01-1. The Nature of Matter: What is that substance?

What do you think?
This section is intended to elicit students’ initial understanding of the terms. Do not expect the students to produce correct responses at this point. Just hear what they have to say, and then continue the activity. The terms are encountered again in the activity, at which point you can assure that the students have acquired the correct understanding.

1. See Application section #1.
2. See Got It! section #1.

Exploration
This section guides students in processing the preceding Information section.

1. As described in the Information section, chemists use the word substance to mean a pure substance that is either a single element or a single compound. In casual conversation, any matter might be called a substance, e.g. oily dirt.
2. (a) Oxygen and hydrogen explosively combine chemically to form a compound, water. Oxygen and nitrogen combine physically to form air, which is a mixture of these two elements. (b) Air is a homogeneous mixture; any sample of air looks like any other.
3. Similarities: Both are homogeneous. Both are gases. Differences: Distillation can separate oxygen from nitrogen in air but not oxygen from hydrogen in water. Oxygen in air can support combustion, but oxygen in water cannot support combustion, in fact water is used to douse fires.
4. A chemical process changes one pure substance into one or more other pure substances while a physical process does not cause such a change. Examples of chemical processes are producing carbon dioxide from baking soda and vinegar, producing carbohydrates by photosynthesis, and fruit ripening. Examples of physical processes are breaking glass, bending a wire, water condensing, and snow forming.

Application
1. (a) Helium is a pure substance and an element. (b) Table salt is a pure substance and a compound. (c) Blood is a heterogeneous mixture. (d) Air is a solution. (e) Tea is a solution. Note: A homogeneous mixture is a solution, and a heterogeneous mixture often is just called a mixture. Students may not think air is a solution because it is a gas; they also may think blood is a solution because it looks homogeneous, but it is not homogeneous when seen through a microscope.
2. (a) Rusting is a chemical change because two pure substances combine to form a third pure substance: iron combines with oxygen to form iron oxide. (b) Water evaporating is a physical process because the pure substance is water in the liquid
form and in the gaseous form. (c) Sugar dissolving in water is a physical process because the pure substance is sugar in the solid form and in a solution with water. (d) Water freezing is a physical process because the pure substance is water in the liquid form and water in the solid form. (e) Food digesting is a chemical process because the initial pure substances in the mixture obviously change into other pure substances in another mixture.

Got It!

1. An element is a pure substance that cannot be broken down into other pure substances. A compound is a pure substance that can be broken down into other pure substances called elements. A pure substance is matter consisting of only one element or one compound. A mixture, which is better called an inhomogeneous mixture, is matter consisting of two or more pure substances combined inhomogeneously, which means that one macroscopic region, as seen visually or with a microscope, differs from another. A solution is matter of two or more pure substances combined homogeneously, which means that all macroscopic regions are the same. A solution also can be called a homogeneous mixture. Note: Many students retain the idea that when you mix two things together you get a mixture, so sodium chloride is a mixture. This misconception should be explicitly addressed at some point. It lies at the heart of chemistry: mixing sodium and chlorine will produce sodium chloride (table salt), which is a compound and a pure substance, not a mixture.

2. A chemical process changes one pure substance into one or more other pure substances while a physical process does not cause such a change. Similarities: In both cases a change occurs and the way matter looks can change. Differences: In a physical process the initial situation usually can be restored easily, while in a chemical process such restoration can be difficult, if not impossible, because new pure substances have been formed.

3. Have students identify additional examples on their own, and have the class validate their examples.

4. Provide students with additional examples to consider.
01-2. Scientists Love to Measure:  
Which athlete is heavier, taller, faster?

What do you think?
This section is intended connect with students’ initial knowledge. Do not expect the students to produce correct responses at this point. Just hear what they have to say, and then continue the activity. These questions are encountered again in the Got It! section, at which point you can assure that the students now have the correct responses.

Exploration – 1
1.1. mass = kilograms, length = meters, and volume = liters
1.2. kilo = k = 10^3, centi = c = 10^{-2}, milli = m = 10^{-3}, micro = μ = 10^{-6}, and nano = n = 10^{-9}
1.3. grams with a kilo prefix so the number of digits in the number would be tractable, like 2 or 3 digits
1.4. A human hair is approximately 10^{-6} to 10^{-3} meters in diameter, so meters with a prefix of micro would be appropriate such that the number could be expressed without an exponent
1.5. Scientific notation uses a factor of 10 exponent to position the decimal point in a number. As a result, the number can be written without including numerous 0’s to position the decimal point.

Exploration – 2
2.1. Both sides of an equivalence statement can be divided by the quantity on the left or by the quantity on the right to produce two unit conversion factors.

2.2 (a) 15 gal \left( \frac{3.785 L}{1 gal} \right) = 57 L,  (b) 15 gal \left( \frac{1 gal}{3.785 L} \right) = 4.0 gal^2 / L ,
(c) In (a) gal/gal = 1 so the units are L, which makes sense. In (b) the units are gal^2/L, which is nonsense. Also note, the multiplier has two significant figures so the answer has two significant figures.

Application
1. (a) 1365 kg and approximately 2730 lbs.
\[ 1,365,000 g \left( \frac{1 kg}{1000 g} \right) = 1365 kg \]
(b) \[ 1365 kg \left( \frac{2.205 lbs}{1 kg} \right) = 3010 lbs \]
2. (a) pico is 10^{-12}, nano is 10^{-9}, so a picosecond is shorter than a nanosecond.
(b) The value in ps will be larger than the value in ns.
(c) 0.15 ns \left( \frac{10^{-9} s}{ns} \right) \left( \frac{1 ps}{10^{-12} s} \right) = 150 ps , which is consistent with the answer to (b)
3. (a) The length of each side of the cube must be converted from centimeters to meters as shown below. Also, since the volume is $cm^3$ the conversion factor must have $cm^3$ for the units to cancel and produce $m^3$.

$$10 cm \times \left( \frac{1m}{100 cm} \right) \times 10 cm \times \left( \frac{1m}{100 cm} \right) \times (10 cm)^3 \times \left( \frac{1m}{100 cm} \right)^3$$

(b) $1L \left( \frac{1000 cm^3}{1L} \right) \left( \frac{1m}{100 cm} \right)^3 = 0.001 m^3$

4. The volume of the baseball divided by the volume per atom will provide the number of atoms in a baseball. The volumes need to be expressed in the same units so the units cancel producing a number without units.

$$\frac{200 cm^3 \left( \frac{1m}{100 cm} \right)^3 \left( \frac{1nm}{10^{-9} m} \right)^3}{0.004 nm^3} = 5 \times 10^{25}$$

5. One needs to find how many pounds of sucrose in a case, then one can multiply by the price per pound to obtain the cost. Note when it comes to money in a problem like this one, people round to the nearest cent irregardless of the significant figures.

$$\frac{1 case \left( 12 bottles \right)}{1 case \left( 1 kg \right)} \left( \frac{5.00 \ kg}{1 \ bottle} \right) \left( \frac{2.205 \ lbs}{1 \ kg} \right) \left( \frac{1 \ bottle}{1 \ kg} \right) \left( \frac{1 \ lb}{1 \ kg} \right) = $1561.14$$

Got It!

1. $105 \ kg \left( \frac{2.205 \ lbs}{1 \ kg} \right) = 232 \ lbs$ so Peyton is heavier.

2. $1.93 \ m \left( \frac{1.094 \ yd}{1 \ m} \right) \left( \frac{36 \ in}{1 \ yd} \right) = 76.0 \ in$ so Candace and Kia are the same height

3. Convert Apolo’s time to seconds.

$$41,518 \ m/s \left( \frac{1 \times 10^{-3} \ s}{1 \ m/s} \right) = 41.518 \ s$$ so Jennifer is faster on the long track
02-1. The Nuclear Atom: 
What is the smallest particle of an element?

Exploration
1. An atom is made up of protons, neutrons, and electrons.
2. The protons and neutrons are located in the central nucleus, and the electrons are located in the surrounding space.
3. The letters provide a symbol for the name of the element, the left superscript is the total number of protons and neutrons (the mass number), and the left subscript is the number of protons (the atomic number).
4. The number of protons and the number of electrons are equal in a neutral uncharged atom.

Got It!

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Z</th>
<th>A</th>
<th>N</th>
<th>Number of Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine-37</td>
<td>(^{37}\text{Cl})</td>
<td>17</td>
<td>37</td>
<td>20</td>
<td>17</td>
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<tr>
<td>Chloride-37</td>
<td>(^{37}\text{Cl}^-)</td>
<td>17</td>
<td>37</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>Chlorine-35</td>
<td>(^{35}\text{Cl})</td>
<td>17</td>
<td>35</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>Oxygen-16</td>
<td>(^{16}\text{O})</td>
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<td>16</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Carbon-12</td>
<td>(^{12}\text{C})</td>
<td>6</td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Carbon-13</td>
<td>(^{13}\text{C})</td>
<td>6</td>
<td>13</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>(Sodium-23)(^+)</td>
<td>(^{23}\text{Na}^+)</td>
<td>11</td>
<td>23</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>(Silver-107)(^+)</td>
<td>(^{107}\text{Ag}^+)</td>
<td>47</td>
<td>107</td>
<td>60</td>
<td>46</td>
</tr>
<tr>
<td>Sulfide-32</td>
<td>(^{32}\text{S}^-)</td>
<td>16</td>
<td>32</td>
<td>16</td>
<td>18</td>
</tr>
</tbody>
</table>
02-2. The Mole and Molar Mass: Can you count atoms and molecules by weighing them?

What do you think?
The intent is to seed a discussion of how objects can be counted by determining the total mass and the average mass of the individual objects. The number of objects is given by the total mass divided by the average mass. The activity then guides students in applying this idea first to pennies and then to atoms.

Exploration
1. The number of pennies can be determined by dividing the total mass of 10 pounds by the average mass of a single penny, 2.509 g. Of course, the units have to be converted so they are the same.
2. \[ N_p = \frac{M_t}{m_p} \]
3. \[ \frac{10 \text{ lbs}}{2.205 \text{ lbs}} \left( \frac{1 \text{ kg}}{2.205 \text{ lbs}} \right) \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) = 1808 \text{ pennies} \]
4. (a) $18.08  (b) The purchase was a good deal since I got $18 worth of pennies for $10.
5. number of Pt atoms = mass of the Pt bar ÷ average mass of a Pt atom
6. \[ \frac{1 \text{ kg}}{195.08 \text{ amu}} \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) = 3.087 \times 10^{24} \text{ Pt atoms} \]
   (interpret 1. kg as exactly one kg to justify the sig figs in this calculation)
After reading the Information section introducing the mole, ask students, “How many moles of atoms are there in a bar of platinum that has a mass of exactly 1 kg?” Or you can wait; this question is posed later (Application #8).
\[ \frac{3.087 \times 10^{24} \text{ atoms}}{6.0221 \times 10^{23} \text{ atoms/mol}} = 5.1263 \text{ mol} \]

Application
1. 1 dozen apples = 12 apples
2. 1 mol apples = 6.0221 × 10^{23} apples
3. \( \left( \frac{$3.00}{12} \right) 6.0221 \times 10^{23} = 1.5055 \times 10^{23} \text{ dollars} \)
4. \( \left( \frac{2.0 \text{ kg}}{12} \right) 6.0221 \times 10^{23} = 1.0 \times 10^{23} \text{ kg} \)
5. \[ 195.08 \text{ amu} \left( \frac{1.6605 \times 10^{-24} \text{ g}}{1 \text{ amu}} \right) \left( \frac{6.0221 \times 10^{23}}{\text{ mol}} \right) = 195.08 \text{ g/mol} \]

6. From #5 we see that the two conversion factors multiply to give 1, so the molar mass of chlorine (Cl₂) is 70.90 g/mol.

7. The average mass in atomic mass units of a particle comprising a substance and the molar mass in grams are equal numerically.

8. (a) \[ \frac{3.0871 \times 10^{24} \text{ atoms}}{6.0221 \times 10^{23} \text{ atoms/mol}} = 5.1263 \text{ mol} \]

   (b) \[ \frac{1000 \text{ g exactly}}{195.08 \text{ g/mol}} = 5.1261 \text{ mol} \]

Got It!

1. grams to moles, divide by the molar mass: \[ \frac{g}{g/\text{mol}} = \text{mol} \]

2. moles to number of particles, multiply by Avogadro’s number: \[ \text{mol} \times \text{number/mol} = \text{number} \]

3. number to moles, divide by Avogadro’s number: \[ \frac{\text{number}}{\text{number/mol}} = \text{mol} \]

4. moles to grams, multiply by the molar mass: \[ \text{mol} \times \text{g/mol} = \text{g} \]
What do you think?
The intent is to stimulate a discussion of what information should be provided in the name of a chemical compound and how that information can be provided. The discussion should end with some ideas about naming conventions that are relevant to water. Di- is used rather than bi- for 2. Maybe dihydrogen monoxygen sounds strange, and dihydrogen monoxide sounds better because the suffix is consistent from one compound to another. Since the only oxides of hydrogen are H₂O and H₂O₂, maybe shorter names would work too: hydrogen monoxide and hydrogen dioxide, or hydrogen oxide and hydrogen peroxide.

Exploration – 1
1.1. There are two different elements in binary compounds.
1.2. The less electronegative element is named first.
1.3. The suffix applied to the root of the more electronegative element is –ide.
1.4. The prefixes are 1 = mono, 2 = di, 3 = tri, 4 = tetra, 5 = penta, 6 = hexa

Exploration – 2
2.1. The metal is named first.
2.2. The suffix applied to the root of the nonmetal is –ide.
2.3. The charge is indicated by Roman numerals in parentheses after the name.
2.4. Similarities: The less electronegative element is named first. The suffix added to the root of the more electronegative element is –ide. Differences: The charge of the metal is indicated for ionic compounds when the charge is variable. Prefixes are used for the number of atoms in covalent compounds.
1. 

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Name</th>
<th>Cation Charge</th>
<th>Anion Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>KBr</td>
<td>Potassium bromide</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>Magnesium chloride</td>
<td>+2</td>
<td>-1</td>
</tr>
<tr>
<td>BaI₂</td>
<td>Barium iodide</td>
<td>+2</td>
<td>-1</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
<td>+2</td>
<td>-2</td>
</tr>
<tr>
<td>CuCl</td>
<td>Copper(I) chloride</td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>Copper(II) chloride</td>
<td>+2</td>
<td>-2</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>Chromium(III) chloride</td>
<td>+3</td>
<td>-1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum oxide</td>
<td>+3</td>
<td>-2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Iron(III) oxide</td>
<td>+3</td>
<td>-2</td>
</tr>
<tr>
<td>FeO</td>
<td>Iron(II) oxide</td>
<td>+2</td>
<td>-2</td>
</tr>
</tbody>
</table>

2. (a) SO₂  (b) SiCl₄  (c) Cr₂O₃

3. (a) cobalt(II) chloride (b) cobalt(III) chloride (c) potassium sulfide  (d) sulfur trioxide

4. (a) Magnesium is an alkaline earth metal in Group 2; it always has a +2 charge and forms ionic compounds.
   (b) The Roman numeral II specifies a +2 charge so two −1 ions like chloride are needed and saying dichloride would be redundant.
03-2. Determining Empirical and Molecular Formulas: Why can different molecules have the same percent composition by mass?

Exploration

Complete Table I

<table>
<thead>
<tr>
<th>Name</th>
<th>Structural Formula</th>
<th>Molecular Formula</th>
<th>Percent by Mass Carbon</th>
<th>Percent by Mass Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pair 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td>( \text{H} \equiv \text{C} \equiv \text{H} )</td>
<td>( \text{C}_2\text{H}_2 )</td>
<td>92.26%</td>
<td>7.74%</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>( \text{C}_6\text{H}_6 )</td>
<td>92.26%</td>
<td>7.74%</td>
</tr>
<tr>
<td><strong>Pair 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethene</td>
<td>( \text{H} \equiv \text{C} \equiv \text{H} )</td>
<td>( \text{C}_2\text{H}_4 )</td>
<td>85.63%</td>
<td>14.37%</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td>( \text{C}<em>2\text{H}</em>{12} )</td>
<td>85.63%</td>
<td>14.37%</td>
</tr>
</tbody>
</table>

1. They all contain carbon and hydrogen. Each pair has the same percent composition even though their molecular formulas differ. Each pair has the same ratio of hydrogen atoms to carbon atoms, 1:1 for Pair 1, 2:1 for Pair 2.

2. Similarities: All involve carbon and hydrogen. The ratios of hydrogen to carbon are the same for each pair. Differences: The total number of atoms and the total number of each kind of atom varies.

3. The molecular formula cannot be determined from the mass percent composition because different compounds can have the same mass percent composition.

4. Compounds have the same mass percent composition if the ratios of atoms are the same, e.g. H:C for the examples in the table.

5. \( \text{CH}_2 \)

Application

1. \( 56.34 \text{ g} \div 30.97 \text{ g/mol} = 1.819 \text{ mol} \)
2. \( 43.66 \text{ g} \div 16.00 \text{ g/mol} = 2.729 \text{ mol} \)
3. As described in the activity, the ratio O atoms : P atoms = 3:2
4. The empirical formula is \( \text{P}_2\text{O}_3 \)
5. molar mass = 2(30.97) + 3(16.00) = 109.94 g/mol
6. 219.9 g/mol ÷ 109.94 g/mol = 2.000
7. The molecular formula must be $\text{P}_4\text{O}_6$

**Got It!**

Moles P in 100 g:
43.64 g ÷ 30.97 g/mol = 1.409 mol

Moles O in 100 g:
56.36 g ÷ 16.00 g/mol = 3.523 mol

Mole ratio:
O/P = 3.523 / 1.409 = 2.500 / 1

Empirical formula:
$\text{P}_2\text{O}_5$ with molar mass 141.94 g/mol

Molecular formula:
283.89 g/mol ÷ 141.94 g/mol = 2.000

Therefore, $\text{MF} = 2 \times (\text{EF}) = 2(\text{P}_2\text{O}_5) = \text{P}_4\text{O}_{10}$
04-1. Reaction Stoichiometry:
How much do I need to get what I want?

Exploration

1. (a) The balanced reaction equation is needed to relate the number of molecules/ions of the reactants to the number of molecules/ions that are produced as products. The number of molecules/ions is measured in units of moles.
   (b) Steps 2 and 3 make clear what information is given and what needs to be found. Molecules/ions react and molecules/ions are produced, so the units to keep track of reactants turning into products must be moles, which specify the number of molecules and/or ions.
   (c) The stoichiometric coefficients specify the minimum number of molecules/ions that are involved in the reaction. The actual number must be some integer multiple of these values. Consequently the mole ratio of amounts is equal to the mole ratio of the stoichiometric coefficients.

2. Students should reflect on the need for each of the steps.

3. Students may suggest alternative or shorter methods. Any method that logically produces a correct answer is acceptable.

4. Answers may vary, but here are 5 possibilities. (1) Collecting and organizing the information in the problem statement clarifies what is given and what needs to be found. (2) Stoichiometry problems only can be solved if you have a balanced reaction equation. (3) Stoichiometry problems must be solved in terms of moles of reactants and products because the number of molecules involved as reactants and products needs to be tracked. (4) Amounts of reactants and products can be specified in different ways; it is important to be able to convert between these different units. (5) Having a multi-step methodology for solving stoichiometry problems helps guarantee success.

