

April 2007 Teacher's Guide

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About the Guide

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NOTE: articles from past issues of *ChemMatters* can be accessed from a CD that is available from the American Chemical Society for \$25. The CD contains all *ChemMatters* issues from 1983 to 2003.

The 2006 *ChemMatters* Print Index can be purchased for \$12 and covers all issues from 1983 to 2006.

Purchase information can be found online at: <u>http://chemistry.org/chemmatters/cd3.html</u>

Student Questions

Paintball!

- 1. What is the source of the gelatin that makes up the outer coating of paintballs?
- 2. Name the substance that comprises most of the fill in a paintball.
- 3. Name the type of bond in which the partially positive charge around a hydrogen atom is attracted to a non-bonding electron pair in an oxygen atom.
- 4. What is the typical propellant used in paintball markers?
- 5. In m/s, what is the initial velocity of a paintball shot from a marker?
- 6. In what decade did the sport of paintball begin?

Gold in Your Tank

- 1. What is the name for compounds composed only of carbon and hydrogen?
- 2. What are saturated molecules?
- 3. Name three methods petroleum geologists use to help them find crude oil underground.
- 4. What physical property is the basis for fractional distillation?
- 5. What two factors affect intermolecular (London) forces?
- 6. What is the name of the hydrocarbon with a positive charge? Does the name make sense to you? Why?
- 7. Name two ways petroleum chemists can create more gasoline from each barrel of crude oil.
- 8. What does an octane rating of 87 mean?

Retiring Old Tires

- 1. About how many used tires are discarded each year in the United States?
- 2. How much oil can an average tire produce when it burns?
- 3. Who discovered vulcanization of rubber?
- 4. Why are tires shredded before they are burned as fuel?
- 5. What pollutants found in emissions from burning coal are not found in the emissions from burning tire derived fuels?
- 6. What substances are used to cool tires before they are ground into smaller bits of rubber?

The Captivating Chemistry of Coins

- 1. Why were coins originally made from precious metals such as gold or silver rather than cheaper metals such as copper?
- 2. What kind of metal is bronze? How does it differ from brass?
- 3. What is meant by the term ferromagnetic?
- 4. What is the major difference in metal composition of Canadian coins compared with American ones?

- 5. Chemically speaking, how does applying hotdog mustard to a coin detect the presence of silver metal?
- 6. What alloy is presently used to produce the appearance of silver on coins without the presence of any silver whatsoever?

The Death of Alexander Litvinenko

- 1. When radioactive Polonium 210 decays, it emits alpha particles. What is the composition of an alpha particle?
- 2. What is the origin of the name Polonium?
- 3. What is meant by a half-life in radioactive decay?
- 4. How is polonium produced?
- 5. What happens to an element when it undergoes beta decay?
- 6. What countries produced polonium 210?
- 7. In nuclear terms what is meant by a "dirty" bomb?

Answers to Student Questions

Paintball!

- 1. What is the source of the gelatin that makes up the outer coating of paintballs? Collagen is the source of the gelatin that makes up the outer coating of paintballs.
- 2. Name the substance that comprises most of the fill in a paintball. Polyethylene glycol is the name of the substance that comprises most of the fill in a pantball.
- 3. Name the type of bond in which the partially positive charge around a hydrogen atom is attracted to a non-bonding electron pair in an oxygen atom. The hydrogen bond is the name of the type of bond in which the partially positive charge around a hydrogen atom is attracted to a non-bonding electron pair in an oxygen atom.
- 4. What is the typical propellant used in paintball markers? Carbon dioxide is the typical propellant used in paintball markers.
- 5. In m/s, what is the initial velocity of a paintball shot from a marker? The initial velocity of a paintball shot from a marker is 91 m/s.
- 6. In what decade did the sport of paintball begin? The 1980's is the decade in which the sport of paintball began.

Gold in Your Tank

- 1. What is the name for compounds composed only of carbon and hydrogen? Compounds made of only carbon and hydrogen are called hydrocarbons.
- 2. What are saturated molecules? Saturated molecules are molecules containing only single bonds.
- 3. Name three methods petroleum geologists use to help them find crude oil underground.

Petroleum geologists use: 1) **satellite images** to examine surface terrain; 2) **cameras** to reveal ocean floor features; 3) **instruments to detect changes in the Earth's gravitational field**; 4) **instruments to detect changes in the Earth's magnetic field**; 5) **explosions or thumper trucks** with seismological instruments to detect pockets of oil in rock structures underground.

- **4. What physical property is the basis for fractional distillation?** *The physical property that is the basis for fractional distillation is boiling point.*
- 5. What two factors affect intermolecular (London) forces? The two factors that affect intermolecular forces are molecular size and surface area.
- 6. What is the name of the hydrocarbon with a positive charge? Does the name make sense to you? Why?

The name of the hydrocarbon with a positive charge is a **carbocation**. The name should make sense, since it contains carbon atoms (carbo-), and it is a positive ion (cation), hence carbocation..

