\text{SO}_4) \left(\frac{98.09 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right)$$

$$= 642.58 \text{ g (unrounded)}$$

$$\frac{w_{\text{max}}}{\text{Reactant Mass}} = \left(\frac{-3.936588 \times 10^5 \text{ J}}{642.58 \text{ g}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = -0.612622 = \mathbf{-0.613 \text{ kJ/g}}$$

$$\begin{aligned}\text{Cell III: Mass of reactants} &= (2 \text{ mol Na}) \left(\frac{22.99 \text{ g Na}}{1 \text{ mol Na}} \right) + (1 \text{ mol FeCl}_2) \left(\frac{126.75 \text{ g FeCl}_2}{1 \text{ mol FeCl}_2} \right) \\ &= 172.73 \text{ g (unrounded)} \\ \frac{w_{\max}}{\text{Reactant Mass}} &= \left(\frac{-4.534795 \times 10^5 \text{ J}}{172.73 \text{ g}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = -2.625366 = \mathbf{-2.62 \text{ kJ/g}}\end{aligned}$$

Cell I has the highest ratio (most energy released per gram) because the reactants have very low mass while Cell II has the lowest ratio because the reactants are very massive.

- 21.98 Examine each reaction to determine which reactant is the oxidizing agent by which reactant gains electrons in the reaction.

From reaction between $\text{U}^{3+} + \text{Cr}^{3+} \rightarrow \text{Cr}^{2+} + \text{U}^{4+}$, find that Cr^{3+} oxidizes U^{3+} .

From reaction between $\text{Fe} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Fe}^{2+}$, find that Sn^{2+} oxidizes Fe.

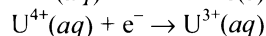
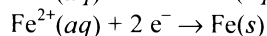
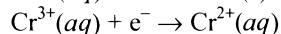
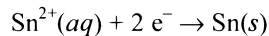
From the fact that no reaction occurs between Fe and U^{4+} , find that Fe^{2+} oxidizes U^{3+} .

From reaction between $\text{Cr}^{3+} + \text{Fe} \rightarrow \text{Cr}^{2+} + \text{Fe}^{2+}$, find that Cr^{3+} oxidizes Fe.

From reaction between $\text{Cr}^{2+} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Cr}^{3+}$, find that Sn^{2+} oxidizes Cr^{2+} .

Notice that nothing oxidizes Sn, so Sn^{2+} must be the strongest oxidizing agent. Both Cr^{3+} and Fe^{2+} oxidize U^{3+} , so U^{4+} must be the weakest oxidizing agent. Cr^{3+} oxidizes iron, so Cr^{3+} is a stronger oxidizing agent than Fe^{2+} .

The half-reactions in order from strongest to weakest oxidizing agent:



- 21.101 Place the elements in order of increasing (more positive) E° .

Reducing agent strength: $\text{Li} > \text{Ba} > \text{Na} > \text{Al} > \text{Mn} > \text{Zn} > \text{Cr} > \text{Fe} > \text{Ni} > \text{Sn} > \text{Pb} > \text{Cu} > \text{Ag} > \text{Hg} > \text{Au}$

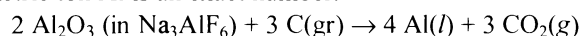
Metals with potentials lower than that of water (-0.83 V) can displace hydrogen from water by reducing the hydrogen in water. These can displace H_2 from water: Li, Ba, Na, Al, and Mn

Metals with potentials lower than that of hydrogen (0.00 V) can displace hydrogen from acids by reducing the H^+ in acid. These can displace H_2 from acid: Li, Ba, Na, Al, Mn, Zn, Cr, Fe, Ni, Sn, and Pb

Metals with potentials above that of hydrogen (0.00 V) cannot displace (reduce) hydrogen.

These cannot displace H_2 : Cu, Ag, Hg, and Au

- 21.102 a) Use the stoichiometric relationships found in the balanced chemical equation to find mass of Al_2O_3 . Assume that 1 metric ton Al is an exact number.



$$\begin{aligned}\text{mass Al}_2\text{O}_3 &= (1 \text{ t Al}) \left(\frac{10^3 \text{ kg}}{1 \text{ t}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{2 \text{ mol Al}_2\text{O}_3}{4 \text{ mol Al}} \right) \left(\frac{101.96 \text{ g Al}_2\text{O}_3}{1 \text{ mol Al}_2\text{O}_3} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1 \text{ t}}{10^3 \text{ kg}} \right) \\ &= 1.8895478 = \mathbf{1.890 \text{ metric tons Al}_2\text{O}_3}\end{aligned}$$

Therefore, **1.890 tons of Al_2O_3** are consumed in the production of 1 ton of pure Al.

- b) Use a ratio of 3 mol C: 4 mol Al to find mass of graphite consumed.

$$\begin{aligned}\text{mass C} &= (1 \text{ t Al}) \left(\frac{10^3 \text{ kg}}{1 \text{ t}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{3 \text{ mol C}}{4 \text{ mol Al}} \right) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1 \text{ t}}{10^3 \text{ kg}} \right) \\ &= 0.3338584 = \mathbf{0.3339 \text{ tons C}}\end{aligned}$$

Therefore, **0.3339 tons of C** are consumed in the production of 1 ton of pure Al, assuming 100% efficiency.

- c) The percent yield with respect to Al_2O_3 is **100%** because the actual plant requirement of 1.89 tons Al_2O_3 equals the theoretical amount calculated in part (a).

- d) The amount of graphite used in reality to produce 1 ton of Al is greater than the amount calculated in (b). In other words, a 100% efficient reaction takes only 0.3339 tons of graphite to produce a ton of Al, whereas real production requires more graphite and is less than 100% efficient. Calculate the efficiency using a simple ratio:

$$(0.45 \text{ t}) (x) = (0.3338584 \text{ t}) (100\%)$$

$$x = 74.19076 = \mathbf{74\%}$$

e) For every 4 moles of Al produced, 3 moles of CO₂ are produced.

$$\text{moles C} = (1 \text{ t Al}) \left(\frac{10^3 \text{ kg}}{1 \text{ t}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left(\frac{3 \text{ mol CO}_2}{4 \text{ mol Al}} \right) = 2.7798 \times 10^4 \text{ mol CO}_2 \text{ (unrounded)}$$

The problem states that 1 atm is exact. Use the ideal gas law to calculate volume, given moles, temperature and pressure.

$$V = nRT / P = \left(\frac{(2.7798 \times 10^4 \text{ mol CO}_2)(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 + 960.) \text{ K}}{1 \text{ atm}} \right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \right)$$

$$= 2.812601 \times 10^3 = \mathbf{2.813 \times 10^3 \text{ m}^3}$$

21.103 a) The reference half-reaction is: $\text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu}(s) \quad E^\circ = 0.34 \text{ V}$

Before the addition of the ammonia, $E_{\text{cell}} = 0$. The addition of ammonia lowers the concentration of copper ions through the formation of the complex $\text{Cu}(\text{NH}_3)_4^{2+}$. The original copper ion concentration is $[\text{Cu}^{2+}]_{\text{original}}$, and the copper ion concentration in the solution containing ammonia is $[\text{Cu}^{2+}]_{\text{ammonia}}$.

The Nernst equation is used to determine the copper ion concentration in the cell containing ammonia.

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

$$0.129 \text{ V} = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$0.129 \text{ V} = - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$(0.129 \text{ V})(-2/0.0592) = \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$-4.358108108 = \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$4.3842154 \times 10^{-5} = \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[0.0100]_{\text{original}}}$$

$$[\text{Cu}^{2+}]_{\text{ammonia}} = 4.3842154 \times 10^{-7} \text{ M (unrounded)}$$

This is the concentration of the copper ion that is not in the complex. The concentration of the complex and of the uncomplexed ammonia must be determined before K_f may be calculated.

The original number of moles of copper and the original number of moles of ammonia are found from the original volumes and molarities:

$$\text{Original moles of copper} = \left(\frac{0.0100 \text{ mol Cu}(\text{NO}_3)_2}{\text{L}} \right) \left(\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu}(\text{NO}_3)_2} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (90.0 \text{ mL})$$

$$= 9.00 \times 10^{-4} \text{ mol Cu}^{2+}$$

$$\text{Original moles of ammonia} = \left(\frac{0.500 \text{ mol NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.0 \text{ mL}) = 5.00 \times 10^{-3} \text{ mol NH}_3$$

Determine the moles of copper still remaining uncomplexed.

$$\text{Remaining mol of copper} = \left(\frac{4.3842154 \times 10^{-7} \text{ mol Cu}^{2+}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100.0 \text{ mL})$$

$$= 4.3842154 \times 10^{-8} \text{ mol Cu}$$

The difference between the original moles of copper and the copper ion remaining in solution is the copper in the complex (= moles of complex). The molarity of the complex may now be found.

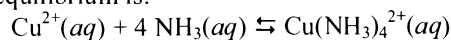
$$\begin{aligned}\text{Moles copper in complex} &= (9.00 \times 10^{-4} - 4.3842154 \times 10^{-8}) \text{ mol Cu}^{2+} \\ &= 8.995615 \times 10^{-4} \text{ mol Cu}^{2+} \text{ (unrounded)}\end{aligned}$$

$$\begin{aligned}\text{Molarity of complex} &= \left(\frac{8.995615 \times 10^{-4} \text{ mol Cu}^{2+}}{100.0 \text{ mL}} \right) \left(\frac{1 \text{ mol Cu(NH}_3)_4^{2+}}{1 \text{ mol Cu}^{2+}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 8.995615 \times 10^{-3} \text{ M Cu(NH}_3)_4^{2+} \text{ (unrounded)}\end{aligned}$$

The concentration of the remaining ammonia is found as follows:

$$\begin{aligned}\text{Molarity of ammonia} &= \left(\frac{(5.00 \times 10^{-3} \text{ mol NH}_3) - (8.995615 \times 10^{-4} \text{ mol Cu}^{2+}) \left(\frac{4 \text{ mol NH}_3}{1 \text{ mol Cu}^{2+}} \right)}{100.0 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ &= 0.014001753 \text{ M ammonia (unrounded)}\end{aligned}$$

The K_f equilibrium is:



$$K_f = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{[8.995615 \times 10^{-3}]}{[4.3842154 \times 10^{-7}][0.014001753]^4} = 5.34072 \times 10^{11} = \mathbf{5.3 \times 10^{11}}$$

b) The K_f will be used to determine the new concentration of free copper ions.

