



February 2010 Teacher's Guide

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About the Guide

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Student Questions

The Many Colors of Blood

1. What is the range of colors for blood in animals?
2. What is a respiratory pigment?
3. What metal is present in the respiratory pigment of humans and what metal is present in the respiratory pigment of horseshoe crabs?
4. What is the function of the metal in a respiratory pigment?
5. What are the differences between hemoglobin and hemocyanin?
6. What produces the different hues of color (dull red, bright red) in human blood?
7. How can the blood of the horseshoe crab be either blue or colorless?
8. How do fish that live in cold water compensate for the fact that their blood does not carry enough oxygen per liter for respiration?
9. Why does cold water contain more oxygen than warm water?
10. What condition produces yellow skin in humans and green skin in skinks?
11. How is the enzyme tyrosinase related to the survival of prehistoric organisms that were not able to tolerate (toxic) oxygen in the atmosphere?

Anesthesia: Chemistry in the Operating Room

1. When was the general anesthetic, nitrous oxide, first discovered?
2. For what non-medical purpose was nitrous oxide first used?
3. When was the first experiment performed to show the anesthetic (analgesic) effect of nitrous oxide?
4. What is meant by the term “inhalation” anesthetic?
5. What is meant by the term “halogenated ether”?
6. What is the advantage of using halogenated ethers instead of non-halogenated ethers as anesthetics?
7. What are some of the undesirable side effects caused by general anesthetics?

Battling Wildfires: When Water Won't Cut It

1. What is the “fire triangle”?
2. How does the fire triangle show how a fire can be prevented or extinguished?
3. What are the two ways in which a wildfire can be attacked?
4. What do firefighters use to battle flames directly?
5. Why are the foams and gels more effective than water?
6. What are the two types of foams developed to fight fires?
7. How do class A foams work?
8. How do gels work at fighting fires?
9. What are some of the chemicals used as fire retardants?
10. By what mechanism do the two ammonium phosphates work?
11. What is one of the most recent advances in fighting wildfires?

Green Gasoline: Fuel from Plants

1. What are three advantages to using green gasoline?
2. Why is green gasoline preferred over other biofuels, such as ethanol?
3. Why has gasoline been the transportation fuel of choice for the past century?
4. What is a hydrocarbon?
5. What gases are heated in the internal combustion engine?
6. Why does green gasoline help reduce the problem of global climate change?
7. Why can't wood be used to fuel cars?
8. Why are carbohydrates poorer fuels than their corresponding hydrocarbons?
9. What is meant by the term, plant "leftovers"? What are some examples?
10. What is the role of a zeolite catalyst?
11. What logistical problems face the production and use of green gasoline?

The Makeup of Mineral Makeup

1. What are the two main chemical components of mineral makeup?
2. Identify two synthetic chemicals present in some mineral makeup products.
3. The oxides of what transition metal are used as pigments in mineral makeup?
4. Which color pigments have crystalline structures?
5. Why does bismuth oxychloride irritate skin when used in mineral makeup even though it is often used in traditional makeup and is not an irritant?
6. What type of bond holds boron and nitrogen together within the layers of boron nitride?
7. How do the bonds within layers differ from those holding the layers together (between the layers)?

Answers to Student Questions

The Many Colors of Blood

- 1. What is the range of colors for blood in animals?**
The colors of blood in animals include red, blue, green and no color (colorless).
- 2. What is a respiratory pigment?**
A respiratory pigment is a large molecule that binds to oxygen used in the respiration process (cellular) and imparts a color that depends on the metal ion that is part of the pigment's molecular structure.
- 3. What metal is present in the respiratory pigment of humans and what metal is present in the respiratory pigment of horseshoe crabs?**
Iron is present in human respiratory pigments called hemoglobin (heme—referring to iron) and copper is found in horseshoe crab pigment, called hemocyanin.
- 4. What is the function of the metal in a respiratory pigment?**
The function of the metal, for both iron and copper, in a respiratory pigment is to bind oxygen atoms to these metal atoms.
- 5. What are the differences between hemoglobin and hemocyanin?**
Hemoglobin utilizes iron atoms to bind to oxygen while hemocyanin uses copper atoms. A single hemoglobin structure contains four iron atoms binding to four oxygen atoms. The hemocyanin contains 96 pairs of copper atoms binding to 160 oxygen molecules making the hemocyanin a much larger molecule than the hemoglobin. Finally, the hemoglobin molecules are found within a cell-like structure (minus the biological nucleus), the red blood cell. The hemocyanin molecules float freely in the blood medium.
- 6. What produces the different hues of color (dull red, bright red) in human blood?**
The presence of oxygen atoms within the hemoglobin causes a twisting of the heme's part of the molecular structure that in turns changes its light absorption/emission properties producing a brighter red color than when the heme is in a relaxed state without the oxygen atom.
- 7. How can the blood of the horseshoe crab be either blue or colorless?**
When the copper in the hemocyanin is in the cuprous state (Cu^{1+}), it does not absorb visible light, hence it is colorless. When oxygen binds to the copper to change it to the cupric state (Cu^{2+}), the copper absorbs the red component of visible light, leaving more of the blue part of the visible spectrum to be more apparent.
- 8. How do fish that live in cold water compensate for the fact that their blood does not carry enough oxygen per liter for respiration?**
Fish living in cold waters reduce their demand for oxygen by being less active, have larger volumes of blood to carry enough oxygen for their needs, and benefit from the fact that cold water has a higher solubility for oxygen than warmer waters, allowing for more oxygen exchange into the less "capable" (for oxygen transport) but more voluminous blood supply.
- 9. Why does cold water contain more oxygen than warm water?**
Cold water contains more oxygen than warm water because there is an inverse relationship between gas solubility in water and its temperature. You can also look at it in terms of the fact that dissolving a gas into a solvent such as water is exothermic. Therefore, raising the temperature of the water reverses the process, forcing more dissolved gas particles [O_2 (aq)] back to the gaseous state [O_2 (g)], escaping from the water system (Le Chatelier's Principle). On the molecular level, warm water molecules move faster and collide with more force, resulting in the oxygen (and other gaseous) molecules being bumped right out of the

solution, resulting in lower solubility. Cooler water molecules don't move as fast and thus often collide with gas molecules with insufficient force to push them out of solution, allowing for greater solubility.

10. What condition produces yellow skin in humans and green skin in skinks?

The presence of the hemoglobin breakdown product, bilirubin, produces the yellow color when it builds up in the surface blood vessels of the skin in humans. The green color in the skin of skinks is due to another breakdown product of hemoglobin called biliverdin.

11. How is the enzyme tyrosinase related to the survival of prehistoric organisms that were not able to tolerate (toxic) oxygen in the early atmosphere?

Tyrosinase is an enzyme that facilitates the oxidation of tyrosine to melanin. This meant that free molecular oxygen was no longer able to negatively affect some aspects of the organism's metabolism that functioned normally in an oxygen-free (anaerobic) or very low-level oxygen environment.

Anesthesia: Chemistry in the Operating Room

1. When was the general anesthetic, nitrous oxide, first discovered?

The discovery of nitrous oxide happened toward the end of the 18th century.

2. For what non-medical purpose was nitrous oxide first used?

People would pay to inhale the gas for entertainment—it caused them to laugh without reason.

3. When was the first experiment performed to show the anesthetic (analgesic) effect of nitrous oxide?

The first experiment to show the anesthetic effect of nitrous oxide was done in 1844 to demonstrate a painless dental procedure (a tooth extraction) on a dentist, Horace Wells. He suggested that nitrous oxide could be used after seeing a lecture/show about nitrous oxide given by a former medical student, Gardner Colton.

4. What is meant by the term “inhalation” anesthetic?

An inhalation anesthetic is one that is inhaled into the lungs then distributed to the blood system rather than given as a direct injection of a drug into the blood vessels.

5. What is meant by the term “halogenated ether”?

An ether is a molecule which has an oxygen atom that connects two organic groups. A halogenated ether means that hydrogen atoms are replaced by halogen atoms (halogen atoms are substituted for hydrogen atoms).

6. What is the advantage of using halogenated ethers instead of non-halogenated ethers as anesthetics?

Halogenated ethers are “...nonflammable and less toxic than earlier general anesthetics.”

7. What are some of the undesirable side effects caused by general anesthetics?

General anesthetics can cause nausea, pain, unconsciousness and even memory loss.

Battling Wildfires: When Water Won't Cut It

1. What is the “fire triangle”?

The “fire triangle” is a diagram used to explain what causes a fire. The three parts are oxygen, fuel, and heat.

2. How does the fire triangle show how a fire can be prevented or extinguished?

The fire triangle shows that a fire can be prevented or extinguished in one of three ways:

- maintain a temperature below the fuel's ignition point;
- minimize the amount of oxygen surrounding the fuel; and
- remove the fuel. (In the case of wildfires, the fuel is the vegetation.)

3. **What are the two ways in which a wildfire can be attacked?**
A wild fire can be attacked directly or indirectly. A direct attack consists of fighting a fire very near where it is burning and an indirect attack involves working at some distance away, so that a fire is put out once it reaches the site that has been worked on.
4. **What do fire fighters use to battle flames directly?**
To battle flames directly, firefighters use mostly solutions that contain foams or gels. Foams are made of water, air bubbles, and chemicals called surfactants that allow the foam to spread. Gels are essentially thickened water with a consistency between that of cream and Jell-o.
5. **Why are the foams and gels more effective than water?**
Foams and gels are more effective than water because water, by itself, evaporates too quickly in a hot fire to be effective.
6. **What are the two types of foams developed to fight fires?**
Class A foams were developed for fighting wildfires and class B foams were designed for use against flammable liquids.
7. **How do class A foams work?**
Class A foams contain surfactants which lower the surface tension of the water allowing the chemicals in the foam to penetrate the surface of the plant more easily.
8. **How do gels work at fighting fires?**
Gels consist of a network of polymers in the shape of a honeycomb. When dry the polymers are in a powder form in which the chains are coiled and lined with carboxyl groups (-COOH). In the presence of water, the chains uncoil and the carboxyl groups form hydrogen bonds with water. The gels often absorb 400-800 times their mass in water. The thick layer of water-containing polymer on the surface of the vegetation protects the plant from the heat of the flames.
9. **What are some of the chemicals used as fire retardants?**
Sodium calcium borate was first used in the 1950's. This chemical has the disadvantage of preventing vegetation from growing again. Its use was discontinued in 1955. Either monoammonium phosphate or diammonium phosphate is currently used.
10. **By what mechanism do the two ammonium phosphates work?**
When either phosphate is heated, it decomposes to form ammonia (NH₃) and phosphoric acid, H₃PO₄. The ammonia escapes as a gas. It and the water vapor cool the fire and the phosphoric acid acts as a catalyst to form a char, graphite, which is more difficult to burn.
11. **What is one of the most recent advances in fighting wildfires?**
One of the most recent advances in wildfire fighting is a unit called a Modular Aerial Fire Fighting System (MAFFS) that consists of tanks, an air compressor, and associated plumbing installed in aircraft that can deliver from 3,000 to 10,000 gallons, depending on the size of the aircraft.

Green Gasoline: Fuel from Plants

1. **What are three advantages to using green gasoline?**
Three advantages to using green gasoline are:
 - a) *it would reduce our dependency on foreign oil*
 - b) *it is better for the environment because*
 - i) *it releases fewer pollutants than oil-derived fuels and*
 - ii) *plants (the source of green gasoline) absorb some pollutants emitted by automobiles*
 - c) *it is renewable*
2. **Why is green gasoline preferred over other biofuels, such as ethanol?**

Green gasoline is preferred over ethanol and other biofuels because it can directly replace oil-derived gasoline in today's cars. No new cars, refineries or pipelines would have to be built just to use it.

3. **Why has gasoline been the transportation fuel of choice for the past century?**

Three reasons exist for gasoline being the fuel of choice for cars:

- a) gasoline is stable
- b) it is non-corrosive
- c) it "packs a high energy punch", meaning it has a high-energy content

4. **What is a hydrocarbon molecule?**

A hydrocarbon molecule is a long chain or ring of carbon and hydrogen atoms.

5. **What gases are heated in the internal combustion engine?**

Gases heated in the internal combustion engine include:

- a) carbon dioxide
- b) water vapor
- c) gasoline vapors
- d) other gases (oxygen and nitrogen from the air, pollutant gases)

6. **Why does green gasoline help reduce the problem of global climate change?**

Plants absorb carbon dioxide and through photosynthesis they incorporate the carbon into their cell structure. When they are burned the carbon is recombined with oxygen and they release the CO₂ back into the atmosphere. This is referred to as being "carbon neutral".

7. **Why can't wood be used to fuel cars?**

There are two reasons wood can't be used to fuel cars: wood is a solid, and therefore would not flow through the car's fuel system, as gasoline does, and wood does not contain as much energy as does gasoline—"you would need to carry three times as much weight in wood to go the same distance as with gasoline."

8. **Why are carbohydrates poorer fuels than their corresponding hydrocarbons?**

Carbohydrates are poorer fuels than their corresponding hydrocarbons because they already contain oxygen atoms. Since energy is produced as carbon and hydrogen atoms combine with oxygen atoms, some of the energy that carbohydrates would produce as they burn and combine with oxygen is not realized.

9. **What is meant by the term, plant "leftovers"? What are some examples?**

Plant leftovers are those parts of plants that presently have no commercial use or value. Examples include cornstalks and sawdust, and switchgrass and other grasses that can be grown easily.

10. **What is the role of a zeolite catalyst?**

The zeolite catalyst has pores that trap anhydro sugar molecules. These molecules then lose oxygen and reform into ring-shaped hydrocarbon molecules similar to cyclohexane, but with fewer hydrogen atoms.

11. **What logistical problems face the production and use of green gasoline?**

Logistical problems facing researchers of green gasoline technology include large-scale collection of cornstalks, etc., from farmers to a central location, and scaling up the laboratory-scale reactions to commercial production facilities.

Mineral Makeup

1. **What are the two main chemical components of mineral makeup?**

The article says that mica powder and talc are the main ingredients with titanium dioxide and zinc oxide also being important components.

2. **Identify two synthetic chemicals present in some mineral makeup products.**

The article identifies bismuth oxychloride and boron nitride as synthetic chemicals.

3. **The oxides of what transition metal are used as pigments in mineral makeup?**

The pigments in mineral makeup are oxides of iron— Fe_2O_3 , FeOOH and Fe_3O_4 .

4. **Which color pigments have crystalline structures?**

Red and black pigments have crystalline structures. Fe_2O_3 has a hexagonal structure and Fe_3O_4 has a cubic structure.

5. **Why does bismuth oxychloride irritate skin when used in mineral makeup even though it is often used in traditional makeup and is not an irritant?**

BiOCl can cause skin irritation when used in mineral makeup but not in traditional makeup because it is used in much higher concentrations in mineral makeup than in traditional makeup.

6. **What type of bond holds boron and nitrogen together within the layers of boron nitride?**

The bonds between boron and nitrogen within layers of boron nitride are strong covalent bonds.

7. **How do the bonds within layers differ from those holding the layers together (between the layers)?**

While the bonds within layers are strong covalent bonds, those between the layers are weaker van der Waals forces. This allows the layers to slip past one another easily.

ChemMatters Puzzle: Chemical Ronion

This nonsensical title contains two letter triplets, ION and RON. Here are two puzzles that feature these triplets. For each we'll show you the three letters and spaces for any other letters needed to generate terms often heard in science classes. Then below we'll show you clues to identify that term, but NOT in order ! You can cross off those you recognize as you proceed.

As an example, the term _ _ _ _ _ RON _ clued by the phrase "released in oxidation" yields ELECTRONS. Good luck in identifying all sixteen !!

THE TERMS WITH ION

ION _ _ _ _ _
 _ I ON _ _
 _ _ _ _ _ ION
 _ _ _ _ _ ION
 _ _ _ ION _
 _ _ ION
 _ _ ION _ _ _
 _ _ ION

THE TERMS WITH RON

_ _ RON
 _ _ _ _ RON
 _ RON _ _
 _ _ _ _ _ RON
 _ _ RON _
 _ RON
 _ _ RON _ _ _ _
 _ _ RON _ _ _ _

THE CLUES for "ION" (scrambled)

(scrambled)

1. Attracted to - terminal of a battery
2. $A + B \rightarrow C + D$, for example
3. Neutral molecules breaking into charged particles
4. Electrons being gained
5. A salt of thionyl acid (which is rich in S) transistors
6. Positively charged ions
Lawrence in 1931
7. An abnormal protein in mad cow disease
8. Relating to artificial limbs or organs
examples

THE CLUES for "RON"

1. Element #26
2. An alloy of copper and tin, primarily
3. "Discovered" by Chadwick in 1932
4. Describes HCl and H₂SO₄, but not HF or
5. Element of sometimes used in "doping"
6. First of the atom smashers, built by
7. An alkaline earth element
8. Neil Armstrong and Sally Ride, as

Answers to the *ChemMatters* Puzzle

IONIZING	Neutral molecules breaking into charged particles
BIONIC	Relating to artificial limbs or organs
REDUCTION	Electrons being taken in
REACTION	$A + B \rightarrow C + D$, for example
CATIONS	Attracted to - terminal of a battery
ANION	A positively charged ion
THIONATE	A salt of thionic acid (which is rich in sulfur)
PRION	An abnormal protein in mad cow disease

The CLUES for “RON”

BORON	Element often used in “doping” transistors
NEUTRON	“discovered” by Chadwick in the 1930’s
BRONZE	An alloy of copper and tin, primarily
CYCLOTRON	First of the atom smashers, built by Lawrence in 1916
STRONG	Describes HCl and H ₂ SO ₄ , but not HF or HCH ₃ COO
IRON	Element #26
ASTRONAUT	Neil Armstrong and Sally Ride, as examples
STRONTIUM	An alkaline earth element

NSES Correlation

National Science Education Content Standards Addressed

National Science Education Content Standard Addressed As a result of activities in grades 9-12, all students should develop understanding	The Many Colors of Blood	Anesthesia	Battling Wildfires	Green Gasoline	The Makeup of Mineral Makeup
Science as Inquiry Standard A: about scientific inquiry.	✓	✓	✓	✓	
Physical Science Standard B: of the structure and properties of matter.	✓	✓	✓	✓	✓
Physical Science Standard B: of chemical reactions.	✓		✓	✓	
Life Science Standard C: about biological evolution.	✓				
Life Science Standard C: matter, energy and organization in living systems.	✓				
Science and Technology Standard E: about science and technology.	✓	✓	✓	✓	✓
Science in Personal and Social Perspectives Standard F: of personal and community health.		✓			✓
Science in Personal and Social Perspectives Standard F: about natural resources.				✓	
Science in Personal and Social Perspectives Standard F: about environmental quality.			✓	✓	
Science in Personal and Social Perspectives Standard F: of science and technology in local, national, and global challenges.	✓	✓	✓	✓	✓
History and Nature of Science Standard G: of science as a human endeavor.	✓	✓	✓	✓	✓
History and Nature of Science Standard G: of the nature of scientific knowledge.	✓	✓	✓	✓	
History and Nature of Science Standard G: of historical perspectives.		✓	✓		

Anticipation Guides

Anticipation guides help engage students by activating prior knowledge and stimulating student interest before reading. If class time permits, discuss students' responses to each statement before reading each article. As they read, students should look for evidence supporting or refuting their initial responses.

Directions for all Anticipation Guides: *Before reading*, in the first column, write "A" or "D," indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

The Many Colors of Blood

Directions: *Before reading*, in the first column, write “A” or “D” to indicate your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Some animals on Earth have colorless blood.
		2. The color of an organism’s blood depends on the respiratory pigment molecule in the organism.
		3. Hemoglobin (found in humans) and hemocyanin (found in crabs) differ only in the identity of the metal ion found in the middle of the heme.
		4. Respiratory pigments are the same color regardless of whether they are bound to oxygen.
		5. Only transition metals bind oxygen in respiratory pigments.
		6. Animals without a respiratory pigment are only found in very cold water.
		7. Green-blooded skinks from New Guinea have red blood cells containing hemoglobin.
		8. Organisms that existed before the Oxygen Catastrophe 2.4 billion years ago needed more oxygen than is currently in the atmosphere.
		9. The purpose of respiratory pigments in animals is to transport oxygen.

Anesthesia: Chemistry in the Operating Room

Directions for all Anticipation Guides: *Before reading*, in the first column, write “A” or “D” to indicate your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. People have used natural substances to relieve pain for thousands of years.
		2. Scientists now know how anesthetics work at the cellular and molecular level.
		3. Both local and general anesthetics work by preventing nerves from carrying pain signals to the brain.
		4. Patients dream during surgery when general anesthetics are used to induce loss of consciousness.
		5. Nitrous oxide was originally used to induce laughter in people.
		6. Nitrous oxide increases the oxygen content in living tissues.
		7. Halogenated ethers are the most common inhalation anesthetic used today.
		8. Sodium ions are involved in carrying electric current from one nerve cell to the next.

Battling Wildfires: When Water Won't Cut It

Directions: *Before reading*, in the first column, write “A” or “D” to indicate your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Firefighters today use the same chemicals that were used 40 years ago.
		2. Both direct and indirect attacks to extinguish wildfires use chemicals.
		3. Foams and gels used in firefighting both contain water.
		4. Foams and gels both consist of a network of polymers in a honeycomb shape.
		5. Long-term fire retardants remain effective after water from the solution sprayed on the plants evaporates.
		6. Plants coated with long-term fire retardants produce flammable gases such as methane and alcohols.
		7. Esters used in long-term fire retardants decompose to form water and graphite, which does not burn.
		8. Large aircraft such as DC-10s and Boeing 747s can be used to fight wildfires.

Green Gasoline: Fuel from Plants

Directions: *Before reading*, in the first column, write “A” or “D” to indicate your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Green gasoline is a nonrenewable source of energy.
		2. Green gasoline would directly replace gasoline derived from crude oil.
		3. When hydrocarbons burn, carbon dioxide and water are produced, and a large amount of energy is released.
		4. Green gasoline is the only biofuel that can recycle carbon dioxide in the atmosphere.
		5. Molecules containing oxygen produce more energy per pound than molecules containing only hydrogen and oxygen.
		6. Only the leaves of plants can be used to produce green gasoline.
		7. The researchers who have produced green gasoline in the lab must first heat the plant material to 500 °C or more.
		8. Large scale production of green gasoline has been demonstrated to work.

The Makeup of Mineral Makeup

Directions: *Before reading*, in the first column, write “A” or “D” to indicate your agreement or disagreement with each statement. As you read, compare your opinions with information from the article. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Me	Text	Statement
		1. Mineral makeup contains no synthetic or processed ingredients.
		2. Some ingredients in makeup protect the skin from ultraviolet radiation.
		3. Iron oxide pigments contain only red shades ranging from light salmon to a deep blue-red.
		4. All iron oxide pigments have a hexagonal crystalline structure.
		5. Some brands of mineral makeup contain a chemical that can irritate or burn the skin.
		6. The structure of boron nitride is similar to graphite, providing it with properties desirable for mineral makeup.
		7. Nitrogen and boron attract electrons equally.
		8. Boron nitride has only recently been developed.

Reading Strategies

These matrices and organizers are provided to help students locate and analyze information from the articles. Student understanding will be enhanced when they explore and evaluate the information themselves, with input from the teacher if students are struggling. Encourage students to use their own words and avoid copying entire sentences from the articles. The use of bullets helps them do this. If you use these reading strategies to evaluate student performance, you may want to develop a grading rubric such as the one below.

Score	Description	Evidence
4	Excellent	Complete; details provided; demonstrates deep understanding.
3	Good	Complete; few details provided; demonstrates some understanding.
2	Fair	Incomplete; few details provided; some misconceptions evident.
1	Poor	Very incomplete; no details provided; many misconceptions evident.
0	Not acceptable	So incomplete that no judgment can be made about student understanding

Question From the Classroom: What is the most deadly poison in the world?