Application

1. Need to balance the reaction equation.
   \[ 2\text{NH}_4\text{NO}_3(s) \rightarrow 2\text{N}_2(g) + 4\text{H}_2\text{O}(g) + \text{O}_2(g) \]
   so setting the ratios equal
   \[ \frac{4\text{mol H}_2\text{O}}{2\text{mol NH}_4\text{NO}_3} = \frac{x}{0.5\text{mol NH}_4\text{NO}_3} \]
   \[ x = 1\text{mol H}_2\text{O} \]
   \[ \frac{1\text{mol O}_2}{2\text{mol NH}_4\text{NO}_3} = \frac{96\text{mol O}_2}{x} \]
   \[ x = 192\text{mol NH}_4\text{NO}_3 \]
3. \( \text{CCl}_4 + 2 \text{HF} \rightarrow \text{CCl}_2\text{F}_2 + 2 \text{HCl} \)

\[
231 \text{ g} \\
231 \text{ g} ÷ 154 \text{ g/mol} = 1.50 \text{ mol CCl}_4 \\
\text{mole ratio is 1:1, so one gets 1.50 mol of CCl}_2\text{F}_2 \\
1.50 \text{ mol of CCl}_2\text{F}_2 \times 121 \text{ g/mol} = 181 \text{ g CCl}_2\text{F}_2
\]

**Got It!**

1. \( \text{K}_2\text{PtCl}_4 + 2 \text{NH}_3 \rightarrow \text{PtCl}_2(\text{NH}_3)_2 + 2 \text{KCl} \)

\[
? \text{ 1000 g} \\
1000 \text{ g} / 300 \text{ g/mol} = 3.33 \text{ mol cisplatin} \\
mole ratio ammonia: cisplatin is 2:1 so twice as much ammonia is required \\
2 x 3.33 \text{ mol} = 6.66 \text{ mol ammonia} \\
6.66 \text{ mol ammonia} \times 17.03 \text{ g/mol} = 114 \text{ g ammonia}
\]

2. \( 4 \text{ C}_3\text{H}_5(\text{NO}_3)_3(\text{l}) \rightarrow 12 \text{ CO}_2(\text{g}) + 10 \text{ H}_2\text{O}(\text{g}) + 6 \text{ N}_2(\text{g}) + \text{O}_2(\text{g}) \)

\[
\text{4 mol nitroglycerine (NG) produces 29 mol gas} \\
227 \text{ g of NG} ÷ 227 \text{ g/mol} = 1 \text{ mol NG} \\
\frac{29 \text{ mol gas}}{4 \text{ mol NG}} = \frac{x}{1 \text{ mol NG}} \\
x = 7.25 \text{ mol gas}
\]

**Additional Practice Problems**

1. (a) \( \text{C}_12\text{H}_22\text{O}_{11} + 12 \text{ O}_2 \rightarrow 12 \text{ CO}_2 + 11 \text{ H}_2\text{O} \)

\[
\text{(b) 42.4 g sucrose ÷ 342 g/mol} = 0.124 \text{ mol sucrose} \\
\text{mole ratio = 11:1 for water so 11 x 0.124 mol = 1.36 mol water} \\
\text{mole ratio = 12:1 for carbon dioxide so 12 x 0.124 mol = 1.48 mol carbon dioxide} \\
\text{(c) mass water = 1.36 mol water x 18.0 g/mol = 24.5 g water} \\
\text{mass carbon dioxide = 1.48 mol carbon dioxide x 44.0 g/mol = 65.1 g CO}_2
\]

2. (a) Need a balanced reaction equation.

\[
2 \text{ SO}_2(\text{g}) + 2 \text{ CaCO}_3(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ CaSO}_4(\text{s}) + 2 \text{ CO}_2(\text{g}) \\
\text{1000 g} \\
1000 \text{ g sulfur dioxide ÷ 64.1 g/mol} = 15.6 \text{ mol sulfur dioxide} \\
\text{mole ratio is 1:1 so 15.6 mol CaCO}_3 \text{ x 100 g/mol} = 1560 \text{ g = 1.56 kg CaCO}_3 \\
\text{(b) mole ratio is 1:1 so 15.6 mol CaSO}_4 \text{ x 136 g/mol} = 2120 \text{ g = 2.12 kg CaSO}_4 \\
\text{(c) mole ratio is 1:1 so 15.6 mol CO}_2 \text{ x 44.0 g/mol} = 686 \text{ g = 0.686 kg CO}_2
\]

3. \( \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{ CO(\text{g})} \rightarrow 2 \text{ Fe(\text{s})} + 3 \text{ CO}_2 \)

\[
\text{1000 kg} \\
10^6 \text{ g ÷ 160 g/mol} = 6,250 \text{ mol iron(III) oxide} \\
\text{the mole ratio is 2:1 so 2 x 6,250 mol = 12,500 mol iron} \\
\text{12,500 mol iron x 55.9 g/mol = 699,000 g iron = 699 kg iron} \\
\text{699 kg iron (1 metric ton /1000 kg) = 0.699 metric ton iron}
\]
04-2. Limiting Reactants:
How much will I get with what I have?

Exploration
1. 5 slices cheese and 10 leaves of lettuce
2. bread
3. Answers may vary. One method is to see how many sandwiches can be made with each ingredient. The ingredient that produces the fewest sandwiches is limiting.
4. Four nitrogen molecules furnish eight nitrogen atoms to produce eight ammonia molecules. Six hydrogen molecules produce 12 hydrogen atoms to produce four ammonia molecules. Hydrogen is limiting, so four ammonia molecules can be produced.
5. $H_2:N_2$ ratio in the reaction equation is 3:1. The ratio of reactants is 6:4 = 3:2 = 1.5:1, which is too small, meaning there is not enough hydrogen to react with all the nitrogen. So hydrogen is limiting.

Application
1.

2. The stoichiometric ratio ammonia:chlorine is 2:1, but have 15:15 = 1:1, so we have excess chlorine, and ammonia is limiting. So 7.5 mol chlorine will react to produce 7.5 mol hydrazine since the mole ratio chlorine:hydrazine is 1:1.

Got It!
1. $2\text{ Al} + 3 \text{ Cl}_2 \rightarrow \text{ Al}_2\text{Cl}_6$
2. $710 \text{ g chlorine} \div 70.9\text{ g/mol} = 10.0 \text{ mol chlorine}$
   $270 \text{ g aluminum} \div 27.0 \text{ g/mol} = 10.0 \text{ mol aluminum}$
   Stoichiometric ratio chlorine:aluminum = 3:2 = 1.5:1, have 10:10 = 1:1, which is too small, so chlorine is limiting.
3. The stoichiometric ratio Cl$_2$:Al$_2$Cl$_6$ is 3:1 so 10 mol chlorine will produce 10/3 mol Al$_2$Cl$_6$, which is 3.33 mol.
4. No chlorine will be left over, and 3.33 mol aluminum will be left over.
   \[
   (2 \text{ mol Al}/3\text{ mol Cl}_2) = (x/10 \text{ mol Cl}_2)
   \]
   \[x = 6.66 \text{ mol Al used}\]

5. Theoretical yield = 3.33 mol AlCl₃ x 267 g/mol = 888 g
   Percent yield = 750 g x 100 ÷ 888 g = 84.5%

**Additional Practice Problems**

1. \[2 \text{ C}_7\text{H}_6\text{O}_3(s) + \text{C}_4\text{H}_6\text{O}_3(l) \rightarrow 2 \text{ C}_9\text{H}_8\text{O}_4(s) + \text{H}_2\text{O}(l)\]
   
   \[
   \text{SA} = \text{salicylic acid}; \text{AA} = \text{acetic anhydride}
   \]
   100 g ÷ 138 g/mol = 0.725 mol SA
   100 g AA ÷ 102 g/mol = 0.980 mol
   Need \(\text{SA}:\text{AA} = 2:1\), actual ratio 0.725:0.980 is too small so SA is limiting.
   Ratio SA:Aspirin = 1:1 so can produce 0.725 mol aspirin.
   0.725 mol aspirin x 180 g/mol = 131 g aspirin

2. \[2 \text{ LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}\]
   10 g ÷ 23.9 g/mol = 0.418 mol LiOH
   20 g CO₂ ÷ 44.0 g/mol = 0.455 mol CO₂
   The balanced stoichiometric ratio LiOH:CO₂ = 2:1. Actual ratio is less than 1, so LiOH is limiting and CO₂ is in excess. 0.418 mol/2 = 0.209 mol of CO₂ is needed to react with all the LiOH, leaving 0.455 mol – 0.209 mol = 0.246 mol, which is 0.246 mol x 44.0 g/mol = 11 g (2 sig figs because 2 sig figs were given initially.)

3. \[2 \text{ C(s)} + 2 \text{ H}_2\text{O}(g) \rightarrow \text{CH}_3\text{OH}(l) + \text{CO}(g)\]
   1000 g ÷ 12.0 g/mol = 83.3 mol C
   1000 g H₂O ÷ 18.0 g/mol = 55.6 mol H₂O
   The stoichiometric ratio is 1:1, but the actual ratio is 83.3/55.6 = 1.5, so water is limiting.
   methanol:water ratio is 1:2 so can produce 55.6 mol ÷ 2 = 27.8 mol methanol
   27.8 mol methanol x 32.0 g/mol = 890 g methanol
   890 g methanol ÷ 0.79 g/mL = 1100 mL = 1.1 L (to 2 sig figs)
4. \( \text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow 2 \text{ NH}_3 + \text{CO}_2 \)

20 lbs/acre  0.25 inches rain

Question asks per acre, so do the calculation for one acre.

Moles of urea = (20 lbs)(454 g/lb)÷(60.1 g/mol) = 151 mol urea

Volume of water = (0.25 in)(2.54 cm/in)(1 acre)(4047 m\(^2\)/acre)(100 cm/m)\(^2\)

= 2.57x10\(^7\) cm\(^3\)

Moles of water = (2.57x10\(^7\) cm\(^3\))(1.00 g/cm\(^3\))÷(18.0 g/mol) = 1.43x10\(^6\) mol water

Clearly there is much excess water, and all the urea most likely reacts.

(a) So 151 mol urea would react and (b) none would remain

(c) The ammonia:urea stoichiometric ratio is 2:1, therefore 2 x 151 mol = 302 mol ammonia would be produced per acre
05-1. Types of Chemical Reactions:
What happens in a chemical reaction?

What do you think?
Responses will vary. Here is an example. In a chemical reaction, molecules combine with each other in different ways to produce new molecules. I have seen a gas forming when I mixed baking soda and vinegar together, a solid forming when we mixed sodium chloride and silver nitrate solutions together in high school chemistry class, and starch turned into sugar by saliva as indicated by an iodine test for starch.

Exploration
1. (a) \( s = \text{solid}, \ g = \text{gas}, \ l = \text{liquid}, \ aq = \text{aqueous solution}, \) which is a solution made with water as the solvent.
(b) An ionic compound is formed from two or more elements with electrons being transferred from one element to another.
(c) To dissolve means to go into solution.
(d) A solution is a homogeneous mixture of two or more pure substances.
(e) An acid is a proton donor, and a base is a proton acceptor (Brönsted-Lowry definition).
(f) Hydronium ion is \( H_3O^+ \), hydroxide ion is \( OH^- \).
2. The characteristics are given in the first column of Table I.
3. Acid ionization, base ionization, acid-base neutralization
4. 2 silver ions and 2 silver atoms are needed to balance the charge.
5. \( Ag^+(aq) + Cl^- (aq) \rightarrow AgCl(s) \)

Application
1. \( Na_2SO_4(s) \rightarrow 2 Na^+(aq) + SO_4^{2-}(aq) \)  
Dissociation
2. \( CO_3^{2-}(aq) + 2 H_2O(l) \rightarrow H_2CO_3(aq) + 2 OH^- (aq) \)  
Base ionization
3. \( Fe^{3+}(aq) + 3 OH^- (aq) \rightarrow Fe(OH)_3(s) \)  
Precipitation
4. \( H_3PO_4(aq) + 3 NaOH(s) \rightarrow Na_3PO_4(aq) + 3 H_2O(l) \)  
Acid-base neutralization
5. \( HOCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO^- (aq) \)  
Acid ionization
6. \( 2 Ca(s) + O_2(g) \rightarrow 2 CaO(s) \)  
Oxidation - reduction
7. \( Sr(OH)_2(aq) \rightarrow Sr^{2+}(aq) + 2 OH^- (aq) \)  
Base dissociation
Got It!

1. (a) \( \text{Pb(NO}_3\text{)}_2(\text{s}) \rightarrow \text{Pb}^{2+}(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) \)
(b) \( \text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \)
(c) \( \text{Pb}^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) \)

2. \( \text{Na}_2\text{CO}_3(\text{s}) \rightarrow 2 \text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \)
   \( \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCO}_3^-(\text{aq}) + \text{OH}^- \)
   \( \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^- \)

3. Oxidation – reduction
   \( \text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \)

4. (a) \( \text{HNO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \)
(b) \( \text{NaOH}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^- (\text{aq}) \)
(c) \( \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \) (net ionic equation)
05-2. **Solutions: What are they, what do they look like, and how are they prepared?**

**What do you think?**
Answers will vary, e.g. beer, soda, whiskey, tea, coffee, soup broth, vinegar.

**Exploration – 1**

1.1. Sodium chloride is the electrolyte because you can see ions. Methanol is the nonelectrolyte because ions are not formed. A similarity is that both solutes are surrounded by water molecules. A difference is that ions are formed in one but not in the other.

1.2. The oxygen is closest to Na\(^+\) because oxygen is electronegative and has lots of electrons to be attracted to the positive ion.

1.3. The hydrogen is closest to Cl\(^-\) because hydrogen is electropositive and is attracted to the negative charge of the chloride ion.

**Exploration – 2**

2.1. \(\frac{11.1 \text{ g}}{111 \text{ g/mol}} = 0.100 \text{ mol}\)

2.2. (a) \(250.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.250 \text{ L}\)
   \(0.100 \text{ mol} / 0.250 \text{ L} = 0.400 \text{ moles/liter or 0.400 mol/L}\)
   (b) One CaCl\(_2\) unit produces one calcium ion so \(0.400 \text{ mol/L} \times 1 \text{ L} = 0.4 \text{ mol}\)
   (c) One CaCl\(_2\) unit produces two chloride ions so \(2 \times 0.400 \text{ mol/L} \times 1 \text{ L} = 0.8 \text{ mol}\)

2.3. (a) \((100.0 \text{ mL})(1\text{L}/1000 \text{ mL})(0.100 \text{ M}) = 0.0100 \text{ mol}\)
   (b) \(0.0100 \text{ mol}\)
   (c) \(0.0100 \text{ mol} / 1.00\text{L} = 0.0100 \text{ M}\)
   (d) Each formula unit produces 2 potassium ions so their concentration will be 0.0200 M

**Exploration – 3**

3.1. \(\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}\)

3.2. \((250.0 \text{ ml})(1 \text{ L}/1000 \text{ mL})(6.0 \text{ M}) = 1.5 \text{ mol}\)

3.3. The stoichiometry is 1:1 so 1.5 mol are required.

3.4. \(\text{volume} \times 3.0 \text{ M} = 1.5 \text{ mol}\)
   \(\text{volume} = 0.50 \text{ L} = 500 \text{ mL}\)

**Got It!**

1. All nitric acid molecules will ionize because it is a strong acid, so it is a strong electrolyte. Only a few acetic acid molecules ionize so it is a weak electrolyte. Essentially no propanol molecules ionize so it is a nonelectrolyte.

2. \(\text{Ba}^{2+}\) will have a concentration of 0.12 M. \(\text{Cl}^-\) will have a concentration of 0.24 M.

3. \((0.25 \text{ mol} / 250.0 \text{ mL})(1000 \text{ mL}/1 \text{ L}) = 1.0 \text{ M}\)

4. \(10.0 \text{ mL} \times 12.5 \text{ M} = 500.0 \text{ mL} \times \text{M}_d\)
   \(\text{M}_d = 125/500 = 0.25 \text{ M}\)
5. \[ V_c \times 12.0 \text{ M} = 250.0 \text{ mL} \times 3.00 \text{ M} \]
   \[ V_c = \frac{250.0 \times 3.00}{12.0} = 62.5 \text{ mL} \]

6. \[ 322 \text{ g} \div 158 \text{ g/mol} = 2.04 \text{ mol} \]
   \[ \text{volume} \times 2.06 \text{ M} = 2.04 \text{ mol} \]
   \[ \text{volume} = 0.990 \text{ L} \]

7. \[
   \text{Ba(OH)}_2 + 2 \text{HNO}_3 \rightarrow \text{Ba(NO}_3)_2 + 2 \text{H}_2\text{O} \\
   25.0 \text{ mL} \times 0.125 \text{ M nitric acid} = 3.125 \text{ mmol nitric acid} \\
   \text{stoichiometry is 1:2 so require half as much barium hydroxide} \ (1.563 \text{ mmol}) \\
   (1.563 \text{ mmol})(1 \text{ mol / 1000 mmol})(171 \text{ g/mol}) = 0.267 \text{ g} 
   
\]

**Additional Practice Problems**

1. \[ 0.50 \text{ M NH}_4^+ \text{ and 0.25 M SO}_4^{2-} \]

2. \[ 250.0 \text{ mL} \times 0.0125 \text{ M} = 3.125 \text{ mmol} \]
   \[ 3.125 \text{ mmol (158 g/mol)} = 494 \text{ mg} = 0.494 \text{ g} \]

3. \[ 0.500 \text{ M} = \text{moles needed/} 0.500 \text{ L} \]
   \[ \text{moles needed} = 0.250 \text{ mol} \]
   \[ 0.250 \text{ mol x 263 g/mol} = 65.8 \text{ g of nickel sulfate hexahydrate} \]

4. \[ 5.00 \text{ mL} \times 0.0250 \text{ M} = 100.0 \text{ mL} \times \text{M}_d \]
   \[ \text{M}_d = 0.00125 \text{ M Na}_3\text{PO}_4 \]
   \[ [\text{Na}^+] \text{ is 3x that} = 0.00375 \text{ M} \]

5. \[ \text{NaHCO}_3(s) + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{CO}_2(g) + \text{H}_2\text{O(l)} \]
   \[ 125 \text{ mL} \times 6 \text{ M HCl} = 750 \text{ mmol} = 0.750 \text{ mol HCl} \]
   \[ \text{stoichiometry is 1:1 so need 0.750 mol sodium hydrogen carbonate} \]
   \[ 0.750 \text{ mol x 84.0 g/mol} = 63.0 \text{ g sodium hydrogen carbonate} \]

6. The volume and concentration of the sulfuric acid that spilled are the same as for HCl in the preceding problem. Sulfuric acid is a diprotic acid so it will take twice as much baking soda, 126 g.

7. (a) \[ \text{C}_2\text{H}_6\text{O}_6(aq) + \text{Br}_2(aq) \rightarrow \text{C}_6\text{H}_6\text{O}_6(aq) + 2 \text{HBr(aq)} \]
   \[ 27.85 \text{ mL} \times 0.102 \text{ M} = 2.841 \text{ mmol bromine} \]
   \[ \text{stoichiometry is 1:1 so have 2.841 mmol vitamin C} \]
   \[ 2.841 \text{ mmol x 176 g/mol} = 500. \text{ mg} = 0.500 \text{ g} \]
   \[ (b) \ 0.500 \text{ g/1.00 g} = 50.0\% \text{ vitamin C} \]

8. \[ \text{C}_3\text{H}_5\text{O(COOH)}_3(aq) + 3 \text{NaOH(aq)} \rightarrow \text{Na}_3\text{C}_3\text{H}_5\text{O(COO)}_3(aq) + 3 \text{H}_2\text{O(l)} \]
   \[ 7.55 \text{ mL} \times 0.125 \text{ M} = 0.944 \text{ mmol NaOH} \]
   \[ \text{stoichiometry is 1:3 so citric acid (CA) is 1/3 as much, 0.315 mmol} \]
   \[ 0.315 \text{ mmol x 192 g/mol} = 60.4 \text{ mg CA in 10 mL} \]
   \[ \text{so 6.04 mg in 1 mL} = 6.04 \times 10^{-3} \text{ g} \]
06-1. Energy: How do you know how much you have gained or lost?