Moles uncomplexed ammonia before the addition of new ammonia =

$$(0.014001753 \text{ mol NH}_3 / \text{L}) (10^{-3} \text{ L / mL}) (100.0 \text{ mL}) = 0.001400175 \text{ mol NH}_3$$

Moles ammonia added = $5.00 \times 10^{-3} \text{ mol NH}_3$ (same as original mol of ammonia)

From the stoichiometry:

	$\text{Cu}^{2+}(\text{aq})$	+	$4 \text{NH}_3(\text{aq})$	\rightarrow	$\text{Cu(NH}_3)_4^{2+}(\text{aq})$
Initial moles:	$4.3842154 \times 10^{-8} \text{ mol}$		0.001400175 mol		$8.995615 \times 10^{-4} \text{ mol}$
Added moles:			$5.00 \times 10^{-3} \text{ mol}$		
Cu^{2+} is limiting:	$-(4.3842154 \times 10^{-8} \text{ mol})$		$-4 (4.3842154 \times 10^{-8} \text{ mol})$		$+(4.3842154 \times 10^{-8} \text{ mol})$
After the reaction:	0		0.006400 mol		$9.00000 \times 10^{-4} \text{ mol}$

Determine concentrations before equilibrium:

$$[\text{Cu}^{2+}] = 0$$

$$[\text{NH}_3] = (0.006400 \text{ mol NH}_3 / 110.0 \text{ mL}) (1 \text{ mL} / 10^{-3} \text{ L}) = 0.0581818 \text{ M NH}_3$$

$$\begin{aligned}[\text{Cu(NH}_3)_4^{2+}] &= (9.00000 \times 10^{-4} \text{ mol Cu(NH}_3)_4^{2+} / 110.0 \text{ mL}) (1 \text{ mL} / 10^{-3} \text{ L}) \\ &= 0.008181818 \text{ M Cu(NH}_3)_4^{2+}\end{aligned}$$

Now allow the system to come to equilibrium:

	$\text{Cu}^{2+}(\text{aq})$	+	$4 \text{NH}_3(\text{aq})$	\rightleftharpoons	$\text{Cu(NH}_3)_4^{2+}(\text{aq})$
Initial molarity:	0		0.0581818		0.008181818
Change:	+ x		+ 4 x		- x
Equilibrium:	x		$0.0581818 + 4x$		$0.008181818 - x$

$$K_f = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{[0.008181818 - x]}{[x][0.0581818 + 4x]^4} = 5.34072 \times 10^{11}$$

Assume -x and +4x are negligible when compared to their associated numbers:

$$K_f = \frac{[0.008181818]}{[x][0.0581818]^4} = 5.34072 \times 10^{11}$$

$$x = [\text{Cu}^{2+}] = 1.3369 \times 10^{-9} \text{ M Cu}^{2+}$$

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{ammonia}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$E = - \frac{0.0592 \text{ V}}{2} \log \frac{[1.3369 \times 10^{-9}]}{[0.0100]}$$

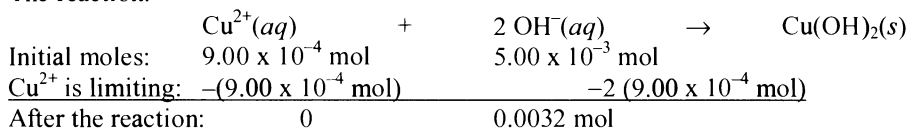
$$E = 0.203467 = \mathbf{0.20 \text{ V}}$$

c) The first step will be to do a stoichiometry calculation of the reaction between copper ions and hydroxide ions.

$$\text{Moles OH}^- = \left(\frac{0.500 \text{ mol NaOH}}{\text{L}} \right) \left(\frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.0 \text{ mL}) = 5.00 \times 10^{-3} \text{ mol OH}^-$$

The initial moles of copper ions were determined earlier: $9.00 \times 10^{-4} \text{ mol Cu}^{2+}$

The reaction:

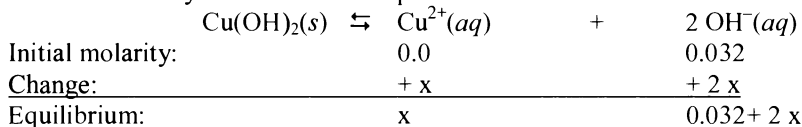


Determine concentrations before equilibrium:

$$[\text{Cu}^{2+}] = 0$$

$$[\text{NH}_3] = (0.0032 \text{ mol OH}^- / 100.0 \text{ mL}) (1 \text{ mL} / 10^{-3} \text{ L}) = 0.032 \text{ M OH}^-$$

Now allow the system to come to equilibrium:



$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-20}$$

$$K_{\text{sp}} = [x][0.032 + 2x]^2 = 2.2 \times 10^{-20}$$

Assume $2x$ is negligible compared to 0.032 M .

$$K_{\text{sp}} = [x][0.032]^2 = 2.2 \times 10^{-20}$$

$$x = [\text{Cu}^{2+}] = 2.1487375 \times 10^{-17} = 2.1 \times 10^{-17} \text{ M}$$

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$E = - \frac{0.0592 \text{ V}}{2} \log \frac{[2.1487375 \times 10^{-17}]}{[0.0100]}$$

$$E = 0.434169 = \mathbf{0.43 \text{ V}}$$

d) Use the Nernst equation to determine the copper ion concentration in the half-cell containing the hydroxide ion.

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[\text{Cu}^{2+}]_{\text{original}}}$$

$$0.340 = - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$(0.340 \text{ V}) (-2 / 0.0592) = \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$-11.486486 = \log \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$3.2622256 \times 10^{-12} = \frac{[\text{Cu}^{2+}]_{\text{hydroxide}}}{[0.0100]}$$

$$[\text{Cu}^{2+}]_{\text{hydroxide}} = 3.2622256 \times 10^{-14} \text{ M (unrounded)}$$

Now use the K_{sp} relationship:

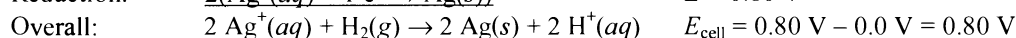
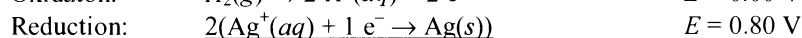
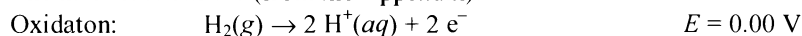
$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^{-}]^2 = 2.2 \times 10^{-20}$$

$$K_{\text{sp}} = [3.2622256 \times 10^{-14}][\text{OH}^{-}]^2 = 2.2 \times 10^{-20}$$

$$[\text{OH}^{-}]^2 = 6.743862 \times 10^{-7}$$

$$[\text{OH}^{-}] = 8.2121 \times 10^{-4} = 8.2 \times 10^{-4} \text{ M OH}^{-} = \mathbf{8.2 \times 10^{-4} \text{ M NaOH}}$$

21.105 The half-reactions are (from the Appendix):



The hydrogen ion concentration can now be found from the Nernst equation.

$$E = E^{\circ} - \frac{0.0592 \text{ V}}{2} \log Q$$

$$0.915 \text{ V} = 0.80 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{H}^{+}]^2}{[\text{Ag}^{+}]^2 P_{\text{H}_2}}$$

$$0.915 \text{ V} - 0.80 \text{ V} = - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{H}^{+}]^2}{[0.100]^2 (1.00)}$$

$$(0.915 \text{ V} - 0.80 \text{ V}) (-2 / 0.0592 \text{ V}) = \log \frac{[\text{H}^{+}]^2}{[0.100]^2 (1.00)}$$

$$-3.885135 = \log \frac{[\text{H}^{+}]^2}{[0.0100]}$$

$$1.30276 \times 10^{-4} = \frac{[\text{H}^{+}]^2}{[0.0100]}$$

$$[\text{H}^{+}] = 1.1413851 \times 10^{-3} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}^{+}] = -\log (1.1413851 \times 10^{-3}) = 2.94256779 = \mathbf{2.94}$$

Chapter 22 The Transition Elements and Their Coordination Compounds

FOLLOW-UP PROBLEMS

- 22.1 **Plan:** Locate the element on the periodic table and use its position and atomic number to write a partial electron configuration. Add or subtract electrons to obtain the configuration for the ion. Partial electron configurations do not include the noble gas configuration and any filled *f* sublevels, but do include outer level electrons (*n*-level) and the *n*–1 level *d* orbitals. Remember that *ns* electrons are removed before *n*–1 electrons.

Solution:

- a) Ag is in the fifth row of the periodic table, so *n* = 5, and it is in group 1B(11). The partial electron configuration of the element is $5s^1 4d^{10}$. For the ion, Ag^+ , remove one electron from the 5*s* orbital. The partial electron configuration of Ag^+ is $4d^{10}$.
- b) Cd is in the fifth row and group 2B(12), so the partial electron configuration of the element is $5s^2 4d^{10}$. Remove two electrons from the 5*s* orbital for the ion. The partial electron configuration of Cd^{2+} is $4d^{10}$.
- c) Ir is in the sixth row and group 8B(9). The partial electron configuration of the element is $6s^2 5d^7$. Remove two electrons from the 6*s* orbital and one from 5*d* for ion Ir^{3+} . The partial electron configuration of Ir^{3+} is $5d^6$.
- Check:** Total the electrons to make sure they agree with configuration.
- a) Ag^+ should have $47 - 1 = 46 \text{ e}^-$. Configuration has 36 e^- (from Kr configuration) plus the 10 electrons in $4d^{10}$. This also totals 46 e^- .
- b) Cd^{2+} should have $48 - 2 = 46 \text{ e}^-$. Configuration is the same as Ag^+ , so 46 e^- as well.
- c) Ir^{3+} should have $77 - 3 = 74 \text{ e}^-$. Total in configuration is 54 e^- (noble gas configuration) plus 14 e^- (in *f* sublevel) plus 6 e^- (in the partial configuration) which equals 74 e^- .

- 22.2 **Plan:** Name the compound by following rules outlined in section 22.2. Use Table 22.6 for the names of ligands and Table 22.7 for the names of metal ions. Write the formula from the name by breaking down the name into pieces that follow naming rules.

Solution:

- a) The compound consists of the cation $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]^{2-}$ and anion Cl^- . The metal ion in the cation is chromium and its charge is found from the charges on the ligands and the total charge on the ion.

$$\text{total charge} = (\text{charge on Cr}) + 5(\text{charge on H}_2\text{O}) + (\text{charge on Br}^-)$$

$$-2 = (\text{charge on Cr}) + 5(0) + (-1)$$

$$\text{charge on Cr} = +3$$

The name of the cation will end with chromium(III) to indicate the oxidation state of the chromium ion since there is more than one possible oxidation state for chromium. The water ligand is named aqua (Table 22.6). There are five water ligands, so pentaqua describes the $(\text{H}_2\text{O})_5$ ligands. The bromide ligand is named bromo. The ligands are named in alphabetical order, so aqua comes before bromo. The name of the cation is pentaquabromochromium(III). Add the chloride for the anion to complete the name:

pentaquabromochromium(III) chloride.

- b) The compound consists of a cation, barium ion, and the anion hexacyanocobaltate(III). The formula of the anion consists of six (from hexa) cyanide (from cyano) ligands and cobalt (from cobaltate) in the +3 oxidation state (from (III)). Putting the formula together gives $[\text{Co}(\text{CN})_6]^{n+}$. To find the charge on the complex ion, calculate from charges on the ligands and the metal ion:

$$\text{total charge} = 6(\text{charge on CN}^-) + (\text{charge on cobalt ion})$$

$$= 6(-1) + (+3)$$

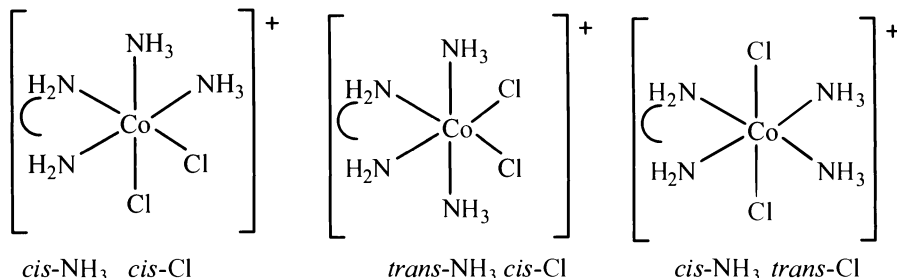
$$= -3$$

The formula of complex ion is $[\text{Co}(\text{CN})_6]^{3-}$. Combining this with the cation, Ba^{2+} , gives the formula for the compound: $\text{Ba}_3[\text{Co}(\text{CN})_6]_2$. The three barium ions give a +6 charge and two anions give a –6 charge, so the net result is a neutral salt.

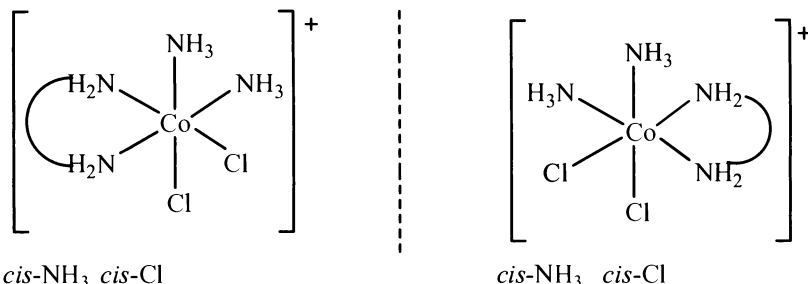
- 22.3 **Plan:** The given complex ion has a coordination number of 6 (*en* is bidentate), so it will have an octahedral arrangement of ligands. Stereoisomers can be either geometric or optical. For geometric isomers, check if the ligands can be arranged either next to (*cis*) or opposite (*trans*) each other. Then, check if the mirror image of any of the geometric isomers is not superimposable. If mirror image is not superimposable, the structure is an optical isomer.