Vocabulary

- poison
- chronic
- acute
- LD₅₀
- inhalation
- absorption
- intravenous
- intramuscular
- subcutaneous
- intraperitoneal

Metric prefixes

- kilo- (k)
- milli- (m)
- micro- (μ)
- nano- (n)

The Many Colors of Blood

Directions: As you read, compare and contrast the properties of hemoglobin and hemocyanin in the chart below.

Hemoglobin	Hemocyanin
Similarities	

Anesthesia: Chemistry in the Operating Room

Directions: As you read, please complete the chart below comparing different general anesthetics.

Anesthetic	Formula & Brief History, including Use	Advantages	Disadvantages
Nitrous oxide			
Diethyl ether			
Halogenated ether			

Battling Wildfires: When Water Won't Cut It

Directions: As you read, complete the chart below comparing foams, gels, and fire retardants.

Fire-fighting product	Used for Direct or Indirect Attack?	Chemicals used
Foam		
Gel		
Fire Retardant		

Green Gasoline: Fuel from Plants

Directions: As you read, please complete the chart below describing green gasoline.

Advantages			
Who is working to develop it?			
What have they tried?			
What problems must still be solved?			

The Makeup of Mineral Makeup

Directions: As you read, please complete the chart below to describe the ingredients in mineral makeup.

Ingredient	Used for slip, adhesion, and/or color?	Properties
Talc		
Mica		
Titanium dioxide		
Zinc oxide		
Iron oxide pigments		
Bismuth oxychloride		
Boron nitride		

The Many Colors of Blood

Background Information

More on properties of blood

Blood as a mixture is a complicated chemical concoction that, over evolutionary time, has performed a variety of functions vital to the existence of many different types of organisms, including humans. As a mixture, it contains a variety of suspended particles, some as large as the red blood cell with a diameter of 5 microns. There are also many specific chemical compounds that help to maintain a necessary equilibrium when the internal environment of an organism is subjected to a variety of changes from the surrounding external environment. Think in terms of: temperature, pH, amount of dissolved gases including oxygen, salts, viruses and bacteria, among others. There is also a variety of protein-based compounds and larger molecules with specific structural shapes that tie directly to their mode of operation. One such large molecular structure is hemoglobin whose primary, though not sole, function is to transport oxygen from the exterior to the interior of an organism at the cellular level.

Hemoglobin consists of four peptide chains (made from amino acids) that enclose a structure known as *heme* which consists of a central ferrous ion (Fe^{+2}) held in place by molecular linkage to the four peptide chains. It is this ferrous ion that is able to loosely bond to molecular (as opposed to atomic) oxygen. This bonding is not a normal covalent, nor an ionic bond. Normally a free ferrous ion forms unstable complexes with molecular oxygen in solution because of solution water. But this same ferrous ion in the heme part of hemoglobin can form a more stable complex because the folds of the four peptide chains have hydrophobic regions that keep away enough water to provide a more stable complex. In any case, it is important that the oxygen not be too tightly bonded or the transfer of oxygen between the blood environment and the cells of an organism would be difficult because it would be too slow to be of biological value.

Why couldn't a simple water solution be used to transport oxygen instead of a special structure like hemoglobin? One has to look at the amount of oxygen that can dissolve in water compared with hemoglobin. One way to look at this issue is to realize, that in human blood, 98.5% of the oxygen is carried by the hemoglobin and only 1.5% is in simple solution. Affinity as well as efficiency is at work here! (See the reference, <http://en.wikipedia.org/wiki/Blood>, p.16)

A second gas that is transported by blood is carbon dioxide that is produced in the metabolic process known as respiration. Again, the blood is nicely designed chemically to handle carbon dioxide. First, carbon dioxide is much more soluble in plasma and water than oxygen. Second, there is a specific enzyme (catalyst), carbonic anhydrase, that increases the rate of dissolving for carbon dioxide in water, producing an important ion, the bicarbonate ion (HCO_3^-), which is highly soluble and which also plays a part in buffering the blood to maintain a fairly steady pH of around 7.2. ($\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^{-1} + \text{H}^{+1}$)

But the blood uses the bicarbonate ion to move what was originally carbon dioxide from the cells to the lungs or functionally equivalent structure. And the same enzyme is used when it is necessary to convert the bicarbonate ion back to CO_2 gas for diffusion out of the blood into a lung or the external environment.

In nature, metal complexes (metal ions bonded to "complicated" protein structures, such as hemoglobin) are also found in such variations as chlorophyll molecules where the iron ion is

replaced by magnesium, Mg. In the hemoglobin of some arthropods (horseshoe crabs) and mollusks, copper ion is substituted for iron, producing a true “blue” blood of the animal kingdom! The copper ion is part of a protein called hemocyanin which is colorless without oxygen and dark blue when oxygenated. The hemocyanin carries oxygen in extra-cellular fluid rather than within cells (red blood cells).

Color changes in blood containing hemoglobin also are due to the amount of oxygen present. Arterial blood is higher in oxygen and brighter red because of the oxygen bound to the iron of the heme. Venous blood (deoxygenated) is darker red. For those familiar with blood donation, the pints of donated blood appear dull red due to non-exposure to oxygen, yet the drop of blood taken to test the blood before the donation is bright red because it is exposed to oxygen in the air.

Other conditions in which hemoglobin changes brightness of color include carbon monoxide and cyanide poisonings. In carbon monoxide poisoning, the carbon monoxide molecule binds more strongly to the heme than oxygen and is very difficult to remove. It forms a carboxyhemoglobin which is brighter red than normal hemoglobin. In cyanide poisoning, the oxygen in the blood is not able to be utilized (the cyanide interferes with certain enzymes necessary for cellular respiration). As a result, the venous blood turns brighter red than normal.

A medical condition known as sickle cell anemia is an example of a genetic error that affects protein synthesis (the order of amino acids) that makes for abnormal hemoglobin. In this particular instance, just one amino acid called valine is incorrectly utilized in the hemoglobin chain instead of the normal one, glutamic acid. The glutamic acid is dissociated into a charged (-1) anion molecule whereas the valine, which remains undissociated, is neutral. This difference seems to make part of the hemoglobin chain less soluble and causes precipitation of the hemoglobin within the red blood cell. This in turn changes the shape of the red blood cell from circular to curved (“sickle” shape). This structural change means that the blood cells have a difficult time circulating in the tiny blood vessels, the capillaries, which in turn essentially clogs up the blood vessels, creating pain and reduced oxygen-carrying capacity for the victim. Long term, the sickle cell condition can become both debilitating as well as fatal. The only good aspect of sickle cell anemia is that individuals with the condition are less prone to malarial infection and attacks, for reasons not fully explained.

Another interesting medical condition involving the synthesis of the heme portion of hemoglobin is known as porphyria. There is a sequence of eight steps in the synthesis of the heme molecule, each catalyzed by a separate enzyme. If any step fails because of a genetic mutation or an environmental toxin, the chemical chain of events is interrupted with a back-up of what are known as porphyrin intermediates. These porphyrins can accumulate to toxic levels. Exposed to light (as in the skin), these compounds can turn caustic, destroying tissue. (They also can be excreted in feces and urine, turning to a purple [port wine] color.) That said, these porphyrin compounds have a potentially beneficial use, attacking tumors for instance. The effectiveness of this particular application again depends on the porphyrin being exposed to light. These are known as phytochemicals. For more on the condition of porphyria and some interesting history that includes werewolves and vampires, refer to the following two articles: “*New Light on Medicine*”; by Nick Lane, *Scientific American*, January 2003; <http://www.sciam.com/article.cfm?articleID=000B4130-5C6C-1DF7-9733809EC588EEDF> and <http://www.sciam.com/article.cfm?id=born-to-the-purple-the-st>

Another interesting facet of blood is the existence of some animals, particularly fish, some frogs, as well as some insects, which have evolved some chemical additives to their blood

that act as an anti-freeze compound to survive in very cold environments, both on land and in water. In these different organisms, the anti-freeze substances are special proteins (antifreeze proteins, AFPs) that prevent the formation of ice crystals within the animal's cells, thereby preventing ice crystals from puncturing the cell membrane resulting in the fatal loss of the cells' liquid contents. (See <http://www.gi.alaska.edu/ScienceForum/ASF15/1560.html> and <http://news.nationalgeographic.com/news/2007/02/070220-frog-antifreeze.html>.)

With blood acting as the transport medium for gases, particularly oxygen and carbon dioxide, mammalian bodies have adaptive mechanisms for certain stressful conditions that are potentially hazardous. But these adaptations in some instances make use of the blood circulatory system. One such adaptation actually occurs in the unborn child in which dissolved oxygen levels from mother to fetus (at the exchange point, called the placenta) are not as high as needed. As a result, the fetus has available a modified hemoglobin called "hemoglobin F" that has a higher affinity for oxygen. Under low oxygen conditions for adults, as in high altitude situations, the adult is not able to produce this hemoglobin "F".

Two other adaptations however are possible. One is the production of more red cells which usually takes several days to accomplish once the person is in a lower oxygen situation. The other adaptation, a genetic one, is found in certain populations who are born and live in high altitude conditions. An example is the Sherpas of Tibet. Living at altitudes averaging 4500 meters (3 miles!) above sea level, these people do not suffer from the condition known as altitude sickness because they are able to increase their blood flow rate through the production of nitric oxide (NO) in the linings of their blood vessels. The nitric oxide dilates the blood vessels, allowing for large volumes of blood flow in the arteries and capillaries. More information on this topic can be found in Scientific American magazine: <http://www.sciam.com/article.cfm?articleID=ED53255A-E7F2-99DF-36FFDF78DD9F2F36>.

More on artificial blood and blood substitutes

Although the article on the Colors of Blood does not deal with the topic of artificial blood, the topic may be useful to pursue with students in terms of understanding the requirements for blood to function and what chemistry can be used to simulate naturally occurring blood. Since there is a variety of disease conditions that could be avoided with artificial blood, the pursuit of artificial blood concoctions continues.

A substantive series of articles on artificial blood can be found in one place, *Scientific American's* site called "Ask the Experts": <http://www.sciam.com/article.cfm?id=how-do-scientists-make-ar>. Included in this website are additional references primarily from scientific journals rather than popular texts. The second article in this series discusses why modified hemoglobin extracts must be part of artificial blood and what the complications are for using straight hemoglobin. Included in this discussion are the bioengineering techniques used to modify hemoglobin. The reason for trying to find ways to incorporate stable forms of hemoglobin into synthetic blood mixtures is because hemoglobin can carry much more dissolved oxygen than something like the perfluorochemicals. Therefore, the use of perfluorochemicals has some limitations (and some advantages as well) unless a way can be found to increase oxygen-carrying capacity.

At the following website, you can find a video-based program on "Additional Thoughts on Blood Substitutes" from the PBS "*Wired Science*" series: http://www.pbs.org/kcet/wiredscience/video/196-additional_thoughts_on_blood_substitutes.html.

And from “13 Video” you can see two other Wired Science Videos on artificial blood at: <http://watch.thirteen.org/video/1321275343/>.

In addition, how artificial blood is made, complete with background, history, design, raw materials and manufacturing techniques can be found at <http://www.madehow.com/Volume-5/Artificial-Blood.html>.

There is also a discussion about the results of recent field tests of one blood substitute called “Polyheme” at ABC News Videos (3 videos in the series): (<http://abcnews.go.com/search?searchtext=Artificial+Blood+controversy&r=old>).

There are also three specific news reports on the Polyheme from ABC news: <http://abcnews.go.com/Blotter/story?id=4741427&page=1>, http://blogs.abcnews.com/theblotter/2007/05/test_of_controv.html and <http://abcnews.go.com/WNT/story?id=2166058&page=1>.

Another view of the issues regarding both effectiveness and hazards of blood substitutes is found at <http://www.sciam.com/article.cfm?id=blood-substitutes-hemoglobin-anemia&print=true>.

This article from *The Scientist* describes the most current idea about creating an artificial blood based on the red blood cell itself instead of simply a 'cocktail' of chemicals to simulate the plasma component of blood. The design of the red blood cell allows it to carry oxygen as well as to be visualized through an MRI: <http://www.the-scientist.com/blog/display/56218/>

More on myoglobin and neuroglobin

Although one associates hemoglobin as a carrier of oxygen in blood, there are two other protein-based oxygen carriers, one long known (myoglobin) and one more recently identified (neuroglobin) that both utilize iron for oxygen attachment. Myoglobin is found in muscle tissue and neuroglobin is found in the nervous system, primarily in the brain. Compared with hemoglobin, myoglobin contains higher concentrations of oxygen at much lower partial pressures in the surrounding tissue (which affects transfer rates). Because of this higher “holding” capacity of oxygen in myoglobin, organisms can hold their breath longer which is particularly important in animals that dive in water systems.

And for some chemistry minutiae, the red color of meat is due to the oxidation state of the iron in the myoglobin molecule. When meat is in the raw state, the iron is in the +2 oxidation state. Cooking meat to a brown color is due to the iron in the +3 oxidation state, having lost an additional electron and now coordinated to a water molecule (In the +2 state, the iron is bound to an oxygen molecule, O₂). Interestingly enough, if meat is exposed to nitrites (cured meats such as corned beef and ham) before cooking, it may appear more pink than brown during cooking due to the iron binding to nitric oxide (NO). Grilled meats may take on a pink color (inside a “smoke ring”) produced when iron binds a molecule of carbon monoxide, CO, to give what is termed metmyoglobin. This same chemistry can be used in the meat packing process to produce fresh-looking meat. The meat is exposed to carbon monoxide in the packing process to produce the pink smoke ring. This artificially produced color can persist up to a year, assuming the meat can be preserved, as in the frozen condition!

Myoglobin is released from damaged tissue and can be detected in the blood. Therefore, it is used as one of the markers indicating a heart attack.

Neuroglobins are more recently identified as possible carriers of oxygen in the nervous system and may be a future tool for reducing the effects of a stroke in which blood supply to the sensitive brain has been compromised. It has been shown that under stress conditions in which oxygen concentration is reduced in the brain, particularly the cerebral cortex, neuroglobins increase in concentration, suggesting that their increased concentration in affected areas is an attempt to provide additional oxygen. Better understanding of the role of neuroglobins may lead to specific forms of treatment post-stroke. (See <http://www.scitopics.com/Neuroglobin.html> and <http://www.scientificamerican.com/article.cfm?id=study-suggests-protein-pl>.) New studies also propose a possible link between concentrations of neuroglobins (deficiencies) and the development of Alzheimer's. (<http://www.news-medical.net/news/2009/05/06/49227.aspx>)

More on hemocyanin

Extracts from hemocyanin of the marine Keyhole Limpet are being developed for use in treating certain cancers based on the fact that these extracts, known as KLH (Keyhole Limpet Hemocyanin) can act as vaccine carriers for certain antigens. These antigens provoke a reaction against cancer cells through the immune system's antibodies congregating on cancer cells that are marked with these specific antigens. Some of the cancers that respond to KLH-based vaccines include non-Hodgkin's lymphoma, cutaneous melanoma, and breast and bladder cancers. (Reference for the details of KLH can be found at <http://www.horseshoecrab.org/med/med.html>.)

More on blood physiology in diving animals

For diving animals such as the seal, the whale and others, there is a need for circulatory and respiratory systems that can deal with the effect of water pressure and temperature on dissolved gases in both the circulation and musculature systems. It is found that in deep-diving, whales and seals rely on large oxygen stores in their muscle and blood. How is this accomplished? Compared with land animals, the divers have blood volumes that are 3-4 times larger than terrestrials (200-250 milliliters of blood per kilogram body mass compared to 70 milliliters per kilogram in humans). The concentration of hemoglobin in the divers is nearly twice that of humans. And finally, the concentration of myoglobin in divers is 10 times that of human muscle.

An aside on this issue concerns the fact that various other gases besides oxygen are dissolved in the blood plasma and respond to pressure changes just as in non-biological physical systems. With an increase in pressure more gases dissolve in the blood of a diver. To avoid this from happening (and later to avoid the rapid release of gases with decrease in environmental pressures as a diver returns to the surface, creating the "bends"), the lungs of these diver animals actually collapse, preventing the absorption of gases, particularly nitrogen, between the lungs and the blood. This mechanical adaptation prevents both the problem of nitrogen narcosis from excess absorption of nitrogen as well as the aforementioned "bends".

More on hemolymph of horseshoe crabs

The hemolymph of horseshoe crabs was shown to have anti-bacterial properties in the late 1950s by Frederick Bang. Bang isolated the chemical in the blood that causes bacteria to

clump—both a telltale sign of the presence of bacteria as well as a bactericide for the horseshoe crab itself. Since then, the extract named LAL (*Limulus* Amoebocyte Lysate) is used routinely to detect for the presence of endotoxin-producing bacteria on anything that goes into the body, including vaccines and various fluids. The detection of these particular bacteria is very important because they can withstand sterilization. (See <http://www.horseshoecrab.org/med/med.html>.)

The component of the horseshoe crab's blood that is active in providing immunity is an amoebocyte blood cell that contains the active ingredient that causes the bacteria to clump. The extraction of this reagent in horseshoe crab blood is done very simply using distilled water in which the blood cells are suspended. Because the blood cells contain a high concentration of salt compared with essentially salt-less distilled water, the cells rupture (lyse, hence the word lysate in the name of the extract, LAL) from osmotic pressures created by water diffusing into the cells. This technique developed by Bang and a colleague, Jack Levin, is still used today in the commercial process to isolate LAL.

Connections to Chemistry Concepts

1. **Polymers**—Large molecules made from joining together many smaller molecules are particularly useful in the biological world, where such things as hair, skin, and various proteins (known as polypeptides), some of which act as catalysts, are all polymers. Much of the large size of polymers depends upon the extensive bonding (networks) that is possible because of carbon atoms. The plastics of blood collection bags, for example, are polymers and are carbon-based.
2. **Organic compound**—Any chemical that contains carbon (except carbon monoxide, carbon dioxide and metal carbonates) is considered an organic compound. Because of the bonding based on the carbon atom, organic compounds have an almost infinite number of configurations with important “functional” groups attached. The size of organic compounds is wide ranging. It is thought that a truck tire of synthetic or natural rubber, a polymer, is a single molecule!
3. **Gas solubility**—Solubility is a property of gases that is dependent on both the molecular structure of the gas and the chemical properties of the solvent in which the gas dissolves. For biological organisms, the solvent is usually water. Both temperature and atmospheric pressure affect the extent of dissolving and escaping of the gases.
4. **Catalysts/Enzymes**—Enzymes are organic catalysts that accelerate rates of biochemical reactions. One example is the use of the enzyme carbonic anhydrase to accelerate the rate at which carbon dioxide dissolves in the blood or is removed from the blood through the formation of the bicarbonate ion (HCO_3^{-1}).
5. **Amino Acids**—Organic acids which contain the functional amine group ($-\text{NH}_2$) as well as the carboxyl group ($-\text{COOH}$) and are fundamental to the various structures of living organisms are called amino acids. These acids are linked together through the carboxyl and amine groups (a peptide bond) to form very long chains that are known as polypeptides and/or proteins. Through hydrogen bonding between various points on the polypeptide, various shapes of a molecule can be produced which are specific enough to provide “identification” within living systems (think enzymes, pharmaceuticals, allergens, antibodies, DNA, among other things).
6. **pH**—pH is the term given to the numerical range of acidity through alkalinity that is important in the biological world. Among other things, certain enzymes will only function in a narrow pH range (think enzymes in the acid environment of the stomach vs. the alkaline

environment of the intestine). For the blood, a pH in the range of 6.8-7.2 is necessary and is maintained through the use of buffers, including the bicarbonate ion, HCO_3^- .

7. **Buffers**—The hydrogen carbonate ion is part of the blood's $\text{CO}_2/\text{H}_2\text{CO}_3$ buffered equilibrium.
8. **Polymers and cross-linking**—In polymeric materials including thermoplastics and proteins like hemoglobin, linkage between several chains of atoms can be produced through covalent bonding of atoms such as sulfur between the chains, as in the vulcanization of rubber or hydrogen bonding within the strands of DNA and the large protein molecules such as hemoglobin.
9. **Transition elements**—Metals contained in the protein-based blood respiratory pigments are from the transition elements including copper, iron, and vanadium, and they bind oxygen to the protein portion of the pigment molecules.

Possible Student Misconceptions

1. **“Blood inside our bodies is blue, but it turns red when exposed to air.”** *No, blood is always red. It only looks blue in the veins close to our skin (at the wrists, for instance) because shorter wavelength red light can penetrate farther into the skin than longer wavelength blue light. If blood in veins is just far enough beneath the surface of the skin, the red light is absorbed by the blood, while the blue light is reflected back to our eyes before it reaches the blood. The reflected light is what we see coming back at us; hence, the blood in that vein appears blue. While this isn't a scientific site, it offers a simple explanation of the phenomenon: <http://www.colourlovers.com/blog/2007/07/26/color-in-science-is-my-blood-really-blue/>. Here's a more scientific explanation from Discover Magazine, for the naturally curious: <http://discovermagazine.com/1996/dec/theskinnyonblue954>.*
2. **“Plasma is not real blood.”** *Plasma is part of blood and therefore is real.*
3. **“People of royalty have blue blood compared with non-royals.”** *The term “Blue Bloods” comes from the Spanish, **sangre azul**. (Sangre=blood, azul= blue). It refers to royalty and has its origins in Spain at a period after the re-conquest of Spain from the Moors. The Moors, who had earlier conquered and settled Spain, produced offspring who had a mix of skin colors. Darker skin from the Moors' ancestors made it difficult to see the color of veins at the surface that are bluish in lighter skinned people. Long after the Moors left and monarchies were re-established, many of these people were light skinned which allowed for the more visible blue veins to be noticed. So there was this association between royalty and blue “blood” (veins)—see Misconception #1 above. The term was eventually adapted by monarchies in other countries. See http://books.google.com/books?id=VTYBbGybtNEC&pg=PA29&lpq=PA29&dq=Spanish+blue+blood&source=bl&ots=MBG_OSTpAq&sig=A1XThfV0QSjVDID_kH8qeYB2FTE&hl=en&ei=nsMCS8TGDZDFIAfNuc3gAQ&sa=X&oi=book_result&ct=result&resnum=8&ved=0CCqQ6AEwBw#v=onepage&q=Spanish%20blue%20blood&f=false.*

Demonstrations and Lessons

1. The information on the history of blood from the PBS program, “Red Gold” that can be found at <http://www.pbs.org/wnet/redgold/resources.html> is a treasure trove of information that you could use with students in a variety of lessons and writing projects, including the history of and the characters involved in discovering various things about the human body's circulatory system and its many components, particularly blood itself. The site includes video clips with

some of the scientists talking about their work. There are also useful timelines with short biographies attached of various scientists.

Another page of the “Red Gold” site, <http://www.pbs.org/wnet/redgold/education/index.html>, has 2 classroom lessons, one a high school plan, “Exploring the Complexity of Blood”, and one for middle school, “Uncovering the History and Science of Blood.”