Exploration
1. 27.4 – 18.1 = 9.3°C
2. If the same amount of energy were used to heat half as much water, the temperature rise should be twice as large because the same amount of energy going into less water should have a larger effect on the temperature.
3. If a different substance were heated by the iron bar, then the temperature change would be different because the amounts may not be the same and different substances require different amounts of energy to increase their temperature.
4. The units of specific heat capacity are J/g °C so to get units of energy, one needs to multiply by the mass of the substance in grams and the temperature change in °C.
5. \( q = c \cdot m \Delta T \)

Application
1. \( q = (4.184 \text{ J/g °C})(500. \text{ mL})(1.00 \text{ g/mL})(9.3 \text{ °C}) = 19 \text{ kJ} \)
2. The equation in #1 is applicable, if we reduce 500 mL by a factor of \( \frac{1}{2} \) then the change in temperature needs to double to give the same result for the energy of 19 kJ, so the change in temperature is 18.6°C.
3. \( \Delta T = \frac{19 \text{ kJ}}{(2.42 \text{ J/g °C})(500. \text{ mL})(1.11 \text{ g/mL})} = 14 \text{ °C} \)
4. \( \Delta T = \frac{1.1 \text{ kJ}}{(0.902 \text{ J/g °C})(110 \text{ g})} = 11 \text{ °C} \)
   Final temperature = 23 + 11 = 34°C

Got It!
1. Since the mass and amount of energy used in each case are the same, the substance with the smaller specific heat capacity will get hotter. The values in the table reveal that iron has the smaller specific heat capacity and therefore will get hotter.
2. Since the rate of energy transfer, the mass, and the temperature change are the same in each case, iron with the smaller specific heat capacity will reach body temperature first because less energy needs to be transferred so it will take less time.
### 06-2. Enthalpy: How much energy is produced by a chemical reaction under different conditions?

#### Exploration

1. \[ \text{C}_8\text{H}_{18}(l) + \frac{25}{2} \text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(g) \]

2. Experiment 1, constant V: \[ \Delta T = 41.607 - 21.560 = 20.047 \, ^\circ\text{C} \]
   Experiment 2, constant P: \[ \Delta T = 43.695 - 23.693 = 20.002 \, ^\circ\text{C} \]

3. Experiment 1, constant V: \[ q = (25.370 \, \text{kJ/}^\circ\text{C})(20.047 \, ^\circ\text{C}) = 508.59 \, \text{kJ} \]
   Experiment 2, constant P: \[ q = (25.370 \, \text{kJ/}^\circ\text{C})(20.002 \, ^\circ\text{C}) = 507.45 \, \text{kJ} \]

   \[
   \frac{11.42 \, \text{g}}{114.23 \, \text{g/mol}} = 0.1000 \, \text{mol}
   \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Isooctane consumed (moles)</th>
<th>Energy transferred, q</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 constant V</td>
<td>0.1000 mol</td>
<td>508.59 kJ</td>
</tr>
<tr>
<td>#2 constant P</td>
<td>0.1000 mol</td>
<td>507.45 kJ</td>
</tr>
</tbody>
</table>

4. In experiment 1, the volume was kept constant and the pressure in the calorimeter increased. In experiment 2, the pressure was kept constant and the volume of the calorimeter increased.

5. The total change in energy of the reacting system is given by the results of experiment 1 because the piston did not move, therefore all the energy went into heating the calorimeter. In experiment 2, some of the energy was used to move the piston.

6. (a) The energy of the reacting system decreased because the energy was transferred to heating the calorimeter in both experiments and also moving the piston in experiment 2.
   (b) \( q_{\text{system}} \) should be negative. A negative sign should be added to the entries in the above table.

7. Since \( \Delta E_{\text{system}} = q_{\text{system}} + w_{\text{system}} \) and \( \Delta E_{\text{system}} \) is given by experiment 1, one can solve for the work in experiment 2: \[ w_{\text{system}} = -508.59 \, \text{kJ} - (-507.45 \, \text{kJ}) = -1.14 \, \text{kJ} \]. The value is negative because this value represents the work done by the system on the piston.

#### Got It!

1. The enthalpy change is obtained in a constant pressure experiment.
   \[ \Delta H = q_{p, \text{system}} = -(25.370 \, \text{kJ/}^\circ\text{C})(5.392 \, ^\circ\text{C}) = -136.8 \, \text{kJ} \]
   \[
   \frac{4.607 \, \text{g}}{46.07 \, \text{g/mol}} = 0.1000 \, \text{mol}
   \]
   molar enthalpy of combustion = \(-136.8 \, \text{kJ} \div 0.1000 \, \text{mol} = -1368 \, \text{kJ/mol} \)

2. The total change in energy is obtained in a constant volume experiment.
   \[ \Delta E = q_{v, \text{system}} = -(25.370 \, \text{kJ/}^\circ\text{C})(5.412 \, ^\circ\text{C}) = -137.3 \, \text{kJ} \]
4.607 g ÷ 46.07 g/mol = 0.1000 mol

Total change in energy for 1 mol reacting = –137.3 kJ ÷ 0.1000 mol = –1373 kJ/mol

3. Work done by the system is negative, work done on the piston is positive.

\[ w_p, \text{system} = \Delta E - \Delta H = -1373 \text{ kJ/mol} - (-1368 \text{ kJ/mol}) = -5 \text{ kJ/mol} \]

\[ w_p, \text{piston} = -w_p, \text{system} = 5 \text{ kJ/mol} \]

**Application**

1. Heating Oil: \( q_{\text{system}} = - (50.745 \text{ kJ/oC})(2.128 \text{ oC}) = -108.0 \text{ kJ} \)

\[ 2.261 \text{ g ÷ 226.00 g/mol} = 0.01000 \text{ mol} \]

\[ \Delta H_{\text{combustion}} = -108.0 \text{ kJ/0.01000 mol} = -10,800 \text{ kJ/mol} \]

LPG: \( q_{\text{system}} = - (50.745 \text{ kJ/oC})(4.020 \text{ oC}) = -204.0 \text{ kJ} \)

\[ 4.411 \text{ g ÷ 44.10 g/mol} = 0.1000 \text{ mol} \]

\[ \Delta H_{\text{combustion}} = -204.0 \text{ kJ/0.1000 mol} = -2040 \text{ kJ/mol} \]

2. Heating Oil: \( (10,800 \text{ kJ/mol}) ÷ (226.00 \text{ g/mol}) = 47.79 \text{ kJ/g} \)

LPG: \( (2040 \text{ kJ/mol}) ÷ (44.10 \text{ g/mol}) = 46.26 \text{ kJ/g} \)

Heating oil has a better fuel value in terms of energy/gram.

3. Heating Oil: \( (47.79 \text{ kJ/g})(0.80 \text{ g/mL}) = 38 \text{ kJ/mL} \)

LPG: \( (46.26 \text{ kJ/g})(0.51 \text{ g/mL}) = 24 \text{ kJ/mL} \)

Heating oil has a better energy density in terms of energy/mL.

4. Heating Oil: \( \text{C}_{16}\text{H}_{34} + \frac{49}{2} \text{O}_2 \rightarrow 16 \text{ CO}_2 + 17 \text{ H}_2\text{O} \)

\[ (10,800 \text{ kJ/mol}) ÷ (16 \text{ mol CO}_2/\text{mol}) = 675 \text{ kJ/mol CO}_2 \]

LPG: \( \text{C}_3\text{H}_8 + 5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 4 \text{ H}_2\text{O} \)

\[ (2040 \text{ kJ/mol}) ÷ (3 \text{ mol CO}_2/\text{mol}) = 680 \text{ kJ/mol CO}_2 \]

The environmental value is about the same; LPG is a bit better, more energy per mole of CO\(_2\) produced.

5. Heating Oil: \( (38 \text{ kJ/mL})(1000 \text{ mL/L})(3.785 \text{ L/gal}) ÷ ($2.50/gal) = 58 \text{ MJ/$} \)

LPG: \( (24 \text{ kJ/mL})(1000 \text{ mL/L})(3.785 \text{ L/gal}) ÷ ($2.50/gal) = 36 \text{ MJ/$} \)

Heating Oil is the much better economic value in terms of energy per dollar if both are priced the same.
07-1. Photoelectron Spectrum of Argon:
How do we learn about the electronic structure of atoms?

Are You Prepared to Explore?

1. \( E = \frac{hc}{\lambda} \)
   
   \[
   \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})}{3500 \text{ eV} \left( \frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right)} = 3.543 \times 10^{-10} \text{ m}
   \]
   
2. A photon is absorbed by the material and the energy is used to eject an electron.
3. The electron current or rate at which electrons are produced is plotted on the y-axis, and the kinetic energy of the electrons is plotted on the x-axis.
4. The binding energy decreases and the kinetic energy of the emitted electron increases as the principal quantum number increases.

Exploration

1.

2. Table I. Argon Photoelectron Data

<table>
<thead>
<tr>
<th>( E_{\text{kinetic}} ) (eV)</th>
<th>3485</th>
<th>3470</th>
<th>3250</th>
<th>3175</th>
<th>295</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{binding}} ) (eV)</td>
<td>15</td>
<td>30</td>
<td>250</td>
<td>325</td>
<td>3205</td>
</tr>
<tr>
<td>( n ) value</td>
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<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>( l ) value</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3. Values in the first two rows of Table I sum to 3500 eV because of energy conservation. The energy of the photon, 3500 eV, is used to overcome the binding energy of an electron in the atom, and the excess energy goes into the kinetic energy of the electron.

4. See Table I above.
Application – 1

The nucleus has a charge of +18. In order of increasing radius, the subshells are \((1,0), (2,0), (2,1), (3,0),\) and \((3,1)\).

Research

According to the Pauli Exclusion Principle each electron must have a different set of quantum numbers \((n, l, m_l, m_s)\). Since there are two possible values for \(m_s\), two electrons
can have the same values for $n$, $l$, and $m_l$. When $l = 0$, $m_l$ must also equal 0, so there is only one set of these quantum numbers, and consequently only two electrons can be accommodated in the $l = 0$ shells. When $l = 1$, $m_l$ can equal 1, 0, –1, so there are three sets of these quantum numbers, and consequently six electrons can be accommodated in the $l = 1$ shells.

**What do you predict?**

1. Potassium will have a larger radius than argon because the radius of the shells increases as the principal quantum number $n$ increases.

2. It will require less energy to remove an electron from potassium than from argon because in potassium the $n = 4$ electron is further away from the positively charged nucleus than the $n = 3$ electrons in argon. Also, the $n = 4$ electron in potassium is shielded by all the other electrons that are between it and the nucleus.

**Application – 2**

1. Since the range is so large, 14 to 14,000 eV, it is necessary to plot the spectrum in three pieces. Electron current is plotted on the y-axis, and binding energy is plotted on the x-axis. The binding energies for the peaks are, from left to right: 14.1, 27.5, 94.5, 218, 293, 1704, 1921, and 14326 eV.

2. 

\[ \begin{align*}
\text{Energy} & \\
-14.1 \text{ eV, } (n,l) &= (4,1) \\
-27.5 \text{ eV, } (n,l) &= (4,0) \\
-94.5 \text{ eV, } (n,l) &= (3,2) \\
-218 \text{ eV, } (n,l) &= (3,1) \\
-293 \text{ eV, } (n,l) &= (3,0) \\
-1704 \text{ eV, } (n,l) &= (2,1) \\
-1921 \text{ eV, } (n,l) &= (2,0) \\
-14,326 \text{ eV, } (n,l) &= (1,0)
\end{align*} \]
3. The nucleus has a charge of +36. In order of increasing radius, the subshells are \((1,0)\), \((2,0)\), \((2,1)\), \((3,0)\), \((3,1)\), \((3,2)\), \((4,0)\), and \((4,1)\).
**07-2. Periodic Trends in Properties of Elements: How much can you learn from the Periodic Table?**

**Exploration – 1**

1.1. The atomic radius decreases across a period from left to right.

1.2. The number of protons and the number of electrons increase in going across a period.

1.3. The effect of electron-nucleus attraction dominates in going across a period because the atomic radius decreases.

1.4. The atomic radius increases in going down a group.

1.5. The number of protons and the number of electrons increase in going down a group.

1.6. Since the atomic radius increases in going down a group, the effect of electron–electron repulsion dominates. Also, the outermost electrons are in a shell that has a larger radius in going down a group from one period to the next.

1.7. In going across a period, electrons are added to the same shell. These electrons don’t repel each other very well, consequently the effective nuclear charge increases, pulling the electrons in and making the atom smaller.

1.8. In going down a group from one period to the next, electrons are added to a new shell that has a larger radius. Consequently the distance of the outer electrons from the nucleus increases and the atom gets larger. Also, the outermost electrons are repelled very well by the electrons in the inner shell, therefore the effective nuclear charge is small and the electrons are not pulled very strongly toward the nucleus.

**Exploration – 2**

2.1. The ionization energy generally increases in going across a period.

2.2. The changes in atomic radius and ionization energy in going across a period are consistent with an increase in the electron-nucleus attraction which pulls the electrons closer to the nucleus and increases the energy required to remove an electron from the atom.

2.3. In going down a group, the ionization energy decreases.

2.4. The changes in atomic radius and ionization energy in going down a group from one period to the next are consistent with an increase in the distance of an electron from the nucleus and an increase in the electron-electron repulsion which leads to an increase in the atomic radius and a decrease in the energy required to remove an electron from the atom.

**Application**

1. N is larger than O because it is to the left of O in Period 2.

H is larger than He because it is to the left of He in Period 1.

Br is larger than Cl because it is further down Group 17.

Na is larger than Mg because it is to the left of Mg in Period 3.

Si is larger than C because it is further down Group 14.

Ge is larger than Si, which is above it in Group 14, and Si is larger than P, which is to the right of it in Period 3, consequently Ge must be larger than P (Ge > Si > P).
2. He has a higher ionization energy than H.  
   Ne has a higher ionization than Ar.  
   Ne has a higher energy than Na because it is at the end of Period 2, and Na is at the beginning of Period 3. Ne has a higher ionization energy than Li because they are at the opposite ends of Period 2. Li has a higher ionization energy than Na because it is above Na in Group 1 so Ne > Li > Na.

**Exploration – 3**

3.1. Group 17, the halogens, has the largest electron affinities.

3.2. Group 2, the alkaline earths, and Group 18, the noble gases, have electron affinities that are 0 or near 0.

3.3. Ne with 10 electrons is on the left. Ne\(^-\) with 11 electrons is on the right.

The additional electron in Ne\(^-\) is in the outer 3s subshell that is far from the nucleus, and this electron is very effectively repelled by the 10 electrons in the inner shells, therefore the effective nuclear charge experienced by this electron is essentially 0, and the anion is not stable.
3.4. F with 9 electrons is on the left. F\(^{-}\) with 10 electrons in on the right.

The additional electron in F\(^{-}\) is in the same shell as the other \(n=2\) electrons. Consequently it is close to the nucleus and not repelled very well by these electrons. It therefore experiences a strong attraction and this ion is very stable as indicated by the large electron affinity.

3.5. N: 1s\(^{2}\) 2s\(^{2}\) 2p\(^{3}\)
N\(^{-}\): 1s\(^{2}\) 2s\(^{2}\) 2p\(^{4}\)

In the anion, the additional electron has to pair up with another electron in the same atomic orbital because there are only three 2p orbitals; this pairing is accompanied by a significant electron-electron repulsion energy that destabilizes the anion producing an electron affinity that is 0.

3.6. Be: 1s\(^{2}\) 2s\(^{2}\)
Be\(^{-}\): 1s\(^{2}\) 2s\(^{2}\) 2p\(^{1}\)

In the anion, the additional electron goes into the p-subshell which is further from the nucleus. The electron in the p-subshell also is repelled by the inner electrons. Consequently the attraction for the nucleus is insignificant, the anion is not stable, and the electron affinity is zero.
**08-1. Lewis Structures:**

*What strategy produces the correct Lewis structure every time?*

**Exploration**

1. The number of valence electrons is given by the column number (IA through VIIA) for the main group elements.
2. Usually the central atom is the one that is written first in the molecular formula, is the most electropositive, and can form the most bonds with other atoms.
3. Extra electrons are placed on the central atom to give that atom more than an octet of electrons, which is OK for elements in Period 3 and higher since they have empty d-orbitals in the valence shell.
4. A double or triple bond is used when necessary to give each atom an octet of electrons.
5. Resonance structures are used to represent bonds that are a composite of single and double bond(s).
6. To determine the formal charge of an atom in a Lewis structure, subtract the number of lone pair electrons and half the number of bonding electrons associated with that atom from the number of valence electrons the atom contributed.
7. Formal charge is used to help identify which of several possible Lewis structures is the best representation of the lowest energy state of a molecule. The idea is that separating charge increases the energy. The lowest energy state will have 0 (zero) formal charge on all the atoms if possible. If that is not possible, then the structure with the smallest charges and with the negative charge on the most electronegative atoms will have the lowest energy.

**Application**

1. hydrofluoric acid: formal charge 0 on all atoms

   ![Hydrofluoric acid Lewis structure]

2. ammonia: formal charge 0 on all atoms

   ![Ammonia Lewis structure]

3. phosphate: formal charge -1 on the three singly bonded O, 0 on doubly bonded O, and 0 on P. Three additional resonance structures can be written with the double bond moved to each of the other three oxygens and appropriate changes in the electron lone pairs.

   ![Phosphate Lewis structure]

4. butane: formal charge 0 on all atoms

   ![Butane Lewis structure]

5. ethanol: formal charge 0 on all atoms

   ![Ethanol Lewis structure]

6. carbon dioxide: formal charge 0 on all atoms

   ![Carbon dioxide Lewis structure]
acetylene: formal charge 0 on all atoms
chloroethene: formal charge 0 on all atoms

chlorine trifluoride: formal charge 0 on all atoms

nitrate: formal charge +1 on N, 0 on doubly bonded oxygen, -1 on each singly bonded oxygen. Two additional resonance structures can be written with the double bond moved to each of the other two oxygens and appropriate changes in the electron lone pairs.

2. In the OCS structure the formal charge is 0 on all the atoms. In the COS structure, the formal charges are -2 on C, +2 on O, and 0 on S. In the CSO structure, the formal charges are -2 on C, +2 on S, and 0 on O. Because there is no charge separation on OCS, this structure is predicted to be the most stable.

Got It!
In the SCN structure, the formal charges are -1 S, 0 C, and 0 N.
In the SNC structure, the formal charges are -1 S, -1 C, and +1 N.
The charge separation in the SNC structure makes this structure unfavorable so SCN⁻ is predicted to be the more stable anion.
08-2. Electronegativity and Bond Properties: Which atom attracts more electron density?

Exploration – 1

1.1. Elements in the upper right corner of the periodic table have high ionization energies, electron affinities, and electronegativities.

1.2. Elements in the lower left corner of the periodic table have low ionization energies, electron affinities, and electronegativities.