7. Name two ways petroleum chemists can create more gasoline from each barrel of crude oil.

Petroleum chemists can produce more gasoline from a barrel of crude oil by: **cracking** (breaking larger molecules into smaller ones), **unification** (combining smaller molecules into larger ones), and **alteration** (changing the structure of molecules).

8. What does an octane rating of 87 mean? An octane rating of 87 means that the gas mixture has the same resistance to preignition as a mixture of 87% iso-octane and 13% heptane.

Retiring Old Tires

- 1. About how many used tires are discarded each year in the United States? About 3 million tires are discarded each year in the U.S.
- 2. How much oil can an average tire produce when it burns? An average tire can release about two gallons of oil when burning.
- 3. Who discovered vulcanization of rubber? Charles Goodyear discovered vulcanization.
- 4. Why are tires shredded before they are burned as fuel? Tires are shredded to increase surface area.
- 5. What pollutants found in emissions from burning coal are not found in the emissions from burning tire derived fuels? Nitrogen oxides (NO_x) are found in coal emissions, but not in tire derived fuel emissions.
- 6. What substances are used to cool tires before they are ground into smaller bits of rubber?

Liquid nitrogen or supercooled air is used to cool the tires.

The Captivating Chemistry of Coins

1. Why were coins originally made from precious metals such as gold or silver rather than cheaper metals such as copper? The coins value was determined by the value of the metal itself. Only later were cheaper metals used because the value of the coin was determined by the deposits of

gold or silver in a "bank" which the coin represented. 2. What kind of metal is bronze? How does it differ from brass? Bronze is not a single metal but a mixture of metals known as an alloy (if a liquid metal,

such as mercury, is used in the mixture, it is known as an amalgam). For bronze, the mixture is copper and tin. For brass, the alloy is a mixture of copper and zinc.

- 3. What is meant by the term ferromagnetic? Ferromagnetic refers to magnetic properties of metals similar to iron (ferro- refers to iron).
- 4. What is the major difference in metal composition of Canadian coins compared with American ones?

Canadian coins contain a high percentage of nickel which is ferromagnetic. American coins contain 25% or less of nickel, the rest being copper. There is not enough nickel to make the coin ferromagnetic.

5. Chemically speaking, how does applying hot dog mustard to a coin detect the presence of silver metal?

Mustard contains certain chemical compounds that have sulfur in them. The sulfur reacts with silver to form a black precipitate, silver sulfide (Aq₂S), which is visible on the surface of a silver-containing coin. This same black color is found on "silverware" when it "tarnishes" dues to hydrogen sulfide in the air reacting with the silver in eating utensils. forming the same black precipitate, silver sulfide, Ag_2S .

6. What alloy is presently used to produce the appearance of silver on coins without the presence of any silver whatsoever?

The alloy used is a copper-nickel mixture.

Alexander Litvinenko

1. When radioactive Polonium 210 decays, it emits alpha particles. What is the composition of an alpha particle?

An alpha particle is a helium nucleus, 2 protons and 2 neutrons which equals four mass units. The two protons represent the atomic number.

2. What is the origin of the name Polonium? The name polonium is based on the Latin word for Poland, the birth country of Marie-Sklodowska-Curie, who, along with her husband, discovered Polonium, originally called Radium F by the Curies.

What is meant by a half-life in radioactive decay? A half-life is the time it takes for half of a radioactive substance to decay to new products.

4. How is polonium produced?

Starting with Bismuth-209, neutrons from Uranium-235 bombard the Bismuth, causing it to become Bismuth-210 when one of the neutrons joins the nucleus of the Bismuth-209. In turn the unstable Bismuth-210 emits a beta particle from a neutron, producing a proton in the bismuth nucleus. With the total number of protons now at 84, a new element exists, which is Polonium-210.

5. What happens to an element when it undergoes beta decay?

In beta decay, a neutron in the nucleus ejects a beta particle with the mass of an electron. The remaining material of the neutron now possesses a positive charge but the same mass of one, hence a proton. With the addition of a proton, the atomic number and characteristics of the element change to a new element, that with the next highest atomic number on the periodic table.

6. What countries produce polonium 210? As far as is known, only Russia produces polonium-210.

7. In nuclear terms what is meant by a "dirty" bomb?

A dirty bomb is one in which regular explosives are used to create an explosion of material that contains radioactive substances such as polonium and uranium. A nuclear explosion is not involved but the effect of dispersing radioactive material into the environment is similar, though not was extensive, depending on a variety of environmental conditions – including how far off the ground the explosion takes place.

ChemMatters Puzzle: GRID QUOTE

In the squares below appears a two sentence quote, to be read left to right, top to bottom. A black square marks the end of a word. But to make things interesting, we've broken the grid into 15 boxes, each 4x4. In each box there are groups of 1, 2, 3, or 4 letters, which we supply to you below the grid (in alphabetical order, shortest to longest). A little logic and shrewd guessing will allow you to place each combination in its proper spot, and the quote will reveal itself. We will place a few letters in the 1A box to get you started. Note that in that box, there are three one-letter groups, four two-letter groups but <u>no</u> three or four-letter sets.