2. You might consider doing a forensic science unit with your class(es), depending on the level of chemistry and the time available in your curriculum. You might want to focus particularly on that part of forensics that involves detecting blood at a crime scene. There are many high school textbooks with lab activities about forensic science. There are also science supply companies that have a variety of kits for detecting the presence of blood, the type of blood, blood spatter pattern analysis, and comparing blood from different animal species. There is also the important detection of DNA at a crime scene and various procedures to examine, by electrophoresis, the content of the DNA, then try to match the banding patterns against various “suspects” DNA that is provided.
3. Students can test the idea of incompatibility of blood because of different antigen-antibody reactions by using special blood testing kits that are available from science supply companies. These kits do not contain real blood, to avoid the possibility of exposing students to any human blood that may be contaminated.
4. To simulate the color change of blood upon exposure to oxygen, you can do the classic blue bottle demonstration, involving the oxidation of glucose in an alkaline solution. Methylene blue helps to oxidize the glucose and is itself oxidized, changing from blue to colorless. Upon standing, the blue color returns and the cycle is repeatable. You can see the demonstration online at several sites listed here, and an online search of the “blue bottle” demonstration will give more.
 - a) This citation describes the demonstration: <http://chemistry.about.com/od/chemistrydemonstrations/ss/bluebottle.htm>.
 - b) This site presents the blue bottle as a student experiment, and includes material for more advanced classes. It also provides a fuller description of the chemistry involved: http://www.union.edu/academic_depts/chemistry/faculty/fox/Chemical%20Demonstrations/docs/10%20Blue%20Bottle.pdf.
 - c) And this site, Dave Brooks’ “Doing Chemistry” site, provides a very thorough lesson plan, including a description of the activity, its hazards, student handouts, Teachers Guide, lab hints, time, disposal, etc. It even includes a video clip showing the demonstration, if you are unable to do the demo “live”: <http://dwb4.unl.edu/Chemistry/DoChem/DoChem006.html>.
5. To reinforce the idea of blood changing hues of red depending upon oxygen concentration, you might mention to students (or remind them, if they have already been blood donors) that pints of donated blood are dull red (see http://www.pathologyprinceton.com/WhatisPath_files/image010.jpg), while the blood oozing from the finger stick is bright red (see <http://www.idph.state.il.us/heartstroke/fingerstick.jpg>). This is because the blood in the flexible bag has not been exposed to the air—from the donor’s arm to the needle, through the tubing to the receiving bag, no air has gotten to the blood. In the finger-stick, however, the drop of blood is exposed to oxygen in the air as soon as the blood leaves the wound.
6. You can show the effects of the hydrogen carbonate ion on the $\text{H}_2\text{CO}_3/\text{CO}_2$ equilibrium system in an aqueous solution to simulate this system in the blood. Do this by preparing two aqueous solutions. The first should contain water, universal indicator and a large amount of baking soda (sodium hydrogen carbonate), the buffer. The second solution should contain water, universal indicator and just enough sodium hydroxide to make the color of the solution with indicator the same blue-green color as the buffered solution. Pour each solution into a cylinder and place both side by side. Now drop chunks of dry ice into each cylinder. Carbon dioxide from the dry ice dissolves into the solution producing carbonic acid.

As a result, the unbuffered solution will rapidly change from blue-green to green, yellow and then orange, becoming more acidic, as more dry ice puts more CO_2 into the solution. But in the buffered solution the color will remain blue-green because the H^+ ions react with HCO_3^{-1} ions to neutralize the added acid ions. A very short video clip (0:15) that shows this change is available from the University of California, Berkeley's chemistry department and can be viewed at <http://www.cchem.berkeley.edu/demolab/images/CO2Buf.mpg>. The demonstrator discusses the two cylinders and states that for the unbuffered solution "pH dramatically changes" and that, for the buffered solution there's "no change". You will probably need to show the clip several times, possibly with your own narration, for students to really see and understand what's happening.

Student Projects

1. Students could investigate the development of synthetic blood and write/give a report on their findings.
2. A most unusual and fascinating project for students combines religious history, miracles, and "mysterious" chemistry. The project is based upon the martyred death of a Saint Januarius and the annual celebration of his blood turning from a gel to a liquid on the anniversary of his death more than 1600 years ago. The blood (in a vial kept in Naples Italy) is supposed to be that of Saint Januarius. Some Italian chemists have tried to determine if this is real blood or not by trying to make a concoction known as a thixotropic mixture. The formula for making this mixture that goes from solid (gel) to liquid by shaking is found in the Feb. 1993 issue of *ChemMatters* (p.15) along with the story behind this religious miracle and the chemical sleuthing done by the three Italian chemists ("Saint's Blood", Robin Meadows, pp.12-14). It makes for an interesting bit of chemistry for students.
3. Students could get into forensic science, particularly the part that involves detecting blood at a crime scene. There are many high school textbooks with lab activities about forensic science. There are also science supply companies that have a variety of kits for detecting the presence of blood, the type of blood, blood spatter pattern analysis, and comparing blood from different animal species. There is also the important detection of DNA at a crime scene and various procedures to examine, by electrophoresis, the content of the DNA, then try to match the banding patterns against various "suspects" DNA that is provided.
4. As mentioned before, the information on the history of blood from the PBS program, "Red Gold" that can be found at <http://www.pbs.org/wnet/redgold/resources.html> is a treasure trove of information for students to use in a variety of writing projects, including the history of and the characters involved in discovering various things about the human body's circulatory system and its many components, particularly blood itself. The site includes video clips with some of the scientists talking about their work. There are also useful timelines with short biographies attached of various scientists.
5. Students might find it instructive to research the various aspects of horseshoe crabs (which are really not crabs but relatives of the spider or arachnid family). There are concerns about present day environmental issues that impact on the survival of these "crabs" which in turn impact on the use of the "crabs" in medical research and applications, such as the LAL reagent for detecting bacteria-infected solutions and devices that go into a human body as a medical procedure. A good starting point would be <http://www.horseshoecrab.org/med/med.html>. Included in this website are the categories of the "crab's" natural history, evolution, anatomy, conservation, and medical uses. Other useful sites include <http://horseshoe-crabs.com/horseshoe-crab-blood/> and http://www.oar.noaa.gov/spotlite/archive/spot_delaware.html.

6. Students can research the history and status of artificial blood and report. A good place to start might be the ABC News web site at <http://abcnews.go.com/search?searchtext=Artificial+Blood+controversy&r=old>. Numerous videos and news reports are listed there.

Anticipating Student Questions

1. **“If iron is found in blood (in the heme part of hemoglobin) why doesn’t blood show signs of rust?”** *Iron is in the form of the ferrous ion, Fe^{+2} , not elemental iron, Fe . For rust to occur (oxidation), molecular oxygen could only react with elemental iron, not iron ion, based on standard reduction potentials.*
2. **“How can a red blood cell function if it is not alive?”** *It is true that a red blood cell lacks a nucleus as found in other biological cells. But the red blood cell essentially operates through a variety of chemical reactions, the principle one being the binding of oxygen molecules to the ferrous ion in the heme portion of the hemoglobin found in the red blood cell. The gain and loss of the oxygen is dependent on the partial pressures of oxygen within the cell and the partial pressure of the oxygen in the surrounding tissue cells. It is a non-biological process that is not dependent on a functioning live cell.*
3. **“Why can’t you just use a water-based solution containing salts as a blood substitute since sea water has oxygen dissolved in it and fish do just fine ‘breathing’?”** *It is a question of how much oxygen will dissolve in a water-based solution compared with how much oxygen can be attached to hemoglobin (“dissolved”) for exchange at the cell membrane barrier. And for the amount of oxygen needed by a blood-carrying animal, not enough would simply dissolve in a water-based liquid compared with how much attaches to hemoglobin. In the blood, more than 95 % of the oxygen attaches to the hemoglobin compared with 2% found dissolved in the plasma (water-based) portion of the blood.*
4. **“Is there such a thing as artificial blood?”** *Yes, there are a number of artificial bloods that have been developed but are still not 100% reliable. You can read more about these blood substitutes in another ChemMatters issue for April, 1998, p.13 and at this reference, <http://www.scientificamerican.com/article.cfm?id=blood-substitutes-hemoglobin-anemia>. Also check “Websites for Additional Information, More sites on artificial blood”, below.*

References

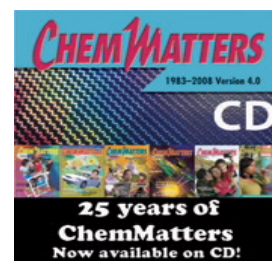
The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site:

<http://www.acs.org/chemmatters>. (Click on the *ChemMatters* CD image at the right of the online screen.)

Selected articles and the complete set of Teacher’s Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher’s Guides are available on the 25-year CD for all past issues, up to 2008.)

(<http://www.acs.org/chemmatters>)

Goldfarb, Brian. Synthetic Blood: Supply from a Different Vein. *ChemMatters*. April, 1998. pp. 13-15. This article is a complete and readable article for students on artificial blood.



This article focuses on the use of this artificial blood for people who may have difficulty breathing and is used as a stopgap measure. It has also been used with premature babies to increase oxygen levels in the blood. There is also a teacher's guide that accompanies the article and elaborates on the chemistry behind hemoglobin's role in carrying oxygen.

Meadow, Robin. Saint's Blood. *ChemMatters*. February, 1993. pp. 12-15. Here is another interesting article in *ChemMatters* that concerns a religious relic alleged to be the blood of Saint Januarius. Investigations by some Italian chemists suggest that the "blood" is really a special gel that can turn to liquid when gently mixed. This special concoction is called a thixotropic gel which students can make, using the recipe found in the article, along with the chemistry behind the properties of this gel.

Web Sites for Additional Information

More sites on the history of blood

The following reference provides a lot of detail on the history of the ideas behind blood using a detailed timeline under which one can find more information about any one era. Important concepts behind blood, be it myth, scientific discovery, war, or AIDS, are substantively described here: <http://www.pbs.org/wnet/redgold/history/index.html>.

More sites on blood and topics biological

<http://www.daviddarling.info/encyclopedia/B/blood.html> This website is a science encyclopedia with emphasis on the biological. One can find various topics using the alphabet tool bar.

<http://www.sciam.com/article.cfm?id=000B4130-5C6C-1DF7-9733809EC588EEDF&page=2> This reference in *Scientific American* makes a good read for students who are interested in seeing the connections between basic biochemistry and specialized applications of biochemistry for treating medical conditions. The specifics involve the use of certain organic compounds, particularly porphyrins, that are altered by exposure to light, subsequently creating toxic products that might be useful in treating cancer, as an example. It is related to the reference on the condition known as porphyria.

Another article about the basics of blood, including antigens, blood type, blood detection in forensics (including some chemistry about the detection reactions) is found in another *ChemMatters* article, February 2008; p. 4. The reference to **past issues of ChemMatters** can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site: <http://www.acs.org/chemmatters>. Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)

More sites on defective hemoglobin conditions

<http://www.sciam.com/article.cfm?id=what-is-thalassemia> This website discusses another genetic disease involving defective hemoglobin synthesis called Thalassemia or Mediterranean anemia (compare with Porphyria). Included in the article is a good “color-coded” picture of normal hemoglobin’s structure (alpha and beta chain positions).

More sites on artificial blood

A useful article about the present state of artificial blood is found at <http://www.scientificamerican.com/article.cfm?id=blood-substitutes-hemoglobin-anemia>.

Another web site on synthetic blood from WNET, a 50-minute video from Wired Science, can be viewed at http://www.pbs.org/kcet/wiredscience/story/65-beyond_blood.html

Anesthesia: Chemistry in the Operating Room

Background Information

More on anesthesia

For a more detailed article on the workings of anesthetics, go to a previous *ChemMatters* article, “You’re Getting Sleepy” by Claudia Vanderborght, published in February, 2004; pp. 4-6. There is also useful information in the Teacher’s Guide that accompanies that issue. Back issues of *ChemMatters* and Teacher Guides can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site: <http://www.acs.org/chemmatters>. Selected articles and the complete set of Teacher’s Guides for all issues from the past five years are also available free online at this same site. (Full articles and Teacher’s Guides are available on the 25-year CD for all past issues, up to 2008.)

More on the nervous system

As anesthesia affects the nervous system, either through localized or systemic application, it is worth looking at the basic components of that system, specifically the nerve cells or neurons where one would expect the anesthesia molecules to act. The neurons themselves are very interesting and dynamic chemical systems associated with the propagation of nerve impulses.

Neurons have many of the intracellular structures associated with all other animal cells—a nucleus, cell membrane, cytoplasm, and mitochondria, among other things. In addition, they have what are known as cytoplasmic vesicles that play an important role in transmission of a nerve impulse from one neuron to the next. Their specific functioning will be outlined later. But the most distinguishing feature of the neuron cell compared with other cells is the chemical changes that take place when a nerve impulse is being generated.

Specifically, a so-called “resting” neuron has a concentration of potassium ions that exceeds that of the surrounding extracellular fluid. The cell maintains this concentration against the tendency of the potassium to flow out of the cell (efflux) following a natural concentration gradient. In addition, there are protein macromolecules that are negatively charged but in concentrations greater than potassium, giving a net negative charge to the cell. So we have what is termed a polarized cell. Should the cell come under the influence of a nerve impulse from an adjacent nerve cell, it undergoes rapid chemical changes in which the cell membrane becomes permeable (special channels open) to potassium ions that follow the concentration gradient, flowing out of the cell into the surrounding intercellular fluid. At the same time sodium ions from the intercellular fluid flow into the neuron (influx) in large enough amounts to make the cell positive which is referred to as depolarization. Again the cell membrane changes its molecular structure to be more permeable to sodium ions which are at higher concentrations on the outside than on the inside of the cell.

This change in the flow of the sodium and potassium ions and the resulting depolarization of the cell is associated with a nerve impulse. Now, with the excess of sodium ions and a deficiency of potassium ions inside the cell with a resultant positive polarity of the

cell, the cell immediately begins restoring the previous concentration of potassium and sodium ions inside the cell by actively “pumping” the appropriate ions into and out of the cell, restoring the original negative polarity of the cell—the resting state. The impulse continues down the neuron’s elongated body as a series of localized depolarizations with the efflux/influx of potassium/sodium ions as described. When the impulse reaches the end of the neuron (called the bouton or boot), other changes take place that are required for an impulse to “jump” a physical gap (synapse) that exists between neurons. A good illustration of these changes with partial animation can be found at http://www.bris.ac.uk/synaptic/public/basics_ch1_2.html and with a video at <http://www.youtube.com/watch?v=SCasruJT-DU&feature=related>.

For an impulse to go across the synapse between neurons, various chemical changes take place. In actuality, an impulse does not cross the synapse. Rather, specialized chemicals called neuroregulators will diffuse across the synapse. First, sacs called vesicles within the neuron become attached to the cell membrane at the end of the neuron when the nerve impulse causes release of calcium ions within the cytoplasm. These vesicles, now attached to the neuron’s cell membrane at the synapse, release specific chemicals called neuroregulators that diffuse across the synapse to the next neuron’s “bouton” (boot). These neuroregulators are important for two reasons. First, they provide one way direction for an impulse—neurons cannot distinguish direction of nerve impulse flow. Second, the use of these chemical regulators prevents a “blur” of impulses coming from different neurons to any one “receiver” neuron. The chemical regulators are very specific in terms of source and reception. (See a video of the physical-chemical action at the synapse at <http://www.youtube.com/watch?v=HXx9qlJetSU&feature=related>.)

With the neuroregulators diffusing across the synapse and into the receiver neuron, depolarization is initiated with the generation of another localized impulse that continues down the neuron to the next synapse. (<http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/S/Synapses.html>)

An animation of neurotransmission can be found at <http://www.brainexplorer.org/anim/anim1.html>.

More on neuroregulators

The two most important neuroregulators are norepinephrine and acetylcholine. There are also three other chemicals that help to regulate the transmission of nerve impulses. They are serotonin, dopamine, and gamma amino butyric acid (known as GABA). These three chemicals are known as neuromodulators and have a variety of functions. GABA has been implicated in recent years with changes in the neurons to produce the anesthetic effects of various drugs by changing the permeability of the neuron for an influx of chloride ions, which in turn makes the cell more negative, remaining in the resting state (depolarized).

Serotonin and dopamine are both associated with certain mental and physical conditions when not available in sufficient amounts in specific locations of the brain. Deficient amounts of serotonin produce a depressed mental state. Deficient concentrations of dopamine are associated with the condition of Parkinson’s. Dopamine cannot pass across the blood-brain barrier if administered into the blood stream for treating the deficient state. Knowing the molecular structure of dopamine has allowed chemists to design a molecule called DOPA that is similar to dopamine but is able to pass across the blood-brain barrier. (<http://www.o2demand.com/bloodbrainbarrier> ;

http://www.elp.manchester.ac.uk/pub_projects/2002/MNQJ9PP2/Webpages/bloodbrainbarrier.htm)

After passing into the brain, this analogue of dopamine is converted to dopamine through the removal of a carbon dioxide molecule. Although DOPA relieves some of the symptoms of Parkinson's, it does not cure the problem.

Other drugs have been developed to deal with a variety of mental conditions that are associated with incorrect levels of dopamine in the brain. They include a variety of psychiatric conditions, certain addictions including nicotine, as well as attention deficit disorders (ADHD). Recreational drugs such as methamphetamines increase dopamine levels. The same drug can be used to control excessive eating by decreasing one's appetite.

A chart summarizing the various neurotransmitters and additional details about neurotransmission and associated chemicals can be found at <http://themedicalbiochemistrypage.org/nerves.html>.

More on the neuromodulator, GABA

The neuromodulator GABA (gamma amino butyric acid) is thought to be involved with producing anesthetic effects when anesthesia reaches the nerve cells of a patient. GABA is labeled a neuromodulator rather than a neuroregulator because it is thought to, quite literally, moderate the extent of depolarization of neurons rather than initiating the depolarization as do the neuroregulators, norepinephrine and acetylcholine. Normally, GABA is released by a nerve impulse at the boutons of a pre-synaptic junction. The GABA molecules diffuse across the synaptic space and into the post-synaptic bouton. There are special channels and receptors for the GABA molecules.

It is thought that GABA interacts with anesthesia molecules at the synapse of two neurons, causing the cell membrane to release more chloride ions (negative) into the postsynaptic neuron, countering the effect of the influx of positive sodium ions normally associated with depolarization and a neural impulse. This change to a negative interior of the neuron keeps the neuron in the resting state. There are special channels that are associated with the inflow of GABA, called GABA receptors. It is thought that anesthetics bind to these special channels. When they do so, they prolong the channel openings that admit more than the normal amount of chloride ions, leading to the prolonged negative polarization of the neuron and no impulse generation in the post-synaptic neuron. You can find an article describing the process at <http://www.general-anaesthesia.com/misc/anesthesia.html>. (The actual article appears in the June, 2007 issue of *Scientific American*, pp. 54-61.) More detailed biochemistry on GABA can be found at <http://www.benbest.com/science/anatmind/anatmd10.html#gaba>.

More on neurohormones

Neurohormones are hormones produced in neurosecretory cells such as those of the hypothalamus (located in the brain) and released into the bloodstream, the cerebrospinal fluid, or intercellular spaces of the nervous system. There are three groups of neurohormones; one group includes the endorphins and enkephalins. They circulate in the blood and bind to the so-called opioid receptors in the brain (endorphins) or in the spinal cord (enkephalins). Their general modus operandi is to modify the way in which neurons respond to nerve transmitters such as norepinephrine and acetylcholine, thereby reducing the sensation of pain.

More on acupuncture

Acupuncture has been used in the Chinese culture for centuries to relieve pain associated with a variety of medical situations including childbirth. When it was revealed to the American public in mid-20th century, it was not allowed by government regulatory agencies because there were no scientific studies done, even though American medical personnel traveled to China to witness the application of the technique. But it was used surreptitiously by patients and self-appointed healers, mostly of Oriental descent, in the USA.

In 1999, clinical researchers reported that inserting acupuncture needles into specific body points triggers the production of endorphins. In another study, higher levels of endorphins were found in cerebrospinal fluid after patients underwent acupuncture. In addition, naloxone appeared to block acupuncture's pain-relieving effects. It is known that naloxone blocks the action of endorphins by blocking the same receptors in the brain for opioids such as morphine. This seemed to give an explanation for the manner by which acupuncture reduced or blocked the sensation of pain and gave credibility to the technique that is now available to patients from certified practitioners of the "art".

More on endorphins

Four types of endorphins are created in the human body. They are named *alpha* (α), *beta* (β), *gamma* (γ) and *sigma* (σ) endorphins. The four types have different numbers and types of amino acids in their molecules; they have between 16 and 31 amino acids in each molecule. <http://www.encyclopedia.com/topic/endorphins.aspx>

Beta-endorphins (β -endorphins) are the most powerful endorphins in the body. They are usually found in the hypothalamus and pituitary gland. Beta-endorphin is released into the blood (from the pituitary gland) and into the spinal cord and brain from hypothalamic neurons. The beta-endorphin that is released into the blood cannot enter the brain in large quantities because of the blood-brain barrier. More endorphins are released in the pituitary gland during times of pain or stress. Exercise increases the endorphin release too. For the same reason, exercise results in a better mood. It is also thought that consumption of chocolate stimulates the release of endorphins, contributing to a "good" mood (heightened awareness). (<http://simple.wikipedia.org/wiki/Endorphin>)

Individuals respond differently to pain based on genetic differences in the opioid receptors for both endorphins and opiates such as morphine and codeine. Recent studies have verified this genetic difference in the structure of these receptors. (See <http://www.scientificamerican.com/article.cfm?id=personal-pain>.)

Connections to Chemistry Concepts

1. **Organic chemistry**—Ethers are organic compounds which are most useful as the basis for anesthetic-type molecules. But they are flammable or explosive without the addition of some halogen atoms to prevent the creation of peroxides when an ether is exposed to oxygen for prolonged periods of time.
2. **Halogens**—Members of this chemical family can be added to ether molecules (replace hydrogen atoms) to prevent the formation of peroxides that are unstable, therefore explosive upon exposure to flame or electric spark.

3. **Solubility**—The extent of solubility of different types of anesthesia determines whether they are used to induce anesthesia or to maintain that medicated state. If the molecule is more soluble, it is used to induce anesthesia; lower solubility means the molecule would be used to maintain anesthesia. Lower solubility of the anesthetic molecule means it will leave the blood system sooner which means quicker recovery from the anesthetic effects.
4. **Ions**—Their presence in the nervous system creates electrical potentials through the gain and loss of both anions and cations that in turn promotes electrical discharge between nerve cells (neurons).

Possible Student Misconceptions

1. **“I pity the poor people who needed surgery before the mid-1800s—they had no anesthetics.”**—OK, part of this statement isn’t a misconception; people who needed surgery prior to the mid-1800s didn’t have a whole of lot of choice regarding anesthetics—there wasn’t much available for them. However, while anesthetics didn’t come into their own until the 1800s, there had been many attempts at finding anesthetics over many centuries preceding the 1800s. Many drugs had been tried and over time for their sedative/anesthetic properties: heroin, marijuana, belladonna, mandrake from the mandragora plant, opium and alcohol, just to name a few. Remains of ancient people show evidence of broken bones that had been realigned and healed, and even some amputees with healed bone ends, indicating surgery had been done successfully. You can read more about this in the Teachers Guide for the February, 2004 issue of ChemMatters, referring to the article, “You’re Getting Sleepy”. See “More on anesthesia”, above, for the details for accessing the article and Teachers Guide.

Demonstrations and Lessons

1. Some general references show how the nervous system (neurons) operates at the cellular level. http://www.bris.ac.uk/synaptic/public/basics_ch1_2.html
<http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/S/Synapses.html>
<http://www.brainexplorer.org/anim/anim1.html>
<http://www.scientificamerican.com/article.cfm?id=lifting-the-anesthesia-fog> (need printed copy of *Scientific American*—URL is for article summary; original article found in the June, 2007 issue, pp. 54-61).
2. Several YouTube videos that show the generation of a nerve impulse and transmission across the synapse include:
<http://www.youtube.com/watch?v=HXx9qIJetSU&feature=related> and
<http://www.youtube.com/watch?v=SCasruJT-DU&feature=related>.

Student Projects

1. Students could research the history of developing anesthesia and what was done to alleviate pain prior to the use of ether and nitrous oxide. <http://www.general-anaesthesia.com/first-anaesthetics.html> (a listing of the 46 “first anesthetics” in the world)
<http://www.wordfocus.com/anesthes-wrd-hist.html>
<http://www.dent.ucla.edu/pic/members/carranza/anesthesia.html> and <http://www.general-anaesthesia.com/seishuhanaoka.html> (a series of references to the work of the 18th C Japanese pioneer in analgesics and anesthesia, Seishu Hanaoka)

2. Could hallucinogens, used in various “native” cultures, be effective as analgesics? What are these hallucinogens?
3. What are endorphins that increase in the body under stressful situations, relieving or modifying the effects of pain? What analogues exist that imitate the endorphin effects?
4. Students could research the topics of endorphins and enkephalins as neuromodulators; what stimulates their production in the body? (Chocolate and strenuous exercise such as running are some of the known stimulants.)
5. There is much history and interesting medical usages of various opiate-based analgesics such as straight opium, morphine, and heroin. What are the differences? What are the similarities and relationships between these three substances? What is the chemistry behind their production? How do they compare with marijuana in the effects that they produce?
6. Research the cultural (Chinese) history behind acupuncture and the very recent incorporation of the practice into American medicine.