1.3. Nonmetals are more electronegative.

1.4. As the electronegativity difference between two elements in a bond increases, then the bond polarity increases.

Got It!

1.1. Fluorine is more electronegative than chlorine, so in the Cl-F bond, F is slightly negative, and Cl is slightly positive.

   Chlorine is more electronegative than bromine, so in the Cl-Br bond, Cl is slightly negative, and Br is slightly positive.

   The electronegativity difference is greater for Cl-F, so Cl-F is more polar than Cl-Br.

1.2. The answer to this question will depend on the electronegativity data being used as the tabulations vary. If one uses H(2.1), C(2.5), and Si(1.8), then for Si-H, H is slightly negative, and Si is slightly positive. For C-H, C is slightly negative, and H is slightly positive, and C-H would be more a bit polar than Si-H. However on the scale of bond polarity, both C-H and Si-H bonds are considered to be nonpolar.

1.3. In both these bonds, Cl is slightly negative and P and S are slightly positive. P-Cl is more polar than S-Cl.

1.4. In both these bonds, C is slightly positive and O and N are slightly negative. C-O is more polar than C-N.

1.5. In both these bonds, O is slightly negative and C and Si are slightly positive. Si-O is more polar than C-O.

Exploration – 2

2.1. As the multiplicity increases, the bond length decreases.

2.2. As the multiplicity increases, the bond strength increases.

2.3. As the multiplicity increases, the electron density between the two nuclei increases. This negative charge attracts the two nuclei closer together and increases the energy it takes to separate them.

2.4. N is to the right of C in Period 2, it therefore has a smaller radius, so when 2 N atoms form a single bond, the bond will be shorter than for the case of 2 C atoms forming a single bond.
Got It!

2.1. C-H compared to C-C will be shorter and have the higher bond energy because the H atom is much smaller than a C atom.

2.2. C=O compared to C=N will be shorter and have the higher bond energy because O is a smaller atom than N.

2.3. C-Cl compared to C-Br will be shorter and have the higher bond energy because Cl is a smaller atom than Br.

24. C≡N compared to C=N will be shorter and have the higher bond energy because a triple bond has higher electron density between the two nuclei than a double bond.
09-1. VSEPR Model:
How can the geometry or shape of a molecule be predicted?

Exploration
1. See the activity on Lewis structures: count the number of valence electrons, write the bonding framework connecting the atoms with single bonds, add the remaining electrons so each atom has an octet if possible, check for exceptions to the octet rule, add double or triple bonds if necessary, put excess electrons on the central atom, determine the formal charges, draw resonance structures if necessary.
2. Electrons repeal each other. Maximizing their separation minimizes the electron-electron repulsion energy.
3. The lone pairs would be positioned at 180° to each other because maximizing their separation is most important in minimizing the electron-electron repulsion.

<table>
<thead>
<tr>
<th>Number of bonds and lone pairs</th>
<th>Electron Geometry</th>
<th>Sketch of the Electron Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td><img src="image" alt="Be" /></td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td><img src="image" alt="B" /></td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td><img src="image" alt="C" /></td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td><img src="image" alt="Cl" /></td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td><img src="image" alt="S" /></td>
</tr>
</tbody>
</table>
## Got It!

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Lewis Structure</th>
<th>Electron Geometry</th>
<th>Molecular Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>H—O—H</td>
<td>tetrahedral</td>
<td>bent</td>
</tr>
<tr>
<td>I₃⁻</td>
<td>[I—I—I]⁻</td>
<td>trigonal bipyramidal</td>
<td>linear</td>
</tr>
<tr>
<td>SeCl₆</td>
<td><img src="image" alt="SeCl6 structure" /></td>
<td>octahedral</td>
<td>octahedral</td>
</tr>
<tr>
<td>SbF₅</td>
<td><img src="image" alt="SbF5 structure" /></td>
<td>trigonal bipyramidal</td>
<td>trigonal bipyramidal</td>
</tr>
<tr>
<td>H₂CO</td>
<td>O:</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>SeO₃²⁻</td>
<td><img src="image" alt="SeO3^2- structure" /></td>
<td>tetrahedral</td>
<td>trigonal pyramidal</td>
</tr>
<tr>
<td>SiF₄</td>
<td><img src="image" alt="SiF4 structure" /></td>
<td>tetrahedral</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>Molecule</td>
<td>Structure</td>
<td>Shape</td>
<td>Geometric Shape</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>-------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>KrF₄</td>
<td><img src="image1" alt="KrF₄ Structure" /></td>
<td>octahedral</td>
<td>square planar</td>
</tr>
<tr>
<td>SF₄</td>
<td><img src="image2" alt="SF₄ Structure" /></td>
<td>trigonal bipyramidal</td>
<td>seesaw</td>
</tr>
<tr>
<td>ICl₃</td>
<td><img src="image3" alt="ICl₃ Structure" /></td>
<td>trigonal bipyramidal</td>
<td>T-shaped</td>
</tr>
<tr>
<td>BrF₅</td>
<td><img src="image4" alt="BrF₅ Structure" /></td>
<td>octahedral</td>
<td>square pyramidal</td>
</tr>
</tbody>
</table>
09-2. Hybrid Atomic Orbitals: How can atomic orbitals describe all the different electron geometries found in molecules?

Exploration

1. sp, sp², sp³, sp³d, sp³d²

2. two sp, three sp², four sp³, five sp³d, six sp³d²

3. sp requires two (s, pₓ)
   sp² requires three (s, pₓ, pᵧ)
   sp³ requires four (s, pₓ, pᵧ, p₂)
   sp³d requires five (s, pₓ, pᵧ, p₂, d)
   sp³d² requires six (s, pₓ, pᵧ, p₂, d, d)

4. Comparing answers to #2 and #3 shows that the number of hybrid orbitals obtained equals the number of atomic orbitals used to form them.

5. 180° for sp, 120° for 2p², 109.5° for sp3, 90° and 120° for sp³d, and 90° for sp³d²

6. sp³

7. sp

8. sp²

9. The geometry of the molecule and the location of the electron density produce the lowest energy situation. Orbitals are used to describe the electron density. Atomic orbitals do not conform to the geometry of the molecules so hybrid orbitals with the correct geometry are needed.

Application

1. methane: 4 sigma bonds, 0 pi bonds
   ethylene: 5 sigma bonds, 1 pi bond
   acetylene: 3 sigma bonds, 2 pi bonds

2.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electron Geometry</th>
<th>Molecular Geometry</th>
<th>Central Atom Hybridization</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon tetrafluoride CF₄</td>
<td>tetrahedral</td>
<td>tetrahedral</td>
<td>sp³</td>
<td>109.5°</td>
</tr>
<tr>
<td>ozone O₃</td>
<td>trigonal planar</td>
<td>bent</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td>formaldehyde H₂CO</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td>carbonate anion CO₃²⁻</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td>sulfur dioxide SO₂</td>
<td>trigonal planar</td>
<td>bent</td>
<td>sp²</td>
<td>120°</td>
</tr>
<tr>
<td>nitrate anion NO₃⁻</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
<td>sp²</td>
<td>120°</td>
</tr>
</tbody>
</table>
Number the carbons 1 – 5 from left to right.
C1 is sp³ hybridized and the bond angles are 109.5°.
C2 and C3 are sp² hybridized and the bond angles are 120°.
C4 and C5 are sp hybridized and the bond angles are 180°.
09-3. Organic Functional Groups: What determines the properties of complicated organic molecules?

What do you know about functional groups already?
The diagram and text help identify two aromatic rings, four ethers, a nitrile, an amine, and alkanes.

Exploration
Alkene has a carbon-carbon double bond.
Alkyne has a carbon-carbon triple bond.
Aromatic ring has a hexagon of six carbons with alternating double and single bonds in two resonance structures. The instructor in discussion should generalize this to larger aromatic rings with illustrations, e.g. naphthalene, anthracene, etc.
Alcohol has an –OH group.
Halide has a halogen bonded to a carbon.
Amine has a nitrogen singly bonded to hydrogen and/or carbon.
Ether has a carbon-oxygen-carbon linkage.
Nitrile has a carbon-nitrogen triple bond.
Carbonyl has a carbon-oxygen double bond.
Aldehyde has a carbonyl bonded to a carbon and a hydrogen.
Ketone has a carbonyl bonded to two carbons.
Carboxyl has a carbonyl bonded to a hydroxyl group.
Acid halide has a carbonyl bonded to a halogen.
Ester has a carbonyl bonded to an ether linkage.
Amide has a carbonyl bonded to an amine linkage.

Got It!
1. aromatic ring, carboxyl, and amine
2. a carboxylic acid because it has hydroxyl groups bonded to carbonyl groups
3. carboxyl, aromatic ring, ester
4. Testosterone has a hydroxyl group instead of a ketone group.
5. D) Neither has ester groups.
Making Connections

1.

<table>
<thead>
<tr>
<th>Atom &amp; Functional Group</th>
<th>Atomic Orbital Hybridization</th>
<th>Local Molecular Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>C atom in an alkane</td>
<td>sp(^3)</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>C atom in an alkene</td>
<td>sp(^2)</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>C atom in an alkyne</td>
<td>sp</td>
<td>linear</td>
</tr>
<tr>
<td>O atom in an alcohol</td>
<td>sp(^3)</td>
<td>bent</td>
</tr>
<tr>
<td>O atom in an ether</td>
<td>sp(^3)</td>
<td>bent</td>
</tr>
<tr>
<td>N atom in an amine</td>
<td>sp(^3)</td>
<td>trigonal pyramidal</td>
</tr>
<tr>
<td>C atom in a nitrile</td>
<td>sp</td>
<td>linear</td>
</tr>
<tr>
<td>C atom in a carbonyl</td>
<td>sp(^2)</td>
<td>trigonal planar</td>
</tr>
</tbody>
</table>

2. (a) The molecule is planar because of the trigonal planar geometry at both carbon atoms.
   (b) All except the two hydrogens attached to the nitrogen and possibly the hydrogen attached to the oxygen because all the carbons have a trigonal planar structure.
   (c) Nitrogen is sp\(^3\) hybridized, the carbon atoms are all sp\(^2\) hybridized, the oxygen atom in the carbonyl group is sp\(^2\) hybridized, and the oxygen atom in the hydroxyl group is sp\(^3\) hybridized. Hydrogens are never hybridized since they only use 1s orbitals for bonding.

3. (a) sp\(^3\) hybridized, trigonal pyramidal geometry
   (b) No, because they are connected by an alkane chain that has a tetrahedral structure at each carbon atom, also the rings can rotate about carbon-carbon single bonds.
   (c) The oxygen atoms are in ether linkages, are sp\(^3\) hybridized, and have a bent local geometry.
   (d) No because there is a tetrahedral structure at each carbon atom in the alkane chain and there can be rotation about the carbon-carbon single bonds in the chain.
10-1. Gases and the Ideal Gas Law: 
How much air does it take to fill a balloon?

What do you predict?
This section is intended to connect with a student’s experience and prior knowledge about the properties of gases. Promote discussion among students, but do not expect correct answers. Students are asked to reconsider their responses at the end of the activity.

Exploration
1. The units must be the same as those used for the gas constant, R: volume in liters, pressure in atmospheres, amount of substance in moles, and temperature in degrees Kelvin.
2. \[ R = \frac{PV}{nT} = \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(1.00 \text{ mol})(273 \text{ K})} = 0.0821 \text{ L atm / mol K} \]
3. (a) The pressure will double.  
(b) The pressure will decrease by \( \frac{1}{2} \).  
(c) The volume must increase.

Application
1. \( P_2V_2 = P_1V_1 \) since \( nRT \) hasn’t changed.  
\( P_2 = P_1 \frac{V_1}{V_2} \)  
\( P_2 = (5 \text{ atm})(10 \text{ L})/(25 \text{ L}) = 2 \text{ atm} \)
2. Pressure is directly proportional to the Kelvin temperature.  
\( ^\circ\text{F} = (\frac{9}{5})^\circ\text{C} + 32^\circ\text{F} \)  
\( ^\circ\text{C} = (\frac{5}{9})(^\circ\text{F} – 32^\circ\text{F}) \)  
\( ^\circ\text{C} = (\frac{5}{9})(-34^\circ\text{F} – 32^\circ\text{F}) = -37^\circ\text{C} \)  
\( ^\circ\text{C} = (\frac{5}{9})(103^\circ\text{F} – 32^\circ\text{F}) = +39^\circ\text{C} \)  
\( T_1 = 273 – 37 = 236 \text{ K} \)  
\( T_2 = 312 \text{ K} \)  
\( \frac{P_2}{P_1} = \frac{T_2}{T_1} \)  
\( P_2 = (30 \text{ lb / in}^2) \left( \frac{312 \text{ K}}{236 \text{ K}} \right) = 40 \text{ lb / in}^2 \)
3. \( P = (1.00 \text{ g} ÷ 18.0 \text{ g/mol})(0.08205 \text{ L atm/mol K})(423 \text{ K}) ÷ (10.0 \text{ L}) = 0.193 \text{ atm} \)
4. The volume is directly proportional to the Kelvin temperature and inversely proportional to the pressure.  
\( \frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2} \)  
\( V_2 = (1000 \text{ L}) \frac{240 \text{ K}}{293 \text{ K}} \frac{745 \text{ torr}}{600 \text{ torr}} = 1017 \text{ L} \)
Got It!

1. (a) and (b) contain the same number of molecules because P, V, and T are the same for both. (c) has a higher temperature and a lower pressure so it must contain fewer molecules. (d) has the same temperature and a higher pressure so it must contain more molecules. So (d) has the largest and (c) has the fewest molecules.

2. The temperature increased by 4X but the pressure didn’t change so the number of molecules must be ¼ the original so ¾ of the molecules escaped.

3. Disagree, gas pressure changes in direct proportion to the Kelvin temperature not the Celcius temperature.
   Agree, gas pressure changes in direct proportion to the number of molecules in a container; if half are removed, both the mass and the pressure will decrease by a factor of 2.
   Disagree, within the ideal gas approximation all gas samples in the same volume and at the same pressure and temperature will contain the same number of molecules. The size of the molecules is not relevant because the molecules are so far apart that their size is negligible.
10-2. Partial Pressures:
What determines the total pressure of a mixture of gases?

What do you think?
Students may have a variety of answers to these questions. Elicit the basis for their ideas and then go on with the activity and revisit these questions at the end.

Exploration
1. (a) \(n(\text{oxygen in 1}) = \frac{PV}{RT}
   \begin{align*}
   & = \frac{(1.0 \text{ atm})(1.0 \text{ L})}{(0.08205 \text{ L atm/mol K})(300 \text{ K})} = 0.041 \text{ mol} \\
   \end{align*}
\(n(\text{nitrogen in 2}) = \frac{PV}{RT}
\begin{align*}
& = \frac{(1.0 \text{ atm})(1.0 \text{ L})}{(0.08205 \text{ L atm/mol K})(300 \text{ K})} = 0.041 \text{ mol}
\end{align*}

(b) moles in 3 = 0.041 mol + 0.041 mol = 0.082 mol

(c) \(P(\text{container 3}) = \frac{nRT}{V}
\begin{align*}
& = \frac{(0.082 \text{ mol})(0.08205 \text{ L atm/mol K})(300 \text{ K})}{1.0 \text{ L}} = 2.0 \text{ atm}
\end{align*}

(d) \(P_{O2} = \frac{nO2RT}{V} = \frac{(0.041 \text{ mol})(0.08205 \text{ L atm/mol K})(300 \text{ K})}{1.0 \text{ L}} = 1.0 \text{ atm}
\)

(e) \(P_{N2} = \frac{nN2RT}{V} = \frac{(0.041 \text{ mol})(0.08205 \text{ L atm/mol K})(300 \text{ K})}{1.0 \text{ L}} = 1.0 \text{ atm}
\)

2. \(P_{O2}/P_{\text{total}} = 1.0 \text{ atm} / 2.0 \text{ atm} = \frac{1}{2}
\)

3. \(n_{O2}/n_{\text{total}} = 1 \text{ mol} / 2 \text{ mol} = \frac{1}{2}
\)

4. The values are equal. The ratio of partial pressure to total pressure equals the mole ratio.
\[
\frac{P_{O2}}{P_{\text{total}}} = \frac{n_{O2} \frac{RT}{V}}{n_{\text{total}} \frac{RT}{V}} = \frac{n_{O2}}{n_{\text{total}}}
\]

Got It!
1. \(P_{O2} = X_{O2} P_{\text{total}} = (0.15)(3000 \text{ psi}) = 450 \text{ psi}
\(P_{\text{He}} = X_{\text{He}} P_{\text{total}} = (0.85)(3000 \text{ psi}) = 2550 \text{ psi}
\)
   Note to Students: \(P_{O2} + P_{\text{He}} = P_T; 450 + 2550 = 3000 \text{ psi}
\)

2. \[
\frac{V_2}{V_1} = \frac{P_1}{P_2} \frac{T_2}{T_1}
\]
   \[
   V_2 = (18 \text{ L}) \left(\frac{450 \text{ psi}}{14.7 \text{ psi}}\right) \left(\frac{273 \text{ K}}{303 \text{ K}}\right) = 496 \text{ L}
   \]

3. \[
\frac{V_2}{V_1} = \frac{P_1}{P_2} \frac{T_2}{T_1}
\]
   \[
   V_2 = (18 \text{ L}) \left(\frac{2550 \text{ psi}}{14.7 \text{ psi}}\right) \left(\frac{273 \text{ K}}{303 \text{ K}}\right) = 2800 \text{ L}
   \]
4. \[ n_{O_2} = \frac{(1.0 \text{ atm})(496 \text{ L})}{(0.08205 \text{ L atm / mol K})(273 \text{ K})} = 22 \text{ mol} \]
\[ n_{He} = \frac{(1.0 \text{ atm})(2800 \text{ L})}{(0.08205 \text{ L atm / mol K})(273 \text{ K})} = 125 \text{ mol} \]

5. total mass = (22 mol)(32 g/mol) + (125 mol)(4.0 g/mol) = 1200 g
(1200 g)(1 kg/1000g) = 1.2 kg
(1.2 kg)(2.2 lb/kg) = 2.6 lbs
11-1. Phases of Matter: As water cools, does the temperature continue to drop as ice forms?

What do you think?
Have students document their thoughts on these questions and then come back to them at the end of the activity.

Exploration
1. Spacing: molecules in the solid are very close to each other, in the liquid they are a bit further apart, and in the gas they are quite far apart.
   Motion: molecules in the solid are in fixed positions, in the liquid they can rotate and move in short steps, and in the gas they are free to move from one side of the container to the next.
   Order: molecules in the crystal have long-ranger order (one part of the solid is exactly like any other part), in the liquid there is short-range order (molecules are organized next to each other but that order is not repeated at long distances), and in the gas the molecules are totally disordered (arranged randomly and constantly moving).
   Compressibility: Solids are almost incompressible, liquids can be compressed slightly, and gases are very compressible.
2. melting, subliming, and vaporizing
3. freezing, depositing, and condensing
4. (a) A is solid water, C is liquid water, E is gaseous water
   (b) It is melting.
   (c) It is vaporizing (becoming a gas).
   (d) All the ice has melted (B) or become a gas (D).
5. The length of the line in the figure is proportional to the amount of energy added. It takes the most energy to vaporize 100 g of liquid water.