Hint 1: try crossing off sets as you place them: *Hint* 2: be on the lookout for some names of elements. The quote is taken from the book VALENCE, a classic chemistry text written in 1923 by G.N. Lewis, of Lewis dot diagrams and Lewis acid/base theory fame.



- 1C С S OF UT WE LEME 1D NTS IGHT INCR TRIC 1E S IO TLY EASI WERE T INT LE DINE XYGE 2A 2B N O AN TH WOU ELLU 2C B E D GR LD SU RIUM 2D E FO OUP WOU LFUR 2E F O LD OF WHI RCED 3A NS ALL NICK TION A A S OF SO EL AMON 3B 3C G R RE TH COB LSO
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GRID QUOTE: ANSWERS

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]	Ι	Ν	Т	0		Т	Н	Е		G	R	0	U	Р		0	F		0
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L	Е		Т	Е	L	L	U	R		U	М		W	0	U	L	D		F
А	L	L		А	Μ	0	Ν	G		Т	Н	Е		Н	Α	L	0	G	Е
Ν	S	٠		S	0		А	L	S	0		Т	Н	Е		Р	0	S	Ι
Т	Ι	0	Ν	S		0	F		С	0	В	Α	L	Т		Α	Ν	D	
N	Ι	С	K	E	L		А	R	E		R	E	V	E	R	S	E	D	•

Content Reading Guide

National Science Education Content Standard Addressed

National Science Education Content Standard Addressed As a result of activities in grades 9-12, all students should develop understanding	Paintball!	Gold in Your Tank	The Captivating Chemistry of Coins	The Death of Alexander Litvinenko	Polymers in Iraq	Retiring Old Tires
Science as Inquiry Standard A: about scientific inquiry.	~	~	~	~	~	~
Physical Science Standard B : of the structure of atoms.	~			~		
Physical Science Standard B : of the structure and properties of matter.	~	~	~	~	~	~
Physical Science Standard B : of chemical reactions.	~	~	~			~
Physical Science Standard B: of motions and forces.	~				~	
Physical Science Standard B: of interaction of energy & matter.		~		~		
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: of environmental quality.	~	~		~		~
Science in Personal and Social Perspectives Standard F: of natural and human-induced hazards.	~	~		~	~	~
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 their 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: 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.

Question From the Classroom: Polymers in Iraq

Ме	Text	Statement
		1. Dyneema, considered to be the strongest polymer in the world, is denser than water.
		2. Kevlar is a polymer that offers the same protection as steel on the floor of Blackhawk helicopters.
		3. Sodium polyacrylamide absorbs thousands of times its weight in water.
		4. Polymers can sniff out explosives such as TNT.
		5. Silly String is used to find trip wires in buildings.

Paintball!

Ме	Text	Statement
		1. More than a billion paintballs are produced each year.
		2. Paintballs are made to deform when they strike someone so that the force
		3. The best paintballs are made using gelatin from horse hooves.
		4. Paintballs contain water-soluble compounds, but no water.
		5. If a paintball is dropped into water, it will shrink.
		electrons to itself more than the hydrogen atoms do, creating a polar bond.
		7 All molecules with polar bonds are polar
		8 Hydrogen bonds are weak intermolecular forces
		9. The CO ₂ inside a gas cartridge is in gaseous form.
		10. The pressure inside a CO_2 gas canister used for launching paintballs is
		more than 60 time atmospheric pressure.

Gold in Your Tank

Ме	Text	Statement
		1. If you could use gasoline for fuel, it would provide you with enough food for two days.
		2. Most molecules from refined crude oil have many double bonds.
		3. Flowing oil underground can cause very small changes in the Earth's gravitational or magnetic fields.
		4. Crude oil is a mixture of about a dozen chemicals.
		5. The hydrocarbons in crude oil are separated according to their boiling points.
		6. As molecules become larger, the attractive forces between molecules decrease.
		7. About 75% of the crude oil that comes out of the distillation column is gasoline.
		8. Cracking involves breaking large hydrocarbons down into smaller hydrocarbons such as those found in gasoline.
		9. Chemical engineers at oil refineries are constantly creating new catalysts.

Retiring Old Tires

Ме	Text	Statement
		1. Burning tires release volatile toxins and carcinogens into the atmosphere.
		2. Rurning tires become toxic oil that can contaminate soil
		3. In order to be useful for making tires, natural rubber must be vulcanized by adding sulfur at high temperatures
		4. Old tires cannot be made into a useful fuel with our current technology.
		5. Shredded used tires improve drainage, so they are used in septic drain fields as well as landfills.
		6. If rubber is separated from the steel in used tires, it is just as useful as virgin rubber.
		7. We currently reuse only 25% of our used tires.