Anticipating Student Questions

1. **“What is the difference between an analgesic and an anesthetic?”** *An analgesic is a substance that relieves or lowers the level of a pain sensation, generally while conscious. An anesthetic is a substance that produces a loss of sensation (such as pain) in a specific area of the body or causes a loss of consciousness.*
2. **“Is a runner’s ‘high’ due to excess sugar in the blood?”** *There is good evidence that a runner’s “high” is produced by increased levels of endorphins that are produced naturally by the body under stressful conditions including excess pain from a bodily wound. This euphoric-type of “high” can also be produced by consumption of chocolate and possibly caffeine.)*

References

An extensive reference on all topics related to anesthesia including history, investigators, known anesthetics and their actions can be found at <http://www.general-anaesthesia.com/refs/index.html>.

Since anesthesia is used to prevent pain, another aspect of the pain issue is controlling chronic pain of conscious individuals not undergoing surgery. New studies identify a source of pain for bodily injuries involving glial cells that are associated with neurons and accentuate the pain sensation. Rather than use the standard pain killers that work on the brain (at opioid-binding sites for things like morphine and endorphins), new research suggests using chemicals that interfere with glial cell activity. A reference that clearly illustrates the function of both neurons and the supporting glial cells as well as the relationship between glial cells and tissue pain is found in *Scientific American*, November 2009; “New Culprits in Chronic Pain”, R. Douglas Fields, pp 50-57.

Web Sites for Additional Information

More sites on mechanisms of anesthetic action

Fluorescent tags on anesthetic molecules are used to identify what regions of the brain take up the anesthetic and what cells are affected.

(<http://www.sciencedaily.com/releases/2009/04/090403181505.htm>)

Another interesting idea on the mechanism of action of anesthetics concerns the swelling of brain proteins by the anesthetic. A simple experiment using myristic acid (a fatty acid common in many foods) in gold fish seems to confirm the basic idea that anesthetic effects are due to expansion of brain protein molecules. The experimental description can be found at <http://www.scientificamerican.com/article.cfm?id=explaining-general-anesth>.

More sites on specific anesthetic molecules

Chloroform, its history and chemistry can be found at <http://www.general-anaesthesia.com/images/chloroform.htm>.

The specifics on the action of desflurane are found at <http://www.general-anaesthesia.com/desflurane.html> and <http://en.wikipedia.org/wiki/Desflurane>.

The specifics on the action of Isoflurane are found at <http://www.general-anaesthesia.com/isoflurane.html> and <http://metrohealthanesthesia.com/edu/inhalational/isoflurane1.htm>.

The specifics on the action of Propofol are found at <http://www.general-anaesthesia.com/propofol.html>.

The specifics on the anesthetic Sevoflurane are found at <http://en.wikipedia.org/wiki/Desflurane>

More sites on history of anesthesia

A detailed description of Horace Wells' use of nitrous oxide anesthesia along with related incidents, individuals, footnotes and references can be found at <http://www.dent.ucla.edu/pic/members/carranza/anesthesia.html>.

Another very comprehensive list of references on the history of anesthesia can be found at <http://www.general-anaesthesia.com/anaesthesia.html>.

In addition, there are some specific references about the use of anesthesia in 18th C. Japan at <http://www.general-anaesthesia.com/seishu-hanaoka.html>.

More sites on modern anesthesiology

An article on the present-day practice of administering anesthesia and related issues, "Anesthesia Without a Knockout Punch " in the 27 July 2004 issue of the *New York Times*, Is found at <http://www.general-anaesthesia.com/misc/anesthesia.html>. It includes issues surrounding errors and the safeguards needed when applying an anesthetic. It reports on the decrease in application of general anesthesia in favor of local and regional anesthesia

applications. It should not be read by anybody about to undergo surgery! There are additional references attached to the article.

Battling Wildfires: When Water Won't Cut It

Background Information

More on surfactants

Surfactants (from the combination of terms, **surface**, **active** and **agent**) are chemicals, usually organic, that are large enough in size to have both hydrophilic and hydrophobic properties, hence amphiphilic. Their general function is to reduce the surface tension of a liquid such as water by forming an interface between water and some other chemical that would normally have very limited solubility, such as an oil. The surfactant's hydrophilic and hydrophobic ends (of the molecule) provide a "bridge" connecting the water (hydrophilic end) with the oil (hydrophobic end). (Visuals or diagrams of this action at the molecular level can be found at <http://www.cem.msu.edu/~reusch/VirtualText/lipids.htm#soap>. This results in a lowering of the surface tension of the water, meaning the strong hydrogen bonds between polar water molecules are interrupted by the surfactant, allowing oil molecules to get in between water molecules. As mentioned in the CM article, surfactants are used in fire-retardant foams to dissolve a water insoluble chemical in water that in turn reduces what one could call "clumping" of the water, producing a spray-like (thin) condition with the water more spread out over forest vegetation that is to be protected from fire.

Surfactants are also commonly used in detergents, which means that the bodily oils found in soiled clothing will be able to dissolve in the large volume of water used in the washing cycle. (See the *ChemMatters* article, "Detergents", April, 1985, pp. 4-7). The surfactants used in detergents are classified according to the "active" part of the molecule. There are *anionics*, *cationics*, and *nonionics*. Obviously anionics have a negative end to the part of the surfactant molecule that interacts with the polar water. A cationic has a positive end and nonionics have neither positive nor negative end. All have a large (long) non-polar hydrocarbon chain that would interact with the non-polar oil molecules. But the nonionics that are without a charged end to their molecule rely on the many oxygen atoms *within* the molecule that have slight negative charges.

Surfactants are used in a whole host of applications. One important non-detergent application is for treating paper that is being recycled. In the recycling process, surfactants are utilized to help remove inks (that are usually oil-based) from the paper that is to be recycled. The reverse is to add to paper in its manufacturing stages something called sizing, a starch or gelatin-based material that, like a surfactant, has hydrophobic and hydrophilic ends. The purpose of this paper coating is to make the cellulose surface resistant (hydrophobic) to water so that inks do not spread into or across the paper surface (bleeding). Some inks contain solvents that evaporate rapidly.

A listing of applications and sources of surfactants can be found at http://en.wikipedia.org/wiki/Wetting_Agents. In addition, a reference on how detergents work can be found at <http://chemistry.about.com/od/howthingswork/f/detergentfaq.htm>.

More on Surface Tension of Water

In nature, there are two interesting situations that depend either on the use of the very strong surface tension of water or the breaking of this surface tension. The movement of water from soil into a plant and to the interior of the plant's photosynthesizing cells depends on the strong hydrogen bonds between polar water molecules. This strong intermolecular bonding creates an unbroken chain of water molecules in the water-transporting tubules of the plant. In the case of trees, for example, we are talking about moving water from the soil to the top of the tree. These chains of water molecules are unbroken in the process of being "pulled" to the leaves' interior from the soil surrounding the plant's roots. The pull involves the evaporative process taking place inside a leaf and is known as transpiration. Students can easily see the effect of this strong surface tension by trying to separate two glass slides with a small drop of water uniformly spread between the glass surfaces. (<http://hyperphysics.phy-astr.gsu.edu/hbase/surten.html> and http://en.wikipedia.org/wiki/Surface_tension)

In comparison, such a strong surface tension of water is potentially detrimental to the physical process of breathing. Within the lungs, at the level of the microscopic breathing sacs called alveoli, inflation of these sacs is obviously dependent on being able to stretch their elastic surface. But these alveoli are surrounded by water-based solutions. The surface tension of the water would normally prevent the inflation of the alveoli. But our bodies produce a detergent that once again breaks the water's surface tension on the alveoli, allowing them to stretch. Without this detergent, breathing would not be possible. Some children are born without enough of this detergent and risk death (known as Infant Respiratory Distress Syndrome; see http://en.wikipedia.org/wiki/Infant_respiratory_distress_syndrome). To prevent this condition in premature babies, the mother is given special hormones called glucocorticoids to speed up the production of the detergent in the fetus.

More on fire-fighting foams

Without question, the most familiar chemical used to extinguish fires is plain water. Its high heat capacity lowers the temperature of the fire and in so doing, removes one of the "fire triangle" requirements for combustion—temperature. Heat released from the fire might also evaporate some of the water, which has a beneficial effect in firefighting. The resulting steam dilutes the available oxygen needed for combustion and so slows the fire's spread.

As long ago as the 1800's, foams were used to fight fires, in addition to water. These early foams were chemical foams, a mixture of water and carbon dioxide bubbles. Modern fire-fighting foam is just a mixture of water with other chemicals to produce what can be considered a colloidal dispersion of a gas phase in a liquid phase. In modern foams the bubbles are air rather than CO₂, and other chemicals, like the surfactants the article describes, are added to stabilize the foam, making it last longer. (See "More on Surfactants")

Modern-day foams are called mechanical foams because they are produced by mixing a solid or liquid foaming agent with water and then aerating the mixture to produce the foam. The foaming agent may be sprayed directly into the air or forced through an aerating tube. The resulting blanket of bubbles—the foam—extinguishes the fire.

How do fire-fighting foams improve water's ability to extinguish fires? Water, which makes up 99% of most foams, lowers the temperature of the fuel below its ignition temperature.

Foams penetrate flames and spread over them, blocking access to oxygen. In Class B fires, the layer of bubbles prevents the fuel vapors from escaping into the air and re-igniting. Inevitably some of the water in the foam is vaporized, creating steam, a process which is endothermic and which also displaces air above the fire and restricts oxygen availability. Foams typically act over a longer period of time than plain water.

As the article states, there are two types of foams used to fight fires—Class A foams and Class B foams. These designations are related to the type of fire they are used to extinguish. The four general classes of fires are:

- Class A — ordinary combustible materials such as wood, paper, cloth, trash, etc.
- Class B — flammable liquids such as gasoline, acetone, kerosene, etc.
- Class C — electrical fires from transformers, live wires, etc.
- Class D — combustible metals.

Foams, however, are recommended only for Type A and Type B fires.

Class A Foams are primarily water with surfactants and rust inhibitors added. Class B foams come in several forms, depending on whether the foaming agent is protein-based or synthetic. Protein foams use natural proteins as foaming agents. One of the earliest of these was developed from soy protein by Percy Lavon Julian in the early 1940's. For more on Julian, see <http://www.chemheritage.org/scialive/julian/history/7.html>.

Protein-based foams include fluoroprotein foam (FP), film-forming fluoroprotein (FFFP), and alcohol-resistant film-forming fluoroprotein (AR-FFFP). Synthetic foams include aqueous film-forming foams (AFFF) and alcohol-resistant aqueous film forming protein (AR-AFFF). Compounds like sodium alkyl sulfate or any number of fluorine-containing compounds are synthetic surfactants. Surfactants lower the surface tension of water and allow it to spread and penetrate more easily. For more information on the various types of foams see this site produced by Kidde, one of the leading foam manufacturers: <http://www.kidde-fire.com/utcfs/Templates/Pages/Template-50/0,8061,pageId%3D3497%26siteId%3D465,00.html>

The article says that there is a new generation of environmentally friendly foams used for fighting fires. For an extensive summary of the environmental concerns about fire-fighting foams, see http://www.haifire.com/publications/Environmental_Impacts_of_Firefighting_Foams.pdf.

More on gels

Gels are “the new kid on the block” when it comes to fire fighting agents. Firefighting history has it that a Florida veteran firefighter, John Bartlett, observed that a disposable baby diaper had not burned up in a trash fire and applied the polymer gel used in disposable diapers to fire fighting.

The gel in question here is potassium polyacrylate, also known as a “superabsorber” because it can absorb hundreds of times its own weight in water. The water molecules are trapped within the coils of the long chains of polymer macromolecules, as explained in the article. It is this water trapped inside the structure of the polymer that makes these gels so successful as firefighting tools.

When water only is used on a fire, as soon as the water hits the trees and shrubs in the fire, the heat of the fire causes the water to rapidly evaporate (or even boil) away, so that is no

longer present to protect the trees and shrubs in the wildfire. But when fire-blocking gels are used, they stick to the plants in the fire and, since there is much more water present in these macromolecules and because it is trapped inside the polymer structure, it takes much longer for this water to evaporate away. While the gel remains coating objects, it continues to absorb the heat of the fire, thereby reducing the devastating effects of the blaze on the remaining plants.

Gels provide more long-lasting protection from fire than water, certainly, but they also last longer than foams firefighting agents. That's because foams consist of air bubbles in a matrix of water and surfactant. When the water evaporates (from the heat of the fire) in a foam, the bubbles burst and the foams collapse and the protection ceases. But when the water in gels evaporates, there are still more layers of water within the polymer molecules to evaporate. When most of the water evaporates, the gels eventually collapse and fire protection from the gels ceases, just like for the foams. It just takes a lot longer for that to happen with gels.

In addition to being used in forest fires, gels are now being used in "normal" fires, like house and industrial fires. These gels' adhesion properties allow them to stick when applied to homes, so that houses and other buildings in the path of an oncoming forest fire can be coated with the gel. As long as the gel sticks to the building, it continues to protect the house from flames and embers from the fire. Many homes have been spared the ravages of fire through the use of these gels. And after the fire has passed, the gel can be washed off the buildings with water and a hose. The material is biodegradable and non-toxic as well.

In this use, the gel is used as an indirect method of attacking the fire—prevention and protection, and in this method it can also be applied to landscape surrounding buildings as an indirect way of attacking a fire—preventing it from ever getting to the buildings themselves.

Bartlett has established a company that produces Barricade® fire-blocking gel for commercial use. The company produces kits for home use as well as commercial applications. The website, <http://www.firegel.com/pages/Home>, has a number of television news broadcasts (including ABC World News Tonight with Peter Jennings) reporting on the product and showing how it works. The site also has numerous testimonials from homeowners whose homes had been saved from destruction by fire through the use of Barricade®.

Other fire-blocking gel products include Wildfire AFG Firewall®, Thermo-Gel®, and PHOS-CHeK AquaGel-K® Fire Suppressant Gel. The PHOS-CHeK AquaGel-K® Fire Suppressant Gel is sold as a dry powder. It must be mixed with water (0.1 to 1.2% gel by weight). The other four are all sold as liquid concentrates that must be mixed with water via the adapter and hose. All four gels are rated by the USDA Forest Service as approved "water enhancers". (http://www.fs.fed.us/rm/fire/documents/gpl_we.pdf) All the gels are also advertised as being very slippery when wet (hazardous), especially when they are being washed off buildings after use.

More on indirect attack of wildfires (flame retardants)

In the (really) old days of wildfire-fighting, forest rangers used to just dig long shallow trenches through a wooded area threatened by wildfire, and clear underbrush from either side of the trenches, in the hopes of creating a fire-break, a vegetation-free line across which the forest fire couldn't travel. Unfortunately, they rarely worked because, even though the flames themselves might not be able to get across the divide on the ground due to a lack of fuel (no plants), burning branches falling from burning trees could cross the barrier. Also, burning

embers carried by the hot winds could get to the other side and begin the burn on the “protected” side. More was needed.

In the 1950s, as the article states, the US Forest Service worked to produce chemical fire retardants. The sodium calcium borate described in the article was the first of these chemicals. It was successful at extinguishing wildfires, as evidenced by its widespread (if short-lived) use in the early '50s. But the drawbacks became clear—re-growth of old trees and new forest growth after use of the retardant on wildfires didn't happen. More was needed (with an ecological bent).

Enter the ammonium phosphate fire retardants in the 1960s. These had the benefit of longevity—they work even after drying out, so they continued working after the immediate threat was over. But they have the added, crucial advantage of having minimal aftereffects.

Typical flame retardant chemicals work on several fronts. These include:

- They promote char formation on the plant (carbon in the form of graphite, which does not burn easily)
- They convert volatile gases from the burning fuel to non-ignitable gases
- They form a glaze barrier at the surface of the plant
- They form an intumescent (swells with heat) foam barrier at the surface
- They terminate free radicals in the gas phase, stifling the combustion reaction

The approved list of long-term retardants approved by the USDA Forest Service can be found at http://www.fs.fed.us/rm/fire/documents/gpl_r_r.pdf.

Having said that long-term retardants are ecologically benign, that may not be the whole story (it rarely is). Researchers from the Institute of Chemical Technology in Prague, Czech Republic, have reported that historical buildings that had been treated with ammonium phosphate and ammonium sulfate fire retardants are showing signs of roof timber deterioration. This occurred after repeated applications of the chemicals. Attempts at neutralizing the effects have worked, but the treatments need to be repeated to maintain proper pH of the wood. (Of course, this is not a typical wildfire situation, wherein the wood being treated is the entire forest.)

Connections to Chemistry Concepts

1. **Combustion**—The fire or combustion triangle provides an entry point for discussion of the role of oxygen in combustion reactions, what makes up a fuel, and how heat completes the triangle.
2. **Kinetic-molecular theory**—Examples of KMT abound throughout the article (and demonstrations, lessons and projects in the Teachers Guide); heat being absorbed by the water, foams and gels used to extinguish fires (and paper cup not burning due to water molecules absorbing heat from burner).
3. **Latent heat of vaporization**—Heat is absorbed by water as it evaporates/boils off plants in a forest fire, thus reducing the temperature of the plant surface (hopefully protecting the plant itself from burning).
4. **Foams and gels**—To battle flames directly, firefighters use mostly solutions that contain foams and gels. The foams are made of water, air bubbles, and chemicals called surfactants that allow the foam to spread. Gels are jelly-like materials made of polymers arranged like a honeycomb in water. Gels are essentially thickened water, and their consistency varies between that of cream and Jell-O.

5. **Polarity**—Water is a classic example of a polar molecule that is produced through a combination of bonding angles and the elements' electronegativities. In turn, the intermolecular bonds between water molecules are strong enough to keep these relatively low-weight molecules in the liquid rather than the gaseous state—which is a good thing for life on earth!
6. **Surface tension**—The surfactants used in foams rely on their ability to reduce the surface tension of water. Of special interest are the details of what causes water to have such a high surface tension (hydrogen bonding) and what can be done to reduce the effects of the high surface tension.
7. **Hydrophilic, hydrophobic, amphiphilic**—Some large organic molecules have both polar ends (hydrophilic) and non-polar ends (hydrophobic). [Both hydrophilic and hydrophobic—amphiphilic] Detergents and surfactants having this kind of structure can be used when combining two chemicals that are not normally miscible such as oil and water or fire retardant chemicals used in foams and gels.
8. **Surfactants**—These molecules with both polar and non-polar characteristics are also called wetting agents because they can reduce the interfacial tension between water and some other chemical not miscible in water, such as an oil or between water and certain types of soil components.
9. **Esters**—These compounds are formed from an alcohol and an organic acid. These esters are also formed when plant materials, covered with fire retardant, are exposed to the heat of a forest fire. The phosphoric acid present in the retardant reacts with the cellulose of the plant, to form a phosphate ester. The ester in turn decomposes to form water that, along with ammonia, formed separately, cools the fire around the plant.
10. **Polymer properties**—The sodium polyacrylate superabsorbers used in the firefighting gels are similar to the polymers used in a variety of popular demos which demonstrate the water absorbing capability of the polymers. The polymers are used in diapers as well as in plant hydrating agents.
11. **Chemical nomenclature**—Sodium calcium borate, monoammonium phosphate, diammonium phosphate, phosphoric acid, organic esters, phosphate esters are among the chemicals used in fire fighting agents. The names used may not be the IUPAC names, e.g. what the article calls monoammonium phosphate should be named monoammonium dihydrogen phosphate and what was called diammonium phosphate should be named diammonium monohydrogen phosphate.

Possible Student Misconceptions

1. **“Fighting fires all involve the same techniques. The difference lies in the scale of the fire.”** *Each fire has unique characteristics which must be accounted for in fighting the fire. The article describes direct and indirect methods of fighting fires. Each method employs a variety of chemical solutions.*
2. **“Only water is used in fighting forest fires.”** *From a distance, the liquids seen dropping from airplanes or helicopters, or that being used by firefighters on the ground may be assumed to be water flown in or carried in to fight the fire. In fact, the liquid probably is not pure water, but a variety of chemical solutions/suspensions that more effectively fight the fire.*
3. **“Lightning is the principal cause of most forest fires.”** *Actually, lightning causes few (~12%) of the forest fires in the US, except for the Southwest, where 60-70% of forest fires are started by lightning. (Source: “Forest Fire in the American Southwest” at <http://forestfire.nau.edu/lightning.htm>)*

4. **“Molecules are either polar or non-polar—they can’t be both.”** No, if a molecule is large enough (such as an organic molecule), part of one end of the molecule can have polar characteristics and the other end can be non-polar (such as a carbon chain with only hydrogen atoms attached).
5. **“When adding soap to water to create bubbles, it is the soap that forms the bubbles, not the water.”** No, the added soap is probably less than 5% of the volume of the water-soap mixture in the bubble. But the water without soap cannot form bubbles because of the very high surface tension that keeps the water “bunched up” rather than “stretching” over a bubble-forming device. The soap reduces the surface tension of the water by getting in between the water molecules, allowing a film of water and soap to stretch over that bubble-forming device.
6. **“All foams can fight fires.”** There may be some truth to this statement, especially if the foams are water-based, but NOT all foams are designed to fight fires. There’s a difference.
7. **“All gels can fight fires.”** See #4 above. In addition, one of the Demonstrations & Lessons items [#2] describes how to make a Sterno®-like gel, and that surely won’t put out fires!

Demonstrations and Lessons

1. Bottoms Up Fire Fighting—Have the **students read the following article** that appeared in People Weekly, on July 26, 1999. (<http://www.firegel.com/pages/news#6>, Click on “Hot Stuff”). After reading the article, have the **students explain the chemistry** that allowed the diaper to survive the dumpster fire. What are some of the properties of the material that make it “the best invention since the fire truck? Bartlett’s keen sense of observation allowed him to make the connection between an un-burnt diaper and the development of a tool to revolutionize firefighting—both home fires and wild fires. (Here’s the article, FYI.)

Firefighter John Bartlett picked up a dirty diaper and found a new way to swaddle misbehaving flames. Bartlett says his gel can stanch fires as hot as 2,000 degrees. “The fire goes out and stays out,” says one fire chief.

When a fire roared through their Palm Coast, Florida, neighborhood in June, 1998, Jim and Debby Hodges fled so quickly they had to leave their beloved mutt Elvis behind. But that was before off-duty firefighter John Bartlett, from Jupiter, Florida, sprayed the Hodges’ property with his experimental fire-stopping gel. The next morning, they found not only their house untouched by flames but also Elvis’s doghouse blessedly intact ‘with its hunk-a, hunk-a tail-waggin’ love safe inside, burning only with gratitude. “That gel,” says Jim Hodges, “is the best invention since the fire truck.”

Call it a doggone miracle; call it a revolution in firefighting technology. But be sure to call it the best invention ever to come from a dirty diaper. Because if Bartlett hadn’t picked up the one surviving remnant of a Dumpster fire in 1993, he would never have figured out that the super absorbent material used in diapers also has a phenomenal ability to repel heat. Bartlett turned the substance into a sprayable goo, which Bill Kramer, a former fire chief who teaches fire science at the University of Cincinnati, calls “a quantum leap in firefighting.”

Now Bartlett, 45, and his partner Bruce Hill, 42, are marketing the product they call Barricade to homeowners and fire departments alike. The duo have yet to make money, but the Los Angeles Fire Department and Indianapolis International Airport are using it, and with the Federal Aviation Administration wanting to study its uses on airplanes, the inventors hope their fire-safe formula leads to smokin’ profits. After all, says Bartlett, the married father of one son, “we developed it from the bottom up.”