Solution:

The complex ion contains two NH_3 ligands and two chloride ligands, both of which can be arranged in either the *cis* or *trans* geometry. The possible combinations are 1) *cis*- NH_3 and *cis*-Cl, 2) *trans*- NH_3 and *cis*-Cl, and 3) *cis*- NH_3 and *trans*-Cl. Both NH_3 and Cl *trans* is not possible because the two bonds to ethylenediamine can be arranged only in this *cis*-position, which leaves only one set of *trans* positions.



The mirror images of the second two structures are superimposable since two of the ligands, either ammonia or chloride ion, are arranged in the *trans* position. When both types of ligands are in the *cis* arrangement, the mirror image is not a superimposable optical isomer:



There are four stereoisomers of $[\text{Co}(\text{NH}_3)_2(\text{en})\text{Cl}_2]^+$.

- 22.4 **Plan:** Compare the two ions for oxidation state of the metal ion and the relative ability of ligands to split the *d*-orbital energies.

Solution:

The oxidation number of vanadium in both ions is the same, so compare the two ligands. Ammonia is a stronger field ligand than water, so the complex ion $[\text{V}(\text{NH}_3)_6]^{3+}$ absorbs visible light of higher energy than $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ absorbs.

- 22.5 **Plan:** Determine the charge on the manganese ion in the complex ion and the number of electrons in its *d*-orbitals. Since it is an octahedral ligand, the *d*-orbitals split into three lower energy orbitals and two higher energy orbitals. Check the spectrochemical series for whether CN^- is a strong or weak field ligand. If it is a strong field ligand, fill the three lower energy orbitals before placing any electrons in the higher energy *d*-orbitals. If it is a weak field ligand, place one electron in each of the five *d* orbitals, low energy before high energy, before pairing any electrons. After filling orbitals, count the number of unpaired electrons. The complex ion is low-spin if the ligand is a strong field ligand and high-spin if the ligand is weak field.

Solution:

Figure the charge on manganese:

$$\text{total charge} = (\text{charge on Mn}) + 6(\text{charge on } \text{CN}^-)$$

$$\text{charge on Mn} = -3 - [6(-1)] = +3$$

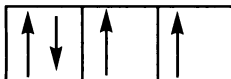
The electron configuration of Mn is $[\text{Ar}]4s^23d^5$; the electron configuration of Mn^{3+} is $[\text{Ar}]3d^4$.

The ligand is CN^- , which is a strong field ligand, so the four *d* electrons will fill the lower energy *d*-orbitals before any are placed in the higher energy *d*-orbitals:

Higher energy d -orbitals



Lower energy d -orbitals



Two electrons are unpaired in $[\text{Mn}(\text{CN})_6]^{3-}$. The complex is **low spin** since the cyanide ligand is a strong field ligand.

END-OF-CHAPTER PROBLEMS

- 22.1 a) All transition elements in Period 5 will have a “base” configuration of $[\text{Kr}]5s^2$, and will differ in the number of d electrons (x) that the configuration contains. Therefore, the general electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^x$.
 b) A general electron configuration for Period 6 transition elements includes f sublevel electrons, which are lower in energy than the d sublevel. The configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^4 5d^x$.
- 22.4 a) One would expect that the elements would increase in size as they increase in mass from Period 5 to 6. Because there are 14 inner transition elements in Period 6, the effective nuclear charge increases significantly. As effective charge increases, the atomic size decreases or “contracts.” This effect is significant enough that Zr^{4+} and Hf^{4+} are almost the same size but differ greatly in atomic mass.
 b) The size increases from Period 4 to 5, but stays fairly constant from Period 5 to 6.
 c) Atomic mass increases significantly from Period 5 to 6, but atomic radius (and thus volume) hardly increases, so Period 6 elements are very dense.
- 22.7 a) A paramagnetic substance is attracted to a magnetic field, while a diamagnetic substance is slightly repelled by one.
 b) Ions of transition elements often have unfilled d -orbitals whose unpaired electrons make the ions paramagnetic. Ions of main group elements usually have a noble gas configuration with no partially filled levels. When orbitals are filled, electrons are paired and the ion is diamagnetic.
 c) The d -orbitals in the transition element ions are not filled, which allows an electron from a lower energy d orbital to move to a higher energy d -orbital. The energy required for this transition is relatively small and falls in the visible wavelength range. All orbitals are filled in a main-group element ion, so enough energy would have to be added to move an electron to a higher energy level, not just another orbital within the same energy level. This amount of energy is relatively large and outside the visible range of wavelengths.
- 22.8 a) V: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ Check: $2 + 2 + 6 + 2 + 6 + 2 + 3 = 23 e^-$
 b) Y: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^1$ Check: $2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 1 = 39 e^-$
 c) Hg: $[\text{Xe}]6s^2 4f^{14} 5d^{10}$ Check: $54 + 2 + 14 + 10 = 80 e^-$
- 22.10 Transition metals lose their s orbital electrons first in forming cations.
 a) The two $4s$ electrons and one $3d$ electron are removed to form Sc^{3+} :
 Sc: $[\text{Ar}]4s^2 3d^1$; Sc^{3+} : $[\text{Ar}]$ or $1s^2 2s^2 2p^6 3s^2 3p^6$. There are **no unpaired electrons**.
 b) The single $4s$ electron and one $3d$ electron are removed to form Cu^{2+} :
 Cu: $[\text{Ar}]4s^1 3d^{10}$; Cu^{2+} : $[\text{Ar}]3d^9$. There is **one unpaired electron**.
 c) The two $4s$ electrons and one $3d$ electron are removed to form Fe^{3+} :
 Fe: $[\text{Ar}]4s^2 3d^6$; Fe^{3+} : $[\text{Ar}]3d^5$. There are **five unpaired electrons** since each of the five d electrons occupies its own orbital.
 d) The two $5s$ electrons and one $4d$ electron are removed to form Nb^{3+} :
 Nb: $[\text{Kr}]5s^2 4d^3$; Nb^{3+} : $[\text{Kr}]4d^2$. There are **two unpaired electrons**.

- 22.12 The elements in Group 6B(6) exhibit an oxidation state of +6. These elements include **Cr, Mo, and W**. Sg (Seaborgium) is also in Group 6B(6), but its lifetime is so short that chemical properties, like oxidation states within compounds, are impossible to measure.
- 22.14 Transition elements in their lower oxidation states act more like metals. The oxidation state of chromium in CrF_2 is +2 and in CrF_6 is +6 (use -1 oxidation state of fluorine to find oxidation state of Cr). **CrF_2** exhibits greater metallic behavior than CrF_6 because the chromium is in a lower oxidation state in CrF_2 than in CrF_6 .
- 22.16 Oxides of transition metals become less basic (or more acidic) as oxidation state increases. The oxidation state of chromium in CrO_3 is +6 and in CrO is +2, based on the -2 oxidation state of oxygen. The oxide of the higher oxidation state, **CrO_3** , produces a more acidic solution.
- 22.19 The coordination number indicates the number of ligand atoms bonded to the central metal ion. The oxidation number represents the number of electrons lost to form the ion. The coordination number is unrelated to the oxidation number.
- 22.21 Coordination number of two indicates **linear** geometry.
 Coordination number of four indicates either **tetrahedral** or **square planar** geometry.
 Coordination number of six indicates **octahedral** geometry.
- 22.24 a) The oxidation state of nickel is found from the total charge on the ion (+2 because two Cl^- charges equals -2) and the charge on ligands:

$$\text{charge on nickel} = +2 - 6(0 \text{ charge on water}) = +2$$
 Name nickel as nickel(II) to indicate oxidation state. Ligands are six (hexa-) waters (aqua). Put together with chloride anions to give **hexaaquanickel(II) chloride**.
 b) The cation is $[\text{Cr}(\text{en})_3]^{3+}$ and the anion is ClO_4^- , the perchlorate ion (see Chapter 2 for naming polyatomic ions). The charge on the cation is +3 to make a neutral salt in combination with 3 perchlorate ions. The ligand is ethylenediamine, which has 0 charge. The charge of the cation equals the charge on chromium ion, so chromium(III) is included in the name. The three ethylenediamine ligands, abbreviated en, are indicated by the prefix tris because the name of the ligand includes a numerical indicator, di-. The complete name is **tris(ethylenediamine)chromium(III) perchlorate**.
 c) The cation is K^+ and the anion is $[\text{Mn}(\text{CN})_6]^{4-}$. The charge of 4- is deduced from the four potassium ions in the formula. The oxidation state of Mn is $-4 - \{6(-1)\} = +2$. The name of CN^- ligand is cyano and six ligands are represented by the prefix hexa. The name of manganese anion is manganate(II). The -ate suffix on the complex ion is used to indicate that it is an anion. The full name of compound is **potassium hexacyanomanganate(II)**.
- 22.26 The charge of the central metal atom was determined in 22.24 because the Roman numeral indicating oxidation state is part of the name. The coordination number, or number of ligand atoms bonded to the metal ion, is found by examining the bonded entities inside the square brackets to determine if they are unidentate, bidentate, or polydentate.
 a) The Roman numeral "II" indicates a +2 oxidation state. There are 6 water molecules bonded to Ni and each ligand is unidentate, so the coordination number is **6**.
 b) The Roman numeral "III" indicates a +3 oxidation state. There are 3 ethylenediamine molecules bonded to Cr, but each ethylenediamine molecule contains two donor N atoms (bidentate). Therefore, the coordination number is **6**.
 c) The Roman numeral "II" indicates a +2 oxidation state. There are 6 unidentate cyano molecules bonded to Mn, so the coordination number is **6**.
- 22.28 a) The cation is K^+ , potassium. The anion is $[\text{Ag}(\text{CN})_2]^-$ with the name dicyanoargentate (I) ion for the two cyanide ligands and the name of silver in anions, argentate(I). The Roman numeral (I) indicates the oxidation number on Ag. O.N. for Ag = $-1 - \{2(-1)\} = +1$ since the complex ion has a charge of -1 and the cyanide ligands are also -1. The complete name is **potassium dicyanoargentate(I)**.
 b) The cation is Na^+ , sodium. Since there are two +1 sodium ions, the anion is $[\text{CdCl}_4]^{2-}$ with a charge of 2-. The anion is the tetrachlorocadmiate(II) ion. With four -1 chloride ligands, the oxidation state of cadmium is +2 and the name of cadmium in an anion is cadmate. The complete name is **sodium tetrachlorocadmiate(II)**.

c) The cation is $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Br}]^{2+}$. The $2+$ charge is deduced from the 2Br^- ions. The cation has the name tetraammineaquabromocobalt(III) ion, with four ammonia ligands (tetraammine), one water ligand (aqua) and one bromide ligand (bromo). The oxidation state of cobalt is $+3$: $2 - \{4(0) + 1(0) + 1(-1)\}$. The oxidation state is indicated by (III), following cobalt in the name. The anion is Br^- , bromide. The complete name is **tetraammineaquabromocobalt(III) bromide**.

22.30 a) The cation is tetramminezinc ion. The tetraammine indicate four NH_3 ligands. Zinc has an oxidation state of $+2$, so the charge on the cation is $+2$. The anion is SO_4^{2-} . Only one sulfate is needed to make a neutral salt. The formula of the compound is **$[\text{Zn}(\text{NH}_3)_4]\text{SO}_4$** .

b) The cation is pentaamminechlorochromium(III) ion. The ligands are 5 NH_3 from pentaammine, and one chloride from chloro. The chromium ion has a charge of $+3$, so the complex ion has a charge equal to $+3$ from chromium, plus 0 from ammonia, plus -1 from chloride for a total of $+2$. The anion is chloride, Cl^- . Two chloride ions are needed to make a neutral salt. The formula of compound is **$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$** .

c) The anion is bis(thiosulfato)argentate(I). Argentate(I) indicates silver in the $+1$ oxidation state, and bis(thiosulfato) indicates 2 thiosulfate ligands, $\text{S}_2\text{O}_3^{2-}$. The total charge on the anion is $+1$ plus $2(-2)$ to equal -3 . The cation is sodium, Na^+ . Three sodium ions are needed to make a neutral salt. The formula of compound is **$\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$** .

23.32 Coordination compounds act like electrolytes, i.e., they dissolve in water to yield charged species. However, the complex ion itself does not dissociate. The “number of individual ions per formula unit” refers to the number of ions that would form per coordination compound upon dissolution in water.