The Captivating Chemistry of Coins

Ме	Text	Statement
		1. Alloys are harder and more durable than the metals from which they are made.
		2. Brass can be made from copper, zinc, manganese, and nickel.
		3. Today's pennies are only 2.5% copper.
		4. If you can't see the date, it is difficult to tell the difference between pennies made before 1982 and those made after 1982.
		5. If a child swallows a post-1982 penny, he should be watched carefully.
		6. Dimes, quarters, half dollars, and silver dollar coins still have a silver coating.
		7. You can use mustard to test to see if a coin contains silver.
		8. Vending machines use fewer than 10 tests to verify whether the coin is genuine.
		9. Most coins minted in the United States are magnetic.
		10. Nickel expands more rapidly and shrinks more quickly than copper.

The Death of Alexander Litvinenko

Ме	Text	Statement
		1. One symptom of Litvinenko's radiation poisoning was that his hair fell out.
		2. Polonium-210 is found in abundance in the earth's crust.
		3. Polonium-206 is the most abundant isotope of polonium.
		4. Polonium-210 can be made in nuclear reactors.
		5. Alpha particles are not harmful outside the body.
		6. Polonium-210 is imported into the United States for use in equipment to eliminate static.
		7. Polonium-210 could be used to make a "dirty bomb."

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; deta		Complete; details provided; demonstrates deep		
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	So incomplete that no judgment can be made		
0	acceptable	about student understanding		

Questions from the Classroom: Polymers in Iraq

Directions: As you read, complete the chart below.

Polymer	Polymer description	Uses
Dyneema		
Kevlar		
Sodium polyacrylamide		
SOPs		

Paintball!

Directions: As you read, please complete the chart below. You should be able to list at least 4 bulleted points for each topic.

History of	
Thistory of	
paintballs	
Challenges to	
onanongeo to	
making	
n ain thalla fan	
paintballs for	
sport	
sport	
<u>.</u>	
Chemicals used	
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in making	
in making paintballs	
in making paintballs Chemistry of	
in making paintballs Chemistry of bow the	
in making paintballs Chemistry of how the	
in making paintballs Chemistry of how the paintball	
in making paintballs Chemistry of how the paintball	
in making paintballs Chemistry of how the paintball markers work	

Gold in Your Tank

Directions: As you read, please complete the chart below. Use bullets or number steps for each topic.



Retiring Old Tires

Directions: As you read, please complete the chart below. Use bullets to separate the steps in the processes and each advantage you can find.

Material	How is it created?	Advantages
Vulcanized rubber		
Tire-derived fuel (TDF)		
Tire-derived aggregates (TDAs)		
Crumb rubber products		

The Captivating Chemistry of Coins

Directions: Compare and contrast old, new, and Canadian coins in the chart below.

COIN	Old	New	CANADIAN
Penny			
Nickel			
Dimes & Quarters			
Dollar			

The Death of Alexander Litvinenko

Directions: As you read the article, please complete the chart below about Polonium-210.

Discovery of polonium-	
210	
Production of	
polonium-210 today	
Properties of polonium-	
210	
Uses for polonium 210	
Uses for polonium-210	

Paintball!

Background Information

More on Paintball Composition

The article says that paintballs consist of a soft outer capsule, which is made of gelatin along with glycerin and sorbitol and a liquid fill that is made primarily of polyethylene glycol and a coloring agent. To learn more about the gelatin that makes up the soft gel capsule see "More on Collagen/Gelatin", below. And to learn more about the fill material see "More on Paint Contents, below".

Paintballs are made by machine in a process called softgel encapsulation, a process pioneered by the pharmaceutical industry to make softgel (see "More on Softgels", below) tablets for drugs. The capsule is made by passing two heated strips of gelatin over two rotating wheels that contain semi-circular holes. As the two holes meet the gelatin is pressed into the semi-circular molds, each forming one half of a paintball. At the same time the fill material is injected into the ball. The two halves of the ball are pressed against each other and sealed. The completed paintballs are then dropped into a tumbler to dry.

According to the trade journal "Paintball Competitions and Ratings International (PCRI)" there are a number of quantitative properties of paintballs. They include the R-factor, weight, shell wall thickness, and burst strength.

The article says that most paintballs are 68 caliber. This means that their diameter is .68 inches, or 1.7 cm. However, according to PCRI, most paintballs are not perfectly round, and this variation affects their accuracy and reliability. The rounder the paintball the more accurate it will be. On the other hand, according to industry experts, paintballs that are out-of-round actually break more easily on impact with a target. The R-factor of a ball measures its roundness. It is calculated by measuring the diameter at the seam (see paragraph below on how paintballs are manufactured) and at right angles to the seam (called "the poles"), finding the difference and dividing by two to get the average. In general, R-Factors for paintballs tested can range from 1-9.

The average paintball has a mass of about 3.2 g. This average paintball increased slightly in mass from 1992 to 1999, from 3.19 g to 3.29 g.

The gelatin-based shell wall of a paintball can range from 0.0098 inch to 0.0102 inch, depending on the manufacturer.

The burst strength of a paintball is the energy (or work) required on impact to make it rupture. PCRI measured the "burst strength" of paintballs on the market and found that if the paintball strikes on its seam, it will burst much more easily than if it hits the target on one of its poles. Average seam burst strength is 11.4 ft-lbs (15.4 joules) and average polar burst strength is 23.3 ft-lbs (31.57 joules).