- Analysis of Ray Bradbury's Novel Fahrenheit 451. A number of your chemistry students may have read Fahrenheit 451 as a reading assignment in an English class. Have students summarize the story and explain the significance of the title. The temperature 451 degrees Fahrenheit is often cited as the kindling temperature of paper—the lowest temperature at which paper will spontaneously catch on fire. This assumption is incorrect. The actual kindling temperature of paper is 450°Celsius or 842°Fahrenheit (Source: Handbook of Physical Testing of Paper, Vol. 2, 2nd .ed., Borch et al. (http://books.google.com/books?id=ga-l8QAOUL8C&pg=PA406&lpg=PA406&dq=flash+point+of+paper&source=web&ots=FjB5FslcKK&sig=Vlr2cc8M2-TWY3qkdWzGUeK-vnM&hl=en&sa=X&oi=book_result&resnum=10&ct=result#v=onepage&q=flash%20point%20of%20paper&f=false). Why did Bradbury choose the number 451 and not 450 and why Fahrenheit and not Celsius? The reference by Dexter listed below discusses the issue. Dexter, Gary (October 2007). *Why Not Catch 21: The Stories Behind the Titles*. Apparently, Bradbury thought Fahrenheit sounded better than Celsius for a book title!
- You can demonstrate **boiling water in a paper cup** to show the ability of water to absorb heat. Visit this site: (https://www.physics.purdue.edu/demos/display_page.php?item=3B-04). This Montana State site shows photos of this demonstration done by heating the cup on the side, rather than on the bottom: http://www.physics.montana.edu/demonstrations/video/4_thermodynamics/demos/boilingwaterinapapercup.html
- A variation on #3, above, is to **heat water in a balloon** partially filled (with water), using an open flame. View the demonstration procedure and video clip at <http://www.cmste.uregina.ca/Quickstarts/unbreakableballoons.html>.

Surface tension

- Demonstrating surface tension can be done in a number of ways. Take two 50-100 mL graduated cylinders and fill each to the top, one with water and the other with ethanol. As you reach the rim of the cylinder, continue to add the liquid using a medicine dropper. It will be apparent that the water will form a convex surface above the rim of the cylinder which will not be true of the alcohol.
- The classic demonstration of surface tension is to carefully **place** a clean **needle** or paper clip **on the surface of water** in a large (500 mL) beaker using clean tweezers. Try this demo with water of different temperatures. Is there any difference? Another approach is to add water, drop by drop (count), to the surface of a clean penny until the water begins to roll off the surface. (Ask students to predict the number first.) Repeat using ethanol. Why the difference in number of drops for each liquid?
- Another demo to show **differences in surface tension between water and alcohol** utilizes two very clean microscope glass slides. Apply a drop of water to one of the two glass slides. Place the second slide on top of the first slide and move around to spread the drop of liquid. Repeat the process with a drop of ethanol on another pair of glass slides. Have a student attempt to separate the two pairs of glass slides, noting the difference in surface tension between the liquid and glass.
- Breaking the surface tension of water can be demonstrated by putting water in a shallow pan. Carefully **cover** the **water surface** with a **very thin layer of lycopodium powder** (see your biology teachers). Touch a **small drop** of liquid **detergent** to the powdered surface and note the movement of the powder as the water's surface tension is "broken". These results can be compared with placing black pepper on the surface instead of the powder. How to interpret the results? (See # 12, below for a variation on the use of lycopodium powder.) Here's a 1-minute video clip of the same phenomenon using ground pepper and water: http://www.metacafe.com/watch/1256649/awesome_pepper_and_soap_trick/.

9. A fun thing to do with surface tension is to cut out the basic shape of a boat (top view) from a 3 x 5 card with a pointed front and a straight back. On the back end, cut out a small rectangular area. Place the flat boat on water in a pan. Add a drop of detergent to the back of the card at the cut-out. Note the action of the boat. Have students explain what is happening. At Questacon Science Squad's web site you can view a unique version of this phenomenon (and finally, a use for that bread tie that we all throw away!) at <http://www.youtube.com/watch?v=5u8ED8d6qb0>.
10. The strong intermolecular bonds between water molecules that are due to the polarity of the water molecules can be demonstrated in an eye-catching fashion by **rubbing** a charge-holding material such as a hard **Bakelite rod**, a plastic ruler **or comb to attract the water stream** coming out of a burette. For comparison, the demo can be repeated using a non-polar liquid such as cyclohexane.
11. The Royal Society of Chemistry (UK), on their web site, "Practical Chemistry", has a list of a **series of experiments/demonstrations** that can be done with chemistry classes on the topic of surface tension. After the procedures, a brief description of what happens is given. View the experiments at <http://www.practicalchemistry.org/experiments/detergents-soaps-and-surface-tension.301.EX.html>.
12. Here's a demonstration that is not in the list from #11 above (but see #8): the "**Powder Glove**" **demonstration**, using lycopodium powder to dip one's hand into water without it getting wet. This site also has a video clip illustrating the process, but it's more impressive done "live". (<http://www.cmste.uregina.ca/Quickstarts/powderglove.html>.)
13. If you want to demonstrate **surface tension in microgravity**, view a NASA astronaut in space doing some "Saturday Morning Science" demonstrations. The first video demonstrates water droplets forming from a film of liquid water in a "2-dimensional beaker" at http://www.youtube.com/watch?v=B8yFxFG_6nIQ&feature=related. The next video shows the same astronaut producing a 5-cm sphere of water forming around a thin wire loop and then he injects a drop of cloudy liquid ("tracer particles") that forms a vortex ring inside the sphere: <http://www.youtube.com/watch?v=qRcE5N2BHmq&feature=related>
14. **Magic Sand®** is based on the principle of hydrophobicity. See a quick video clip at <http://www.youtube.com/watch?v=vIUMj5baNHM>.

Fire-fighting foams

15. Here's a guide to the chemistry of fire fighting, including student activities, from the US Forest Service: <http://www.fs.fed.us/r3/resources/coned/fe-curriculum/hs-chem-72.pdf>.
16. Here's a procedure for **making a fire-fighting foam** in the lab: http://blog.makezine.com/science_room/chemistry/laboratory_182_produce_firefighting/.
17. This demonstration requires a **microwave oven**, but **produces a foam** very nicely: <http://chemistry.about.com/od/demonstrationexperiments/a/soaptrick.htm>.

Fire-suppressant gels

18. On the outside chance that students might think all gels are able to extinguish fires, you can do the "Canned Heat" demonstration using calcium acetate and ethyl alcohol to **make a gel** similar to Sterno®. You can find the *ChemMatters* source in the Reference section below
19. A **complete lesson plan on forest fires** is available at <http://school.discoveryeducation.com/lessonplans/programs/forestfires/> The plan is structured to accommodate students from grades 6-12 and allows the students to understand (1) the benefits and problems associated with fire and (2) the role that fire plays in maintaining healthy ecosystems. Eight activities with procedures are included. Adaptations are available for younger students. Extensions, evaluations, added readings, vocabulary, and links to the National Science Standards are included. An extension on the

“Fire Triangle” connects directly with the article. An additional resource, the film “Understanding Fire,” a Discovery Channel video, could be rented from a local library.

Student Projects

1. Study the properties of the sodium polyacrylate polymers described in the article. Samples of the “snow powder” are available from chemical suppliers. Hobby stores such as Hobby Lobby and Michaels also carry the superabsorbers. Solution concentrations of approximately 1% are described in the article. Prepare solutions of varying concentration. Test the viscosity of the solutions. Test the adherence of the solutions to a flammable surface; e.g., cardboard.
2. Perform a polymer show featuring the superabsorbent polyacrylates. The script and instructions for putting on a polymer show are available at <http://www.princeton.edu/~pccm/outreach/LSCPCCMPolymerShow.pdf> . The show can be used as a model for demonstrating the properties of the superabsorbent polymers used in the firefighting gels. (Note this show might be best for an elementary student audience (but high school students can still perform the demonstrations).
3. The Center for Polymer Studies at Boston University has created a visualization simulation “Forest Fires and Percolation” (<http://polymer.bu.edu/java/java/blaze/blaze.html>). A cluster of trees that reaches from one side of a forest to the other side is said to have percolated. A forest fire burning all the way across such a cluster is also called a percolation. In the simulation, a student grows a “forest” by hand, following a set of rules. Graph paper, pencil, ruler, green and red markers are the only items required. After the forest is generated a second set of rules allows the students to start a fire in the model forest. After the student completes the hand-generated activity, a “Blaze Applet”—a computer simulation game of forest management and fire fighting, is available for further study. In the game the student is responsible for growing and harvesting trees on a plot of land located in a high-risk fire region. The object of the game is to retain the largest number of unburned trees after the fire, thereby attaining the largest income possible from the harvesting of the trees. In case of a forest fire, the student has the capability of dumping water on the fire using a helicopter. At the conclusion of the game, after the fire has burned out, a game score is produced on the lower right of the screen. The score depends on the number of unburned trees and dryness of the forest. The exercise concludes with a set of questions.
4. Study surface tension by performing the demonstration available at <http://www.ilpi.com/genchem/demo/tension/>. The demo involves observing the effect of a drop of liquid detergent on a layer of sulfur powder floating on the surface of water. A QuickTime video is included. A clear explanation of the observed behavior is included.
5. Students can research and report on the various classes of fires, the appropriate type of fire extinguisher to use on those fires, and explain how the extinguishers work on that specific type of fire.
6. Students could investigate the differences in cleaning action of soap versus detergents. First, students need to understand the difference between soap molecules and detergent molecules. A very good reference on this topic is a *ChemMatters* article on “Detergents”, from April 1985, pp. 4-7. See “References” below for information about obtaining a copy. Also see <http://chemistry.about.com/od/cleanerchemistry/a/how-soap-cleans.htm> and <http://www.sdahq.org/sdalatest/html/soapchemistry1.htm>.
7. Related to #1 is a collection of experiments on testing soaps and detergents that can be found in the ACS publication, “The Best of Wonder Science” available from the American

Chemical Society (www.acs.org) or the publisher, Delmar Publishers at www.delmar.com/delmar.html.

8. From the same publication, “The Best of Wonder Science”, is a whole series of experiments on soap and bubbles. Varying the mix of water plus soap or detergent as well as glycol will produce different results. What is the best ratio of soap (or detergent) with glycol? What is glycol? Adding sugar also prolongs the life of bubbles. There are lots of variables and makes for a good project. (See also a video on the behavior of big sheets of bubbles at <http://www.magnet.fsu.edu/education/tutorials/slideshows/bubblewall/index.html>. Also see <http://chemistry.about.com/od/bubbles/a/bubblescience.htm> for the basics behind bubble formation.)
9. Students can research and report on the history of fire fighting agents, particularly as they apply to wildfires.
10. There are several instrumentation satellites in orbit that track forest fires (among many other natural and man-made phenomena) around the world. Students could research and report on these. (ChemMatters has featured these surveillance satellites in several past issues.)

Anticipating Student Questions

1. **“What is the cause of most wildfires?”** Human carelessness causes the majority of cases of wildfires, especially while people handle fireworks and leave camp fires unattended. Smoking and arson are frequent causes. Slash-and-burn farming (clearing land by burning woodlands and vegetation) is a cause of a number of major wildfires. Lightning is not a common cause of wildfires (~12%), despite the popular belief to the contrary. Three to five major wildfires a year are caused by lightning. Lightning associated with severe thunderstorms infrequently results in wildfires. The dry summer lightning is the greater hazard. Volcanic and underground coal fires are even less frequent causes of wildfires.
2. **“What types of airplanes and helicopters are used in fighting wildfires?”** A number of commercial aircraft have been used over the years. Photos of the different type of aircraft are available at http://winjack3.com/borate_bombers.html
3. **“Won’t a wildfire eventually burn itself out?”** A forest fire probably will burn itself out eventually, *but the key word here is “eventually”.* Many thousands of acres of woodland can be burned before a fire dies out.

References

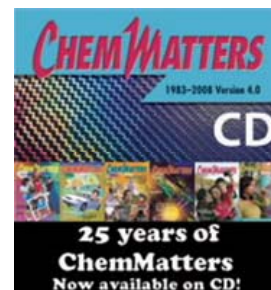
ChemMatters archived articles

The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site:

<http://www.acs.org/chemmatters>. (Click on this *ChemMatters* CD image at the right of the screen.)

Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)

(<http://www.acs.org/chemmatters>)



Becker, Bob. Carbon Dioxide—A Pourable Greenhouse Gas. *ChemMatters*. 19, Special Issue No. 1. September, 2001. pp 10-11. This article is written as an experiment for students to make their own fire extinguisher with baking soda and vinegar. Discussion of the reactions involved are included, as well as extensions for further experiments.

Darrow, Frank. Canned Heat. *Classroom Guide for ChemMatters*. April, 1992. The Teachers Guide for this issue provides a one-page experiment for students to prepare canned heat, a Sterno®-like flammable gel. See Demonstrations and Lessons for the description of its fit in this Teachers Guide.

Lutz, Diana. Hollywood's Special Effects: How Did They Do That? *ChemMatters*. December, 2009. 27:4. pp. 5-8. This article discusses the use of sodium polyacrylate (used in firefighting foams) to make fake snow. The chemistry of the polymer is discussed briefly.

Rimetz, Brendan. The Great Hartford Circus Fire. *ChemMatters*. 23:1. February, 2005. pp 4-7. Although this is not a "wildfire", it was a wild fire! The article discusses the circus fire that occurred in 1944. The fire killed more than 150 people, and injured 700 more. Chemistry solved the puzzle of how and why it happened, but the chemistry of firefighting wasn't advanced enough at the time to prevent/stop it. (The author was a high school junior at the time the article was written.)

Wood, Clair. Detergents. *ChemMatters*. April, 1985. pp. 4-7. This article gives good background on detergents and surfactants.

Wood, Clair. Soap. *ChemMatters*. February, 1985. pp. 4-7. This article gives good background on soap—how it's made and how it works.

Zelaya-Quesada, Myrna. Chemical Foams in the Line of Fire. *ChemMatters*. 19:2. April, 2001. pp 8-9. The article discusses a 450-acre raging forest fire in Los Alamos, NM, in May,

2000, and the foam extinguisher firefighters used to put it out. It discusses the latest in “green” fire extinguishing materials.

Web Sites for Additional Information

More sites on fire, wildfires and firefighting in general

<http://www.ufba.org.nz/downloads/contribute/FirefightingandChemistry.pdf> The pdf files explain why knowledge of chemistry is especially important for firefighters.

T.C. Forensic “Forensic and Scientific Services” provides “Physical Constants for Investigators” on its web site at <http://www.tcforensic.com.au/docs/article10.html>. The page lists much pertinent information about fire, primarily for fire investigators; e.g., auto-ignition temperatures, physical constants of various flammable materials, etc.

Another site providing similar information is “The Engineering Toolbox” at http://www.engineeringtoolbox.com/fuels-ignition-temperatures-d_171.html.

Incident Information System at <http://www.inciweb.org/> provides up-to-date information on current wildfires throughout the US.

<http://www.fs.fed.us/rm/fire/wfcs/index.htm> The website of the US Forest Service, this portion of the site points to Wildland Fire Chemical System, WFCS, which provides National Resource Agencies with detailed information promoting safe and effective Fire Suppression Chemicals and Aerial Delivery Systems. This site contains the approved lists of firefighting foams and “water enhancers” (fire-suppressant gels).

More sites on environmental concerns of current firefighting agents

<http://www.nytimes.com/2008/11/16/us/16wildfires.html> An article describing the environmental concerns surrounding the use of chemicals dropped by air on forest fires.

A study from the University of the Aegean, Greece, on the different types of fire retardants and their residual effects on humans and the environment can be found at http://www.gnest.org/Journal/Vol2_No2/01_kalabokidis.pdf.

More sites on surface tension and surfactants

Answers.com provides a good summary discussion of surface tension, along with nice photos showing the phenomena. The text by the end of the web page becomes rather high level, especially for students. View it at <http://www.answers.com/topic/surface-tension>.

<http://en.wikipedia.org/wiki/Surfactant> The Wikipedia article offers a full discussion on all aspects of surfactants. It is a good entry article for someone wishing to learn more about surfactants.

<http://www.chemistry.co.nz/surfactants.htm> The site provides an introductory lesson on the action of surfactants. It includes a table of the effect of concentration of surfactants on the surface tension of water.

This site provides a lecture about water and all its special properties, including discussion about hydrophilicity and hydrophobicity. View it at <http://mansfield.osu.edu/~sabedon/biol1015.htm>.

This page, from the Brooklyn College, City University of New York, is a one-screen animated model of the effect of hydrophobicity on a mixture of water and a non-polar substance: <http://academic.brooklyn.cuny.edu/biology/bio4fv/page/hydropho.htm>.

<http://www.mechleans.com/content/what-surfactant> shows the first of three screens that describe what a surfactant is, followed by one about surface tension, and followed by one about how a surfactant works. Models are shown to help in understanding. (Click on the three topics in the sidebar at the right of the screen.)

You can view a 13-minute video clip lecture-demonstration, entitled “Water: Hydrophilic and Hydrophobic Substances” at <http://www.5min.com/Video/Water-Hydrophilic-and-Hydrophobic-Substances-150612616>. It describes the terms in the title and culminates in the production of mayonnaise!

This 50-second movie clip captures 5 picoseconds of a molecular dynamics simulation of a hydrophobic Xenon particle dissolved in liquid water at 275 K and ambient pressure conditions. <http://www.youtube.com/watch?v=ETMmH2trTpM>.

Here’s a different use for hydrophobic substances: a wound dressing that binds irreversibly to bacteria: <http://www.cutimeduk.com/cutimed-sorbact.html>.

For the ultimate in hydrophobicity, check out research on superhydrophobic materials at http://www.youtube.com/watch?v=EaE9k-xUtrQ&feature=player_embedded#.

More sites on firefighting foam agents

<http://fireade.com/faqs> This site provides information on FireAde 2000 which the (commercial) site considers the most effective firefighting foam agent manufactured today. “The elimination of ALL aspects of the fire tetrahedron makes FireAde 2000 superior to all other agents. The OXYGEN, HEAT, FUEL, and CHEMICAL REACTION (free radical) are eliminated with FireAde 2000. These unique features ensure the quality and safety of those who use it.” The “Photos/Videos” button at the top of the page shows some pretty impressive fires; e.g., tire fires, tank fire, large pit fires, being put out with FireAde 2000.

More sites on phosphate esters

<http://dl.clackamas.cc.or.us/ch106-04/phosphat.htm> The site is a chemistry lesson on oxyorganic compounds. The specific site deals with esters in general. Structure and properties, nomenclature, formation, reactions, and triesters are discussed along with the section of interest—phosphate esters. Two possible structures for the phosphate esters are presented as well as a discussion justifying the two different representations.

More sites on fire-suppressing gels

Precision Lift, Inc.'s web site has a page that explains the difference between foams and gels. It also lists the commercial fire-blocking gels presently on the market. View it at <http://www.precisionliftinc.com/gel.shtml>.

The commercial gels' websites are listed here:

Thermo-Gel®—<http://www.thermo-gel.com/>

PHOS-CHeK AquaGel-K® Fire Suppressant Gel—<http://phos-chek.com.au/gel/phos-chek-aquagel-k>

Wildfire AFG Firewall®—http://www.baileysonline.com/PDF/AFG_Firewall_instruct.pdf (a 4-slide show about the product) and http://www.wildfire-equipment.com/index.php?page=shop.product_details&flypage=shop.flypage&product_id=5668&category_id=11&manufacturer_id=0&option=com_virtuemart&Itemid=26 for the supplier

Barricade®—<http://www.firegel.com/pages/Home>

More sites on sodium polyacrylate

http://www.alibaba.com/showroom/Sodium_Polyacrylate.html This website features a large number of sources of sodium polyacrylate. Of special interest is the listing of the many uses of sodium polyacrylate.

More sites on flame retardants and fire extinguishers

(http://www.americanchemistry.com/s_ACC/sec_article.asp?CID=22&DID=6138) This is an article originally published in *American Chemistry* by the American Chemistry Council that discusses flame retardants and types of fire extinguishers. This article is one of a series of short pieces aimed at the general public to cite the benefits of chemistry to society.

<http://www.ilpi.com/safety/extinguishers.html> The site describes the basic types of fire extinguishers and how to determine which kind of extinguisher one should use. The site goes on to explain how to use each type of fire extinguisher and how to maintain the fire extinguisher.

The Fireretard.com site contains some background information on the role of fire retardants in fighting fires. View it at <http://www.fireretard.com/main.php?pdf=3-1%20Formulations.pdf&langid=1&itemid=2&subitem=5&subsubitem=>.

More sites on borate bombers

http://winjack3.com/borate_bombers.html A photo collection of aircraft called borate bombers that used to deliver fire fighting chemicals to forest fires.

General Web References

<http://www.firewise.org/> is the site of the national “Firewise Communities” program. This “... is a multi-agency effort designed to reach beyond the fire service by involving homeowners, community leaders, planners, developers, and others in the effort to protect people, property, and natural resources from the risk of wildland fire—before a fire starts. The Firewise Communities approach emphasizes community responsibility for planning in the design of a safe community as well as effective emergency response, and individual responsibility for safer home construction and design, landscaping, and maintenance.

The national Firewise Communities program is intended to serve as a resource for agencies, tribes, organizations, fire departments, and communities across the U.S. who are working toward a common goal: reduce loss of lives, property, and resources to wildland fire by building and maintaining communities in a way that is compatible with our natural surroundings.” The site includes power point presentations and resources for protecting communities from the ravages of wild fires.”

<http://pages.total.net/~unifoam/dialog.html> The Unifoam website includes a detailed introduction to firefighting foams. George Vestergom Jr., the author of the article, is Product Developer at Unifoam Company, Limited. His article includes a history of the development of foams, a description of the types of available foams, and challenges to the acceptance of foams.

<http://www.lbfdtraining.com/RTM/Chapter3%20Fundamentals/Fire%20Behavior%20&%20Chemistry.html> is a website offering a complete discussion of everything related to fires and fire fighting.

More Web Sites on Teacher Information and Lessons

http://www.education-world.com/a_lesson/lesson/lesson026.shtml
The article “Fire Safety: Activities to Spark Learning! “ provides a large number of cross-curriculum activities and fire-related web sites for Fire Prevention Week, the first week in October. Most of these activities are geared toward middle school.

<http://school.discovereducation.com/lessonplans/programs/forestfires/>
The site provides an ecology lesson plan based on forest fires. In completing the lesson, students would understand the benefits and problems associated with fire and the role that fire plays in maintaining healthy ecosystems.

Green Gasoline: Fuel from Plants

Background Information

More on gasoline and its history

Gasoline is a complex mixture composed primarily of hydrocarbons. It is part of crude oil. Gasoline contains more than 500 hydrocarbons having between 3 and 12 carbon atoms, in both saturated and unsaturated molecules. Alkanes (single-bonded carbon atoms, traditionally called paraffins), alkenes (some double-bonded carbon atoms, traditionally called olefins), alkynes (triple-bonded carbon atoms, traditionally called acetylenes) cycloalkanes and arenes (conjugated double bonds between carbon atoms, called aromatics) are all contained in gasoline.

In the early history of petroleum, gasoline was not particularly useful because most of petroleum was refined to produce kerosene for kerosene lamps. Whale oil had been the source of lamp oil, but eventually whale populations declined and whale oil became very expensive. So as petroleum became more abundant, kerosene replaced whale oil.

With the invention and mass-production of the automobile, gasoline became a valuable economic commodity. At first straight-run gasoline, refined directly from crude oil, was good enough. But as more automobiles came on the market, a higher yield of gasoline from petroleum was required. To solve this problem, cracking was needed. Cracking is the process by which longer-chain hydrocarbons are broken down (cracked) into smaller chains, including heptane and octane, that go into making gasoline. Two methods of cracking were developed.

The first of the methods of cracking crude oil was thermal cracking, where larger hydrocarbon molecules in petroleum were heated to high temperatures at high pressure. The second method of cracking is catalytic cracking, invented by Eugene Houdry in the late 1930s. This process applies catalysts to aid the cracking of larger molecules. It can be done at lower temperatures and pressures, resulting in cost savings and greater safety for the refinery. This process also produced more gasoline per barrel and a higher quality gasoline (higher octane rating) than that from thermal cracking.