Got It!
1. Add energy at a constant rate and notice when the temperature stops increasing. At that temperature, a phase transition is occurring.
2. Now students should realize that (1) as long as ice is melting in the Coke, the temperature should not be changing, (2) when water boils the temperature is constant, and (3) the bubbles forming in boiling water may consist of air and water initially but after all the dissolved air has been removed, they consist of gaseous water. A common misconception is that they consist of hydrogen and oxygen gases since water is a liquid.
11-2. Phase Diagrams:
What information can be obtained from a phase diagram?

Exploration
1. (a) vapor pressure curve, vaporization and condensation occur along this line.  
   (b) melting point curve, melting and freezing occur along this line.  
   (c) sublimation curve, sublimation and deposition occur along this line.  
2. solid, liquid, and gas  
3. The distinction between the liquid and the gas disappears, and only one phase is present.

Application
1. 50°C is about half-way between 0.01 and 100°C; a vertical line at that point intersects the vapor pressure curve about 1/5 of the way to 760 torr, producing an estimate of the vapor pressure as 150 torr.
2. Ice will sublime below the triple point. For this to occur, the temperature must be less than 0.01°C and the pressure less than 4.58 torr.
3. The label should be placed at the point where the vapor pressure curve, the melting point curve, and the sublimation curve come together. At this point solid, liquid, and gaseous carbon dioxide can exist simultaneously in equilibrium.
4. (a) As shown by the dotted lines in the figure, 5.2 atm and -57°C.  
   (b) solid  
   (c) gas
5. decreases  
6. increases  
7. For a given mass of water, the volume of the solid is larger than the volume of the liquid. Consequently, increasing the pressure should promote melting to reduce the volume. As a result when the pressure increases, ice melts at a lower temperature.
8. For a given mass of carbon dioxide, the volume of the solid is smaller than the volume of the liquid. Consequently, increasing the pressure should hinder melting because the volume would have to expand against the pressure. As a result, when the pressure increases, carbon dioxide melts at a higher temperature.

Research
The intermolecular interactions in carbon dioxide are weak compared to those in water. In addition to London dispersion interactions, water also has dipole-dipole and hydrogen bonding interactions. Consequently, the molecules of carbon dioxide must be closer together (a higher pressure) and have less energy (a lower temperature) before they will form a solid and a liquid phase.

Got It!
1. two
2. Find a pressure of 1 atm on the y-axis and draw a horizontal line, the point where it intersects the vapor pressure curve corresponds to the normal boiling point on the x-axis.

3. Find a pressure of 1 atm on the y-axis and draw a horizontal line, the point where it intersects the melting point curve corresponds to the normal melting point on the x-axis.

4. The critical point is where the vapor pressure curve ends.

5.
12-1. Solubility: Where do those vitamins go?

What do you think?

Make a list on the blackboard of issues students have with vitamins. Some may be addressed in this activity, but many may not be. A class project might be a literature search to resolve some of these issues.

Exploration

1. Vitamin C has the following interactions: London dispersion, dipole – dipole, and hydrogen bonding. 
   Vitamin E has the following interactions: London dispersion, and smaller dipole-dipole and only one possibility for hydrogen bonding.

2. With all the –OH groups and oxygen atoms, hydrogen bonding should be very important for vitamin C.

3. With the long hydrocarbon chain and aromatic ring, London dispersion interactions should be important for vitamin E.

4. Vitamin C is expected to be hydrophilic because of the interactions are similar to those in water (dipole-dipole and hydrogen bonding). Vitamin E is expected to be hydrophobic because dipole-dipole and hydrogen bonding interactions are not as important. Also, the long hydrocarbon chain would disrupt the hydrogen bonding network in water.

5. The structure of Vitamin E is most similar to that of fatty tissue and phospholipid membranes. It should dissolve in these structures.

6. Vitamin C does not dissolve in the fatty tissue and membranes, rather it remains in the bloodstream and is rapidly eliminated from the body through the kidneys. Vitamin E will dissolve in the fatty tissue and membranes and a low but steady concentration will be maintained in the bloodstream. Vitamin E will remain in the bloodstream longer.

7. Vitamin X actually is vitamin C because it is rapidly eliminated from the blood. Vitamin Y actually is vitamin E because its concentration is maintained in the blood.

8. The half-life of vitamin C in the blood is about 30 minutes. The half-life of vitamin E in the blood is about 50 hours.

9. Vitamin C will reach the 10% level in about 90 minutes. Vitamin E will reach the 10% level in well over 100 hours, maybe 200 hours. It is difficult to tell because the graph doesn’t extend far enough.

10. To keep the concentrations above 50% of the initial concentration, vitamin C should be taken every 30 minutes and vitamin E every 40 hours, i.e. about every two days.
11. As the above graph shows, the concentration can be maintained between 50% and 100% of the initial level by taking half the initial dose every half-life of the vitamin, e.g. two tablets at the beginning followed by one tablet after every half life.

12. It is recommended to take vitamin C hourly, and vitamin E every other day. These times are commensurate with the half-lives of the vitamins in the bloodstream, and are convenient to remember.

Got It!
1. Vitamin B3 is more like vitamin C in structure, and vitamin D is more like vitamin E. Vitamin D will remain in the bloodstream longer because it will be absorbed by the fatty tissue and membranes.

2. It is predicted that amoxicillin has a bloodstream half-life of about 6 hours, and azythromycin has a bloodstream half-life of about 24 hours. Amoxicillin should have more polar groups and groups capable of hydrogen bonding than azythromycin while azythromycin should have large London dispersion interactions that enable it to be retained in fatty tissue and membranes.
12-2. Colligative Properties:
What effect does a solute have on properties of a solvent?

What do you think?
This section connects with students may already know. Revisit it at the end of the activity if necessary to confirm that any misunderstandings have been resolved.

Exploration
1. A colligative property depends only on the number of particles not on their composition.
2. vapor pressure lowering, boiling point elevation, freezing point lowering, osmotic pressure
3. (1) All are caused by adding a nonvolatile solute to a solvent. (2) All of these depend on the van’t Hoff factor. (3) Two involve a change in the temperature at which a phase transition occurs. (4) Two involve molal concentration units.
4. Measure the osmotic pressure produced by a known mass of the polymer. Use the equation and solve for the concentration. For a polymer the van’t Hoff factor equals one. Then use moles polymer = concentration x volume of solution, and molar mass = mass polymer / moles polymer.

Application
1. \[ \Delta T_b = (0.52 \degree C/kg/mol) \left( \frac{15 g}{58.5 g/mol} \right) 1.0 kg \] (2) = 0.27 \degree C
2. \[ m = -\frac{\Delta T_f}{K_f i} = \frac{10 \degree C}{(1.86 \degree C kg/mol)(3)} = 1.79 mol/kg = 1.79 m \]
3. Osmotic pressure depends on the concentration of particles.
   KCl: 0.10 M x 2 = 0.20 M
   Sucrose: 0.10 M x 1 = 0.10 M
   K2SO4: 0.05 M x 3 = 0.15 M
   CaCl2: 0.10 x 3 = 0.30 M
   so Sucrose < K2SO4 < KCl < CaCl2
4. \[ \Pi = cRT_i \]
   \[ c = \frac{(7.60 \text{torr} / 760 \text{torr} / \text{atm})}{(0.08205 L \text{atm} / \text{mol} K)(298 K)(1)} = 4.09 \times 10^{-4} \text{mol/L} \]
   (4.09 \times 10^{-4} \text{mol/L})(0.2000 L) = 8.18 \times 10^{-5} \text{mol}
   MM = 4.40 g \div 8.15 \times 10^{-5} \text{mol} = 53,800 \text{g/mol}
5. \[ \Delta T_f = -K_f m_i \]
   \[ m = (0.28 \degree C) / (30 \degree C \cdot \text{kg/mol})(1) = 9.33 \times 10^{-3} \text{mol/kg} \]
   \[ (9.33 \times 10^{-3} \text{mol/kg})(0.200 \text{ kg}) = 1.87 \times 10^{-3} \text{mol} \]
   MM = 0.48 g \div 1.87 \times 10^{-3} \text{mol} = 257 \text{g/mol}
   257 \text{g/mol} \div 32.1 \text{g/mol S} = 8.01
   Corresponding to the formula S8
Got It!

1. (a) Pure water in beaker B has the higher vapor pressure so water will be transferred from beaker B to beaker A. The level in beaker B will go down, and the level in beaker A will go up.
   (b)

   ![Graph](image)

   concentration in A

   time

2. (a) In both cases water is transported to dilute the salt solution.
   (b) In the osmosis experiment the level of the pure solvent drops and the level of the solution rises.
13-1. Rates of Chemical Reactions: 
*How quickly do reactants turn into products?*

**What do you think?**
These questions are intended to stimulate discussion of change and the rate of change. Many examples are possible. One is given in the prior introductory paragraph.

**Exploration**
1.

<table>
<thead>
<tr>
<th>time (min)</th>
<th>conc ($10^{-6}$ M)</th>
<th>&lt;rate&gt; ($10^{-6}$ M/min)</th>
<th>&lt;rate&gt;/conc (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>48.3</td>
<td>1.7</td>
<td>0.034</td>
</tr>
<tr>
<td>10</td>
<td>35.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>33.9</td>
<td>1.2</td>
<td>0.034</td>
</tr>
<tr>
<td>20</td>
<td>24.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>23.8</td>
<td>0.8</td>
<td>0.033</td>
</tr>
<tr>
<td>30</td>
<td>17.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>16.7</td>
<td>0.6</td>
<td>0.035</td>
</tr>
<tr>
<td>40</td>
<td>12.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>11.7</td>
<td>0.4</td>
<td>0.033</td>
</tr>
<tr>
<td>50</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>8.2</td>
<td>0.3</td>
<td>0.035</td>
</tr>
<tr>
<td>60</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>5.8</td>
<td>0.2</td>
<td>0.033</td>
</tr>
<tr>
<td>70</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>4.0</td>
<td>0.2</td>
<td>0.048</td>
</tr>
<tr>
<td>80</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>81</td>
<td>2.8</td>
<td>0.1</td>
<td>0.035</td>
</tr>
<tr>
<td>90</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>2.0</td>
<td>0.1</td>
<td>0.048</td>
</tr>
</tbody>
</table>
2 & 3

4. The rate decreases as the concentration decreases because the slope of the graph at any point gets smaller as time increases and the concentration decreases.

5. The vertical line is at approximately 20 minutes where the concentration has been reduced to 25 from 50 x 10^-6 M.

6. The reaction rate divided by the concentration is essentially constant.

7. (b) describes the data because Rate/Concentration = k, which is a constant.

Application

1. first order because Rate = k[PAN] and the exponent for the concentration is 1.

2. \[
\frac{\text{Rate}}{\text{Concentration}} \text{ in any small time interval } = k. \]
   Those values are given in Column 4 of Table 1. The average of the first seven measurements is 0.035 min^{-1}. The later measurements are omitted because the concentration is low and they probably are less accurate.

3. Using k, give \( t_{1/2} = 19.8 \text{ min} \) in good agreement with the estimate from the graph.

Got It!

1. A plot of \( \ln[\text{PAN}(t)] \) vs. t should produce a straight line with slope \(-k\) and intercept \(\ln[\text{PAN}]_{t=0}\)

2. (a) \( \text{Rate} = k[\text{Ni(CO)}_4] \)
   (b) \( t_{1/2} = \ln(2) \div 1.879 \text{ s}^{-1} = 0.3689 \text{ s} \)
   (c) \( \ln[\text{Ni(CO)}_4] = -kt + \ln[\text{Ni(CO)}_4]_{t=0} \)
   (d) Rearranging (c) and solving for t gives

\[
    t = \frac{\ln\left(\frac{1}{0.1}\right)}{k} = 1.225 \text{ s}
\]
Additional Practice Problems
1. Doubling X increase the rate by 4 times, halving Y decreases the rate by $\frac{1}{2}$, so the net effect is 4 times $\frac{1}{2} = 2$. The reaction rate doubles.

2. (a) In the first two rows, only the ozone concentration changed, and it changed by a factor of 3. The rate also changed by a factor of 3, so the reaction is first order with respect to ozone. In the first and third rows, both the ozone and ethylene concentrations changed by a factor of 2, and the rate changed by a factor of 4. The ozone contributed one factor of 2 to this change since it is first order, so the ethylene contributed the other factor of 2, so the reaction also is first order with respect to ethylene. Consequently the rate law is Rate = $k[O_3][C_2H_4]$.

(b) Using the data in the first row:
$$k = \frac{\text{Rate}}{[O_3][C_2H_4]}$$
$$= \frac{(1.0 \times 10^{-12} \text{ M s}^{-1})}{(0.50 \times 10^{-7} \text{ M})(1.0 \times 10^{-8} \text{ M})}$$
$$= 2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

(c) Rate = $(2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1})(2.0 \times 10^{-7} \text{ M})^2$
$$= 8.0 \times 10^{11} \text{ M/s}$$
**13-2. Reaction Mechanisms:**
*What determines the rate law for a reaction?*

**What do you think?**
These questions ask students to reflect on what they have just learned.

1. Rate = k[A]
2. Rate = k[A][B]

**Exploration 1**
1.1. (a) yes
   NO + O₂ + NO₃ + NO → NO₃ + 2NO₂
   2NO + O₂ → 2NO₂

   (b) yes
   NO + O₂ + NO + O → NO₂ + O + NO₂
   2NO + O₂ → 2NO₂

1.2. (a) Mechanism 1, Step 2 is a bimolecular elementary reaction.
   Rate = k[NO₃][NO]

   (b) Mechanism 2, Step 1 also is a bimolecular elementary reaction.
   Rate = k[NO][O₂]

1.3. No, the intermediate NO₃ is included in Mechanism 1.

1.4. (a) Replacing [NO₃] and combining the constants give
   Rate = k[NO][O₂][NO] = k[NO]²[O₂]

   (b) Mechanism 1: Rate = k[NO]²[O₂]

   Mechanism 2: Rate = k[NO][O₂]

**Exploration 2**
2.1. by a factor of 2
2.2. so, y = 1
2.3. by a factor of 4
2.4. so, x = 2
2.5. Rate = k[NO]²[O₂]

**Got It!**
1. Mechanism 1 is consistent with the experimentally determined rate law.
2. \[ k = \text{Rate} / [\text{NO}]^2 [\text{O}_2], \text{ using the data in Row 1 gives} \]
   \[ k = (7.0 \times 10^{-3} \text{ M s}^{-1})^2 (1.0 \times 10^{-2} \text{ M})^2 (1.0 \times 10^{-2} \text{ M}) \]
   \[ = 7.0 \times 10^3 \text{ M}^2 \text{s}^{-1} \]
3. (a) IV, VII
   (b) II, V, VI,
   (c) I, III, VIII
4. (a) Summary: Zero order bromine, 1st order hydronium, 1st order acetone
   With acetone constant, hydronium constant, and bromine 2X, rate doesn’t change;
   with acetone constant and hydronium 2X, rate 2X within some experimental error;
   with acetone 1.33X, hydronium constant, rate 1.33X
   so Rate = k[CH₃COCH₃][H₃O⁺]

   (b) zero order wrt bromine, first order with respect to hydronium and acetone

   (c) overall order is 2

   (d) using the data in the first row gives
   k = (5.7x10⁻⁵ M/s)/(0.30 M)(0.05 M) = 3.8x10⁻³ M⁻¹ s⁻¹

   (e) Rate = (3.8x10⁻³ M⁻¹ s⁻¹)(0.01 M)(0.01 M) = 3.8x10⁻⁷ M/s
14-1. Equilibrium Constant and Reaction Quotient: How can the direction of a reaction be identified?

What do you think?
This section elicits students’ understandings of what it might mean to think of a chemical reaction as being complete or coming to an end. A consensus need not be reached until after the activity has been completed.

Exploration
1. The concentrations of the products raised to the power given by the corresponding stoichiometric coefficient.
2. The concentrations of the reactants raised to the power given by the corresponding stoichiometric coefficient.
3. The corresponding stoichiometric coefficient.
4. (1) They both are ratios of products/reactants. (2) They both involve the concentrations of the reactants and the products. (3) They both have the concentrations raised to a power as given by the corresponding stoichiometric coefficient.
5. The value for the equilibrium constant is produced by the concentrations of the reactants and products when the reaction has reached equilibrium, while the reaction quotient can have any value as given by the instantaneous concentrations of reactants and products.
6. If the equilibrium constant is large, then the product concentrations should be higher than the reactant concentrations and the reaction should be product favored.
7. If Q > K then the product concentrations are too large to be at equilibrium, so the reaction should proceed in the reverse direction to produce more reactants.
8. Q will equal K when the reaction has reached equilibrium.

Application
1. \[ K_c = \frac{[NO]^2}{[N_2][O_2]} \]
2. \[ K_c = \frac{1}{[Ca^{2+}][CO_3^{2-}]} \]
3. \[ K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \]
Got It!
1. Products will predominate over reactants when equilibrium has been achieved if the value of the equilibrium constant is much larger than 1.
2. If $Q > K$, then the concentrations of products are too large, and the reaction will proceed in the reverse direction to reach equilibrium by producing more reactants. If $Q < K$, then the concentrations of products are too small, and the reaction will proceed in the forward direction to reach equilibrium by producing more products.
3. $H_2 + I_2 \rightleftharpoons 2 \text{HI}$
   
   (a) $Q = \frac{(5.0 \text{ mol/2.0 L})^2}{(0.5 \text{ mol/2.0 L})(0.5 \text{ mol/2.0 L})} = 100$
   
   (b) $K = 50.0$ and $Q = 100$, so $Q > K$ and HI will decompose to reach equilibrium.
Exploration
1. The stoichiometric coefficients are essential to have in solving equilibrium problems.
2. x in each column would have to be multiplied by the stoichiometric coefficient in that respective column.
3. The last line is important because it gives the amounts that need to be substituted into the equilibrium constant expression in order to solve for x.
4. Answers will vary, but one good insight is the importance of organizing the information and thinking about the solution systematically.

Application
1. \[ K_c = \frac{[CO]^2}{[CO_2]} = \frac{(0.10 \text{ mol} / 2.00 \text{ L})^2}{(0.20 \text{ mol} / 2.00 \text{ L})} = 0.025 \]

Since \( K_c \) is small, expect x to be small compared to 1.00, so neglect 2x in the denominator. 
\[ 4x^2 = 2.0 \times 10^{-5} \]
\[ x = 0.0171 \text{ M} \]
Concentrations are 0.034 M for NO and 0.017 for Cl₂.
Check validity of the approximation: 0.034/1.00 = 3.4%, satisfies the less than 5% convention.

Got It!
1. The example was a bit serendipitous. Taking the square root of both sides eliminated the quadratic equation in x.
2. When the equilibrium constant is small, then the change compared to the initial concentrations will be small (<5%) and can be neglected.
3.

<table>
<thead>
<tr>
<th>R</th>
<th>$H_2(g)$</th>
<th>$I_2(g)$</th>
<th>$\Rightarrow$</th>
<th>$2HI(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.100 M</td>
<td>0.300 M</td>
<td>0</td>
<td>Initial concentrations (mol/L)</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>-x</td>
<td>+2x</td>
<td>Change caused by the reaction (mol/L)</td>
</tr>
<tr>
<td>E</td>
<td>0.100 M-x</td>
<td>0.300 M-x</td>
<td>+2x</td>
<td>Concentrations at equilibrium (mol/L)</td>
</tr>
</tbody>
</table>

Write the balanced reaction equation.

$K_c = \frac{(2x)^2}{(0.100 - x)(0.300 - x)} = 50.0$

Must solve a quadratic equation, because the equilibrium constant is large, meaning much product will be produced.