More on Encapsulation/Soft Gels

As described above, paintball capsules are made from gelatin. The article says that a plasticizer is added to the gelatin to give added strength to the capsules. Glycerol, or glycerine, is the most used plasticizer in paintballs. Its properties include: Glycerol (propane-1,2,3-triol, $C_3H_5(OH)_3$, density = 1.261 g/cm³, m.p. = 18 °C,

b.p. = 290 °C)

Others plasticizers include:

 propylene glycol (propane 1,2-diol, C₃H₈O₂, molecular mass = 76.09 g/mol, density = 1.036 g/cm³, m.p. = -59 °C, b.p. = 188.2 °C)

- sucrose (C₁₂H₂₂O₁₁, molecular mass = 342.29 g/mol, density = 1.587 g/cm³, m.p. = 186°C,)
- sorbitol (C₆H₁₄O₆, molecular mass = 182.17, density = 0.68 g/cm³, m.p. = 95 °C, b.p. = 296 °C)

For an excellent video explaining how paintballs are made see this Discovery Channel video (4:57) <u>http://video.google.com/videoplay?docid=-1232968100512219178</u>

More on Collagen/Gelatin

The outer membrane of a paintball, as the article describes, is made of gelatin. Gelatin is essentially a protein produced by hydrolyzing collagen, the connective tissue found in many animals, including humans. Collagen, also a protein, provides structural support for tissue. It is the principle component of connecting tissue like cartilage, tendons and ligaments. Collagen is in the news a lot recently because of its affect on skin tone and flexibility as people age.

As the article suggests, animal parts are the typical source of collagen. Bones and skin of pigs and cattle are often used. They are treated in acid or lime and washed. Treatment with acid alone produces what is called Type A collagen. Using both acid and lime produces Type B collagen. The gelatin used in paintball outer membranes is then produced by hydrolysis. As the collagen is heated with water, the peptide strands come apart, forming gelatin.

The Gelatin Manufacturers of Europe provides this data on gelatin production for 2005:

	Production (metric tons)
From pig skin	136,600
From bovine hides	84,600
From bones	81,600
Other	4,000
TOTAL	306.800

The main amino acids in collagen are glycine, proline and hydroxyproline. The collagen molecule consists of three polypeptide strands crosslinked by means of both covalent bonds and hydrogen bonds. In the hydrolysis, the hydrogen bonds holding the peptide strands are broken, and the resulting single protein strands form the gelatin. When the material cools, the individual molecules partially revert back to their braided strand, forming gelatin. This kind of hydrolysis can be thought of as the reverse of a condensation reaction for polymers. In a condensation reaction, a molecule of water is removed from each of two monomers to form a polymer. Hydrolysis reverses this process.

The article suggests that gelatin forms a colloidal gel with water. This is due to the fact that within the gelatin structure there are pockets that can absorb water resulting in the formation of the colloid. The gelatin is capable of absorbing up to ten times its own weight of water.

According to the Gelatin Manufacturers Institute of America, gelatin is "slightly yellow to light tan in color, it is a rather tasteless and odorless substance." Also, "Gelatin contains 84-90% protein, 1-2% mineral salts, 8-15% water and is free from additives and preservatives."

The Gelatin Manufacturers Association of Asia Pacific lists these properties for gelatin:

	Туре А	Type B
pH	3.8 - 5.5	5.0 - 7.5
Isoelectric Point	7.0 - 9.0	4.7 - 6.0

Gel strength (bloom)	50 – 300	50 – 300
Viscosity (mps)	15 – 75	20 – 75
Ash (%)	0.3 - 2.0	0.5 - 2.0

Typically the molecular mass of gelatin ranges from 20,000 to 250,000 amu. It is practically tasteless and odorless and is transparent. It is soluble in hot water but not soluble in organic solvents. In water, of course, it forms a gel. It is amphoteric, meaning that it has properties of both acid and base in solution.

Gel strength is the most important property of gelatins, and it is measured in units called blooms. The bloom strength of a gelatin is a measure of the rigidity of a gel of standard composition as made by an instrument called a Bloom gelometer. It measures the force (in grams) required to push a circular plunger of 12.7 mm diameter to a depth of 4 mm under standard conditions. The typical Bloom strength of gelatins ranges from 50-300 bloom. For paintballs filled with polyethylene glycol, a higher bloom strength gelatin is used.

The second most important property of gelatin is viscosity. Viscosity is a property of liquids that measures resistance to flow. The standard method calls for the viscosity of a 6-2/3 % (6.67%) solution at 60°C. As the temperature of a liquid increases, its viscosity decreases.

Again, according the GMIA trade association, "Gelatin has traditionally been used in three major areas: food, pharmaceutical, and photographic industries."

Gelatin use in the food industry is probably best recognized in gelatin desserts and confectionery applications such as marshmallows and gummi candies. It is also used as a binding and/or glazing agent in meats and aspics.