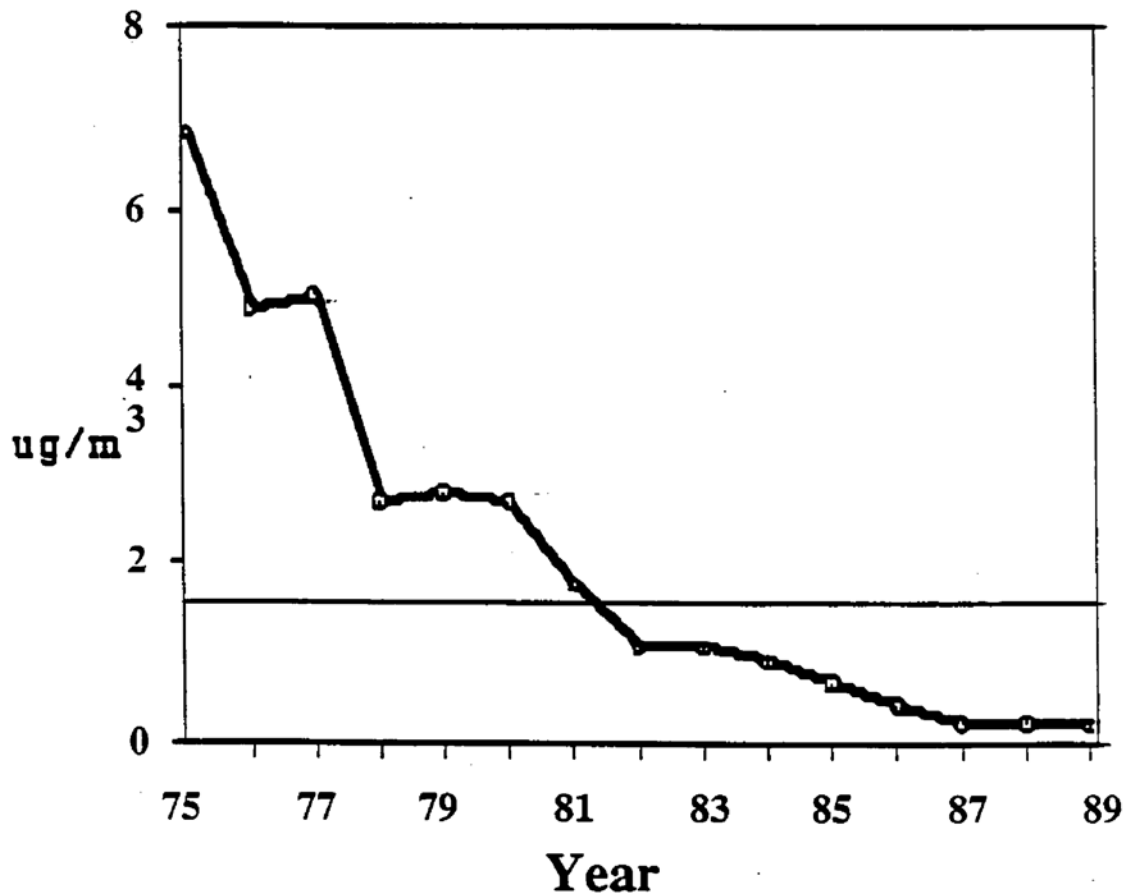
This higher quality gasoline from catalytic cracking was important because newer cars had engines that were more powerful (higher compression) and required gasoline with higher octane ratings (better gasoline). Lower-octane-rated gasoline caused knocking and pinging of engines, indicating incomplete combustion of the fuel and reduced power output, as well as increased engine wear.

Research on additives to gasoline to improve antiknock properties was going on as early as the 1920s. Ethanol had been used as a gasoline additive, but Robert Midgley and his research teams experimented with many materials, leading to organometallic compounds, and eventually they settled on tetraethyl lead. (You might be surprised to learn that iodine was originally the best antiknock compound available.)

Tetraethyl lead was added to gasoline in the 1920s, along with scavenger molecules whose purpose was to remove the metallic lead that would otherwise build up in the engine and exhaust system. The scavengers, ethylene dibromide and ethylene dichloride, contain halogen

atoms that react with the lead producing lead halide salts that are emitted out the exhaust pipe into the air. The environmental hazards of the lead additive were debated from its earliest days, leading in the 1970s to its exclusion from gasoline by law in the US. In 1975, new cars were equipped with catalytic converters designed to reduce pollutant emissions from automobiles. Since these could not work with leaded gasoline, this spelled the demise of tetraethyl lead as an additive to gasoline. The results of this extreme change in fuel composition are glaringly obvious to see. As a result of the government's efforts, lead concentrations in the air decreased dramatically from the mid-1970s to 1990, as this graph of lead content in the air of Los Angeles shows:

Figure 3: Ambient Lead Concentration (Downtown Los Angeles)



Source: http://www.arb.ca.gov/fuels/gasoline/carfg1/P1_ch4.pdf

Although this graph is limited in its geographic coverage, similar results occurred nationwide.

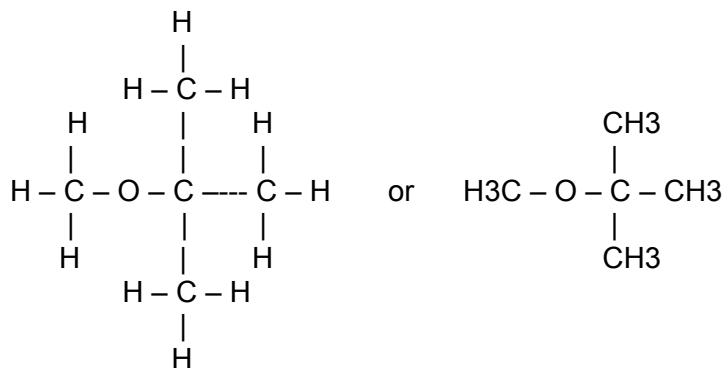
Something was needed, though, to replace tetraethyl lead to maintain its antiknock properties and to increase clean-burning of the fuel. Oxygenates entered the scene in commercial use in the early 1970s. Oxygenates are mostly alcohols or ethers containing 1 to 6 carbon atoms. Their role is to enhance octane rating, thereby reducing knock in engines, while providing increased power to the engine. Their oxygen content helps gasoline to burn more completely (more slowly), thereby reducing exhaust emissions. They also replace aromatic compounds such as benzene, as well as sulfur in gasoline, thereby further reducing toxic emissions.

In 1990 an amendment to the federal Clean Air Act was passed that required fewer and lower levels of toxic exhaust emissions from automobile engines. In 1989-90, winter oxygenated gasoline (WOG) was introduced. Its purpose was to reduce toxic automobile emissions during the winter months, specifically in densely populated urban areas, when toxic emissions were at their highest levels. MTBE was one of the oxygenate additives whose concentrations were increased—to 11-15% ranges. Refineries' first forays into this new market occurred in California cities and the northeast corridor from Washington to New York.

During the 1990s, the petroleum refineries began to produce what are termed "reformulated gasolines" (RFGs). These were gasolines specifically formulated with extra oxygenates to reduce pollution across the country—essentially WOGs country-wide year-round. One of their major targets was ozone reduction. Again, MTBE was the main oxygenate used in RFGs.

Methyl tertiary butyl ether (MTBE), $C_5H_{12}O$, is probably the best known and most widely used oxygenate for gasoline worldwide. (Note, however, that it is estimated that more than 50 countries around the world still use leaded gasoline.) MTBE replaced tetraethyl lead as that compound was phased out of US gasoline. MTBE was favored over ethanol as an oxygenate due to its lower cost and better blending characteristics. It also could be shipped and stored in existing oil product pipes and storage tanks, unlike ethanol, which corroded those containers. Corrosion is a problem with ethanol even today, whether used as an oxygenate or as a direct fuel for automobiles.

MTBE, methyl tertiary butyl ether, is also known by its IUPAC name: 2-methoxy-2-methylpropane. It is an ether with the structural formula $H_3C-O-C(CH_3)_3$. Its principal use is as an oxygenate additive for gasoline.



Because of the two non-bonding pair of electrons on the oxygen atom of MTBE, the molecule is slightly polar. This polarity results in its solubility in water (4.8 g / 100 g H_2O) being much greater than other hydrocarbons found in gasoline.

Since MTBE contains oxygen, it acts as an oxidizer in the automobile engine, reacting with combustion by-products to reduce the amount of carbon monoxide emitted from the tailpipe. In addition MTBE's concentration at approximately 11-15% by volume effectively reduces the relative amounts of other volatile organic compounds (VOCs) present in gasoline, such as benzene, and sulfur compounds. This also contributes to a reduction in air pollution for cars burning gasoline with MTBE added.

Charts from the EPA showing the widespread use of MTBE compared to ethanol and other oxygenates can be found at this web site:

<http://www.epa.gov/otaq/consumer/fuels/mtbe/oxy-type.pdf>. The charts show that in 1995, approximately 87% of all reformulated gasoline contained MTBE.

MTBE was widely used until the early 2000s, when a few states, notably California and New York, in 2004) forced the gasoline industry to begin its phase-out of MTBE. Twenty-five more states had signed legislation banning MTBE by 2005. (The EPA had drafted plans as early as 2000 to phase out MTBE nationwide over four years.

The concern about MTBE was primarily due to the discovery that gasoline leaks from ruptured underground storage tanks at gas stations and oil fields had resulted in the MTBE escaping into local water supplies. MTBE is more soluble than most of the other non-polar organic components of gasoline, so it leaches into water supplies more quickly than other components. Although its toxicity has not been established at low concentrations presently existing in some water supplies, the EPA has classified it as a possible carcinogen at high doses. Regardless of its toxicity, it does impart a distinct (bad) taste to contaminated water, thus making drinking water unpotable. It can be detected even at the parts-per-billion level. It thus serves as a harbinger of other organics that might also be contaminating subsurface water.

An oxygenate that has to some degree replaced MTBE in gasoline is ethyl tertiary butyl ether (ETBE). It has properties similar to MTBE. ETBE is produced from ethanol (which is more expensive than methanol), however, and this makes it more expensive than MTBE, which is produced from methanol (derived from natural gas) and isobutylene (derived from butane that comes from crude oil or natural gas). (Thus MTBE is considered a fossil fuel.) As a result of its higher cost, it is less widely used than a different oxygenate.

Ethanol replaced MTBE as the most recent widely used gasoline oxygenate. See “More on ethanol”, below for more information about ethanol.

More on alternative sources of green gasoline

In addition to making gasoline from corn stover and switchgrass, other researchers are taking different approaches. One such group is working on producing gasoline from bacteria and sugar. The San Francisco, California-based LS9, Inc., “The renewable petroleum company”, has genetically engineered strains of bacteria (and yeast), including *E. coli*, to produce hydrocarbon chains. They’ve succeeded in modifying genetic pathways used by bacteria to store energy. Bacteria, plants and animals store energy as fatty acids, chains of hydrocarbons with carboxylic acid groups attached. The researchers at LS9 have engineered bacteria to produce the hydrocarbon chains without carboxylic acid groups. They’ve modified bacteria to produce and excrete hydrocarbon chains of varying lengths, based on the goal of the individual experiment. Since the company is privately owned, not much detailed information is known about the proprietary biotechnology processes used by LS9.

Their processes produce biofuels that are “fit for purpose”—meaning the products can be made to precisely match the required use. Their products include a crude oil substitute that can be refined to make petroleum-based products.

LS9 says the process is essentially the same as that for making cellulosic ethanol—fermentation. The extraction process is entirely different, however. In ethanol production, the ethanol must be separated from the water medium. Since ethanol and water are both polar, the

ethanol/water mix must be distilled to separate the two. This takes huge amounts of energy. In the LS9 process, the product is hydrocarbons, non-polar molecules. The non-polar organic material separates spontaneously from the water slurry because the two substances are immiscible. This results in a huge energy gain. LS9 claims that their processes are about 65% less energy intensive than ethanol fermentation processes for this reason.

The remaining hurdle for LS9 is to scale up their processes to make it economically feasible to produce these hydrocarbon molecules on an industrial scale. Going from Petri dish laboratory scale experiments to huge vats of the same bacteria producing millions of gallons of hydrocarbons will be a difficult task. LS9 has scaled up to a 1000 liter vat, but even this is a long way from industrial quantities. The company had planned to build a manufacturing facility in 2008 and have products ready for commercial scale within 3-5 years. Stay tuned.

(http://www.huffingtonpost.com/david-roberts/ls9-promises-renewable-pe_b_58388.html)

The BBC has a video of the inside of the LS9 facility and microphotographs of small drops of oil produced by the bacteria at <http://news.bbc.co.uk/2/hi/science/nature/8220278.stm>. And LS9's own web site is here: <http://www.ls9.com/>.

Another company, Amyris, has produced diesel fuel from microbes and sugarcane. They seem to be a step ahead of LS9 in that Amyris has patented their microbes and they've already produced diesel fuel in commercial quantities. They've just signed an agreement with Brazilian companies including Embraer to use their jet/aviation fuel in Embraer commercial jets as a test run. You can find more information at <http://www.amyrisbiotech.com/>. (Beware, though—the web site seems to be designed somewhat strangely. The hot buttons are way off to the right on [off] the screen.) It looks like LS9 has stiff competition.

More on energy content: carbohydrates vs. hydrocarbons

Carbohydrates produce less energy when they burn because some of the carbon or hydrogen atoms have already reacted with oxygen atoms. If fewer C or H atoms are free to react with diatomic oxygen molecules from the air, less energy is emitted because there are fewer atoms reacting.

Another way to look at the problem is from the standpoint of average bond energies. It requires more energy to break a mole of C-O bonds and a mole of O-H bond in an alcohol than it does to break a mole of C-H bonds and ½ mole of O=O bonds in an alkane.

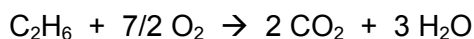
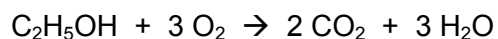
Here are average bond energies (in kJ/mol) needed to solve the following problem:

C-H	413	C-C	347	C-O	358
C=O	799	O-H	467	O=O	495

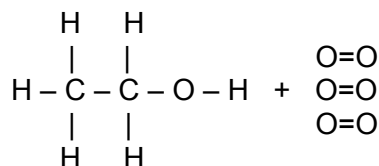
(Source:

<http://butane.chem.uiuc.edu/cyerkes/Chem104ACSpring2009/Genchemref/bondenergies.html>--
Values are referenced from Chemistry by Zumdahl (5th Ed.) Table 8.4, p. 373.)

Take the case of burning a mole of ethanol vs. burning a mole of ethane. The equations for combustion are:



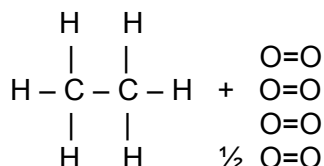
Breaking apart a mole of ethanol molecules and 3 moles of oxygen molecules



for reaction requires the following energies:

5 moles of C–H bonds	5 x 413 = 2065 kJ
1 mole of C–C bonds	1 x 347 = 347 kJ
1 mole of C–O bonds	1 x 358 = 358 kJ
1 mole of O–H bonds	1 x 467 = 467 kJ
3 moles of O=O bonds	3 x 495 = <u>1485 kJ</u>
	4722 kJ

Breaking apart a mole of ethane molecules and 3.5 moles of oxygen molecules

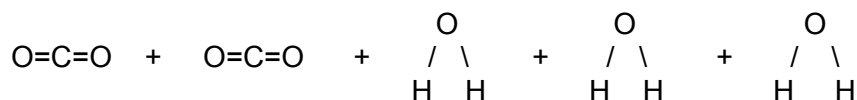


for reaction requires the following energies:

6 moles of C–H bonds	6 x 413 = 2478 kJ
1 mole of C–C bonds	1 x 347 = 347 kJ
3.5 moles of O=O bonds	3.5 x 495 = <u>1732.5 kJ</u>
	4557.5 kJ

Thus it requires 164.5 kJ more energy to break apart a mole of ethanol molecules and the stoichiometric amount of oxygen molecules (3 moles) needed to burn the ethanol than it does to break up a mole of ethane and the stoichiometric amount of oxygen molecules (3.5 moles) needed to burn the ethane. Since the products are identical, the difference in heats of combustion will differ only by the amount of bond energy difference in the reactants.

To complete the calculations and actually find the $\Delta H_{\text{combustion}}$ for each of the fuels, however, we can calculate the energy released when the 2 moles of carbon dioxide and 3 moles of water are formed, by calculating the amount of energy that would be needed to break all those bonds, which is exactly the same value, except the sign of the reaction would be the opposite.



4 moles of C=O bonds	4 x 799 = 3196
6 moles of O–H bonds	6 x 467 = <u>2802</u>
	5998

Since $\Delta H = H_{\text{bonds broken}} - H_{\text{bonds formed}}$, we can calculate ΔH for both reactions:

For ethanol, $\Delta H_{\text{combustion}} = 4722 \text{ kJ/mol} - 5998 \text{ kJ/mol} = -1276 \text{ kJ/mol C}_2\text{H}_5\text{OH}$

For ethane, $\Delta H_{\text{combustion}} = 4557.5 \text{ kJ/mol} - 5998 \text{ kJ/mol} = -1440.5 \text{ kJ/mol C}_2\text{H}_6$

The calculations show that the combustion of one mole of ethane produces 164.5 kJ more energy than the combustion of one mole of ethanol. This should verify the author's claim that combustion of carbohydrates provides less energy than combustion of their hydrocarbon counterparts; e.g., burning glucose produces less energy than burning cyclohexane. (Of course, you could always have students prove this by calculations.)

More on zeolites

Zeolites are silicates, composed of interlocking tetrahedral of SiO_4 and AlO_4 . The requisite empirical formula for a zeolite must result in the following ratio: $(\text{Al} + \text{Si})/\text{O} = \frac{1}{2}$. The aluminosilicate structure has a negative charge, thus attracting cations into the pore structure. More useful zeolites contain interconnecting spaces, producing long tunnels or channels. The open channels allow the zeolites to absorb and release molecules easily. The extent of porosity of these materials explains their low specific gravity.

Zeolites act as molecular sieves, trapping molecules inside their pores. They have been used since the 1970s to help in the refining of gasoline. They have many basic functions: e.g., ion exchange, filtering, sieving, removing odors, and gas absorption.

Since their discovery, they have been used to trap a wide variety of substances. One of their principle uses over the years has been in the water softening industry. The zeolites are used to trap calcium and magnesium ions from hard water. Sodium ions that were trapped in the zeolites pores are exchanged for the calcium and magnesium ions that are removed from the water, resulting in the softening of the water. This means the calcium and magnesium ions aren't present to create soap scum and build-up of scale in the water pipes.

Another group of substances are a prime target for zeolites. Scientists are working on the use of zeolites to trap radioactive substances so they can be removed from the environment. You can listen to a brief podcast from the American Association for the Advancement of Science dealing with using zeolites to remove radioactive strontium from reactors at http://www.sciencenetlinks.com/sci_update.php?DocID=88. The transcript is included, along with questions for students.

More on ethanol

Ethanol, like MTBE, contains an oxygen atom within its molecule ($\text{C}_2\text{H}_5\text{OH}$). Thus it also acts as an oxygenate when added to gasoline. It improves the burn characteristics of gasoline, resulting in less pollution, and its presence in gasoline reduces the volume of other VOCs and sulfur contained in the same volume. (In effect, it dilutes the other constituents.) Both these reasons make it a desirable oxygenate.

According to SRI Consulting, in 2008 the US consumed almost 60% of the world's ethanol used for oxygenating gasoline. Brazil followed with about 33%. The Middle East and Europe used about 50% of the world's MTBE for the same purpose, showing the rapid changeover from MTBE to ethanol. The site cites many reasons for this trend toward ethanol and away from MTBE. (<http://www.sriconsulting.com/CEH/Public/Reports/543.7500/>)

A graph by Dr. Christoph Berg at <http://www.distill.com/World-Fuel-Ethanol-A&O-2004.html> shows the trends in ethanol production worldwide from 1975 (projected) to 2012. Its uses as a fuel, in industrial settings, and as a beverage are highlighted. From the graph it is clear that its uses as a beverage and in industry are relatively unchanged over that time period. On the other hand, ethanol's use as a fuel (or fuel additive) has increased substantially, and it has increased (and will likely continue to do so) at an increased rate since about 2000. He estimates that fuel ethanol accounted for about 70% of world ethanol production in 2003. This site provides 2003 information about ethanol production and consumption worldwide.

One problem with ethanol is that, like MTBE, it is a polar molecule, but one that is more polar than MTBE (0.654 for ethanol vs. 0.124 for MTBE). (Source: <http://virtual.yosemite.cc.ca.us/smurov/orgsoltab.htm>) Its polarity results in its driving off volatile

non-polar hydrocarbons from gasoline, which MTBE does to a much smaller extent. Many of these volatile hydrocarbons are known carcinogens and produce photochemical smog.

Its polarity also makes it water-soluble, like MTBE. Unlike MTBE, however, ethanol dissolved in water quickly breaks down biologically into harmless products. Thus it is much less of a problem than MTBE when it leaks into groundwater from storage and pipeline leaks. In addition, ethanol doesn't have a noticeable bad taste at low concentrations, as does MTBE.

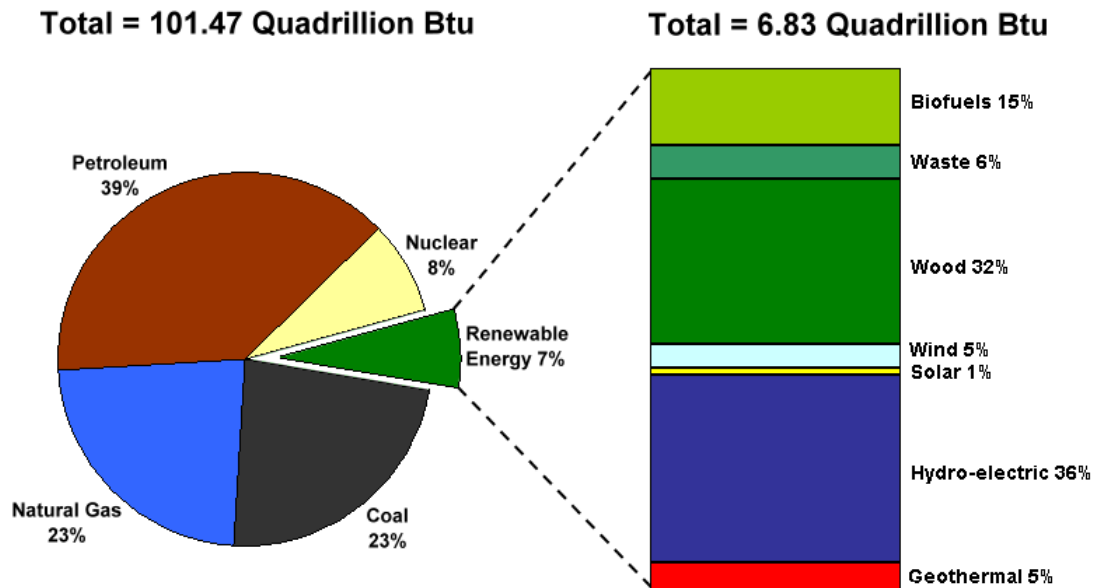
Ethanol also dilutes VOCs in gasoline, but to a lesser extent than MTBE, since less ethanol is needed to meet EPA oxygen requirements.

A major problem with ethanol that does not exist for MTBE is that it is corrosive to metals and for that reason refineries cannot ship it through the same pipeline facilities as gasoline. It also is corrosive to automobile engines, but since it is mixed with gasoline, the effect is much diminished.

The polarity of ethanol also contributes to problems if it were to be used as a direct fuel replacement for gasoline, rather than just using it as an oxygenate additive to gasoline. A concentrated stream of ethanol would corrode pipelines and automobile engines and exhaust systems if used directly as a fuel.

More on biofuels

Figure 1.1
Summary of Biomass Energy Consumption, 2007



Source:

Energy Information Administration. 2008. *Monthly Energy Review*, July, <http://www.eia.doe.gov/emeu/mer/contents.html>.