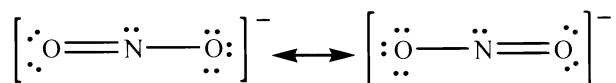
a) The counter ion is SO_4^{2-} , so the complex ion is $[\text{Zn}(\text{NH}_3)_4]^{2+}$. Each ammine ligand is unidentate, so the coordination number is **4**. Each molecule dissolves in water to form one SO_4^{2-} ion and one $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ion, so **2 ions** form per formula unit.

b) The counter ion is Cl^- , so the complex ion is $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$. Each ligand is unidentate, so the coordination number is **6**. Each molecule dissolves in water to form two Cl^- ions and one $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion, so **3 ions** form per formula unit.

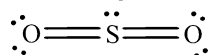
c) The counter ion is Na^+ , so the complex ion is $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$. Assuming that the thiosulfate ligand is unidentate, the coordination number is **2**. Each molecule dissolves in water to form 3 Na^+ ions and one $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ion, so **4 ions** form per formula unit.

22.34 Ligands that form linkage isomers have two different possible donor atoms.

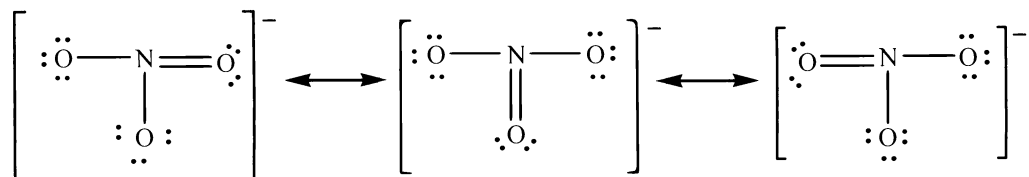
a) The nitrite ion **forms linkage isomers** because it can bind to the metal ion through either the nitrogen or one of the oxygen atoms – both have a lone pair of electrons. Resonance Lewis structures are



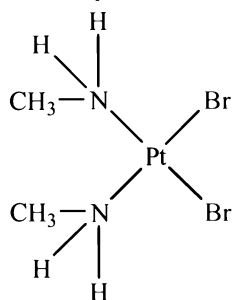
b) Sulfur dioxide molecules **form linkage isomers** because both the sulfur and oxygen atoms can bind metal ions because they both have lone pairs.



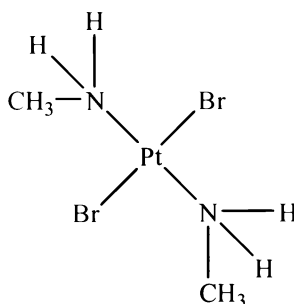
c) Nitrate ions have three oxygen atoms, all with a lone pair that can bond to the metal ion, but all of the oxygen atoms are equivalent, so there are **no linkage isomers**. The nitrogen does not have a lone pair to use to bind metal ions.



- 22.36 a) Platinum ion, Pt^{2+} , is a d^8 ion so the ligand arrangement is square planar. A *cis* and *trans* geometric isomer exist for this complex ion:



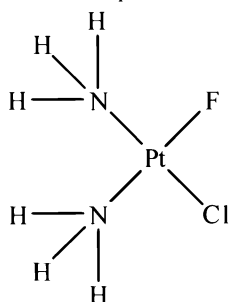
cis isomer



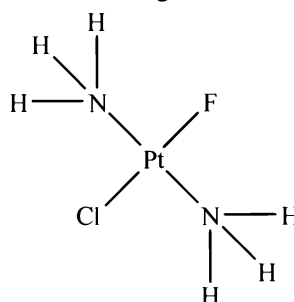
trans isomer

No optical isomers exist because the mirror images of both compounds are superimposable on the original molecules. In general, a square planar molecule is superimposable on its mirror image.

b) A *cis* and *trans* geometric isomer exist for this complex ion. No optical isomers exist because the mirror images of both compounds are superimposable on the original molecules.

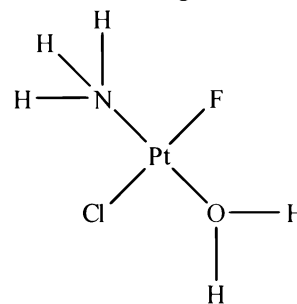
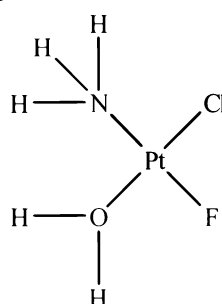
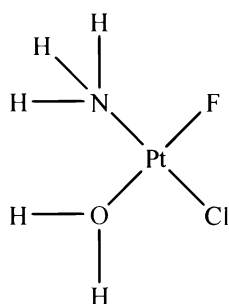


cis isomer



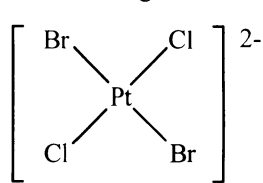
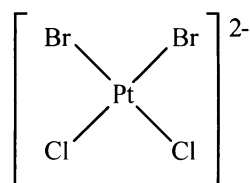
trans isomer

c) Three geometric isomers exist for this molecule, although they are not named *cis* or *trans* because all the ligands are different. A different naming system is used to indicate the relation of one ligand to another.

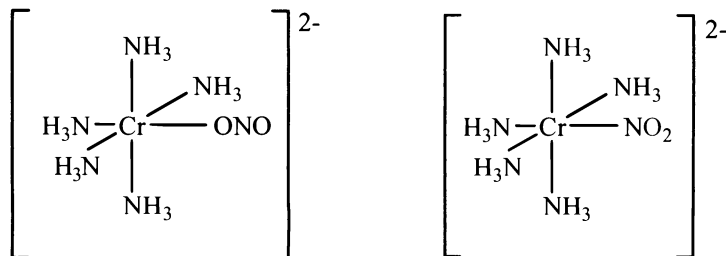


- 22.38 Types of isomers for coordination compounds are coordination isomers with different arrangements of ligands and counterions, linkage isomers with different donor atoms from the same ligand bound to the metal ion, geometric isomers with differences in ligand arrangement relative to other ligands, and optical isomers with mirror images that are not superimposable.

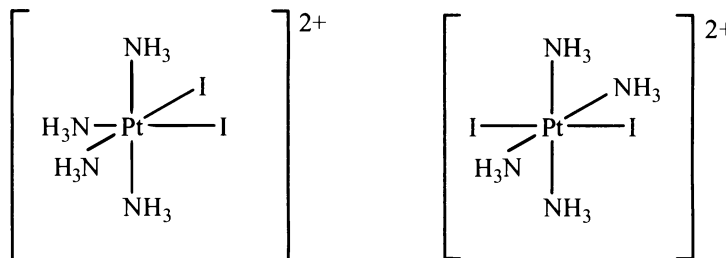
a) Platinum ion, Pt^{2+} , is a d^8 ion, so the ligand arrangement is square planar. The ligands are 2 Cl^- and 2 Br^- , so the arrangement can be either both ligands *trans* or both ligands *cis* to form geometric isomers.



b) The complex ion can form linkage isomers with the NO_2 ligand. Either the N or an O may be the donor.



c) In the octahedral arrangement, the two iodide ligands can be either *trans* to each other, 180° apart, or *cis* to each other, 90° apart.



- 22.40 a) Four empty orbitals of equal energy are “created” to receive the donated electron pairs from four ligands. The four orbitals are hybridized from an s , two p , and one d -orbital from the previous n level to form 4 dsp^2 orbitals.
b) One s and three p -orbitals become four sp^3 hybrid orbitals.
- 22.43 a) The crystal field splitting energy is the energy difference between the two sets of d -orbitals that result from the bonding of ligands to a central transition metal atom.
b) In an octahedral field of ligands, the ligands approach along the x , y , and z axes. The $d_{x^2-y^2}$ and d_{z^2} orbitals are located along the x , y , and z axes, so ligand interaction is higher in energy than the other orbital-ligand interactions. The other orbital-ligand interactions are lower in energy because the d_{xy} , d_{yz} , and d_{zx} orbitals are located between the x , y , and z axes.
c) In a tetrahedral field of ligands, the ligands do not approach along the x , y , and z axes. The ligand interaction is greater for the d_{xy} , d_{yz} , and d_{zx} orbitals and lesser for the $d_{x^2-y^2}$ and d_{z^2} orbitals. The crystal field splitting is reversed, and the d_{xy} , d_{yz} , and d_{zx} orbitals are higher in energy than the $d_{x^2-y^2}$ and d_{z^2} orbitals.
- 22.45 If Δ is greater than E_{pairing} , electrons will preferentially pair spins in the lower energy d -orbitals before adding as unpaired electrons to the higher energy d -orbitals. If Δ is less than E_{pairing} , electrons will preferentially add as unpaired electrons to the higher d -orbitals before pairing spins in the lower energy d -orbitals. The first case gives a complex that is low-spin and less paramagnetic than the high-spin complex formed in the latter case.
- 22.47 To determine the number of d electrons in a central metal ion, first write the electron configuration for the metal atom. Examine the formula of the complex to determine the charge on the central metal ion, and then write the ion's configuration.
a) Electron configuration of Ti: $[\text{Ar}]4s^23d^2$
Charge on Ti: Each chloride ligand has a -1 charge, so Ti has a $+4$ charge $\{+4 + 6(-1)\} = 2-$ ion.
Both of the $4s$ electrons and both $3d$ electrons are removed.
Electron configuration of Ti^{4+} : $[\text{Ar}]$
 Ti^{4+} has **no d electrons**.
b) Electron configuration of Au: $[\text{Xe}]6s^14f^{14}5d^{10}$
Charge on Au: The complex ion has a -1 charge ($[\text{AuCl}_4]^-$) since K has a $+1$ charge. Each chloride ligand has a -1 charge, so Au has a $+3$ charge $\{+3 + 4(-1)\} = 1-$ ion. The $6s$ electron and two d electrons are removed.
Electron configuration of Au^{3+} : $[\text{Xe}]4f^{14}5d^8$
 Au^{3+} has **8 d electrons**.

c) Electron configuration of Rh: $[\text{Kr}]5s^24d^7$

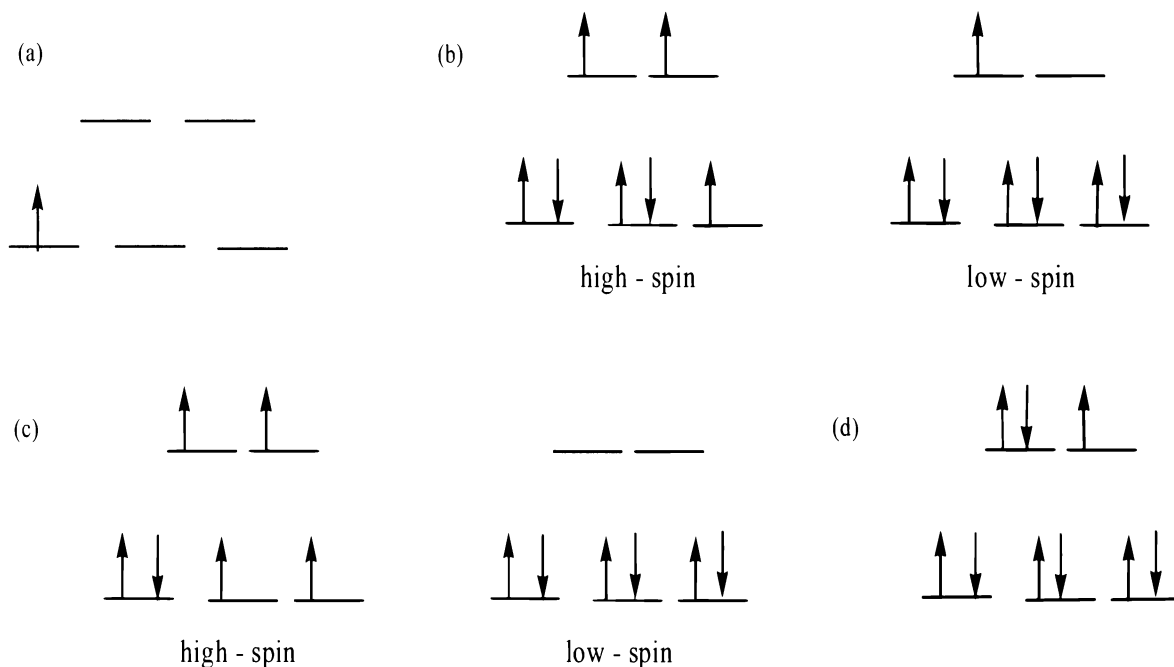
Charge on Rh: Each chloride ligand has a -1 charge, so Rh has a $+3$ charge $\{+3 + 6(-1)\} = 3-$ ion.