In the pharmaceutical health industry, gelatin is used to make the shells of hard and soft capsules for medicines, dietary/health supplements, syrups, etc. It is highly digestible and serves as a natural protective coating for medications.

The unique chemical and physical properties of gelatin make it an important component in the photographic industry. Gelatin serves many useful purposes in the preparation of silver halide emulsions in the production of photographic film.

A new, major application for gelatin is in the paintball industry. The classic-style "war games" are played out using projectiles constructed of gelatin."

More on Paint Contents

The important chemical ingredients in the "paint" in paintballs includes polyethylene glycol and food dye.

Polyethylene glycol (PEG)

The article gives basic properties of PEG and shows its structure. The formula is sometimes shown as $H(OCH_2CH_2)_nOH$ where the subscript "n" shows the number of repeating oxyethylene groups (OCH_2CH_2), which usually ranges from 4 to 180. It is a condensation polymer. Lower molecular weight PEG's (up to about 600) have the properties described in the article—a viscous liquid that is tasteless, odorless and nearly colorless.

Since safety in paintball is important, the fact that the PEG is relatively harmless to humans is critical. The MSDS for PEG indicates these ratings:

Health Rating: 1 - Slight Flammability Rating: 1 - Slight Reactivity Rating: 1 - Slight Contact Rating: 0 - None Lab Protective Equip: GOGGLES; LAB COAT; VENT HOOD; PROPER GLOVES Storage Color Code: Green (General Storage) Further, the MSDS recommends:

Ingestion: If large amounts were swallowed, give water to drink and get medical advice.

Skin Contact: In case of contact, immediately flush skin with plenty of soap and water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. Get medical attention if irritation develops or persists.

Eye Contact: In case of contact, flush eyes with plenty of water for at least 15 minutes. Get medical advice if irritation develops.

Among its uses other than in paintballs are: in cleaners, detergents and soaps; in some laxatives; as a humectant, solvent and lubricant in personal care products like skin creams, eye care lubricants like Visine and in tooth pastes; in laundry starches; in pet, flea and tick products; as a dye carrier in inks (similar to its use in the article); and in the soft drink Dr. Pepper.

More on Food Dye

The dye in paint balls is used primarily to identify the source of the marker from which the ball was fired. The dyes are usually used in higher concentrations than they would be in foods in order to create visual effects. The limiting factor in dye concentration is the need to be able to wash the dyes out of clothing. Typical concentrations are between 1-10%. (Also see *ChemMatters*, Dec. 2006, p. 12)

According to the Food and Drug Administration, these food dyes are approved for use in foods:

Color Additives Certifiable For Food Use

Name/Common Name	Hue	Common Food Uses
FD&C Blue No.1 Brilliant Blue FCF	Bright blue	Beverages, dairy products powders, jellies, confections, condiments, icings, syrups, extracts
FD&C Blue No.2 Indigotine	Royal Blue	Baked goods, cereals, snack foods, ice cream, confections, cherries
FD&C Green No.3 Fast Green FCF	Sea Green	Beverages, puddings, ice cream, sherbert, cherries, confections, baked goods, dairy products
FD&C Red No.40 Allura Red AC	Orange- red	Gelatins, puddings, dairy products, confections, beverages, condiments
FD&C Red No.3 Erythrosine	Cherry- red	Cherries in fruit cocktail and in canned fruits for salads, confections, baked goods, dairy products, snack foods
FD&C Yellow No.5 Tartrazine	Lemon Yellow	Custards, beverages, ice cream, confections, preserves, cereals

FD&C Yellow	Orange	Cereals, baked goods, snack foods, ice
No.6		cream, beverages, dessert powders,
Sunset Yellow		confections

More on Polarity

The article covers in some detail the relationship between electro-negativity, polar bonds, polar molecules and water solubility. This section of the Teachers Guide will not provide additional background since these topics are standard topics in every high school chemistry text. You should note, however, that the article can be used as an example when it comes time for you to teach any of the above concepts. For more on these topics, see

http://dwb.unl.edu/Teacher/NSF/C06/C06Links/www.uis.edu/7Etrammell/organic/introdu ction/polarity.htm or http://www.chemguide.co.uk/atoms/bonding/electroneg.html

More on Hydrogen Bonding

The article attributes the water soluble of the paint in paintballs in part to hydrogen bonding. Hydrogen bonds are one type of intermolecular force. Intermolecular forces (van der Waals forces) account for nearly all of the physical properties of a liquid. There are three types of intermolecular forces. They are (in order of increasing strength) London dispersion forces, dipole-dipole interactions, and hydrogen bonds. The relative energies of intermolecular forces are much less than covalent or ionic bonding energies. The following chart gives an approximation of the relative strengths in kJ/mol:

Covalent bonds	100–1000
Hydrogen bonds	10–40
Dipole-dipole	0.1–10
London forces	0.1–10

While covalent bond energies range from 150 to 800 kJ/mol, the energy required to overcome intermolecular attractions are usually less than 40 kJ/mol. For example, it takes 464 kJ/mol to break the H—O bonds *within* a water molecule and only 41 kJ/mol to break the bonds *between* water molecules.