$46x^2 - 20x + 1.5 = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = \frac{20 \pm \sqrt{400 - (4)(46)(1.5)}}{2(46)}$

$x = \frac{20.0 \pm 11.1}{92}$

$x = 0.338 M \text{ or } x = 0.0967 M$

The larger value is too large, since the initial concentrations were only 0.100 M and 0.300 M. So $x = 0.0967 M$, and the equilibrium concentration of HI is $2x = 0.193 M$ in the 10.0 L container, so 1.93 mol of HI was produced.

**Additional Practice Problems**

1. $K_c = \frac{[Cu^{2+}][Cl^-]^4}{[CuCl_4^{2-}]}$

$K_c = \frac{[HCl]^2}{[H_2O]}$

$K_c = \frac{[H_3O^+][HS^-]}{[H_2S]}$

2. $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.3 \times 10^{-2})(3.9 \times 10^{-3})}{(4.2 \times 10^{-3})} = 1.21$
3. \[ 2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g) \]

Write the balanced reaction equation.

<table>
<thead>
<tr>
<th></th>
<th>2NOCl(g)</th>
<th>(\rightleftharpoons)</th>
<th>2NO(g)</th>
<th>Cl(_2)(g)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.00 M</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-2x</td>
<td>+2x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2.00 M-2x</td>
<td>0.66 M</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Initial concentrations (mol/L)

Change caused by the reaction (mol/L)

Concentrations at equilibrium (mol/L)

From the table, \(2x = 0.66\) M, \(x = 0.33\) M.
Consequently \([\text{NOCl}] = 1.34\) M, \([\text{NO}] = 0.66\) M, and \([\text{Cl}_2] = 0.33\) M

\[ K_c = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080 \]

4. \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]

<table>
<thead>
<tr>
<th></th>
<th>(\text{N}_2)(g)</th>
<th>(\text{O}_2)(g)</th>
<th>(\rightleftharpoons)</th>
<th>2NO(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0.0150 M</td>
</tr>
<tr>
<td>C</td>
<td>x</td>
<td>x</td>
<td>-2x</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>x</td>
<td>x</td>
<td>0.0150-2x M</td>
<td></td>
</tr>
</tbody>
</table>

\[ K_c = \frac{(0.0150-2x)^2}{x^2} = 1.70 \times 10^{-3} \]

The equilibrium constant is small, which means that there will be little product, NO, and lots of reactants, so \(x\) will be large. You can solve the quadratic equation for \(x\), but you can avoid the quadratic equation by noticing that you can take the square root of both sides to eliminate the quadratic.

\[ \frac{(0.0150-2x)}{x} = 0.0412 \]

\[ x = 7.35 \times 10^{-3} \]

So \([\text{N}_2] = [\text{O}_2] = 7.35 \times 10^{-3}\) M, and \([\text{NO}] = 3.00 \times 10^{-4}\) M

5. (a) \( Q = \frac{(0.00150)^2}{(0.0250)^2} = 3.60 \times 10^{-3} \)

\(Q\) is larger than \(K\), so there is too much product, the reaction is not at equilibrium.
(b) Reaction will proceed in the reverse direction to consume NO and produce more \(\text{N}_2\) and \(\text{O}_2\).
\( \text{R} \) | \( \text{N}_2(\text{g}) \) | \( \text{O}_2(\text{g}) \) | \( \triangleq \) | \( \text{2NO}(\text{g}) \) \\
--- | --- | --- | --- | --- \\
I | 0.0250 M | 0.0250 M | | 0.00150 M \\
C | \( x \) | \( x \) | | \(-2x\) \\
E | 0.0250 + \( x \) M | 0.0250 + \( x \) M | | 0.00150 - 2\( x \) M \\

\[
K_c = \frac{(0.00150 - 2x)^2}{(0.0250 - x)^2} = 1.70 \times 10^{-3}
\]

\[
\frac{(0.00150 - 2x)}{(0.0250 - x)} = 0.0412
\]

\( x = 2.30 \times 10^{-4} \)

So \( [\text{N}_2] = [\text{O}_2] = 0.0252 \text{ M}, \) and \( [\text{NO}] = 0.00104 \text{ M} \)
15-1. Acid Ionization Constants: How strong is that acid?

What do you think?
This question is intended to help students connect acids with their experiences. They might not know the names of the acids, and they might not know that apples or some other food products are acidic. Although some examples are included in the activity, have them do some research on these issues and report to the class at the next session. Their report should include the molecular formulas and structural formulas as well.

Exploration
1. A Brønsted-Lowry acid is a proton donor.
2. A Brønsted-Lowry base is a proton acceptor.
3. HF and H$_2$O$^+$ are the acids.
4. H$_2$O and F$^-$ are the bases.
5. Top to bottom corresponds to decreasing $K_a$ or increasing p$K_a$.
6. Acetic acid $K_a = 2.0 \times 10^{-5}$
   Ammonium ion $K_a = 5.0 \times 10^{-10}$
   Nitric acid $pK_a = -1.3$
   Hydrofluoric acid $pK_a = 3.1$
7. \[
\frac{(0.0264)(0.0264)}{0.973} = 7.16 \times 10^{-4}
\]
The concentrations produce the value in the table.
8. \[
\frac{0.9999}{0.0001} = 9,998, \text{ which equals the value in the table to two significant figures.}
\]
9. 0.0264 M / 1.0 = 2.6% ionized
10. 0.9999/1.0 = 99.99% ionized or 100% to two significant figures
11. HF is called a weak acid because its percent ionization is small. HCl is called a strong acid because its percent ionization is large.

Got It!
1. Weak acids are acids that do not ionize completely; percent ionization is much less than 100%.
2. Strong acids are acids that ionize nearly completely, i.e. percent ionization is close to 100%.
3. hydrochloric, sulfuric, and nitric
4. phosphoric, hydrofluoric, nitrous, acetic, carbonic, dihydrogen phosphate, ammonium ion, ethanol, methane (Note ethanol and methane are extremely weak acids and often are not even considered to be acids.)
5. all are weak acids
   Oxalic acid $K_a = 5.9 \times 10^{-2} >$ Malic acid $K_a = 4.0 \times 10^{-4} >$ Lactic acid $K_a = 1.3 \times 10^{-4}$
15-2. Calculations Involving Acid Ionization Constants: How can the pH of an acid solution be determined?

What do you think?
The RICE table consists of four rows.
R = write the balanced reaction equation
I = write the initial amounts of the reactants and products
C = write the change in the initial amounts for the reaction to reach equilibrium
E = write the amounts present at equilibrium
The unknown quantity should be represent by x in these rows, then the equilibrium constant expression is used to solve for x.

Exploration 1
Table I. RICE Table for Strong Acid Ionization

<table>
<thead>
<tr>
<th>R) Reaction eq.</th>
<th>HCl(aq) + H$_2$O(l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + Cl$^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial conc.</td>
<td>0.0020 M 0 0</td>
</tr>
<tr>
<td>C) Change in conc.</td>
<td>-0.0020 M +0.0020 M +0.0020 M</td>
</tr>
<tr>
<td>E) Equilibrium conc.</td>
<td>0 0.0020 M 0.0020 M</td>
</tr>
</tbody>
</table>

pH = $-\log[H_3O^+] = -\log(0.0020) = 2.70$

Exploration 2
Table II. RICE Table for pKa of lactic acid
let L$^- = \text{CH}_3\text{CH}_2(\text{OH})\text{COO}^-$

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>LH(aq) + H$_2$O(l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + L$^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial concentration</td>
<td>0.25 M 0 0</td>
</tr>
<tr>
<td>C) Change in concentration</td>
<td>$-x$ $x$ $x$</td>
</tr>
<tr>
<td>E) Equilibrium concentration</td>
<td>$0.25 - x$ M $x$ $x$</td>
</tr>
</tbody>
</table>

since pH = 2.23, $x = 10^{-2.23}$

$x = 5.9 \times 10^{-3}$ M

$K_a = (5.9 \times 10^{-3})^2 / (0.244) = 1.4 \times 10^{-4}$

(Apply 5% rule and ignore change in initial acetic acid concentration)
pK$_a$ = 3.85
Exploration 3  
**Table III. Rice Table for the pH of rainwater.**

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>H$_2$CO$_3$(aq) + H$_2$O(l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + HCO$_3^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial concentration</td>
<td>1.09x10$^{-5}$ M</td>
</tr>
<tr>
<td>C) Change in concentration</td>
<td>$-x$</td>
</tr>
<tr>
<td>E) Equilibrium concentration</td>
<td>$1.09x10^{-5} - x$</td>
</tr>
</tbody>
</table>

$10^{-6.38} = x^2/(1.09x10^{-5} - x)$

$[H_3O^+] = x = 2.1x10^{-6}$

pH $= 5.68$

**Got It!**

1. The balanced reaction equation is needed to determine how the change in moles of reactants and moles of products are related.
2. When one molecule of lactic acid ionizes, one hydronium ion is produced and one lactate ion is produced.
3. The amount that ionizes is assumed, as an approximation, to be very small and negligible.
4. Answer can vary, but one insight is the benefit of using the RICE table to organize the information and the process.

**Additional Practice Problems**

1.

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>CH$_3$COOH(aq) + H$_2$O(l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + CH$_3$COO$^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial concentration</td>
<td>1.00 M</td>
</tr>
<tr>
<td>C) Change in concentration</td>
<td>$-x$</td>
</tr>
<tr>
<td>E) Equilibrium concentration</td>
<td>$1.00 - x$</td>
</tr>
</tbody>
</table>

$10^{-4.74} = x^2/(1.00 - x)$

$x = 4.3x10^{-3}$

The hydronium ion and acetate ion concentrations are $4.3x10^{-3}$ M, and the acetic acid concentration is 0.996 M. The pH is 2.37.
2. \[ K_a = \frac{[H_2O^+][E]}{[EH^+]} \]

\[ \frac{[E]}{[EH^+] \cancel{[H_2O^+]}} = \frac{K_a}{[H_2O^+]} = \frac{10^{-9.96}}{10^{-7.4}} = 2.8 \times 10^{-3} \]

The acid form, EH\(^+\), dominates in the bloodstream because the hydronium ion concentration is so large. If the hydronium ion concentration and the \( K_a \) were equal then the concentration ratio would be 1.

3. (a) \[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{B} \\
\text{O} \\
\text{H}
\end{array}
\]

(b) Water can react with boric acid because the boron atom does not have an octet of electrons.

(c) \[ K_a = 10^{-9.24} = \frac{x^2}{(0.10 - x)} \]

\[ x = 7.6 \times 10^{-6} \]

\[ pH = 5.12 \]
16-1. Buffers: How can your blood pH be kept near the critical value of 7.4?

Exploration

1. 3.0
2. pOH = 3.0 so pH = 11
3. Since [F\(^-\)] = [HF], pH = pK\(_a\) = 3.14
4.

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>HCl(aq) + F(^-)(aq) ⇌ HF(aq) + Cl(^-)(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial concentration</td>
<td>0.0010 M  0.050 M  0.050 M  0 M</td>
</tr>
<tr>
<td>C) Change in concentration</td>
<td>-0.0010  -0.0010  +0.0010  +0.0010</td>
</tr>
<tr>
<td>E) Equilibrium concentration</td>
<td>0  0.049  0.051  0.0010</td>
</tr>
</tbody>
</table>

\[
\text{pH} = \text{pK}_a + \log\left(\frac{[F^-]}{[HF]}\right)
\]

\[
\text{pH} = 3.14 + \log(0.049 \div 0.051)
\]

\[
\text{pH} = 3.12
\]

5.

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>NaOH(aq) + HF(aq) ⇌ F(^-)(aq) + Na(^+)(aq) + H(_2)O(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial concentration</td>
<td>0.0010 M  0.050 M  0.050 M  0 M</td>
</tr>
<tr>
<td>C) Change in concentration</td>
<td>-0.0010  -0.0010  +0.0010  +0.0010</td>
</tr>
<tr>
<td>E) Equilibrium concentration</td>
<td>0  0.049  0.051  0.0010</td>
</tr>
</tbody>
</table>

\[
\text{pH} = \text{pK}_a + \log\left(\frac{[F^-]}{[HF]}\right)
\]

\[
\text{pH} = 3.14 + \log(0.051 \div 0.049)
\]

\[
\text{pH} = 3.16
\]
6. **Table I. Effect of a strong acid and a strong base on pH**

<table>
<thead>
<tr>
<th>Question</th>
<th>Solution</th>
<th>Amount</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>1.0 L</td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>1</td>
<td>HCl added</td>
<td>0.010 mole added</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>NaOH added</td>
<td>0.010 mole added</td>
<td>11.0</td>
</tr>
<tr>
<td>3</td>
<td>0.50 M in both HF and NaF</td>
<td>1.0 L</td>
<td>3.14</td>
</tr>
<tr>
<td>4</td>
<td>HCl added</td>
<td>0.010 mole added</td>
<td>3.12</td>
</tr>
<tr>
<td>5</td>
<td>NaOH added</td>
<td>0.010 mole added</td>
<td>3.16</td>
</tr>
</tbody>
</table>

The addition of a strong acid or strong base to the HF/NaF solution has little effect on the pH. It only changes by 0.02 units. The addition of the strong acid or base to water has a large effect on the pH; it changes by 4 units.

7. The strong acid was consumed by the fluoride ion that was present, and the strong base was consumed by the hydrofluoric acid that was present, so there was little change in the pH.

**Got It!**

1. The pKₐ of the weak acid.
2. I would pick a weak acid conjugate base system with a pKₐ close to 6.
3. \[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) \]
   \[ \text{pH} = 4.74 + \log \left( \frac{0.300}{0.150} \right) = 5.04 \]

**Application**

1. \[ \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{pK}_a \]
   \[ \left( \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right) = 10^{(7.4 - 7.2)} = 1.6 \]
2.  (a) pH = 4.85  
(b) Let HP = propanoic acid and P⁻ = propanoate  

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>HCl(aq) + P⁻(aq) ⇌ HP(aq) + Cl⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial amount</td>
<td>0.10 mmol 3.0 mmol 3.0 mmol 0</td>
</tr>
<tr>
<td>C) Change in amount</td>
<td>-0.10 -0.10 +0.10 +0.10</td>
</tr>
<tr>
<td>E) Equilibrium amount</td>
<td>0 2.9 3.1 0.10</td>
</tr>
</tbody>
</table>

\[
pH = 4.85 + \log \left( \frac{2.9 \text{ mmol}/11.0 \text{ mL}}{3.1 \text{ mmol}/11.0 \text{ mL}} \right) \\
pH = 4.82
\]

(c) 

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>HCl(aq) + P⁻(aq) ⇌ HP(aq) + Cl⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial amount</td>
<td>1.0 mmol 3.0 mmol 3.0 mmol 0</td>
</tr>
<tr>
<td>C) Change in amount</td>
<td>-1.0 -1.0 +1.0 +1.0</td>
</tr>
<tr>
<td>E) Equilibrium amount</td>
<td>0 2.0 4.0 1.0</td>
</tr>
</tbody>
</table>

\[
pH = 4.85 + \log \left( \frac{2.0 \text{ mmol}/20.0 \text{ mL}}{4.0 \text{ mmol}/20.0 \text{ mL}} \right) \\
pH = 4.55
\]

(d) As more acid or base is added, the change in the pH of the buffer becomes larger so the buffer is less effective.

3.  log([NH₃] / [NH₄⁺]) = pH - pKₐ = 9.00 - 9.25 = -0.25  
[NH₃] / [NH₄⁺] = 10⁻⁰.₂⁵ = 0.56  
(0.050 mol NH₃ ÷500 mL solution) = (0.56)(mol NH₄Cl÷500 mL solution)  
mol NH₄Cl = 0.050÷0.56 = 0.089  
mass NH₄Cl = (0.089 mol)(53.5 g/mol) = 4.8 g
4. (a) let HA = acetic acid and A⁻ = acetate

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>NaOH(aq) + HA(aq) ⇌ A⁻(aq) H₂O(l) + Na⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial amount</td>
<td>1.0 mmol 10.0 mmol 10.0 mmol 0</td>
</tr>
<tr>
<td>C) Change in amount</td>
<td>-1.0 -1.0 +1.0 +1.0</td>
</tr>
<tr>
<td>E) Equilibrium amount</td>
<td>0 9.0 11.0 1.0</td>
</tr>
</tbody>
</table>

Initial pH = pKₐ = 4.74

\[ pH = 4.74 + \log \left( \frac{11.0 \text{ mmol}}{101 \text{ mL}} \right) \]

\[ pH = 4.82 \]

The change is 0.08 units.

(b) Reaction equation

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>NaOH(aq) + HA(aq) ⇌ A⁻(aq) H₂O(l) + Na⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial amount</td>
<td>1.0 mmol 1.0 mmol 1.0 mmol 0</td>
</tr>
<tr>
<td>C) Change in amount</td>
<td>-1.0 -1.0 +1.0 +1.0</td>
</tr>
<tr>
<td>E) Equilibrium amount</td>
<td>0 0 2.0 1.0</td>
</tr>
</tbody>
</table>

The acetic acid has been consumed, and there is no excess NaOH, so the pH is determined by the acetate, with a concentration of 2.0 mmol÷101 mL = 0.020 M

(c) Reaction equation

<table>
<thead>
<tr>
<th>R) Reaction equation</th>
<th>A⁻(aq) + H₂O(l) ⇌ HA(aq) + OH⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Initial amount</td>
<td>0.020 M 0 0</td>
</tr>
<tr>
<td>C) Change in amount</td>
<td>- x x x</td>
</tr>
<tr>
<td>E) Equilibrium amount</td>
<td>0.020 - x x x</td>
</tr>
</tbody>
</table>

\[ 10^{-4.74} = \frac{x^2}{0.020 - x} \]

\[ x = 6.03 \times 10^{-4} \]

pOH = 3.22, pH = 10.78

The change is 6.04 units.

(c) 1.0 mmol of NaOH reacts with 0.10 mmol acetic acid, there is 0.9 mmol excess NaOH

[NaOH] = 0.9 mmol÷101 mL = 0.0089 M

pOH = 2.05, pH = 11.91

The change is 7.20 units.