The $5s$ electrons and one $4d$ electron are removed.

Electron configuration of Rh^{3+} : $[\text{Kr}]4d^6$

Rh^{3+} has **6 d electrons**.

- 22.49 a) Ti: $[\text{Ar}]4s^23d^2$. The electron configuration of Ti^{3+} is $[\text{Ar}]3d^1$. With only one electron in the d -orbitals, the titanium(III) ion **cannot form** high and low spin complexes – all complexes will contain one unpaired electron and have the same spin.
- b) Co: $[\text{Ar}]4s^23d^7$. The electron configuration of Co^{2+} is $[\text{Ar}]3d^7$ and will form high and low-spin complexes with 7 electrons in the d -orbital.
- c) Fe: $[\text{Ar}]4s^23d^6$. The electron configuration of Fe^{2+} is $[\text{Ar}]3d^6$ and will form high and low-spin complexes with 6 electrons in the d -orbital.
- d) Cu: $[\text{Ar}]4s^13d^{10}$. The electron configuration of Cu^{2+} is $[\text{Ar}]3d^9$, so in complexes with both strong and weak field ligands, one electron will be unpaired and the spin in both types of complexes is identical. Cu^{2+} **cannot form** high and low-spin complexes.



- 22.51 To draw the orbital-energy splitting diagram, first determine the number of d electrons in the transition metal ion. Examine the formula of the complex ion to determine the electron configuration of the metal ion, remembering that the ns electrons are lost first. Determine the coordination number from the number of ligands, recognizing that 6 ligands result in an octahedral arrangement and 4 ligands result in a tetrahedral or square planar arrangement. Weak-field ligands give the maximum number of unpaired electrons (high-spin) while strong-field ligands lead to electron pairing (low-spin).

a) Electron configuration of Cr: $[\text{Ar}]4s^13d^5$

Charge on Cr: The aqua ligands are neutral, so the charge on Cr is $+3$.

Electron configuration of Cr^{3+} : $[\text{Ar}]3d^3$

Six ligands indicate an octahedral arrangement. Using Hund's rule, fill the lower energy t_{2g} orbitals first, filling empty orbitals before pairing electrons within an orbital.

b) Electron configuration of Cu: $[\text{Ar}]4s^13d^{10}$

Charge on Cu: The aqua ligands are neutral, so Cu has a +2 charge.

Electron configuration of Cu^{2+} : $[\text{Ar}]3d^9$

Four ligands and a d^9 configuration indicate a square planar geometry (only filled d sublevel ions exhibit tetrahedral geometry). Use Hund's rule to fill in the 9 d electrons. Therefore, the correct orbital-energy splitting diagram shows one unpaired electron.

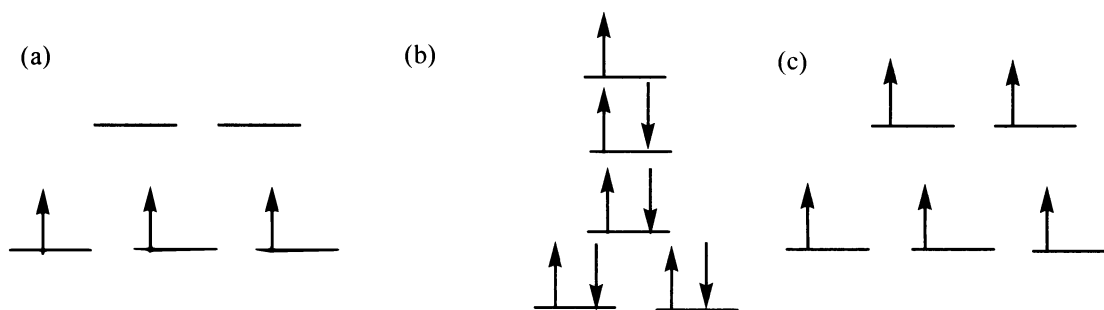
c) Electron configuration of Fe: $[\text{Ar}]4s^23d^6$

Charge on Fe: Each fluoride ligand has a -1 charge, so Fe has a +3 charge to make the overall complex charge equal to -3 .

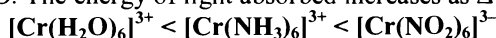
Electron configuration of Fe^{3+} : $[\text{Ar}]3d^5$

Six ligands indicate an octahedral arrangement. Use Hund's rule to fill the orbitals.

F^- is a weak field ligand, so the splitting energy, Δ , is not large enough to overcome the resistance to electron pairing. The electrons remain unpaired, and the complex is called *high-spin*.



22.53 Figure 22.21 describes the spectrum of splitting energy, Δ . NO_2^- is a stronger ligand than NH_3 , which is stronger than H_2O . The energy of light absorbed increases as Δ increases.



22.55 A violet complex absorbs yellow-green light. The light absorbed by a complex with a weaker ligand would be at a lower energy and higher wavelength. Light of lower energy than yellow-green light is yellow, orange, or red light. The color observed would be **blue** or **green**.

22.60 a) The coordination number of cobalt is 6. The two Cl^- ligands are unidentate and the two ethylenediamine ligands are bidentate, so a total of 6 ligand atoms are connected to the central metal ion.

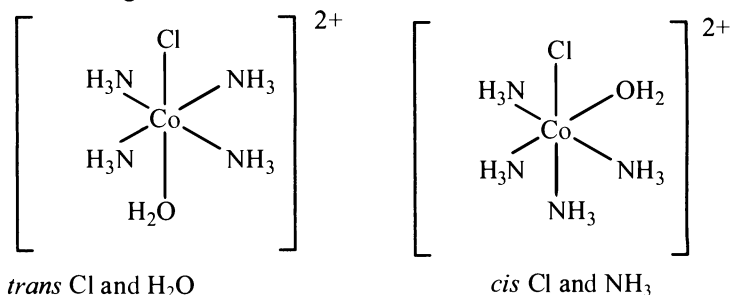
b) The counter ion is Cl^- , so the complex ion is $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. Each chloride ligand has a -1 charge and each en ligand is neutral, so cobalt has a +3 charge: $+3 + 2(0) + 2(-1) = +1$.

c) One mole of complex dissolves in water to yield one mole of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ ions and one mole of Cl^- ions. Therefore, each formula unit yields 2 individual ions.

d) One mole of complex dissolves to form one mole of Cl^- ions, which reacts with the Ag^+ ion (from AgNO_3) to form **one mole of AgCl precipitate**.

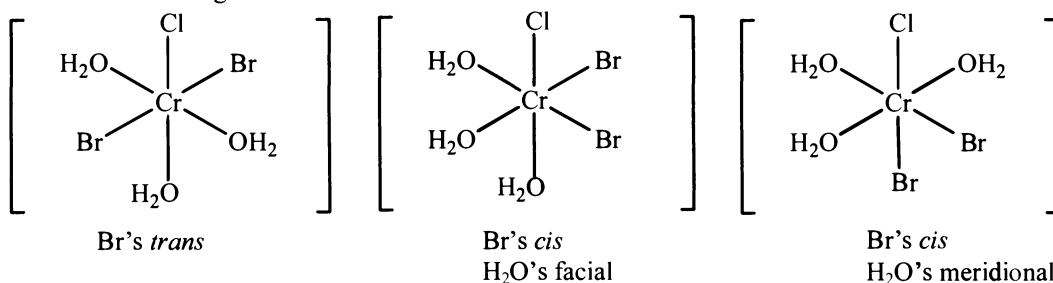
22.64 $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ tetraammineaquachlorocobalt(III) ion

2 geometric isomers



$[\text{Cr}(\text{H}_2\text{O})_3\text{Br}_2\text{Cl}]$ triaquadibromochlorochromium(III)

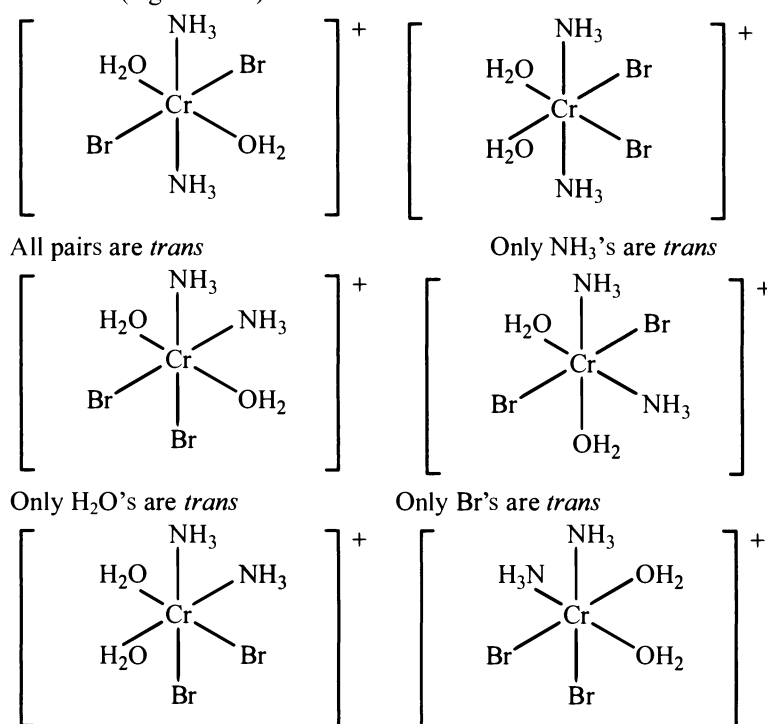
3 geometric isomers



(Unfortunately meridional and facial isomers are not covered in the text. Facial (fac) isomers have three adjacent corners of the octahedron occupied by similar groups. Meridional (mer) isomers have three similar groups around the outside of the complex.)

$[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Br}_2]^+$ diamminediaquadibromochromium(III) ion

6 isomers (5 geometric)



All pairs are *cis*. These are optical isomers of each other.

- 22.69 a) The first reaction shows no change in the number of particles. In the second reaction, the number of reactant particles is greater than the number of product particles. A decrease in the number of particles means a decrease in entropy, while no change in number of particles indicates little change in entropy. Based on entropy change only, the first reaction is favored.
- b) The ethylenediamine complex is more stable with respect to ligand exchange with water because the entropy change is unfavorable.