The pie chart above from the US Department of Energy shows that biomass (biofuels, waste and wood) collectively produced 53% of the renewable energy consumed in the US in

2007. (The figures are essentially the same for 2008.) Realistically, however, this represents a bit less than 4% of the total energy consumed in the US for the same year. Although their uses are increasing substantially, renewable energy sources collectively—and biomass fuels especially—have a long way to go before they become major contributors to our energy needs.

Connections to Chemistry Concepts

1. **Types of chemical reactions, combustion**—Combustion is one of the five types of chemical reactions typically taught in a first-year chemistry course, along with synthesis (direct combination), decomposition, single replacement (displacement), and double replacement (displacement). This whole article features combustion, although the focus is on sustainable fuels.
2. **Combustion**—Reactants and products for the combustion of octane
3. **Polarity in molecules**—Gasoline is non-polar, water is polar; little interaction occurs between unlike substances; hence, it's easy to separate gasoline and water. Ethanol is polar, water is polar; greater dissolution occurs between two polar (or two non-polar) substances—"likes dissolve likes"; hence, it's more difficult to separate ethanol and water.
4. **Distillation**—Manufacturers of ethanol for fuel must separate the ethanol from the yeast/water mixture by distillation, which is highly energy-intensive.
5. **Catalysis**—Zeolites serve as surface catalysts that allow anhydro sugar molecules to enter the pores in the zeolite and lose oxygen atoms to reform into the ring-shaped hydrocarbon molecules.
6. **Organic chemistry**—Basic organic chemistry is shown here with hydrocarbons, in both straight-chain and ring formations, and carbohydrates.
7. **Structural formulas**—Note that the author uses mainly space-filling models to represent organic molecules in the article. There are other types of representations of structural formulas, and you may wish to expose students to these at this time: space-filling models; skeletal formulas (this could also be an example of a Haworth projection), Lewis structures.
8. **Chemical bonding**—Many examples of the tetrahedral bonding of carbon are exhibited throughout the article.
9. **Thermochemistry**—Bond-breaking is endothermic; bond-forming is exothermic. The author mentions bond-breaking between carbon and hydrogen atoms in burning, but he doesn't really connect the energy production with the reforming of the new bonds between carbon and oxygen, and between hydrogen and oxygen. Students may need a clarification on this section.
10. **Sustainability**—Although sustainability is not a concept presently contained in first-year chemistry courses, perhaps it should be. The need to provide a continuous supply of fuels and materials for humanity is a central concern for chemical industry everywhere. Producing green fuels is a step in the right direction—for all of us.

Possible Student Misconceptions

1. **"We'll never run out of oil—why are we so worried about running out? There are millions of barrels of oil still buried underground."** *While this is a true statement, we consume millions of barrels of oil daily. Eventually, we will run out of oil that is presently stored underground. We must find (grow) replacements for this fuel source. [Ed. Note: some scientists believe that oil is being produced today via abiogenic processes deep underground. The hypothesis/theory has been around for decades, mostly supported by*

Russian scientists, but now gaining (a little) ground in geologic circles. See http://www.experiencefestival.com/a/Abiogenic_petroleum_origin_-_Comparison_of_theories/id/1293166 for an introduction to the idea.]

2. **“Breaking bonds releases energy—it says as much in the article: ‘Octane and other hydrocarbons burn by breaking bonds between carbon and hydrogen atoms...’”** *The remaining part of that quote, “...which then grab onto oxygen atoms” finishes the thought, implying that the carbon and hydrogen atoms grabbing onto (bonding with) oxygen atoms is the part that really releases the energy. This misconception is also fueled (excuse the pun) by the discussion in biology classes about ATP releasing energy when it breaks down into ADP.*
3. **“Gasoline must be the only thing produced from crude oil.”** *Au contraire! Crude oil is used in many other types of fuels besides gasoline—diesel, kerosene and jet fuel, just to name a few. Petrochemicals are chemicals derived from petroleum, and they can be found in almost everything we touch—clothing, pharmaceuticals, cosmetics, plastics, paints, rubber products, fibers, paper and textiles, for examples. Our lifestyle without petroleum would be unrecognizable.*
4. **“Ethanol seems like a better deal than the other processes described in the article. There’s less processing needed to make it into a fuel. Let’s just use ethanol as a fuel instead of gasoline.”** *This is a bigger problem than it seems. First, ethanol produced by fermentation of sugars must be separated from the aqueous slurry in which it is produced. This must be done by distillation, which requires tremendous amounts of energy (defeating the purpose of making it into a fuel). Second, ethanol is corrosive to the metals used in the automobile engine and the pipeline used to transport gasoline. The existing infrastructure of refineries, pipelines and storage tanks we use for gasoline would need to be completely revamped for use of ethanol, not to mention the need to redesign the automobile engine. That’s another reason why it’s so important to produce hydrocarbons, rather than carbohydrates for fuel.*

Demonstrations and Lessons

1. Let students discover for themselves the difference in heat content between hydrocarbons and carbohydrates; do a heat of combustion lab (simple Calorimetry) using several hydrocarbon (and carbohydrate) fuels, instead of just measuring the heat of combustion of a burning candle. For example, use propane, butane, kerosene and ethanol or methanol as fuels (with proper safety precautions, of course). Have students measure heats, calculate heats of combustion and compare them as fuels – on a heat per gram basis and a heat per mole basis. Different groups in the class could do different fuels, and then compare results—even across classes, for more data upon which to make a decision.
2. A paper-and-pencil activity involving bond energies could be done to verify for students the decreased energy content of a carbohydrate vs. that of a hydrocarbon. (See “More on energy content: carbohydrates vs. hydrocarbons”, above.)
3. Use molecular models to construct the organic compounds discussed in the article.
4. You can use the following YouTube video clip to begin a class discussion about how combustion in the internal combustion engine really takes place: http://www.youtube.com/watch?v=ST0ktyJKCug&feature=player_embedded. The clip focuses on 2 students burning ethanol and gasoline in separate alcohol lamps. Many safety infractions are shown on the clip, which is a lesson in itself. The focus of the clip is on the relative pollution given off by gasoline vs. that of alcohol. You need to discuss with students

- the effect that vaporizing the gasoline in the carburetor/fuel injection ports has on its combustion efficiency/pollution reduction.
- If students are interested in seeing the internal workings of the 4-cylinder internal combustion engine, you can show them the “real deal” in an animation at http://www.carbibles.com/fuel_engine_bible.html. It can even be enlarged to full-screen mode! And the text is there to describe what’s happening. Another source of information and animations about car engines is the “How Stuff Works” site at <http://auto.howstuffworks.com/engine.htm>.
 - Kennesaw State University hosts a series of case studies in chemistry, called ChemCases.com. One such rather extensive study is the one about Fuels and Society. It is a 3-part study about the rise of the automobile and the energy sources needed to fuel it. The case study appears to be aimed at the non-major chemistry student in college. Each part gives historical background information, pertinent chemistry and a hot-linked concept map to guide students through the study.
 - Part A (1 of 3) of the Kennesaw State University’s Fuels and Society case study investigates how fuels were developed for the automobile—the history of automobile fuels. It assumes some understanding of basic organic chemistry (isomers), thermochemistry (basic ΔH work), and thermodynamics (ΔS and ΔG). This might be better suited as a lesson for Chemistry II or AP Chemistry, or possibly as a student project. (<http://chemcases.com/fuels/index.htm#The%20Chemistry>)
 - Part B of the 3-part study deals with gasoline and automobiles—specifically the rise of lead in gasoline. You can find the site at <http://chemcases.com/tel/index.htm>.
 - Part C deals with “How Lead was Finally Removed from Gasoline”. You could ask students to research and debate the decision to eliminate MTBE as an oxygenate additive to gasoline. (<http://www.chemcases.com/converter/index.htm>)
 - If you want to show students how a distillation tower works to fractionally distill crude oil into useful products including but not limited to gasoline, check out the animated fractional distillation column at the “How Stuff Works” site at <http://science.howstuffworks.com/oil-refining4.htm>. This page is part of the larger sequence of pages on “How Petroleum Refining Works” at <http://science.howstuffworks.com/oil-refining.htm>.
 - Students can learn about the chemistry of petroleum and participate in a lesson plan on “Chemistry of Petroleum” from the American Association for the Advancement of Science’s *Science NetLinks* at <http://www.sciencenetlinks.com/lessons.php?BenchmarkID=4&DocID=469>.
 - If you want students to have a crash mini-course in organic chemistry, you can send them to “An Introduction to Organic Chemistry” at <http://www.krysstal.com/organic.html>. It’s listed as “a beginners’ [sic] guide to the chemistry of Carbon compounds”.
 - The Virtual Chemical Plant is a site that is designed for middle school, but it contains useful information for students of all levels. You must register, but you do so by choosing a name the computer offers from a drop-down menu; e.g., Cal Condensor and Eva Evaporator. There are a lot of flash animations contained within the site. A fractional distillation process is shown in animation, among others. Some parts of the site are game-like, with guessing needed with no firm basis on which to make the guess, and some seem a bit simplistic, but overall students could learn from a visit (or several visits) to the site. Macromedia Flash Player is required (free to download from the site) to view the site. There is a “Teacher’s Corner” that contains a downloadable 74-page User’s Guide to help teachers wade through the site. Activities for students abound. (<http://capt.com.edu/virtualchemplant/>)
 - If students are interested in learning about where oil is located underground, they can work through (play) “Virtual Oil Well”, a simulation/game that gives students the opportunity to use seismic readings and a topographic map to decide where and how deep to drill for oil on a plot of land left to them by their late Aunt Thibodeaux. They can access information for free

from the library, or they can pay experts (from their inheritance from the same aunt). The goal is to make as much money by discovering as much oil as possible. View the site at <http://www.earthscienceworld.org/games/index.html>.

Student Projects

1. Students can research and report on the status of oil exploration/production globally and relate that to the need for research in biofuels and other alternative energy sources.
2. Students can research and report on the status of research in the area of other alternative energy sources (besides biofuels).
3. Students can research and report on the problems associated with ethanol as a biofuel for transportation. The article mentions that green gasoline is preferred because it can be used directly in cars and pipelines, but it does not discuss why ethanol cannot.
4. Students can research and report on other biofuel sources, such as soybeans, switchgrass and algae.
5. Students can compare and contrast existing biofuels in areas such as: fuel efficiency, cost per kJ of energy, land mass needed to grow energy-equivalents of each, energy needed to grow/prepare biofuels, net energy output, etc.
6. Students can research and report on a comparison of MTBE and ethanol, to see which (if either) should be the “oxygenate of choice” for gasoline. Several studies are available on the World Wide Web.
7. A Web Quest on “Alternative Biofuels” by high school chemistry teacher Ron Brandt is available at <http://web-prod-1.shu.edu/~brandtro/indexAF.html>. The student is tasked with working as part of a team of four students to research and report to the President (of the US) about either ethanol or biodiesel as an alternative to fossil fuels. A 3-week timeline is given, with interim reports required at specified intervals. This is very professional-looking, with specific requirements for each step, and an evaluation rubric included. An added feature to this site is a blog students can access to discuss their findings with others and the “President”, and to report progress. (Unfortunately, this is an in-school feature and not available to outside access; nonetheless, it is a worthwhile item to consider in your own class work.)
8. Another WebQuest, “The Great MTBE Controversy”, from the Chemical Heritage Foundation, at <http://www.chemheritage.org/educationalservices/webquest/mtbe.htm>, focuses on the question of the federal government’s banning MTBE. Students must work in pairs to do research using starter sites and focus questions given. One partner researches the benefits of MTBE, the other researches its risks. Then they discuss both sides and come to a team consensus and write a report that supports their position.

Anticipating Student Questions

1. **“Why is green gasoline the only fuel that can be used directly in cars and pipelines without further modifications—why can’t ethanol be used directly in cars and pipelines?”** *Ethanol as a fuel is corrosive to metals in automobile engines, refineries and pipelines. [Note: How much you want to discuss this with students depends upon whether you want them to pursue this question as a research topic (See Student Projects #3, above.)*
2. **“Where does our (US) oil come from?”** *Two thirds of the crude oil imported by the United States (total, 11 million barrels a day) comes from OPEC countries; e.g., Saudi Arabia, Nigeria, Iraq and Venezuela (yes, Venezuela is part of OPEC). The other one-third comes*

from non-OPEC countries; e.g., Canada, Mexico, Russia and Brazil, and even the UK. (Source: http://tonto.eia.doe.gov/dnav/pet/pet_move_net1_a_ep00_IMN_mbb1pd_a.htm.)

3. **“Can cars run on fuels other than gasoline?”** Yes, some cars can use other fuels. Cars with diesel engines, for instance, can run on diesel fuel or other hydrocarbon fuels; e.g., used French fry oil from fast-food restaurants. The original diesel engine was designed (by Rudolf Diesel) to run on vegetable oils, because these plant materials would be readily available in rural agricultural regions, so people wouldn't be dependent on petroleum sources.

References

Nersesian, Roy L. *Energy for the 21st Century*. Armonk, NY: M. E. Sharpe, Inc. 2007
Nersesian's book gives a comprehensive overview of energy sources and extensive tables of data. To quote from Nersesian's preface: "This book examines the role of the principal sources of energy both in the aggregate and by specific types . . . for a balanced view on energy."

ChemMatters archived articles

The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site:

<http://www.acs.org/chemmatters>. (Click on this *ChemMatters* CD image at the right of the screen.)

Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)

(<http://www.acs.org/chemmatters>)

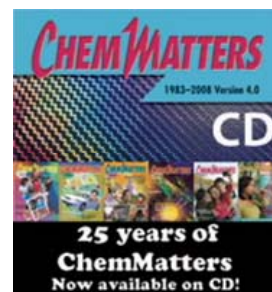
Kirchhoff, Mary. Do You Want Biodiesel with That? *ChemMatters*. April, 2005. 23:2, 7-9. This article focuses on diesel fuel made from vegetable oil, especially used vegetable oil (hence the title, a take on "Do you want fries with that?"). This is one of the first American Chemical Society moves into "green" chemistry for pre-college audiences.

The Teachers Guide for the April, 2005 issue also contains much information about biodiesel fuel and compares diesel fuel to gasoline.

Ryan, Mary Ann. Green Chemistry—Green by Design. *ChemMatters*. December, 1999. 17:4, 9-11. Although this article doesn't deal with ethanol and green gasoline specifically, it does discuss green chemistry in detail.

The Teachers Guide for December, 1999 discusses the 12 principles of green chemistry, as adopted by the U.S. Environmental Protection Agency from Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press. New York. 1998. p. 30.

Haines, Gail. Corn—the A'maiz'ing Grain. *ChemMatters*. December, 2006. 24:4, 4-7. This article deals with corn in many situations—its history, direct use as a food, its biology, a



genetically-modified food, popcorn particulars, biofuel source, and sweetener. Only a small part is devoted to ethanol-production.

The Teachers Guide provides links to sites that deal with ethanol-production.

Rohrig, Brian. NASCAR: Chemistry on the Fast Track. *ChemMatters*. February, 2007. 25:1, 4-7. The article deals with the chemistry of fuels and the safety of drivers in NASCAR race cars. [Ethanol is NOT a feature, but students might get a more complete picture of fuels by reading the article.]

The February, 2007 Teachers Guide contains background information on the history of fuels and cars, and the chemistry of fuels.

Baxter, Roberta. Gold in Your Tank. *ChemMatters*. April, 2007. 25:2, 8-10. Baxter gives a good background treatment of where gasoline comes from, from source (crude oil underground—on land and offshore), through processing (the refinery), to distribution (the gas pump). Chemistry of octane is shown using structural formulas.

Smith, Trevor. Camping Stoves. *ChemMatters*. April, 1992. pp. 7-11. Although the focus of the article is on camping stoves, it does compare the heating efficiency of various fuels. Gasoline and ethanol are compared: gasoline wins (50% more).

Web Sites for Additional Information

More sites on octane and gasoline

Gasoline FAQ, a frequently-asked-questions web site, covers a great deal of discussion about gasoline, including its history and chemistry (a mini-organic course on the basics of hydrocarbons), at <http://stason.org/TULARC/vehicles/gasoline-faq/index.html>.

Did you know that the retail price per gallon for gasoline in 2000 was \$1.29, or that 15.7% of the price we pay for gasoline is for taxes? Who knew? Find out how the price of gasoline has changed over the last 10 years from the Energy Information Administration at <http://tonto.eia.doe.gov/oog/info/gdu/gaspump.html>.

And here's a chart from Zfacts.com that traces gas prices back to 1970 and relates prices to world events: <http://zfacts.com/p/35.html>.

The Bedrock Bioremediation Center at the University of New Hampshire, has prepared a paper in pdf format online that covers in fair detail the dissolving of MTBE in ground water, and ways to remediate the problem. Find it at <http://www.asce.org/pdf/kinnertestimony.pdf>.

California Environmental Protection Agency has published online an update to cleaner burning gasoline, entitled, "Cleaner-Burning Gasoline: An Update". The update lists 8 basic specifications for cleaner burning gasoline, which were put in effect in 1996. They include: reduced sulfur, benzene, other aromatic hydrocarbons and olefins; reduced vapor pressure (less gas evaporates into the air); reduced distillation temperatures; and use of oxygenates. View the list at <http://www.arb.ca.gov/fuels/gasoline/cbgupdat.htm>.

Some time prior to 2002, the Sierra Club published one of their *Sierra Club Conservation Policies* on "Gasoline Additive: MTBE". The document establishes their position on using MTBE,

which is to say, “no—don’t use it.” But their position paper cites reasons why. If students use this document, they need to evaluate the information based on the publishing entity. In other words, they need always to consider the source. View the document at <http://www.sierraclub.org/policy/conservation/mtbe.aspx>.

A British site dealing with tetraethyl lead and other additives for petrol (gasoline) that contains structural formulas for heptanes, octane, tetraethyl lead and MTBE, among others can be found at <http://www.chm.bris.ac.uk/motm/leadtet/leadc.htm>. The structures can be manipulated using Chime, Chemsymphony or VRML applets. A 3-D animation of a tetraethyl lead molecule can be found from the above site at <http://www.chm.bris.ac.uk/motm/leadtet/leadtetraethyl.mol>.

More sites on energy content: carbohydrates vs. hydrocarbons

For a site containing a table of bond energies, as well as a sample calculation of a ΔH calculation and several other practice problems, see <http://www.chalkbored.com/lessons/chemistry-11/bond-energies-worksheet.pdf>.

Another site with more difficult bond energy problems (and their answers) can be found here: <http://www.bishops.k12.nf.ca/science/chem/3202/assign/thermo/SingleBondEnergiesans.doc>.

More sites on zeolites

“The Zeolite Group of Minerals” is a web page from a larger site about minerals in general and can be found at <http://www.galleries.com/minerals/silicate/zeolites.htm>. It explains what zeolites are and what they are used for.

Another site that gives a 1-page basic explanation about zeolites is “What are Zeolites?” at <http://www.bza.org/zeolites.html>.

More sites on ethanol

From CNNMoney.com comes this February, 2006 article: “How to Beat the High Cost of Gasoline. Forever!” at <http://ender.bu.edu/~tgardner/be209/lectures/01/articles/How%20to%20Beat%20the%20High%20Cost%20of%20Gasoline.%20Forever!%20-%20February%202006.%202006.pdf>. It highlights the role of ethanol as an alternative fuel to gasoline.

“‘Green Dreams’, Joel K. Bourne, Jr. This feature story, also available in the print edition of *National Geographic* magazine, October 2007, explores the promises and pitfalls of ethanol and biodiesel produced from a variety of plant sources, from corn and sugar cane to switch grass and algae. This insightful and in-depth story looks at the various sources in terms of their environmental, economic, and human impacts.” [This is quoted from the December 2007 *ChemMatters* Teachers Guide.] (<http://ngm.nationalgeographic.com/2007/10/biofuels/biofuels-text/1>)

Here is an article describing ethanol production, with interviews from the people actually doing the growing and processing: http://www.pbs.org/newshour/bb/science/july-dec07/ethanol_10-09.html.

More sites on other biofuels

“Biofuels in the Transportation Sector”, at <http://www.eia.doe.gov/oiaf/analysispaper/biomass.html>, is a February, 2007 article from the Energy Information Administration. The EIA provides official energy statistics from the Department of Energy. The article includes information about the current (2007) status of the Biofuels Industry.

Biodiesel, like gasoline, has its own backers. You can find a site by the National Biodiesel Board with lots of useful links and basic information about biodiesel fuel at http://www.biodiesel.org/resources/biodiesel_basics/default.shtm.

The “National Biofuels Action Plan”, October, 2008, is a booklet describing the current national fuel challenges, and the ways the government plans to solve these problems. Published by the Biomass Research and Development Board, the report can be found at <http://www1.eere.energy.gov/biomass/pdfs/nbap.pdf>.

General Web References

The Kennesaw State University ChemCases.com web site, at <http://www.chemcases.com/converter/converter-24.htm> has been cited in the body of the Teachers Guide, but it is worth mentioning here also as it is replete with information re: gasoline and its additives.

More Web Sites on Teacher Information and Lessons

The Greater Houston Energy Education Collaborative (GHEEC— I think that’s pronounced “geek “) exists “to foster dialogue, education and collaboration on energy education issues...” This site has a page on which you can “Find great lessons for the classroom”. It also contains a “Find great web sites” page, a “Find multimedia resources” page and a “Find great project ideas” page: <http://hunstem.uhd.edu/GHEEC/#>. The site also allows you to upload your own project and lesson ideas to share with others.

The Makeup of Mineral Makeup

Background Information

More on mineral makeup

Since this article is about mineral makeup, a cautionary word about minerals is in order here. The accepted definition of a mineral requires that the substance be a naturally occurring solid formed by geological processes and with a definite chemical composition, specific properties and an ordered atomic structure (usually crystalline). Until recently, minerals were defined as inorganic substances, but the current definition has been expanded to include organic substances as well.

Companies producing mineral makeup products are allowed to call their product a “mineral” product even though some of the chemicals in the product are not actually minerals from the geochemical point of view. Students should understand that in chemistry terms often have stricter or different meanings than they might have in everyday language. You should remind students as they read this article to think about the differences in the meaning of terms.

For example, the article says that the primary components of most mineral makeup products are talc, mica powder, titanium dioxide, zinc oxide, and iron oxides. These substances qualify as minerals. Other components mentioned in the article are bismuth oxychloride and its replacement, boron nitride, and neither of these should be considered true minerals. Neither bismuth oxychloride nor boron nitride occurs naturally. BiOCl is derived from bismuth, which does occur naturally, but that does not qualify the compound as a mineral. Boron nitride is a completely synthetic compound.

In addition, the fact that the primary components are minerals does not preclude their having been treated chemically in order to prepare them for safe use in the makeup. For example, one method of producing pure titanium dioxide involves reducing the TiO_2 with carbon, then oxidizing with chlorine to produce titanium tetrachloride, which is then distilled and re-oxidized with oxygen to yield pure TiO_2 . All makeup ingredients are processed in some way.

The fact that mineral makeup is a mixture of finely ground solids means that in addition to extraction from the ore and purification processes, each of the ingredients has to be pulverized to produce the powders in the makeup. This process is referred to as “micronization”. Historically solids have been milled or ground to produce the desired particle size. Milling involves placing the solid in a drum which contains steel spheres. As the drum is rotated the spheres collide with the solid particles making them smaller. Grinding reduces particle size by means of blades which crush the particles. (See “More on particle size”, below.)

A new technology called the RESS (Rapid Expansion of Supercritical Solutions) creates smaller particle size by dissolving the solid in a fluid at high temperature and pressure. The supercritical solution is forced through a small nozzle and small fluid particles form. The resulting drop in pressure causes the solid to precipitate out of solution. At the same time the fluid that is trapped in the solid crystal changes to a gas, thus breaking the solid crystal into smaller particle. Particle size on the order of 0.01 μm can be achieved using this method of micronization. (See “More on particle size”, below.)

Using naturally occurring chemical substances as cosmetics is not new. As early as 10,000 BC, natural oils and ointments were used to mask body odor. Henna, chemically known as lawsone (2-hydroxy-1,4-naphthoquinone), was used as a dye for skin and finger nails. Kohl, a dark powder consisting mainly of antimony but often including lead or copper, was used as eyeliner.