London dispersion forces (one of the three forces that are, in aggregate, known as van der Waals forces) arise from temporary charges that arise in non-polar molecules involving atoms with larger number of electrons. Dipole-dipole interactions (the second type of van der Waals forces) are electrostatic forces created by the partial positive and negative charges within neighboring molecules that exhibit some degree of polarity. Hydrogen bonds (the last of van der Waals forces) are the best known of the three and are the attractions between a polar covalently bonded hydrogen atom in one molecule and an electronegative atom with one (or more) nonbonding pair(s) of valence electrons in a neighboring molecule. Hydrogen bonding occurs most often in covalently bonded molecules involving nitrogen, oxygen, fluorine and chlorine.

Connections to Chemistry Concepts

1. Safety – The article does not discuss the usual safety rules for paintball, but all reputable field operators have a list of safety rules for players. A list of typical

rules can be found here:

<u>http://paintball.about.com/od/safetyinfo/a/basicsafety.htm</u> This article might allow you to reinforce the need for safety not only while playing paintball, but also in the chemistry classroom and lab. There is a strong link between chemistry and paintballs, and safety is a requirement for both.

- Hydrogen bonds The article discusses hydrogen bonds as factors in the water solubility of polyethylene glycol. You can use the article for class reading when you discuss hydrogen bonds in class
- 3. Molecular polarity Most high school chemistry courses spend significant time on the shape of molecules and the resulting properties of the substances they make up. Electronegativity and bond polarity are usually part of the content.
- 4. Relationship between microscopic and macroscopic This article provides an example of the fact that observable, macroscopic properties of substances depend upon interactions between molecules (the microscopic). Colloidal dispersions like gelatin and the discussion of the water solubility of the paint in paintballs provide specific examples. This is an important concept for chemistry students to understand.
- 5. Gas Laws/Phase Change Gas laws are not emphasized in the article, but they are the underlying explanation for the propulsion of paintballs from markers along with the phase change of the propellant gas.
- 6. **Polymers** Since both gelatin and polyethylene glycol are polymers, some discussion of polymer basics is possible using the article as a starting point.

Possible Student Misconceptions

- 1. "A paintball is a solution, right? (Or is it a colloid?)" Students easily confuse solutions and colloids. It is not crucial to a general chemistry course that you make the distinction in great detail, but highlighting the differences in properties of solutions and the mechanisms by which they form might help to students to understand the idea that paintballs are biodegradable.
- 2. "Paintball Chemistry. Paintball Chemistry? Paintball Chemistry!" Before reading this article it is unlikely that many students would even think about the chemistry connection to paintball. There is a general student misconception that chemistry is very theoretical and unrelated to things that are interesting to students. Showing students how properties of matter are the basis for many useful (and enjoyable) things in life should be an integral part of what students learn about chemistry.

Demonstrations and Lessons

- Students can do some lab work that illustrates properties of gels and shows how gelatin is formed from collagen. <u>http://www.chemistry.org/portal/a/c/s/1/wondernetdisplay.html?DOC=wondernet</u> <u>%5Cactivities%5Cfood%5Cprotein.html</u>
- 2. Students might perform the standard test for protein on gelatin or on paintballs.

- 3. If you can find carbonless paper, students can investigate the paintball's properties as an example of encapsulation technology. <u>http://mrsec.wisc.edu/Edetc/IPSE/educators/activities/smPapers.html</u>
- 4. To show the fact that water and gelatin interact but do not dissolve you might do an activity involving gummy bears using this procedure: <u>http://www.newton.dep.anl.gov/askasci/chem03/chem03398.htm</u> or this one: <u>http://www.pslc.ws/macrog/kidsmac/activity/bear.htm</u> or this one: <u>http://www.sciencespot.net/Media/mmaniabearlab.pdf</u>
- 5. Activities that illustrate the properties of polymers can be found here. http://www.pslc.ws/macrog/kidsmac/lab.htm
- 6. The article mentions that polyethylene glycol is a viscous liquid. Students can do a lab activity on viscosity here

http://www.seed.slb.com/en/scictr/lab/viscosity/index.htm

- 7. For a demonstration on molecular polarity and solubility see http://www.learner.org/channel/workshops/chemistry/support/act2 c.pdf
- 8. For a lab activity on molecular polarity and solubility see <u>http://www.scienceteacherprogram.org/physics/Flomberg01.html</u>

Suggestions for Student Projects

- 1. Have students find paintball grounds in your area and record the safety rules for games played there.
- 2. Students might research other games, toys or other recreational activities that involve chemistry.
- 3. Since some students in your class may have played paintball, you might ask these students to share their experiences, especially about items in the article, like how much a paintball hurts when it hits, how easily the "paint" washes out of clothing, etc.
- 4. You might find some students who have access to paintball gear. Checking first with your school administrator on policy, you might ask these students to bring their equipment to class. Exhibit caution about asking students to bring in a marker, since it is likely to be against your school's policy about weapons. Within the confines of policies in your school, having paintball equipment available for them to see as they read this article is another method of connecting chemistry to the lives of students.