Chapter 23 Nuclear Reactions and Their Applications

FOLLOW-UP PROBLEMS

- 23.1 **Plan:** Write a skeleton equation that shows an unknown nuclide, ${}^A_Z\text{X}$, undergoing beta decay, ${}^0_{-1}\beta$, to form cesium-133, ${}^{133}_{55}\text{Cs}$. Conserve mass and atomic number by ensuring the superscripts and subscripts equal one another on both sides of the equation. Determine the identity of X by using the periodic table to identify the element with atomic number equal to Z.
- Solution:**
The unknown nuclide yields cesium-133 and a β particle:

$${}^A_Z\text{X} \rightarrow {}^{133}_{55}\text{Cs} + {}^0_{-1}\beta$$
 To conserve atomic number, Z must equal 54. Element is xenon.
 To conserve mass number, A must equal 133.
 The identity of ${}^A_Z\text{X}$ is ${}^{133}_{54}\text{Xe}$.
 The balanced equation is: ${}^{133}_{54}\text{Xe} \rightarrow {}^{133}_{55}\text{Cs} + {}^0_{-1}\beta$
Check: $A = 133 = 133 + 0$ and $Z = 54 = 55 + (-1)$, so mass is conserved.
- 23.2 **Plan:** Nuclear stability is found in nuclides with an N/Z ratio that falls within the band of stability in Figure 23.2. Nuclides with an even N and Z , especially those nuclides that have magic numbers, are exceptionally stable. Examine the two nuclides to see which of these criteria can explain the difference in stability.
- Solution:**
Phosphorus-31 has 16 neutrons and 15 protons, with an N/Z ratio of 1.07. Phosphorus-30 has 15 neutrons and 15 protons, with an N/Z ratio of 1.00. An N/Z ratio of 1.00 when $Z < 20$ could indicate a stable nuclide, but Figure 23.2 indicates a departure from the 1:1 line, even with smaller nuclides. ${}^{31}\text{P}$ has an even N and a slightly higher N/Z ratio, accounting for its stability over ${}^{30}\text{P}$.
- 23.3 **Plan:** Examine the N/Z ratio and determine which mode of decay will yield a product nucleus that is closer to the band.
- Solution:**
a) Iron-61 has an N/Z ratio of $(61 - 26)/26 = 1.35$, which is too high for this region of the band. Iron-61 will undergo β decay.

$${}^{61}_{26}\text{Fe} \rightarrow {}^{61}_{27}\text{Co} + {}^0_{-1}\beta \quad \text{new } N/Z = (61 - 27)/27 = 1.26$$
 b) Americium-241 has $Z > 83$, so it undergoes α decay.

$${}^{241}_{95}\text{Am} \rightarrow {}^{237}_{93}\text{Np} + {}^4_2\text{He}$$
- 23.4 **Plan:** Use the half-life of ${}^{24}\text{Na}$ to find k . Substitute the value of k , initial activity (A_0), and time of decay (4 days) into the integrated first-order rate equation to solve for activity at a later time (A_t).
- Solution:**
 $k = (\ln 2) / t_{1/2} = (\ln 2) / 15 \text{ h} = 0.0462098 \text{ h}^{-1}$ (unrounded)
 $\ln A_0 - \ln A_t = kt$
 $\ln A_t = -kt + \ln A_0 = -(0.0462098 \text{ h}^{-1})(4.0 \text{ days})(24 \text{ h/day}) + \ln(2.5 \times 10^9) = 17.2034$ (unrounded)
 $\ln A_t = 17.2034$
 $A_t = 2.96034 \times 10^7 = 3.0 \times 10^7 \text{ d/s}$
Check: In 4 days, a little more than 6 half-lives (6.4) have passed. A quick calculation on the calculator shows that $(2.5 \times 10^9) / 2 = 1.25 \times 10^9$ (first half-life). Dividing by 2 again shows 6.25×10^8 (second half-life). Continued division by 2 shows that this value comes to $3.9 \times 10^7 \text{ d/s}$ after six divisions by 2. This number is slightly higher than the calculated answer because 6 half-lives have been calculated, not 6.4 half-lives.

- 23.5 **Plan:** The wood from the case came from a living organism, so A_0 equals 15.3 d/min•g. Substitute the current activity of the case (A_t), A_0 and the $t_{1/2}$ of carbon (5730 yr) into the first-order rate expression and solve for t .
Solution:

$$t = \frac{1}{k} \ln \frac{A_0}{A_t} = \frac{1}{\left(\ln 2 / t_{1/2} \right)} \ln \frac{A_0}{A_t} = \frac{1}{\left(\ln 2 / 5730 \text{ yr} \right)} \ln \frac{(15.3 \text{ d/min} \cdot \text{g})}{(9.41 \text{ d/min} \cdot \text{g})} = 4018.2 = 4.02 \times 10^3 \text{ years}$$

Check: Since the activity of the bones is a little more than half of the modern activity, the age should be a little less than the half-life of carbon.

- 23.6 **Plan:** Uranium-235 has 92 protons and 143 neutrons in its nucleus. Calculate the mass defect (Δm) in one ^{235}U atom, convert to MeV and divide by 235 to obtain binding energy/nucleon.

Solution:

$$\Delta m = [(92 \times \text{mass H atom}) + (143 \times \text{mass neutron})] - \text{mass } ^{235}\text{U atom}$$

$$\Delta m = [(92 \times 1.007825 \text{ amu}) + (143 \times 1.008665)] - 235.043924 \text{ amu}$$

$$\Delta m = 1.915071 \text{ amu}$$

$$\text{Binding Energy / nucleon} = [(1.915071 \text{ amu}) (931.5 \text{ MeV/amu})] / (235 \text{ nucleons})$$

$$= 7.591015 = 7.591 \text{ MeV / nucleon}$$

The BE/nucleon of ^{12}C is 7.680 MeV/nucleon. The energy per nucleon holding the ^{235}U nucleus together is less than that for ^{12}C ($7.591 < 7.680$), so ^{235}U is less stable than ^{12}C .

Check: The answer is consistent with the expectation that uranium is less stable than carbon.

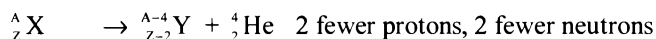
END-OF-CHAPTER PROBLEMS

- 23.1 a) Chemical reactions are accompanied by relatively small changes in energy while nuclear reactions are accompanied by relatively large changes in energy.
 b) Increasing temperature increases the rate of a chemical reaction but has no effect on a nuclear reaction.
 c) Both chemical and nuclear reaction rates increase with higher reactant concentrations.
 d) If the reactant is limiting in a chemical reaction, then more reactant produces more product and the yield increases in a chemical reaction. The presence of more radioactive reagent results in more decay product, so a higher reactant concentration increases the yield in a nuclear reaction.

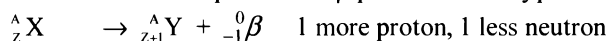
- 23.2 Radioactive decay that produces a different element requires a change in *atomic number* (Z , number of protons).

$$\begin{array}{lll} {}^A_Z\text{X} & A & = \text{mass number (protons + neutrons)} \\ & Z & = \text{number of protons (positive charge)} \\ & \text{X} & = \text{symbol for the particle} \\ & N & = A - Z \text{ (number of neutrons)} \end{array}$$

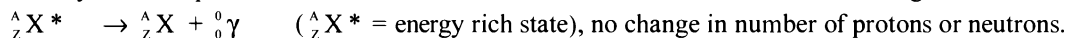
a) Alpha decay produces an atom of a different element, i.e., a daughter with two less protons and two less neutrons.



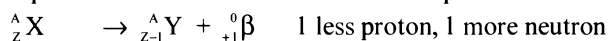
b) Beta decay produces an atom of a different element, i.e., a daughter with one more proton and one less neutron. A neutron is converted to a proton and β particle in this type of decay.



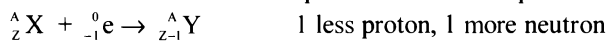
c) Gamma decay does not produce an atom of a different element and Z and N remain unchanged.



d) Positron emission produces an atom of a different element, i.e., a daughter with one less proton and one more neutron. A proton is converted into a neutron and positron in this type of decay.

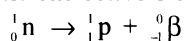


e) Electron capture produces an atom of a different element, i.e., a daughter with one less proton and one more neutron. The net result of electron capture is the same as positron emission, but the two processes are different.

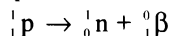


A different element is produced in all cases except (c).

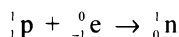
- 23.4 A neutron-rich nuclide decays to convert neutrons to protons while a neutron-poor nuclide decays to convert protons to neutrons. The conversion of neutrons to protons occurs by beta decay:



The conversion of protons to neutrons occurs by either positron decay:

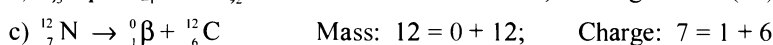
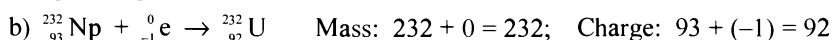
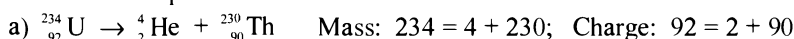


or electron capture:

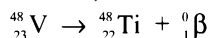


Neutron-rich nuclides, with a high N/Z , undergo β decay. Neutron-poor nuclides, with a low N/Z , undergo positron decay or electron capture.

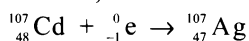
- 23.6 In a balanced nuclear equation, the total of mass numbers and the total of charges on the left side and the right side must be equal.



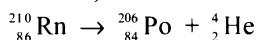
- 23.8 a) In other words, an unknown nuclide decays to give Ti-48 and a positron.



- b) In other words, an unknown nuclide captures an electron to form Ag-107.



- c) In other words, an unknown nuclide decays to give Po-206 and an alpha particle.



- 23.10 Look at the N/Z ratio, the ratio of the number of neutrons to the number of protons. If the N/Z ratio falls in the band of stability, the nuclide is predicted to be stable. Also check for exceptionally stable numbers of neutrons and/or protons – the “magic” number of 2, 8, 20, 28, 50, 82 and ($N = 126$). Also, even numbers of protons and or neutrons are related to stability whereas odd numbers are related to instability.

- (a) ${}_{8}^{20}\text{O}$ appears stable because its Z (8) value is a magic number, but its N/Z ratio ($12:8 = 1.50$) is too high and this nuclide is above the band of stability; ${}_{8}^{20}\text{O}$ is unstable.

- (b) ${}_{27}^{59}\text{Co}$ might look unstable because its Z value is an odd number, but its N/Z ratio ($32:27 = 1.19$) is in the band of stability, so ${}_{27}^{59}\text{Co}$ appears stable.

- (c) ${}_{3}^9\text{Li}$ appears unstable because its N/Z ratio ($6:3 = 2.00$) is too high and is above the band of stability.

- 23.12 a) ${}_{92}^{238}\text{U}$: Nuclides with $Z > 83$ decay through α decay.

- b) The N/Z ratio for ${}_{24}^{48}\text{Cr}$ is $(48 - 24)/24 = 1.00$. This number is below the band of stability because N is too low and Z is too high. To become more stable, the nucleus decays by converting a proton to a neutron, which is positron decay. Alternatively, a nucleus can capture an electron and convert a proton into a neutron through electron capture.

- c) The N/Z ratio for ${}_{25}^{50}\text{Mn}$ is $(50 - 25)/25 = 1.00$. This number is also below the band of stability, so the nuclide undergoes positron decay or electron capture.

- 23.14 Stability results from a favorable N/Z ratio, even numbers of N and/or Z , and the occurrence of magic numbers. The N/Z ratio of ${}_{24}^{52}\text{Cr}$ is $(52 - 24)/24 = 1.17$, which is within the band of stability. The fact that Z is even does not account for the variation in stability because all isotopes of chromium have the same Z . However, ${}_{24}^{52}\text{Cr}$ has 28 neutrons, so N is both an even number and a magic number for this isotope only.

23.18 No, it is not valid to conclude that $t_{1/2}$ equals 1 minute because the number of nuclei is so small (6 nuclei). Decay rate is an average rate and is only meaningful when the sample is macroscopic and contains a large number of nuclei, as in the second case. Because the second sample contains 6×10^{12} nuclei, the conclusion that $t_{1/2} = 1$ minute is valid.

23.20 Specific activity of a radioactive sample is its decay rate per gram. Calculate the specific activity from the number of particles emitted per second (disintegrations per second = dps) and the mass of the sample.

Specific activity = decay rate per gram.

1 Ci = 3.70×10^{10} dps

$$\text{Specific Activity} = \left(\frac{1.66 \times 10^6 \text{ dps}}{1.55 \text{ mg}} \right) \left(\frac{1 \text{ mg}}{10^{-3} \text{ g}} \right) \left(\frac{1 \text{ Ci}}{3.70 \times 10^{10} \text{ dps}} \right) = 2.8945 \times 10^{-2} = \mathbf{2.89 \times 10^{-2} \text{ Ci/g}}$$

23.22 The rate constant, k , relates the number of radioactive nuclei to their decay rate through the equation $A = kN$. The number of radioactive nuclei is calculated by converting moles to atoms using Avogadro's number. The decay rate is 1.39×10^5 d/yr or more simply, $1.39 \times 10^5 \text{ yr}^{-1}$ (the disintegrations are assumed).