(d) The pH changed little in part (a) because the amount of NaOH added was small compared to the amount of acetic acid present. In part (b) all of the NaOH reacted.
with all the acetic acid, the buffer was destroyed, and the pH changed a lot. In part (c) the excess NaOH determined the pH. The main conclusion is that buffers fix the pH in a small range of values as long as the amount of acid or base added is small compared to the components comprising the buffer.
## 16-2. Acid – Base Titrations:

*How much acetic acid is there in an exotic wine vinegar?*

### Exploration

1. **HA = acetic acid, A⁻ = acetate**
   
   Use the RICE table methodology
   
   **R:** \( HA + H_2O \rightleftharpoons H_3O^+ + A^- \)
   
   **I:** 0.100 M
   
<table>
<thead>
<tr>
<th>C</th>
<th>E</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
   
   \[ 10^{-4.74} = \frac{x^2}{0.100 - x} \]
   
   assume \( x \) in the denominator is negligible
   
   \[ x = \sqrt{(0.100)(10^{-4.74})} = 1.35 \times 10^{-3} \text{ M} \]
   
   **pH = 2.87**

2. **Use amounts in mmol rather than concentrations**
   
   **R:** \( HA + OH^- \rightleftharpoons H_2O + A^- \)
   
   **I:** 2.50 mmol 0.50 mmol 0
   
<table>
<thead>
<tr>
<th>C</th>
<th>E</th>
<th>+x</th>
</tr>
</thead>
<tbody>
<tr>
<td>-x</td>
<td>x</td>
<td>+x</td>
</tr>
</tbody>
</table>
   
   all of the hydroxide reacts, so \( x = 0 \)
   
   **pH = 0.50 mmol**

   \[ pH = pK_a + \log(\text{base}/\text{acid}) \]
   
   \[ pH = 4.74 + \log(0.50/2.0) \]
   
   **pH = 4.14**

   You can divide the moles by the volume of the resulting solution to obtain concentrations, but the volumes in the numerator and denominator cancel, so it is not necessary

3. **R:** \( HA + OH^- \rightleftharpoons H_2O + A^- \)
   
   **I:** 2.50 mmol 1.25 mmol 0
   
<table>
<thead>
<tr>
<th>C</th>
<th>E</th>
<th>+x</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.25</td>
<td>-1.25</td>
<td>+1.25</td>
</tr>
</tbody>
</table>
   
   **pH = 4.74 + log(1.25/1.25)**
   
   **pH = 4.74**

4. **R:** \( HA + OH^- \rightleftharpoons H_2O + A^- \)
   
   **I:** 2.50 mmol 2.25 mmol 0
   
<table>
<thead>
<tr>
<th>C</th>
<th>E</th>
<th>+x</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.25</td>
<td>-2.25</td>
<td>+2.25</td>
</tr>
</tbody>
</table>
   
   **pH = 4.74 + log(2.25/0.25)**
   
   **pH = 5.69**
5. \[ \text{R: } \text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^- \]
\[ I: 2.50 \text{ mmol} \quad 2.50 \text{ mmol} \quad 0 \]
\[ C: -2.50 \quad -2.50 \quad +2.50 \]
\[ E: 0 \quad 0 \quad 2.50 \]

\[ \text{R: } \text{Ac}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HAc}(aq) + \text{OH}^- (aq) \]
\[ I: 2.50 \text{ mmol} \quad 0 \quad 0 \]
\[ C: -x \quad x \quad x \]
\[ E: 2.50-x \quad x \quad x \]

\[ 10^{-9.26} = x^2/(2.50-x) \]
Assume x in the denominator is negligible.
\[ x = \{(2.50)(10^{-9.26})\}^{1/2} \]
\[ x = 3.71 \times 10^{-5} \text{ mmol} \]

\[ [\text{OH}^-] = 3.71 \times 10^{-5} \text{ mmol}/75 \text{ mL solution} = 4.95 \times 10^{-7} \text{ M} \]

\[ \text{pOH} = 6.31, \quad \text{pH} = 7.69 \]

6. 5 mL excess NaOH x 0.05 mol/L = 0.25 mmol NaOH

\[ [\text{OH}^-] = 0.25 \text{ mmol}/80.0 \text{ mL} = 3.13 \times 10^{-3} \text{ M} \]

\[ \text{pOH} = 2.51, \quad \text{pH} = 11.49 \]

7. 25 mL excess NaOH x 0.05 mol/L = 1.25 mmol NaOH

\[ [\text{OH}^-] = 1.25 \text{ mmol}/100.0 \text{ mL} = 1.25 \times 10^{-2} \text{ M} \]

\[ \text{pOH} = 1.90, \quad \text{pH} = 12.10 \]

8. Table I. Calculated data for the titration of 25.0 mL of 0.100 M acetic acid with 0.050 M sodium hydroxide.

<table>
<thead>
<tr>
<th>Question</th>
<th>Situation</th>
<th>Major Species</th>
<th>[\text{H}_3\text{O}^+]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Before adding NaOH solution</td>
<td>acetic acid</td>
<td>(1.35 \times 10^{-3} \text{ M})</td>
<td>2.87</td>
</tr>
<tr>
<td>2</td>
<td>10.0 mL NaOH</td>
<td>acetic acid &amp; acetate</td>
<td>(7.24 \times 10^{-5} \text{ M})</td>
<td>4.14</td>
</tr>
<tr>
<td>3</td>
<td>25.0 mL NaOH</td>
<td>acetic acid &amp; acetate</td>
<td>(1.82 \times 10^{-5} \text{ M})</td>
<td>4.74</td>
</tr>
<tr>
<td>4</td>
<td>45.0 mL NaOH</td>
<td>acetic acid &amp; acetate</td>
<td>(2.04 \times 10^{-6} \text{ M})</td>
<td>5.69</td>
</tr>
<tr>
<td>5</td>
<td>50.0 mL NaOH</td>
<td>acetate</td>
<td>(2.04 \times 10^{-8} \text{ M})</td>
<td>7.69</td>
</tr>
<tr>
<td>6</td>
<td>55.0 mL NaOH</td>
<td>hydroxide</td>
<td>(3.24 \times 10^{-12} \text{ M})</td>
<td>11.49</td>
</tr>
<tr>
<td>7</td>
<td>75.0 mL NaOH</td>
<td>hydroxide</td>
<td>(7.94 \times 10^{-13} \text{ M})</td>
<td>12.10</td>
</tr>
</tbody>
</table>
9. **Titration of Acetic Acid with Sodium Hydroxide**

Got It!

1. Before any base is added, the stronger acid will ionize to a greater extent and produce the lower pH. Therefore, Acid 1 is stronger than Acid 2. Also, halfway to the equivalence point, the pH = pK_a, Acid 1 has the smaller pK_a, so it is the stronger acid.

2. Acid 1, pH = 8
   Acid 2, pH = 9

3. At the equivalence point the pH is determined by ionization of the conjugate base of the acid, and the pK_b values are different for these two bases.

4. The acids have different pK_a values and ionize to different extents producing different concentrations of hydronium ion.

5. Past the equivalence point the pH is determined by the excess sodium hydroxide, which is the same in both cases.

6. Halfway to the equivalence point, which in this example is at 25.0 mL. At this point the concentrations of the acid and its conjugate base are the same. So in the Henderson – Hasselbalch equation, pH = pK_a.

7. A buffer is produced from the beginning until the equivalence point is reached. In this region both the acid and conjugate base are present to a significant extent.

8. The buffering effect disappears and the pH is determined by the excess sodium hydroxide. Also it is a property of the log function; as x approaches 1, log(x) changes abruptly.
Application
1. (a) moles sodium hydroxide = moles acetic acid
   \( (84.0 \text{ mL NaOH})(0.500 \text{ M}) = (50.0 \text{ mL HA})(\text{molarity of acetic acid}) \)
   molarity of acetic acid = 0.840 M

   (b) 0.840 mol HA/L solution
   Mass HA in 1 L = 50.4 g
   Mass of 1 L = 1010 g
   Mass percent HA = \( \frac{50.4 \text{ g}}{1010 \text{ g}} = 4.99 \% \)

   (c) The measurement was only good to 3 sig figs, the uncertainty in the calculated
   result is roughly 0.01 so 4.99% is consistent with the claim of 5% (one sig fig?)
17-1. Entropy:

*Why do some things occur spontaneously while others do not?*

**What do you think?**

1. No, an example of an exothermic process that is not spontaneous is given.
2. No, an example of an endothermic process that is not spontaneous is given.
3. A student might conclude that salt dissolving in water and ice melting are examples of endothermic processes that are spontaneous. In each case, a solid becomes a liquid, either a pure liquid or as a solution. So maybe the greater motion that molecules have in liquids has something to do with spontaneity; the molecules become more free to move.
4. A student might then say that some processes occur spontaneously because they increase the freedom of molecules.

Soliciting and discussing student responses might lead to something like the above that then can be connected to an increase in the number of states accessible to the molecules.

**Exploration – 1**

1.1. 10

1.2. One star could be put in any one of 10 circles, the second star then could be put in any one of the other nine for a total number of $10 \times 9 = 90$ possibilities, but since the stars are identical, each possibility would be duplicated so the answer is $90/2 = 45$.

1.3. Pr[energy dispersed] = $45/55 = 82\%$

1.4. I would most likely find it in an energy dispersed state because the probability is higher.

**Exploration – 2**

2.1 No, examples of exothermic processes where the entropy of the system decreases are given in Table II. See the drying agent.

2.2. Yes, an exothermic process always causes the entropy of the surroundings to increase.

2.3. No, the entropy of the system does not always increase for a spontaneous process. See drying agent.

2.4. No, the entropy of the surroundings does not always increase for a spontaneous process. See salt dissolving.
2.5.

<table>
<thead>
<tr>
<th>Process at 298 K</th>
<th>$\Delta S_{\text{total}}$ (J/K)</th>
<th>$\Delta H$</th>
<th>Spontaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron rusting</td>
<td>5619</td>
<td>exo</td>
<td>yes</td>
</tr>
<tr>
<td>$4\text{Fe(s)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose metabolism</td>
<td>9631</td>
<td>exo</td>
<td>yes</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O(\text{l})}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drying agent working</td>
<td>62</td>
<td>exo</td>
<td>yes</td>
</tr>
<tr>
<td>$\text{CaSO}_4(\text{s}) + 2\text{H}_2\text{O(\text{g})} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O(\text{s})}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water decomposing</td>
<td>$-1591$</td>
<td>endo</td>
<td>no</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O(\text{l})} \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt dissolving in water</td>
<td>30</td>
<td>endo</td>
<td>yes</td>
</tr>
<tr>
<td>$\text{NaCl(\text{s})} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ice melting</td>
<td>1.84</td>
<td>endo</td>
<td>yes, above 298 K</td>
</tr>
<tr>
<td>$\text{H}_2\text{O(\text{s})} \rightarrow \text{H}_2\text{O(\text{l})}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water freezing</td>
<td>$-1.84$</td>
<td>exo</td>
<td>no, not above 298 K</td>
</tr>
<tr>
<td>$\text{H}_2\text{O(\text{l})} \rightarrow \text{H}_2\text{O(\text{s})}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The total entropy always increases for a spontaneous process.

2.6. Water decomposing is not spontaneous because the large decrease in entropy of the surroundings is not offset by the small increase in the entropy of the system. In the case of salt dissolving, the decrease in entropy of the surroundings is small and is offset by the increase in entropy of the system.

2.7. The entropy is a measure the number of accessible states, so if the total entropy increases, the total number of accessible states increases, which makes the process spontaneous.
Got It!

1. Above 298 K the total entropy increases for ice melting but decreases for water freezing.

2. (a) For 1 mol ice melting
    \[ \Delta S_{\text{system}} = 22.0 \text{ J/K} \]
    \[ \Delta S_{\text{surroundings}} = -6009 \text{ J/T} \]
    \[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 \]
    \[ 22.0 \text{ J/K} - 6009 \text{ J/T} = 0 \]
    \[ T = \frac{6009 \text{ J}}{22.0 \text{ J/K}} = 273 \text{ K} \]

    (b) For 1 mol water freezing
    \[ \Delta S_{\text{system}} = -22.0 \text{ J/K} \]
    \[ \Delta S_{\text{surroundings}} = 6009 \text{ J/T} \]
    \[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 \]
    \[ -22.0 \text{ J/K} + 6009 \text{ J/T} = 0 \]
    \[ T = \frac{6009 \text{ J}}{22.0 \text{ J/K}} = 273 \text{ K} \]

3. At 273 K, liquid water and ice are in equilibrium, and no spontaneous change will occur. Above 273 K, ice will melt spontaneously because the decrease in entropy of the surroundings is reduced. Below 273 K, water will freeze spontaneously because the increase in the entropy of the surroundings is magnified.

Application

1. (a) Energy flowed from the water to the freezer
    (b) \[ \Delta S_{\text{system}} = - (6010 \text{ J/mol}) \div 273 \text{ K} = -22.0 \text{ J/K mol} \]
    (c) \[ \Delta S_{\text{surroundings}} = (+6010 \text{ J/mol}) \div 258 \text{ K} = 23.3 \text{ J/K mol} \]
    (d) The entropy of the system decreased but the entropy of the surroundings increased more, which means that the total number of accessible states of the system plus surroundings increased, causing the process to be spontaneous.
17-2. Free Energy:
How much work can be obtained from any process?

What do you think?
You might get multiple answers to this question, or you might get a dumbfounded look, in which case just ask about water freezing and ice melting.

Exploration
1. ΔH, the enthalpy change
2. A positive sign for ΔH_{reaction}, means that the energy of the reacting system increases. This energy came from the surroundings, therefore the energy of the surroundings decreased by the amount −ΔH_{reaction}.
3. The reaction of hydrogen and oxygen to produce water is spontaneous because it has a negative ΔG, which corresponds to an increase in the entropy of the universe.
4. The one that can produce the most work will have the most negative ΔG, which will occur for case (c) when ΔH < 0 and ΔS > 0.
5. If ΔG can be 0 at some temperature, because ΔH and ΔS have the same signs, then the reaction will be spontaneous at one temperature but not at another. It will change in spontaneity at the temperature for which ΔG = 0, which is when T = ΔH/ΔS.

Got It!
Table I. Effects of ΔH, ΔS, and temperature on reaction spontaneity.

<table>
<thead>
<tr>
<th>ΔH</th>
<th>ΔS</th>
<th>Sign of ΔG</th>
<th>Spontaneous always, never, at low T, or at high T?</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>depends on T</td>
<td>spontaneous at high T</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>positive</td>
<td>never spontaneous</td>
</tr>
<tr>
<td>&lt; 0</td>
<td>&gt; 0</td>
<td>negative</td>
<td>always spontaneous</td>
</tr>
<tr>
<td>&lt; 0</td>
<td>&lt; 0</td>
<td>depends on T</td>
<td>spontaneous at low T</td>
</tr>
</tbody>
</table>

Application
1. (a) Need to find values for the enthalpy of solvation and the entropy of solvation of ammonium nitrate. Find ΔH = 25.7 kJ/mol, ΔS = 108.7 J/K mol from standard enthalpies of formation and standard entropies.
   At room temperature
   ΔG = 25.7 kJ/mol − (298 K)(108.7 J/K mol)(1 kJ/1000 J)
   ΔG = -6.7 kJ/mol; a negative value indicates that the reaction is spontaneous.
   (b) Since the reaction is endothermic, ΔH is positive, the reaction would be useful in a cold pack.

2. For the decomposition of silver oxide
   ΔH = 2(31.1 kJ/mol) = 62.2 kJ/mol
   ΔS = 4(43) + 205 – 2(121) = 135 J/K mol
   At low temperature the reaction will not be spontaneous, it will switch to spontaneous when T = ΔH/ΔS = 62,200 J/mol÷135 J/K mol = 461 K
18-1. Electrochemical Cells: Where does the energy come from to power your cell phone?

What do you think?

The purpose of this question is to get students thinking about batteries. Just listen, and do not be judgmental. You can revisit the question at the end of the activity. The answer is (C) as the activity should make clear.

Exploration

1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Anode Compartment</th>
<th>Cathode Compartment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode metal (Cu or Zn)</td>
<td>Zn</td>
<td>Cu</td>
</tr>
<tr>
<td>Electron potential (+ or -)</td>
<td>Negative</td>
<td>Positive</td>
</tr>
<tr>
<td>Type of half reaction</td>
<td>Oxidation</td>
<td>Reduction</td>
</tr>
<tr>
<td>Write the half reaction</td>
<td>Zn(s) → Zn^{2+}(aq) + 2e^-</td>
<td>Cu^{2+}(aq) + 2e^- → Cu(s)</td>
</tr>
</tbody>
</table>

2. Zn(s) → Zn^{2+}(aq) + 2e^-  
3. Cu^{2+}(aq) + 2e^- → Cu(s)  
4. Electrons flow from the anode to the cathode.  
5. The concentration of cations in the anode compartment is increasing.  
6. To maintain electrical neutrality, cations flow from the anode to the cathode compartment, and anions flow from the cathode to the anode compartment.  
7. In an oxidation reaction the positive charge on a species increases; in a reduction reaction the positive charge is reduced.  
8. The oxidation and reduction potentials are added together to obtain the cell potential.  
9. E^{o}_{\text{cell}} = E^{o}_{\text{reduction(cathode)}} – E^{o}_{\text{reduction(anode)}}

Got It!

1. Reduction reaction: Ag_2O(s) + H_2O(l) + 2e^- → 2Ag(s) + 2OH^-(aq)  
The other reverses and runs as an oxidation.  
2. E^{o}_{\text{cell}} = 0.34 + 1.22 V = 1.56 V  
3. anode reaction: oxidation  
   Zn(s) + 2OH^-(aq) → ZnO(s) + H_2O(l) + 2e^-  
   cathode reaction: reduction  
   Ag_2O(s) + H_2O(l) + 2e^- → 2Ag(s) + 2OH^-(aq)  
4. Zn(s) + Ag_2O(s) → ZnO(s) + 2Ag(s)  
5. Zn(s) is oxidized, Ag_2O(s), or specifically Ag, is reduced  
6. Zn(s) is the reducing agent, Ag_2O(s) is the oxidizing agent  
7. Hydroxide ions are not produced in the overall reaction; they are produced in one half-reaction and consumed in the other.
**18-2. Electrolytic Cells: How can silver be deposited on nickel to make a beautiful friendship ring?**

**What do you think?**
An external battery is needed to drive the chemical reactions. Electrons flow in the opposite direction, from the anode (+) to the cathode (-).

**Exploration – 1**
1.1. \(2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-\)
1.2. \(\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})\)
1.3. \(2\text{Na}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Na}(\text{s}) + \text{Cl}_2(\text{g})\)
1.4. \(E^\circ_{\text{reduction}} = 1.36\ \text{V for Cl}_2\text{ and -2.71 V for Na}^+\)
1.5. The sodium reaction runs as a reduction, the chlorine reaction runs as an oxidation, so \(\text{-2.71} + (-\text{1.36}) = -\text{4.07 V.}\) The negative sign means the reaction is not spontaneous and a voltage of at least \(\text{4.07 V}\) needs to be applied.
1.6. The magnitudes are the same because the reactions are the same, but the signs are opposite because the reactions run in opposite directions in the two types of cells.

**Exploration – 2**
2.1. \(2\text{Na}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Na}(\text{s}) + \text{Cl}_2(\text{g})\)
To produce 2 moles of sodium and 1 mole of chlorine gas, 2 moles of electrons must be transferred from the anode to the cathode. One mole of sodium and half a mole of chlorine gas are produced per mole of electrons transferred.
2.2. \((10\ \text{A})(1\ \text{C/s÷A})(10\ \text{hrs})(3600\ \text{s/hr})(1\ \text{mol e÷96,485 C}) = 3.73\ \text{mol e}^-\)
2.3. \((1\ \text{mol Na÷1 mol e}^-)(3.73\ \text{mol e}^-) = 3.73\ \text{mol Na}\)
\((0.5\ \text{mol Cl}_2÷1\ \text{mol e}^-)(3.73\ \text{mol e}^-) = 1.87\ \text{mol Cl}_2\)

**Got It!**
1. \(2\ \text{H}_2\text{O(l)} \rightarrow 2\ \text{H}_2(\text{g}) + \text{O}_2(\text{g})\)
2. H in water is reduced, O in water is oxidized.
3. The oxidation potential for the oxidation of O in water is \(\text{-1.23 V.}\) The reduction potential for the reduction of H in water is \(\text{0.00 V.}\) At least \(\text{1.23 V}\) would have to be applied to electrolyze water.
4. \(n = (1\ \text{atm})(22.4\ \text{L})÷[(0.08206\ \text{L atm/mol K})(273\ \text{K})] = 1.00\ \text{mol of H}_2.\)
A complete reaction requires 2 mol e\(^{-}\).
\((1.00\ \text{A})(1\ \text{C s}^{-1}\ \text{A}^{-1})\\text{(t)(1 mol e}^{-}\text{÷96,485 C}) = 2.00\ \text{mol e}^{-}\)
\(t = (2.00\ \text{mol e}^{-})÷(1.036 \times 10^{-5}\ \text{mole e}^{-}\text{s}^{-1}) = 193,000\ \text{s or 53.6 hrs}\)

**Application**
1. From Got It! #4 we learned that a current of 1.00 A will furnish 1 mol e\(^{-}\) in 26.8 hrs. To deposit (1.00 g Ag)(1 mol/108 g) = 0.00926 mol requires 0.00926 mol e\(^{-}\).
\[\frac{x}{0.00926\ \text{mol}} = \frac{26.8\ \text{hr}}{1.00\ \text{mol}}\]
\[x = 0.248\ \text{hr}\]
19-1. Radioactivity: Are there different kinds of radioactivity?