In ancient Egypt, women applied eye coloring made from the copper ore malachite (copper carbonate) and Mesdemet, which is produced from galena (PbS). In Greece, chalk or white lead— $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ —was used to whiten the skin, and ochre clays mixed with red iron were used as lipstick. In the 16th century, arsenic compounds were sometimes used as a whitener instead of lead. Even well into the 19th century, lead and antimony sulfide and mercury(II) sulfide were still being used in cosmetics. By this period in history, zinc oxide, the same ZnO used in mineral makeup, was in use as a cosmetic.

Brands of mineral makeup vary according to their formulation. Each company mixes the basic ingredients (titanium dioxide, zinc oxide, talc, mica, iron pigments, etc.) in a slightly different way. As the article suggests, many of the basic mineral makeup ingredients (like titanium dioxide and zinc oxide) are also found in traditional makeup products.

Talc— $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$

Talc is a common hydrous silicate mineral with the chemical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. The crystal structure of pure talc is a sheet made up of $(\text{Mg}_{12}\text{O}_{12}\text{H}_4)$ sandwiched between two sheets of silica (SiO_2), to form talc layers. This pattern repeats continuously. Each layer is electrically neutral. The layers are held together only by weak van der Waals forces, which can be easily overcome by rubbing. When you rub talc, the layers slide over each other and the talc feels slippery. This is one of the reasons it is used in body and baby powders.

According to the United States Geological Survey, “U.S. talc is used in the production of ceramics (the main domestic use), paint, paper (for improving several paper qualities and in recycling processes), plastics (as a functional filler, providing rigidity to the plastic), roofing, rubber, cosmetics, flooring, caulking, and agricultural applications. As examples, talc is used in the ceramic substrate of catalytic converters and is found in wire and cable insulation, auto body putty, asphalt shingles, caulks, sealants, joint compounds, foam packaging, animal feed, pharmaceuticals, chewing gum, candy, gaskets, hoses, belts, flooring (providing softness and flexibility), insecticide carriers, and of course, baby and body powders.”

(<http://pubs.usgs.gov/fs/fs-0065-00/fs-0065-00textonly.pdf>) Only about 2% of U.S. talc production goes to cosmetics.

Properties

Appearance = white, green or gray crystalline solid
Refractive index = 1.60
Luster = dull to pearly
Hardness (Mohs) = 1
Specific gravity = 2.53-2.83
Solubility (water) = insoluble

Mica

According to the United States Geological Survey, mica production was estimated to be 98,700 tons in 2008. North Carolina accounted for about 37% of U.S. production. The remaining output came from Alabama, Georgia, South Carolina, and South Dakota. The majority of domestic production was processed into small particle-size mica by either wet or dry grinding. Primary uses were joint compound, oil-well-drilling additives, and paint, roofing, and rubber

products. The value of 2008 scrap mica production was estimated to be \$14 million. Ground mica sales in 2007 were valued at about \$50 million and were expected to increase in value in 2008.

(<http://minerals.usgs.gov/minerals/pubs/commodity/mica/mcs-2009-micasc.pdf>)

Properties

Appearance = colorless to silvery

Specific gravity= 2.7-2.8

Hardness – 2.0-3.5

Index of refraction = 1.53-1.70

Luster = vitreous, pearly, metallic

Solubility (water) = insoluble

Most micas are inert. They are stable except to concentrated hydrofluoric and sulfuric acids. Mica is unaffected by UV light, and temperatures up to 1800°C. It is non-flammable and non-toxic.

There is a variety of micas, the most common of which is muscovite, $KAl_2Si_3AlO_{10}(OH,F)_2$. The common chemical component of micas is that they are silicates. They are known as sheet silicates because the crystal structure is a loosely connected set of layers, similar to those in talc. In the case of mica crystals, however, cations separate the layers.

Titanium dioxide (TiO₂)

Titanium dioxide occurs in nature as the minerals rutile, anatase and brookite. The rutile and anatase forms have tetrahedral crystal systems and brookite is an orthorhombic crystal. The ore is refined, as mentioned above, by reducing the TiO₂ with carbon, then oxidizing with chlorine to produce titanium tetrachloride, which is then distilled and re-oxidized with oxygen to yield pure TiO₂. The TiO₂ is micronized for use in makeup. It is used primarily as a white pigment, but in makeup its high refractive index makes it an excellent opacifier. TiO₂ also acts as a sunscreen—actually as a sun block to protect skin by preventing penetration from UV radiation. Both TiO₂ and ZnO block UV radiation from reaching the skin by scattering the incoming light away from the skin. They are referred to as *physical* sun blocks to distinguish them from *chemical* sun blocks which operate by absorbing UVA and UVB radiation and re-emitting it as less harmful radiation. TiO₂ has high opacity and, therefore, is used in makeup to provide coverage.

Properties of TiO₂ include:

Appearance = white solid

Density = 4.23 g/mL

m.p. = 1843°C

b.p. = 2972°C

Refractive index = 2.90

Solubility (water) = insoluble

Zinc oxide (ZnO)

Zinc Oxide is an amorphous white or yellowish powder. Zinc oxide absorbs UVA radiation at wavelengths of 320-400 nm and UVB radiation in the 280-320 nm range. Its opacity is somewhat less than that of titanium dioxide. These two properties make it useful in makeup—opacity to provide coverage and UV absorption to provide SPF of 15. It is also used as a pigment in compounding rubber, as a white pigment in the ceramics industry, as an opaque base in cosmetics, and it has other applications in the paper, paints and optical glass industries.

Properties

Appearance = white solid

Density = 5.61 g/mL
m.p. = 1975°C
b.p. = 2360°C
Solubility (water) = very slightly soluble
Refractive index = 2.00
Hardness (Mohs) = 4.5

Iron oxide pigments

As the article states, iron oxides are used as mineral pigments to impart color to makeup. The three basic iron oxides, hematite (Fe_2O_3), limonites (FeOOH) and magnetite (Fe_3O_4), can be used in combination with each other and with other pigment components like TiO_2 and ZnO to produce a wide variety of makeup colors. In addition, the particle size of the pigments can be manipulated to nuance the color of the makeup.

Color tone also depends on factors like temperature, concentration, pH, and radius of the pigment particle when manufactured. As a colorant, iron oxide pigments impart color and opacity and allow the makeup to slide easily on the skin.

Both natural forms of the oxides and synthetic forms have been used in makeup. The synthetic forms virtually eliminate any impurities in the pigments. Three major methods for the manufacture of synthetic iron oxides are thermal decomposition of iron salts or iron compounds; precipitation of iron salts, usually accompanied by oxidation; and reduction of organic compounds by iron. However, many of the mineral makeup companies prefer to use natural pigments. The U.S. Food and Drug Administration regulates cosmetic pigments. For information of FDA approved color additives, including the iron oxide pigments, see

<http://www.fda.gov/ForIndustry/ColorAdditives/ColorAdditivesinSpecificProducts/InCosmetics/ucm110032.htm>.

Brief profiles of the three main color pigments:

Red iron oxide (Fe_2O_3)

Red iron oxide is a red to brown solid with a metallic to dull luster. Among the other properties of the compound are: a refractive index of 1.49-1.66, a specific gravity of 5.26, and a melting point equal to 1565°C. It is insoluble in water.

This inorganic pigment has high opacity and strong tinting strength, as well as good dispersion. It has outstanding light resistance and is weather proof. These make it attractive for a variety of applications such as: in construction, rubber and painting, as well as cosmetics.

Yellow iron oxide (FeOOH)

This pigment is an insoluble yellow solid with a specific gravity of 4.0. It is widely used in painting, and concrete due to its bright color and high opacity. It has good hiding ability. Depending on particle size, yellow iron oxide takes on different color from green shade yellow and red shade yellow.

Black iron oxide

Magnetite is a black insoluble solid with specific gravity of 5.2 and melting point of 1538°C. The natural mineral, also called lodestone, is magnetic. It is often produced synthetically rather than extracted from the mineral, so that mineral size can be better controlled.

More on boron nitride (BN)

As the article states, boron nitride is a synthetic compound. It was discovered in the 1800s but was not used in consumer products until the 1990s. It can exist in two forms—hexagonal and cubic—similar to the allotropes of carbon, graphite and diamond. The hexagonal form is the one described in the article. In fact, boron nitride is “nicknamed” white graphite. This form is synthesized by reacting boron trioxide with ammonia gas at a high temperature and then heating the resulting BN in nitrogen gas above 1500°C.

The compound is insoluble in water and has a melting point of 2967°C and a boiling point of 3273°C. It is a good lubricant in ceramics, alloys, resins, plastics, and rubbers in addition to cosmetics. It is also used in laser printers and photocopiers.

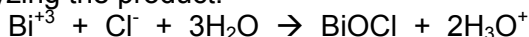
More on bismuth oxychloride (BiOCl)

Bismuth oxychloride is a white crystalline solid used to impart luster and to provide “slip” to makeup (“slip” refers to the ease of application on skin). In small concentrations it is a common ingredient in most traditional makeups.

Properties:

Appearance = white solid
Density = 7.72 g/mL
Refractive index = 2.15
Solubility (water) = insoluble
m.p. = 500°C

BiOCl does not occur in nature. It is produced from bismuth, which is a by-product of the refining of ores of copper, lead, tin, silver and gold, by reacting bismuth with a chloride salt and hydrolyzing the product:



Although the compound is inert, it can irritate the skin, as the article describes. The MSDS says that BiOCl is “slightly hazardous in case of skin contact (irritant).”

So how do the properties of these makeup ingredients translate into properties of the makeup itself?

The fact that there are no dyes, preservatives or fragrances in mineral makeup make them less likely to irritate the skin. The article says that many manufacturers are replacing boron oxychloride—a possible skin irritant—with boron nitride, which is chemically unreactive. In addition, at least two of the chemical components—titanium dioxide and zinc oxide—have anti-inflammatory properties. These latter two chemicals also provide protection against both UVA and UVB radiation. TiO₂, ZnO and BN all also help makeup adhere to the skin. The article details the reason that BN adheres well—van der Waals forces.

Each of the chemicals in mineral makeup is water insoluble, which means that the powders need be applied less often. The luminescent properties often seen in mineral makeup

products are the result of two factors. The first is the unusually high index of refraction of many of the chemical components. These high refractive index chemicals—mica, TiO₂, BN, for example—disperse the light to create both the “shimmer” associated with mineral makeup and the “rainbow of colors” produced by the makeup. The second factor is the carefully regulated particle size of many of the components. By regulating particle size manufacturers also prevent the makeup from clogging pores—a property called non-comedogenic.

More on particle size

Although the article does not emphasize it, the particle size of the solids making up mineral makeup products help to determine the overall properties of the makeup. This would be an opportunity to review with students SI prefixes and units

Value	Prefix	Multiple/Decimal
trillion	tera-	1000000000000 X
billion	giga-	1000000000 X
million	mega-	1000000 X
thousand	kilo-	1000 X
hundred	hecto-	100 X
ten	deca-	10 X
UNIT	_____	1
tenth	deci-	0.1
hundredth	centi-	0.01
thousandth	milli-	0,001
millionth	micro-	0.000001
billionth	nano-	0.000000001
trillionth	pico-	0.000000000001

The particle size of the powders in many mineral makeup products are on the order of 1-30 μm. For example, the smallest TiO₂ particles are between 0.2 and 0.3 μm in diameter. Zinc oxide particles are in the same range. In general mineral pigments fall in the following ranges:

Particle Size	Measurement
Coarse	< 10 μm
Fine	< 2.5 μm
Ultra-fine	< 0.1 μm (nanoparticles)

Manufacturers of mineral makeup create different makeup effects by varying the size of the powdery particles in the product. Makeup hiding power and luster are functions of particle size. For example, makeup particles less than 15 μm in size have good hiding power and low luster. If particle size were to be increased to about 150 μm (larger than the particle size in makeup) the effect is a sparkling luster but the makeup is almost transparent.

Now, nanoparticles all have dimensions less than 100 nm, or less than 0.100 μm. This definition plays a role in mineral makeup because some products are thought to contain particles in the nano range. Some environmental, health and safety groups claim that nanoparticles in mineral makeup could penetrate the skin and be harmful to human health. There is some evidence that in the application process smaller particles in loose (powdered) mineral makeup may be inhaled and cause damage to lungs.

There is little research to back up claims of nanoparticles entering the body through the skin. In fact, it is very unlikely that even nanoparticles could penetrate human skin, which consists of three layers—epidermis, dermis, and subcutaneous layers. On the top of the outer

layer, the epidermis, there is a sub-layer called the stratum corneum, which is a layer of hardened dead cells approximately 10-15 nm thick. This prevents chemical substances from penetrating through to the dermis underneath. Studies have shown that nanoparticles of TiO₂ and ZnO in sunscreen do not penetrate the epidermis.

Given the growing interest in nanotechnology currently, it might be interesting to introduce particle size and nanoparticles to students in connection with this article.

More on van der Waals forces

About the bonding the boron nitride, the article says, "Within each layer, boron and nitrogen atoms form strong covalent bonds, whereas the layers are held together by weak van der Waals forces." There are two types of van der Waals forces: London dispersion forces, which originate from temporary charges that arise in non-polar molecules involving atoms with larger numbers of electrons; and dipole-dipole interactions, which are electrostatic forces created by the partial positive and negative charges within neighboring molecules that exhibit some degree of polarity. The relative energies of van der Waals forces are much less than covalent bonding energies. The following chart gives an approximation of the relative strengths in kJ/mol:

Covalent bonds 100–1000
Dipole-dipole 0.1–10
London forces 0.1–10

The article says that the relatively strong covalent bonds between boron and nitrogen atoms hold the atoms **within** the layers and the weaker van der Waals forces **between** the layers allow the layers to slide over one another. The article also suggests that van der Waals forces help the makeup adhere to skin.

More on evaluating claims

Because mineral makeup is not well regulated by the Food and Drug Administration or other agencies, students should be careful to evaluate claims made by companies and individuals involved in making mineral makeup. This caution should be a general one for all consumers and especially for anyone looking for information on the internet. Some terms that students should view with skepticism include natural, organic, botanical, pure and mineral.

The accuracy of statements made about mineral makeup should also be carefully evaluated. For example, consider this advice about mineral makeup: "Consider bismuth . . . carefully. Bismuth is a mineral that does not occur naturally in the earth. It provides a glow to many bronzers and finishing powders. Some people love it, while others find that it makes them unbearably itchy." (http://www.ehow.com/how_4494680_evaluate-ingredients-mineral-makeup.html) The person making this statement is talking about bismuth oxychloride, but says "bismuth," perhaps without knowing the difference between the element and its compounds.

Or consider the accuracy of this statement about boron nitride: "Boron nitride is a silky, white mineral [yes, it is a NOT a chemical even though it sounds like one] and it is added as an additive to improve the "slip" (i.e. how smoothly the product applies) as well as "adhesion" (i.e. how long it stays on the skin) of the mineral makeup which can range from foundations, blushes, eye shadows and concealers."

Vested interest is another potential problem. The following statement was taken from a “news” website based in California (<http://www.bohemian.com/bohemian/05.02.07/poisonous-cosmetics-0718.html>).

One new alternative to conventional cosmetic chemistry is mineral makeup, which uses naturally occurring minerals as the basis for the products. Not only is mineral makeup free of toxic chemicals, it provides protection from the sun and can even include customized levels of moisturization or oil control.

With conventional makeup, says Tara Voight, owner of the Always Pampered salon in Novato, "women are trying to cover up instead of work with their skin." Instead, she advocates using mineral makeup, which doesn't clog pores and can be customized to complement your skin.

This might sound like reasonable advice from a professional salon owner, but the next statement in the “news” article suggests something different behind the advice:

Voight, who has been working in the skincare business for 14 years, is such a believer in the benefits of mineral makeup that she has developed her own line. She says creating high-quality mineral makeup is just a matter of practice, and her long-term goal for her line is to "make one better than the rest.

The salon owner is also a mineral makeup producer with a vested interest in promoting the use of the product.

Label claims may also be misleading. For example, this description appears on the manufacturer web site <http://www.purminerals.com/Pur-Radiance-Mineral-Powder>

Pür Radiance Mineral Powder makeup is an all-natural mineral powder blush that enhances your complexion with soothing ingredients. Pür Radiance Mineral Powder makeup catches the light from different angles to give skin a radiant, healthy glow. And as with all Pür Minerals makeup products, Pür Radiance Mineral Powder is free of oil, alcohol, talc, fillers, fragrance and chemical dyes. Your wedding day, the first "I love you," a stolen kiss... Pür Radiance Mineral Powder makeup gives you back that warm, healthy glow.

The list of ingredients in this product also appears on this site:

Zea Mays (Corn) Starch, Zinc Stearate, Silica, Butyrospermum Parkii (Shea Butter), Boron Nitride, Tocopheryl Acetate, Methylparaben, Propylparaben May Contain: Mica CI 77019, Titanium Dioxide CI 77891, Iron Oxides CI 77491/CI 77492/CI 77499, Carmine CI 75470

At least one ingredient is not “all-natural” and there are several that may not be natural. Students can research these ingredients to determine which are synthetic.

Students can find many other examples of questionable claims by doing a little internet research. (See “Student Projects” #2, below.)

Connections to Chemistry Concepts

1. **Covalent chemical bonding**—Chemical bonding is an important topic in this article, especially in the discussion of boron nitride. Covalent bonds hold the atoms together within a layer of that compound.
2. **Secondary chemical bonding**—the forces holding together the layers of boron nitride are prime examples of van der Waals forces.
3. **Chemical and physical properties**—There is a great deal of emphasis on the properties of individual compounds and properties of the resulting mixture of powders that comprise mineral makeup.
4. **Particle size**—The bond distances within boron nitride are featured, and the article discusses that the properties of the makeup are related to the particle size in the powder constituents. With nanotechnology becoming such a large feature of scientific research, particle size will become more and more important to the study of chemistry.
5. **Crystal structures**—Hematite’s and magnetite’s crystal structures are hexagonal and cubic, respectively. Other minerals listed in the article; e.g., mica and talc also have specific crystal structures, and several more are listed in the Background Information, above.
6. **Chemistry and personal perspectives**—Much of this article relates to the properties of makeup, the use of which often comes down to personal preferences and choices. It is important for students to learn to make informed choices.

Possible Student Misconceptions

1. “**Aren’t minerals just dirt and rocks? Surely those can’t be part of makeup!**” When we look around us in nature, we may see “rocks and dirt.” But from a chemistry viewpoint we need to think about the chemical compounds that make up the rocks. These chemical compounds can be (and are) extracted from the rocks and purified and used in powder form in makeup.
2. “**I’ve heard so much about cosmetics being petroleum-based. So, the chemicals in mineral makeup are derived from petroleum, right?**” *No. The chemicals described in this article are inorganic minerals which are mined from the earth. The accepted definition for a mineral is “naturally occurring solid formed by geological processes and with a definite chemical composition, specific properties and an ordered atomic structure (usually crystalline).” Petroleum is a mixture of organic compounds, most of which are liquids.*

Demonstrations and Lessons

1. Since mineral makeup is a mixture of powders, students might enjoy doing the “mystery powder” lab activity. Here are several for reference
http://www.knowitall.org/instantreplay/files/gearup_for/Forensics%20Powder%20Lab.pdf or
http://schools.lwsd.org/KiJH/t_palmer/documents/9th%20Grade/Chemistry/Mystery%20Powders%20Lab.pdf or
<http://www.skaggs.adventurejunkie.net/class%20work/unknown%20substance%20lab.pdf>
2. The United States Geological Survey has a booklet of activities about minerals, including one activity on talc (see page 17). (<http://pubs.usgs.gov/qip/2005/17/qip-17.pdf>)

Student Projects

1. Students can research products and ingredients here: <http://www.cosmeticsdatabase.com/index.php>. This page is part of the Environmental Working Group's site. Other sites that provide information on products and ingredients include <http://people.delphiforums.com/tracikenyon/IngredList22405.html> and <http://www.mineral-makeup-reviews.com/Mineral-Makeup-Brands.html>.
2. Students should learn to evaluate the claims made by the manufacturers of any product, and they can gain experience by evaluating mineral makeup claims. See "More on evaluating claims", above. Students can use these resources:
 - a) A National Public Radio transcript about mineral makeup, <http://www.npr.org/templates/story/story.php?storyId=91791886>.
 - b) See this from How Stuff Works, <http://www.howstuffworks.com/framed.htm?parent=mineral-makeup.htm&url=http://www.slate.com/id/2211934/>.
 - c) The Cosmetic Labeling Guidelines from the Food and Drug Administration, <http://www.fda.gov/Cosmetics/CosmeticLabelingLabelClaims/CosmeticLabelingManual/ucm126444.htm>.
 - d) See this web site for reviews on mineral makeup brands: <http://www.mineral-makeup-reviews.com/Mineral-Makeup-Ingredients.html>.
 - e) This web site sells many of the mineral makeup ingredients and provides recipes for preparing mineral makeup. (http://www.pvsoap.com/mineral_makeup_ingredients.asp)

Anticipating Student Questions

1. **"How can something be 'natural' and 'synthetic' or processed at the same time?"**
Many of the chemical compounds discussed in the article can also be synthesized in the lab from other chemicals. The iron oxide pigments are examples. Thus, these kinds of compounds may be either natural or synthetic. In other words, compounds that occur in nature may also be synthesized. In fact, much of chemistry research deals with attempts to synthesize naturally occurring materials. In addition, even if the chemicals are obtained directly from nature, they must be purified or otherwise processed to be usable in a cosmetic product. Titanium dioxide is mentioned in the article as one chemical that undergoes extensive purification. Other compounds, like boron nitride do not exist in nature and are entirely synthetic.
2. **"The article talks about pigments. Are they the same as the pigments found in paint?"**
Yes, chemical compounds like Fe_2O_3 may be used in a variety of ways. The Fe_2O_3 found in mineral makeup is the same chemical that is used as a paint pigment.

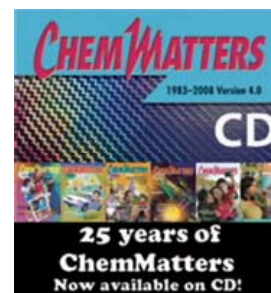
References

The references below can be found on the *ChemMatters* 25-year CD (which includes all articles published during the years 1983 through 2008). The CD is available from ACS for \$30 (or a site/school license is available for \$105) at this site:

<http://www.acs.org/chemmatters>. (Click on this *ChemMatters* CD image at the right of the screen.)

Selected articles and the complete set of Teacher's Guides for all issues from the past five years are also available free online at this same site. (Full *ChemMatters* articles and Teacher's Guides are available on the 25-year CD for all past issues, up to 2008.)

(<http://www.acs.org/chemmatters>)



Fruen, Lois, "Cleopatra's Perfume Factory and Day Spa," *ChemMatters*, October, 2004, pp. 14-15. This article describes some of the history of cosmetics.

Sibley, Lynn, "Lipstick," *ChemMatters*, December, 1985, pp. 8-11. This article includes a discussion of the components of lipstick.

Rohrig, Brian, "Tattoo Chemistry Goes Skin Deep," *ChemMatters*, October, 2001, pp.6-7. Pigments are discussed in this article.

Web Sites for Additional Information

More sites on cosmetics

From the FDA, this site provides information on a variety of cosmetics:
<http://www.fda.gov/Cosmetics/default.htm>.

More sites on minerals

The United States Geological Survey has a book of activities on minerals, including one activity on talc at <http://pubs.usgs.gov/gip/2005/17/gip-17.pdf>.

This site is a huge database providing the chemical composition of minerals—searchable—at <http://webmineral.com/chemical.shtml>.

More sites on talc

The United States Geological Survey has a fact sheet on talc: <http://pubs.usgs.gov/fs/fs-0065-00/fs-0065-00textonly.pdf>.

More sites on health effects of mineral makeup

Friends of the Earth, an environmental group, has published this document regarding potential health effects of products with small particle size:
http://www.foe.org/sites/default/files/final_USA_web.pdf.