Decay rate = $-(\Delta N / \Delta t) = kN$

$$-\frac{1.39 \times 10^5 \text{ atom}}{1.00 \text{ yr}} = k \left(\frac{1.00 \times 10^{-12} \text{ mol}}{10^{-3} \text{ g}} \right) \left(\frac{6.022 \times 10^{23} \text{ atom}}{1 \text{ mol}} \right)$$

$$1.39 \times 10^5 \text{ atom/yr} = k (6.022 \times 10^{11} \text{ atom})$$

$$k = (1.39 \times 10^5 \text{ atom/yr}) / 6.022 \times 10^{11} \text{ atom}$$

$$k = 2.30820 \times 10^{-7} = \mathbf{2.31 \times 10^{-7} \text{ yr}^{-1}}$$

23.24 Radioactive decay is a first-order process, so the integrated rate law is $\ln \frac{N_0}{N_t} = kt$

To calculate the fraction of bismuth-212 remaining after 3.75×10^3 h, first find the value of k from the half-life, then calculate the fraction remaining with N_0 set to 1 (exactly).

$$t_{1/2} = 1.01 \text{ yr} \quad t = 3.75 \times 10^3 \text{ h}$$

$$k = (\ln 2) / (t_{1/2}) = (\ln 2) / (1.01 \text{ yr}) = 0.686284 \text{ yr}^{-1} \text{ (unrounded)}$$

$$\ln \frac{1}{N_t} = (0.686284 \text{ yr}^{-1}) (3.75 \times 10^3 \text{ h}) (1 \text{ day} / 24 \text{ h}) (1 \text{ yr} / 365 \text{ days})$$

$$\ln \frac{1}{N_t} = 0.293785958 \text{ (unrounded)}$$

$$\frac{1}{N_t} = 1.3414967 \text{ (unrounded)}$$

$$N_t = 0.745436 \text{ (unrounded)}$$

Multiplying this fraction by the initial mass, 2.00 mg, gives $1.490872 = \mathbf{1.49 \text{ mg}}$ of bismuth-212 remaining after 3.75×10^3 h.

23.26 Lead-206 is a stable daughter of ^{238}U . Since all of the ^{206}Pb came from ^{238}U , the starting amount of ^{238}U was $(270 \mu\text{mol} + 110 \mu\text{mol}) = 380 \mu\text{mol} = N_0$. The amount of ^{238}U at time t (current) is $270 \mu\text{mol} = N_t$. Find k from the first-order rate expression for half-life, and then substitute the values into the integrated rate law and solve for t .

$$t_{1/2} = (\ln 2) / k$$

$$k = (\ln 2) / t_{1/2} = (\ln 2) / (4.5 \times 10^9 \text{ yr}) = 1.540327 \times 10^{-10} \text{ yr}^{-1} \text{ (unrounded)}$$

$$\ln \frac{N_0}{N_t} = kt$$

$$\ln \frac{380 \mu\text{mol}}{270 \mu\text{mol}} = (1.540327 \times 10^{-10} \text{ yr}^{-1})t$$

$$0.341749293 = (1.540327 \times 10^{-10} \text{ yr}^{-1})t$$

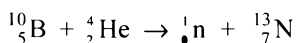
$$t = (0.341749293) / (1.540327 \times 10^{-10} \text{ yr}^{-1}) = 2.21868 \times 10^9 = \mathbf{2.2 \times 10^9 \text{ yr}}$$

23.28 Use the conversion factor, 1 Ci = 3.70×10^{10} disintegrations per second (dps).

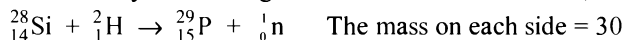
$$\text{Activity} = \left(\frac{6 \times 10^{-11} \text{ mCi}}{\text{mL}} \right) \left(\frac{10^{-3} \text{ Ci}}{1 \text{ mCi}} \right) \left(\frac{3.70 \times 10^{10} \text{ dps}}{1 \text{ Ci}} \right) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) \left(\frac{1000 \text{ mL}}{1.057 \text{ qt}} \right) = 126.0 = \mathbf{1 \times 10^2 \text{ dpm/qt}}$$

23.32 Protons are repelled from the target nuclei due to the interaction of like (positive) charges. Higher energy is required to overcome the repulsion.

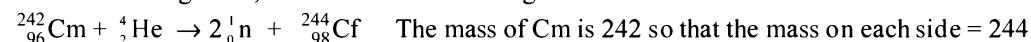
23.33 a) ${}^{10}_5\text{B} + {}^4_2\text{He} \rightarrow {}^1_0\text{n} + \text{X}$ Since the charge on the left, $5 + 2 = 7$, the charge on the right must = 7
Element X has a $Z = 7$ which is nitrogen. The mass is 14 on each side.



b) ${}^{28}_{14}\text{Si} + {}^2_1\text{H} \rightarrow {}^{29}_{15}\text{P} + \text{X}$ Since the charge on the left, $14 + 1 = 15$, the charge on the right must = 15.
P-29 already has a charge of 15 so X must have $Z = 0$, a neutron.



c) $\text{X} + {}^4_2\text{He} \rightarrow 2 {}^1_0\text{n} + {}^{244}_{98}\text{Cf}$ The charge on the right = $0 + 98 = 98$. The charge on the left must = 98.
He-4 has a charge of 2, so element X has a charge of $98 - 2 = 96$. Element 96 is Cm.



23.37 Ionizing radiation is more dangerous to children because their rapidly dividing cells are more susceptible to radiation than an adult's slowly dividing cells.

23.38 a) The rad is the amount of radiation energy absorbed per body mass in kg.

$$\left(\frac{3.3 \times 10^{-7} \text{ J}}{135 \text{ lb}} \right) \left(\frac{2.205 \text{ lb}}{1 \text{ kg}} \right) \left(\frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \right) = 5.39 \times 10^{-7} = \mathbf{5.4 \times 10^{-7} \text{ rad}}$$

b) Conversion factor is 1 rad = 0.01 Gy

$$(5.39 \times 10^{-7} \text{ rad}) (0.01 \text{ Gy/1 rad}) = 5.39 \times 10^{-9} = \mathbf{5.4 \times 10^{-9} \text{ Gy}}$$

23.40 a) Convert the given information to units of J/kg. 1 rad = 0.01 J/kg = 0.01 Gy

$$\text{Dose} = \frac{(6.0 \times 10^5 \beta)(8.74 \times 10^{-14} \text{ J}/\beta)}{70. \text{ kg}} \left(\frac{1 \text{ rad}}{0.01 \text{ J/kg}} \right) \left(\frac{0.01 \text{ Gy}}{1 \text{ rad}} \right) = 7.4914 \times 10^{-10} = \mathbf{7.5 \times 10^{-10} \text{ Gy}}$$

b) Convert grays to rads and multiply rads by RBE to find rems. Convert rems to mrems.

$$\text{rem} = \text{rads} \times \text{RBE} = (7.4914 \times 10^{-10} \text{ Gy}) \left(\frac{1 \text{ rad}}{0.01 \text{ Gy}} \right) (1.0) \left(\frac{1 \text{ mrem}}{10^{-3} \text{ rem}} \right) = 7.4914 \times 10^{-5} = \mathbf{7.5 \times 10^{-5} \text{ mrem}}$$

c) 1 rem = 0.01 Sv

$$\text{Sv} = (7.5 \times 10^{-5} \text{ mrem}) (10^{-3} \text{ rem} / 1 \text{ mrem}) (0.01 \text{ Sv} / \text{rem}) = 7.4914 \times 10^{-10} = \mathbf{7.5 \times 10^{-10} \text{ Sv}}$$

23.42 Use the time and disintegrations per second (Bq) to find the number of ${}^{60}\text{Co}$ atoms that disintegrate, which equals the number of β particles emitted. The dose in rads is calculated as energy absorbed per body mass.

$$\text{Dose} = \left(\frac{475 \text{ Bq}}{1.588 \text{ g}} \right) \left(\frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ dps}}{1 \text{ Bq}} \right) \left(\frac{5.05 \times 10^{-14} \text{ J}}{1 \text{ disint.}} \right) (27.0 \text{ min}) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) \left(\frac{1 \text{ rad}}{0.01 \text{ J/kg}} \right) = 2.447 \times 10^{-3} = \mathbf{2.45 \times 10^{-3} \text{ rad}}$$

23.44 NAA does not destroy the sample while chemical analyses does. Neutrons bombard a non-radioactive sample, "activating" or energizing individual atoms within the sample to create radioisotopes. The radioisotopes decay back to their original state (thus, the sample is not destroyed) by emitting radiation that is different for each isotope.

23.45 The oxygen in formaldehyde comes from methanol because the oxygen isotope in the methanol reactant appears in the formaldehyde product. The oxygen isotope in the chromic acid reactant appears in the water product, not the formaldehyde product. The isotope traces the oxygen in methanol to the oxygen in formaldehyde.

23.48 Apply the appropriate conversions from the chapter or the inside back cover.

$$\text{a) Energy} = (0.01861 \text{ MeV}) \left(\frac{10^6 \text{ eV}}{1 \text{ MeV}} \right) = \mathbf{1.861 \times 10^4 \text{ eV}}$$

$$\text{b) Energy} = (0.01861 \text{ MeV}) \left(\frac{10^6 \text{ eV}}{1 \text{ MeV}} \right) \left(\frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = 2.981322 \times 10^{-15} = \mathbf{2.981 \times 10^{-15} \text{ J}}$$

23.50 Calculate Δm , convert the mass deficit to MeV, and divide by 59 nucleons.

$$\text{Mass of } 27 \text{ } ^1\text{H atoms} = 27 \times 1.007825 = 27.211275 \text{ amu}$$

$$\text{Mass of 32 neutrons} = 32 \times 1.008665 = 32.27728 \text{ amu}$$

$$\text{Total mass} \quad 59.488555 \text{ amu}$$

$$\text{Mass defect} = \Delta m = 59.488555 - 58.933198 = 0.555357 \text{ amu} \quad ^{59}\text{Co} = 0.555357 \text{ g/mol } ^{59}\text{Co}$$

$$\text{a) Binding energy} = \left(\frac{0.555357 \text{ amu } ^{59}\text{Co}}{59 \text{ nucleons}} \right) \left(\frac{931.5 \text{ MeV}}{1 \text{ amu}} \right) = 8.768051619 = \mathbf{8.768 \text{ MeV / nucleon}}$$

$$\text{b) Binding energy} = \left(\frac{0.555357 \text{ amu } ^{59}\text{Co}}{1 \text{ atom}} \right) \left(\frac{931.5 \text{ MeV}}{1 \text{ amu}} \right) = 517.3150 = \mathbf{517.3 \text{ MeV / atom}}$$

$$\text{c) Use } \Delta E = \Delta mc^2$$

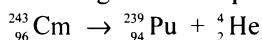
$$\begin{aligned} \text{Binding energy} &= \left(\frac{0.555357 \text{ g } ^{59}\text{Co}}{\text{mol}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(2.99792 \times 10^8 \text{ m/s} \right)^2 \left(\frac{1 \text{ J}}{\text{kg} \cdot \text{m}^2/\text{s}^2} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \\ &= 4.9912845 \times 10^{10} = \mathbf{4.99128 \times 10^{10} \text{ kJ / mol}} \end{aligned}$$

23.53 In both radioactive decay and fission, radioactive particles are emitted, but the process leading to the emission is different. Radioactive decay is a spontaneous process in which unstable nuclei emit radioactive particles and energy. Fission occurs as the result of high-energy bombardment of nuclei with small particles that cause the nuclides to break into smaller nuclides, radioactive particles, and energy.

In a chain reaction, all fission events are not the same. The collision between the small particle emitted in the fission and the large nucleus can lead to splitting of the large nuclei in a number of ways to produce several different products.

23.56 The water serves to slow the neutrons so that they are better able to cause a fission reaction. Heavy water ($^2_1\text{H}_2\text{O}$ or D_2O) is a better moderator because it does not absorb neutrons as well as light water ($^1_1\text{H}_2\text{O}$) does, so more neutrons are available to initiate the fission process. However, D_2O does not occur naturally in great abundance, so production of D_2O adds to the cost of a heavy water reactor. In addition, if heavy water does absorb a neutron, it becomes *tritiated*, i.e., it contains the isotope tritium, ^3_1H , which is radioactive.