What do you think?

Responses will vary. Some examples of uses are to kill cancerous cells, in smoke detectors, kill bacteria to store food at room temperature, monitor chemical reactions, image biological systems, sterilize medical instruments, and produce energy. Dangers are killing human cells and causing DNA to mutate.

Exploration 1

1. Superscript give the mass number, subscript gives the atomic number.

2. \(^4_2\alpha\) or \(^4_2\text{He}^{2+}\)

3. 

Table I. Nuclear Decay Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Symbol</th>
<th>(\Delta Z)</th>
<th>(\Delta A)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha particle emission</td>
<td>(\alpha)</td>
<td>-2</td>
<td>-4</td>
<td>(^{234}U \rightarrow ^{230}\text{Th} + \alpha)</td>
</tr>
<tr>
<td>Beta particle emission</td>
<td>(\beta)</td>
<td>+1</td>
<td>0</td>
<td>(^{239}U \rightarrow ^{239}\text{Np} + \beta)</td>
</tr>
<tr>
<td>Gamma ray emission</td>
<td>(\gamma)</td>
<td>0</td>
<td>0</td>
<td>(^{57}\text{Fe}^* \rightarrow ^{57}\text{Fe} + \gamma) (* = excited state)</td>
</tr>
<tr>
<td>Positron emission</td>
<td>(0^-_1e)</td>
<td>-1</td>
<td>0</td>
<td>(^{207}\text{Po} \rightarrow ^{207}\text{Bi} + 0^-_1e)</td>
</tr>
<tr>
<td>Electron capture</td>
<td>(0^-_1e)</td>
<td>-1</td>
<td>0</td>
<td>(^7\text{Be} + 0^-_1e \rightarrow ^7\text{Li})</td>
</tr>
</tbody>
</table>

4. They must sum to the zero.

5. They must sum to zero.

6. Proton to neutron requires that a positive charge leave the nucleus in the form of a positron. Neutron to proton requires that a negative charge leave the nucleus in the form of an electron (\(\beta\) particle).

Got It!

1. 
\(^{18}_9F \rightarrow ^{18}_8\text{O} + 0^-_1e\)
\(^{26}_{13}\text{Al} + 0^-_1e \rightarrow ^{26}_{12}\text{Mg}\)
\(^{35}_{16}\text{S} \rightarrow ^{35}_{17}\text{Cl} + 0^-_1e\) (\(\beta\) particle)
\(^{218}_{84}\text{Po} \rightarrow ^{214}_{82}\text{Pb} + \alpha\)
\(^{119}_{50}\text{Sn}^* \rightarrow ^{119}_{50}\text{Sn} + \gamma\)
19-2. Rates of Nuclear Decay:
How long does a radioactive substance last?

What do you remember?

Table I. Rate Laws for Reactions

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Rate Law</th>
<th>Integrated Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \frac{d[N]}{dt} = -k )</td>
<td>( [N(t)] = -kt + [N(t=0)] )</td>
</tr>
<tr>
<td>1</td>
<td>( \frac{d[N]}{dt} = -k[N] )</td>
<td>( \ln[N(t)] = -kt + \ln[N(t=0)] )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{d[N]}{dt} = -k[N]^2 )</td>
<td>( \frac{1}{[N(t)']} = kt + \frac{1}{[N(t=0)]} )</td>
</tr>
</tbody>
</table>

Exploration

1. \( _{53}^{131}I \rightarrow _{54}^{131}Xe + _{-1}^0e \)

2. The table gives us the decay rate at different times. If the reaction was zero order, the decay rate would be constant. The numbers change; the decay rate is not constant, therefore the reaction is not zero order.

If the reaction is first order, then the decay rate is proportional to the number of radioactive atoms. Plotting the logarithm of the radioactivity vs. time should produce a straight line if the reaction is first order. The graph is shown below; the reaction is first order.

![Decay of Iodine-131](graph.png)
3. (a) The rate constant can be evaluated from the slope as can be seen from the integrated rate law for a first order reaction.
\[-k = \text{slope} = -0.0036, \text{so } k = 3.6 \times 10^{-3} \text{ /hr}\]

(b) The half-life is when half the atoms have decayed, which means the decay rate will be half the initial value. From the data in the table we can estimate this as 400/2 = 200, which occurs at around 190 hours.
\[t_{1/2} = \ln(2)/k = 193 \text{ h}, \text{ which can be derived from the integrated rate law.}\]

4. Explanation included in 3.

5. The rate law is valid whether concentration units or the total number of atoms is used because concentration is just the number of atoms in some volume.

\textbf{Got it!}

1. Rate = kN = 400 \times 10^6 /s, k = 3.6 \times 10^{-3} /hr from #3 above
\[N = (4.00 \times 10^8 \text{ s}^{-1}) \cdot (3.6 \times 10^{-3} /hr)(1 \text{ hr}/(3.6 \times 10^3 \text{ s}))\]
\[N = 4.00 \times 10^{14}\]
\[(4.00 \times 10^{14})(1 \text{ mol}/6.02 \times 10^{23})(127 \text{ g/mol}) = 8.44 \times 10^{-8} \text{ g}\]

2. \[\ln(N_0/N_t) = kt\]
\[t = \ln(100) / 3.6 \times 10^{-3} \text{ hr}^{-1} = 1280 \text{ hr}\]
\[1280 \text{ hr}(1 \text{ da}/24 \text{ hr}) = 53 \text{ da}\]

3. \[t = \ln(200) / 3.6 \times 10^{-3} \text{ hr}^{-1} = 1470 \text{ hr}\]
\[1280 \text{ hr}(1 \text{ da}/24 \text{ hr}) = 61 \text{ da}\]
Note: half life = 8 da, so doubling the dose requires waiting one more half life

4. 1 mCi = 3.7 \times 10^{10} \text{ decays /s}
\[\ln\{(30 \text{ mCi} / 1 \text{ mCi}) = kt\]
\[t = \ln(30)/3.6 \times 10^{-3} /\text{hr} = 945 \text{ hr} = 39 \text{ da}\]
20-1. Chemistry of the Main Group Elements: Why are some elements more special than others?

What do you know already?
Answers will vary, here are some possibilities.
Oxygen is used in metabolic processes in living organisms and supports the combustion of fuels. It also combines with hydrogen to make water.
Lithium is used in batteries and in medicines.
Sodium combines with chlorine to make sodium chloride, which is table salt. Sodium combines with carbonate and hydrogen carbonate to make baking soda and baking power.
Aluminum is used to make cans for beverages and in building materials.
Nitrogen is used to make explosives and fertilizers.

Exploration
1. The main group elements are in Groups IA through VIIIA so there are 44 elements, neglecting those that have not yet been confirmed with \( Z > 112 \).
2. O, Si, Al, Fe, Ca
3. Electrolysis: sodium and aluminum
   Oxidation/reduction reactions: phosphorous from calcium phosphate, iron from iron oxides
   Decomposition: heating silver oxide
4. Cs is used in photodetectors.
   Sr is used to provide color in fireworks.
   Ga is used in semiconductors.
   Sn is used to provide a noncorrosive coating.
   Pb is used in solder.
   Sb is used in semiconductors.
   S is used to make sulfuric acid, which has many industrial applications.
   Iodine is essential for the synthesis of thyroid hormones.
   He is used in balloons and dirigibles.
5. Carbon, nitrogen, oxygen, and hydrogen are essential for amino acids that are the building blocks of proteins. These elements also are essential for carbohydrates and nucleic acids.
   Phosphorous also is an essential component in nucleic acids.
6. Carbon and hydrogen are the fundamental components of organic molecules that form all sorts of polymers.
   Silicon, germanium, phosphorous, and antimony are used in all sorts of semiconductors and photovoltaic devices.
   Lithium is the material used in high tech batteries.
   Iron, titanium, and aluminum are important structural building materials.
**20-2. Electronic Structure and Properties:**

*How are electronic structure and atomic properties related?*

**What do you remember?**

The three key ideas are electron-nucleus attraction, electron-electron repulsion, and the shell structure of the atom.

In going across a Period, the nuclear charge increases and the number of electrons increases, but the electrons go into the same shell. As a result, electron-nucleus attraction increases more than electron-electron repulsion and the atomic radius decreases.

In going down a group, electrons go into a new shell with a larger radius, consequently electron-electron repulsion increases more than electron-nucleus attraction, combined with the larger radius shell, the atomic radius increases.

**Exploration**

1. The metals are on the left in each Period 2 - 7 through Al, Ga, Sn, Po, and Ra, respectively. The nonmetals are on the right beginning with C, P, Se, I, and Rn, respectively, and including H and He.

2. Nonmetals have the higher ionization energies because the electrons are entering the same shell across a Period, and the effect of electron-nucleus attraction dominates.

3. Nonmetals generally have the higher electron affinities because the electrons are entering the same shell across a Period, and the effect of electron-nucleus attraction dominates, although there are some exceptions.

4. Nonmetals generally have the higher electronegativities because the electronegativity is an average of the ionization energy and electron affinity, see responses to 2 and 3.

5. Cesium is used in photodetectors because it has a low ionization energy and therefore can produce an electrical current through the photoelectric effect in response to very low energy, long wavelength light.

Limestone primarily is calcium carbonate, CaCO₃, which forms because Ca has two valence electrons that can be readily ionized (low ionization energy) to form the ionic compound.

Boron is a semimetal or nonmetal and forms covalent bonds because its electronegativity is relatively high (2.0).

Carbon chemistry is characterized by 4 bonds to carbon because the valence electron configuration of carbon is 2s²2p² and the orbitals are readily hybridized to describe different geometries and provide single, double, and triple bonds.

Nitrogen is a common element in explosives because a product is N₂ which has a very stable triple bond, resulting from the 2s²2p³ atomic configuration, thus much energy is released when it forms. It also is a gas which expands tremendously in the explosion.
Almost all metals are found as their oxides because oxygen has a high abundance on Earth and a high electronegativity (3.5) to readily form ionic compounds.

F is highly reactive because of its large electronegativity, the largest of all elements (4.0).

He is not reactive at all because it has a filled shell, 1s$^2$, which is a very stable electron configuration.
What do you know already?
Responses will vary. Here are some possibilities.
Titanium is used as a structural building material, in jewelry, and titanium(IV) oxide is a white paint pigment.
Chromium is coated on surfaces to make them shiny and mixed with iron to make steel.
Tungsten is used as a filament in light bulbs, and tungsten carbide is very strong and used to make cutting tools.
Iron is used to make magnets, and as a structural building material.
Nickel is used is used in batteries and with iron to make stainless steel.
Platinum is used in jewelry and as a catalyst in automobile catalytic converters.
Zinc is used in batteries and to coat steel to prevent corrosion.
Cadmium is used in batteries and to make colored pigments.
Mercury is used in thermometers and barometers, to make dental amalgams, and to produce ultraviolet light for sterilizing medical instruments.
Copper is used in electrical wiring and to make ornamental objects.
Silver is used to make batteries, jewelry, and silverware table settings.
Gold is used to provide backing for currency and make jewelry and coins.

Exploration
1. The charge on all counter ions has to equal or balance the charge on the metal complex ion.
2. The charge on the complex ion equals the total charge on the ligands plus the oxidation number or charge of the metal.
3. In Table I, 4 ligands are arranged in a tetrahedral geometry, 6 ligands are arranged in an octahedral geometry.

Table I. Examples of Coordination Compounds

<table>
<thead>
<tr>
<th>Coordination Compound</th>
<th>Complex Ion</th>
<th>Ligand</th>
<th>Ligand Geometry</th>
<th>Counter Ion</th>
<th>CN</th>
<th>Charge L+M</th>
<th>Ox</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(H₂O)₆]Cl₂</td>
<td>[Ni(H₂O)₆]²⁺</td>
<td>H₂O</td>
<td>Octahedral</td>
<td>Cl⁻</td>
<td>6</td>
<td>+2</td>
<td>+2</td>
</tr>
<tr>
<td>K₃[Fe(CN)₆]</td>
<td>[Fe(CN)₆]³⁻</td>
<td>CN⁻</td>
<td>Octahedral</td>
<td>K⁺</td>
<td>6</td>
<td>−3</td>
<td>+3</td>
</tr>
<tr>
<td>[Co(NH₃)₃(OH)₃]</td>
<td>None</td>
<td>NH₃,</td>
<td>Octahedral</td>
<td>None</td>
<td>6</td>
<td>0</td>
<td>+3</td>
</tr>
<tr>
<td>Na₂[Hgl₄]</td>
<td>[Hgl₄]²⁻</td>
<td>I⁻</td>
<td>Tetrahedral</td>
<td>Na⁺</td>
<td>4</td>
<td>−2</td>
<td>+2</td>
</tr>
</tbody>
</table>

5. Metal plus ligand(s) are always present.
6. A counter ion is present is some compounds.
7. The square bracket identifies the transition metal complex, which may be an ion or may be neutral.

8.

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Counter Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(H₂O)₆]²⁺ and 2 Cl⁻</td>
<td>not ionic, doesn’t dissociate</td>
</tr>
<tr>
<td>[Fe(CN)₆]³⁻ and 3 K⁺</td>
<td></td>
</tr>
<tr>
<td>[HgI₄]²⁻ and 2 Na⁺</td>
<td></td>
</tr>
</tbody>
</table>

**Got It!**

1. A coordinate covalent bond is formed when one species donates a pair of electrons to form a covalent bond with another species.
   A coordination compound results when ions or molecules form coordinate covalent bonds with a transition metal.
   A complex ion consists of the transition metal and the ions or molecules bonded to it.
   A ligand is an ion or molecule bonded to the transition metal.
   The coordination number is the number of ions or molecules (ligands) bonded to the transition metal.
   Counter ions are the ions associated with the complex ion to produce a compound that is electrically neutral.

**Research**

Responses will vary. Here are some possibilities.

1. Iron is a component in hemoglobin that carries oxygen in the bloodstream.
   There are several transition metals found in enzymes that catalyze a variety of chemical reactions, e.g. zinc, copper, vanadium, molybdenum, tungsten, cobalt, and nickel.
   Platinum is found in cisplatin, a powerful anticancer agent. Titanium, vanadium and niobium compounds also have antitumor activity.
   Vanadium and chromium compounds are being tested for treating diabetes.
   Gold and osmium compounds are used to reduce inflammation in joints.

2. Tungsten and molybdenum oxide films are being used to produce smart windows, windows that darken when sun shines on them.
   Ruthenium compounds are being used in luminescent sensor probes to measure concentrations of small ions/molecules, e.g. of hydronium ion, oxygen, and carbon dioxide.
   Nickel is used as a catalyst for hydrogenation of vegetable oils to make margarine.
   Iron is used as a catalyst in the Haber-Bosch process to make ammonia.
Aluminum, nickel, and cobalt are alloyed with iron and copper to make very high
strength permanent magnets called alnico magnets.
21-2. Magnetism and Color in Coordination Compounds:
Where does all that attraction and beauty come from?

What do you remember?
All of the transition metals except Zn have unpaired electrons.

Exploration 1
1.1. xy, xz, and yz lie between the axes; x²-y² and z² lie along the axes.
1.2. x²-y² and z²
1.3. xy, xz, and yz
1.4. Stronger interactions, Set 1: x²-y² and z²
    Weaker interactions, Set 2: xy, xz, and yz
1.5.

\[
\begin{align*}
&x^2 - y^2 & z^2 \\
xy & xz & yz
\end{align*}
\]

Exploration 2
2.1. cyanide
2.2. The electrons pair up in the strong field complex. In the weak field complex, the electrons only pair up after all five orbitals have been occupied by one electron.
2.3. In the strong field complex, the electrons pair up because the electron-electron repulsion energy is less than the ligand field splitting. In the weak field complex, the ligand field splitting is less than the electron-electron repulsion energy so they don’t pair until all the orbitals are occupied. In the free ion, there is no ligand field splitting, so of course the energy is lower if the electrons stay apart in different orbitals.
2.4. High and low spin states are related to the number of unpaired electrons. This number is largest in the weak field complex, therefore it is appropriate to call the weak field complex high spin.
2.5. The weak field complex is paramagnetic because there are unpaired electrons acting like little magnets with their north and south poles (magnetic moments) lined up. The strong field complex is diamagnetic because all the electrons are paired with their north and south poles pointing in opposite directions, so the magnetic effect of one is cancelled by the opposing magnetic effect of its partner in the orbital.
Exploration 3
3.1. When you look through the solution, you see the wavelengths that are transmitted, not those that are absorbed.

3.2. Longer wavelength has lower energy, so in order of increasing energy of photons absorbed:

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} < [\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+} < [\text{Co(NH}_3\text{)}_5\text{NCS}]^{2+} < [\text{Co(NH}_3\text{)}_6]\]

3.3. \(\Delta \omega = \frac{hc}{\lambda}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Observed</th>
<th>Absorbed</th>
<th>Wavelength (nm)</th>
<th>(\Delta \omega) (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3\text{)}_6])^{3+}</td>
<td>Yellow</td>
<td>Bluish violet</td>
<td>430</td>
<td>4.63x10^{-19}</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{NCS}]^{2+})</td>
<td>Orange</td>
<td>Bluish green</td>
<td>470</td>
<td>4.23x10^{-19}</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+})</td>
<td>Red</td>
<td>Green</td>
<td>500</td>
<td>3.98x10^{-19}</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+})</td>
<td>Reddish purple</td>
<td>Yellowish green</td>
<td>522</td>
<td>3.81x10^{-19}</td>
</tr>
</tbody>
</table>

3.4. \([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} < [\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+} < [\text{Co(NH}_3\text{)}_5\text{NCS}]^{2+} < [\text{Co(NH}_3\text{)}_6]\)

The diagram for each should like the one drawn for #1.5 with increasing splitting of the two sets as one goes across the row from the chloride ligand to the ammonia ligand.

Got It!
1. \([\text{Fe(NCS)}_6]^{3-}\)  \([\text{Fe(NO}_2\text{)}_6]^{3-}\)
2. high spin \([\text{Fe(NCS)}_6]^{3-}\)  low spin \([\text{Fe(NO}_2\text{)}_6]^{3-}\)
3. High spin \([\text{Fe(NCS)}_6]^{3-}\) will be more paramagnetic because it has 5 unpaired electrons, the other complex ion only has 1 unpaired electron. There are five d electrons in Fe^{3+}.
4. 

\[\begin{array}{cccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\
\end{array}\]

\[\text{[Fe(NCS)}_6]^{3-}\]  \[\text{[Fe(NO}_2\text{)}_6]^{3-}\]

5. Longer wavelength means smaller photon energy, which means the smaller ligand field splitting, therefore \([\text{Fe(NCS)}_6]^{3-}\) will absorb the longer wavelength light.