23.60 a) Use the values given in the problem to calculate the mass change (reactant – products) for:



$$\begin{aligned} \Delta \text{mass (kg)} &= [243.0614 \text{ amu} - (4.0026 + 239.0522) \text{ amu}] \left(\frac{1.66054 \times 10^{-24} \text{ g}}{\text{amu}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \\ &= 1.095956 \times 10^{-29} = \mathbf{1.1 \times 10^{-29} \text{ kg}} \end{aligned}$$

$$b) E = \Delta mc^2 = (1.095956 \times 10^{-29} \text{ kg})(2.99792 \times 10^8 \text{ m/s})^2 \left(\frac{1 \text{ J}}{\text{kg} \cdot \text{m}^2 / \text{s}^2} \right) = 9.84993 \times 10^{-13} = \mathbf{9.8 \times 10^{-13} \text{ J}}$$

$$c) E \text{ released} = (9.84993 \times 10^{-13} \text{ J/reaction}) (6.022 \times 10^{23} \text{ reactions/mol}) (1 \text{ kJ} / 10^3 \text{ J}) \\ = 5.9316 \times 10^8 = \mathbf{5.9 \times 10^8 \text{ kJ/mol}}$$

This is approximately 1 million times larger than a typical heat of reaction.

22.62 Determine k for ^{14}C using the half-life (5730 yr):

$$k = (\ln 2) / t_{1/2} = (\ln 2) / (5730 \text{ yr}) = 1.2096809 \times 10^{-4} \text{ yr}^{-1} \text{ (unrounded)}$$

Determine the mass of carbon in 4.38 grams of CaCO_3 :

$$\text{mass} = (4.38 \text{ g CaCO}_3) \left(\frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \right) \left(\frac{1 \text{ mol C}}{1 \text{ mol CaCO}_3} \right) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 0.52556 \text{ g C (unrounded)}$$

The activity is: $(3.2 \text{ dpm}) / (0.52556 \text{ g C}) = 6.08874 \text{ dpm} \cdot \text{g}^{-1}$

Using the integrated rate law:

$$\ln \left(\frac{N_t}{N_0} \right) = -kt \quad N_0 = 15.3 \text{ dpm g}^{-1} \text{ (the ratio of } ^{12}\text{C}:^{14}\text{C} \text{ in living organisms)}$$

$$\ln \left(\frac{6.08874 \text{ dpm g}^{-1}}{15.3 \text{ dpm g}^{-1}} \right) = -(1.2096809 \times 10^{-4} \text{ yr}^{-1})t$$

$$t = 7616.98 = \mathbf{7.6 \times 10^3 \text{ yr}}$$

23.65 Determine how many grams of AgCl are dissolved in 1 mL of solution. The activity of the radioactive Ag^+ indicates how much AgCl dissolved, given a starting sample with a specific activity (175 nCi/g).

$$\text{Concentration} = \left(\frac{1.25 \times 10^{-2} \text{ Bq}}{\text{mL}} \right) \left(\frac{1 \text{ dps}}{1 \text{ Bq}} \right) \left(\frac{1 \text{ Ci}}{3.70 \times 10^{10} \text{ dps}} \right) \left(\frac{1 \text{ g AgCl}}{175 \text{ nCi}} \right) \left(\frac{1 \text{ nCi}}{10^{-9} \text{ Ci}} \right) \\ = 1.93050 \times 10^{-6} \text{ g AgCl/mL (unrounded)}$$

Convert g/mL to mol/L (molar solubility) using the molar mass of AgCl .

$$\text{Molarity} = \left(\frac{1.93050 \times 10^{-6} \text{ g AgCl}}{\text{mL}} \right) \left(\frac{1 \text{ mol AgCl}}{143.4 \text{ g AgCl}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ = 1.34623 \times 10^{-5} = \mathbf{1.35 \times 10^{-5} \text{ M AgCl}}$$

23.66 a) Find the rate constant, k , using any two data pairs (the greater the time between the data points, the greater the reliability of the calculation). Calculate $t_{1/2}$ using k .

$$\ln \left(\frac{N_t}{N_0} \right) = -kt$$

$$\ln \left(\frac{495 \text{ photons/s}}{5000 \text{ photons/s}} \right) = -k(20 \text{ h})$$

$$-2.312635 = -k(20 \text{ h})$$

$$k = 0.11563 \text{ h}^{-1} \text{ (unrounded)}$$

$$t_{1/2} = (\ln 2) / k = (\ln 2) / (0.11563 \text{ h}^{-1}) = 5.9945 = \mathbf{5.99 \text{ h}}$$
 (Assuming the times are exact, and the emissions have three significant figures.)

b) The percentage of isotope *remaining* is the fraction remaining after 2.0 h (N_t where $t = 2.0$ h) divided by the initial amount (N_0), i.e., fraction remaining is N_t/N_0 . Solve the first order rate expression for N_t/N_0 , and then subtract from 100% to get fraction *lost*.

$$\ln\left(\frac{N_t}{N_0}\right) = -kt$$

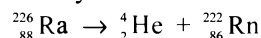
$$\ln\left(\frac{N_t}{N_0}\right) = -(0.11563 \text{ h}^{-1})(2.0 \text{ h}) = -0.23126 \text{ (unrounded)}$$

$$\left(\frac{N_t}{N_0}\right) = 0.793533 \text{ (unrounded)}$$

$$\left(\frac{N_t}{N_0}\right) \times 100\% = 79.3533\% \text{ (unrounded)}$$

The fraction lost is $100\% - 79.3533\% = 20.6467\% = \mathbf{21\%}$ of the isotope is lost upon preparation.

- 23.68 The *production rate* of radon gas (volume/hour) is also the *decay rate* of ^{226}Ra . The decay rate, or activity, is proportional to the number of radioactive nuclei decaying, or the number of atoms in 1.000 g of ^{226}Ra , using the relationship $A = kN$. Calculate the number of atoms in the sample, and find k from the half-life. Convert the activity in units of nuclei/time (also disintegrations per unit time) to volume/time using the ideal gas law.



$$k = (\ln 2) / t_{1/2} = (\ln 2) / [(1599 \text{ yr})(8766 \text{ h/yr})] = 4.9451051 \times 10^{-8} \text{ h}^{-1} \text{ (unrounded)}$$

The mass of ^{226}Ra is 226.025402 amu / atom or 226.025402 g / mol.

$$N = (1.000 \text{ g Ra}) \left(\frac{1 \text{ mol Ra}}{226.025402 \text{ g Ra}} \right) \left(\frac{6.022 \times 10^{23} \text{ Ra atoms}}{1 \text{ mol Ra}} \right) = 2.6643023 \times 10^{21} \text{ Ra atoms (unrounded)}$$

$$A = kN = (4.9451051 \times 10^{-8} \text{ h}^{-1})(2.6643023 \times 10^{21} \text{ Ra atoms}) = 1.3175254 \times 10^{14} \text{ Ra atoms / h (unrounded)}$$

This result means that 1.318×10^{14} ^{226}Ra nuclei are decaying into ^{222}Rn nuclei every hour. Convert atoms of ^{222}Rn into volume of gas using the ideal gas law.

$$\text{moles} = (1.3175254 \times 10^{14} \text{ Ra atoms / h}) (1 \text{ atom Rn} / 1 \text{ atom Ra}) (1 \text{ mol Rn} / 6.022 \times 10^{23} \text{ Rn})$$

$$= 2.1878536 \times 10^{-10} \text{ mol Rn / h (unrounded)}$$

$$V = nRT / P = \frac{(2.1878536 \times 10^{-10} \text{ mol Rn / h}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273.15 \text{ K})}{1 \text{ atm}}$$

$$= 4.904006 \times 10^{-9} = \mathbf{4.904 \times 10^{-9} \text{ L / h}}$$

Therefore, radon gas is produced at a rate of $4.904 \times 10^{-9} \text{ L/h}$. Note: Activity could have been calculated as decay in moles/time, removing Avogadro's number as a multiplication and division factor in the calculation.

- 23.75 a) Kinetic energy = $\frac{1}{2} mv^2 = (1/2) m (3 RT/M_H) = (3/2) (RT / N_A)$

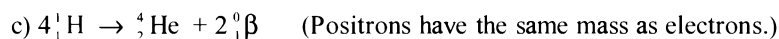
$$\text{Energy} = \left(\frac{3}{2} \right) \frac{(8.314 \text{ J / mol} \cdot \text{K}) (1.00 \times 10^6 \text{ K})}{6.022 \times 10^{23} \text{ atom / mol}} = 2.0709066 \times 10^{-17} = \mathbf{2.07 \times 10^{-17} \text{ J/atom } ^1_1\text{H}}$$

- b) A kilogram of ^1H will annihilate a kilogram of anti- ^1H ; thus, two kilograms will be converted to energy:

$$\text{Energy} = mc^2 = (2.00 \text{ kg}) (2.99792 \times 10^8 \text{ m/s})^2 (\text{J} / (\text{kg} \cdot \text{m}^2/\text{s}^2)) = 1.7975048 \times 10^{17} \text{ J (unrounded)}$$

$$\text{H atoms} = \left(\frac{1.7975048 \times 10^{17} \text{ J}}{1 \text{ kg H}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1.0078 \text{ g H}}{1 \text{ mol H}} \right) \left(\frac{1 \text{ mol H}}{6.022 \times 10^{23} \text{ atoms H}} \right) \left(\frac{\text{H atoms}}{2.0709066 \times 10^{-17} \text{ J}} \right)$$

$$= 1.4525903 \times 10^7 = \mathbf{1.45 \times 10^7 \text{ H atoms}}$$



$$\Delta m = [4(1.007825 \text{ amu})] - [4.00260 \text{ amu} - 2(0.000549 \text{ amu})]$$

$$= 0.027602 \text{ amu} / {}^4_2\text{He}$$

$$\Delta m = \left(\frac{0.027602 \text{ g}}{\text{mol He}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1 \text{ mol He}}{4 \text{ mol H}} \right) \left(\frac{1 \text{ mol H}}{6.022 \times 10^{23} \text{ H atoms}} \right) (1.4525903 \times 10^7 \text{ H atoms})$$

$$= 1.6644967 \times 10^{-22} \text{ kg (unrounded)}$$

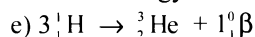
$$\text{Energy} = (\Delta m)c^2 = (1.6644967 \times 10^{-22} \text{ kg}) (2.99792 \times 10^8 \text{ m/s})^2 (\text{J} / (\text{kg} \cdot \text{m}^2/\text{s}^2))$$

$$= 1.4959705 \times 10^{-5} = \mathbf{1.4960 \times 10^{-5} \text{ J}}$$

d) Calculate the energy generated in part (b):

$$\text{Energy} = \left(\frac{1.7975048 \times 10^{17} \text{ J}}{1 \text{ kg H}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1.0078 \text{ g H}}{1 \text{ mol H}} \right) \left(\frac{1 \text{ mol H}}{6.022 \times 10^{23} \text{ atoms H}} \right) = 3.0081789 \times 10^{-10} \text{ J}$$

$$\text{Energy increase} = (1.4959705 \times 10^{-5} - 3.0081789 \times 10^{-10}) \text{ J} = 1.4959404 \times 10^{-5} = \mathbf{1.4959 \times 10^{-5} \text{ J}}$$



$$\Delta m = [3(1.007825 \text{ amu})] - [3.01603 \text{ amu} + 0.000549 \text{ amu}]$$

$$= 0.006896 \text{ amu} / {}^3_2\text{He} = 0.006896 \text{ g} / \text{mol } {}^3_2\text{He}$$

$$\Delta m = \left(\frac{0.006896 \text{ g}}{\text{mol He}} \right) \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left(\frac{1 \text{ mol He}}{3 \text{ mol H}} \right) \left(\frac{1 \text{ mol H}}{6.022 \times 10^{23} \text{ H atoms}} \right) (1.4525903 \times 10^7 \text{ H atoms})$$

$$= 5.5447042 \times 10^{-23} \text{ kg (unrounded)}$$

$$\text{Energy} = (\Delta m)c^2 = (5.5447042 \times 10^{-23} \text{ kg}) (2.99792 \times 10^8 \text{ m/s})^2 (\text{J} / (\text{kg} \cdot \text{m}^2/\text{s}^2))$$

$$= 4.9833164 \times 10^{-6} = \mathbf{4.983 \times 10^{-6} \text{ J}}$$

No, the Chief Engineer should advise the Captain to keep the current technology.