Anticipating Student Questions

1. "Are paintballs really water soluble?" Yes and no. The capsule of a paintball is made of gelatin (see "More on Collagen/Gelatin", above). When gelatin interacts with water a colloidal gel is formed. A colloid differs from a solution in a number of ways, but essentially in a colloid the particles that are dispersed uniformly throughout the medium are larger in size than those in a true solution. The net effect in a paintball is that the gel weakens and the paintball may deform. On the other hand, the "fill" in a paintball is actually soluble in water, as the article describes. Both polyethylene glycol and water are polar molecules and so are miscible. Furthermore, as the article describes, water will pass through the gelatin membrane due to osmotic pressure. These subtle differences in water-

paintball interactions may be difficult to explain in the context of a general chemistry course.

- 2. "How does the speed of a paintball compare to the speed of a bullet?" Paintball markers (guns) are regulated so that paintballs can exit the barrel at a speed no greater than 91 m/sec, less than one third of typical revolver muzzle velocities and about one tenth the muzzle velocity of a rifle.
- 3. "Why don't paintballs break inside the marker?" The "burst strength" of the gelatin shell is large enough to prevent the capsule from rupturing as the molecules of gas propel it forward. Between the elasticity of the "softgel" capsule and the elasticity of the gas, there is enough "give" to keep the paintball from bursting as it is fired. The pressure created by the CO₂ or N₂ gas is regulated so that the capsule will not break in the barrel. However, irregularities in the barrel or in the release of gas propellant can cause paintballs to break in the marker. When the paintball strikes a solid surface, the impact is sufficient to overcome the burst strength of the paintball and it breaks.

Websites for additional Information

For a You Tube video demonstrating the game of paintball, see http://www.youtube.com/watch?v=DR3Kjip6n2Q

For an article on Jello, including information about gelatin, see <u>http://pubs.acs.org/cen/whatstuff/stuff/8120jello.html</u>

For more on gelatin, see the web site of the Gelatin Manufacturers of America at <u>http://www.gelatin-gmia.com/</u>

For more on gelatin, see the web site of the Gelatin Manufacturers Association of Asia pacific at <u>http://www.gmap-gelatin.com/about_gelatin.html</u>

For a history of gelatin, see <u>http://www.gelatine.org/en/gelatine/overview/129.htm</u>

To read more about the properties of gelatin, see <u>http://www.gelatin.co.za/gltn1.html</u>

For technical information on gelatin, including possible health warning as a result of SBE (mad cow disease), see <u>http://www.ams.usda.gov/nop/NationalList/TAPReviews/Gelatin.pdf</u>

For a video explaining how paintballs are made see this Discovery Channel video (4:57) <u>http://video.google.com/videoplay?docid=-1232968100512219178</u>

To read a *Time Magazine* article profiling Robert Pauli Scherer, inventor of the original machine (the rotary die) that now makes gelatin capsules for paintballs see http://www.time.com/time/magazine/article/0,9171,763830,00.html

For the Food and Drug Administration site on food dyes, see <u>http://www.cfsan.fda.gov/~dms/col-regu.html</u>

For an article on the history of food dyes see either <u>http://www.chemistry.org/portal/a/c/s/1/feature_ent.html?DOC=enthusiasts%5Cent_food</u> <u>dyes.html</u> or "The Unadulterated History of Food Dyes." in the December, 1999, edition of *ChemMatters, p. 4*

For an interesting article on molecular polarity and solubility, which also involves polyethylene glycol, see "Lava Lite: A Chemical Juggling Act," in the April, 1997, edition of *ChemMatters*, p. 4

For more on polar bonds, polar molecules and solubility, see http://dwb.unl.edu/Teacher/NSF/C06/C06Links/www.uis.edu/7Etrammell/organic/introdu/ction/polarity.htm or http://www.chemguide.co.uk/atoms/bonding/electroneg.html

Gold in Your Tank

Background Information

More on the History of Crude Oil

The existence of crude oil has been known for thousands of years. The word itself was derived from Latin, petra- rock, and oleum- oil – rock oil, an apt name. Historical records indicate that crude oil was used for medicinal purposes, for paving, for sealing or caulking, and for lighting.

The modern history of crude oil (at least in the U.S.) begins in 1859 in Titusville, Pennsylvania. There on August 27th, Edwin Drake struck oil from his first oil well. The well produced about 25 barrels a day in the beginning, but dropped to 15 barrels a day shortly thereafter. He drilled in Titusville because oil seeps (where oil seeps out on the surface of the land) had been known to exist in that area for years. Evidence exists to show that American Indians living in the region had been collecting the oil for medicinal purposes for centuries before Drake began drilling.

The main fraction of interest from the crude oil that he obtained was kerosene for lighting. Until this time, whale oil lamps were the major type of lamp used, but whales were becoming scarce. Several entrepreneurs had discovered how to distill kerosene from coal, but it was a laborious process. When it was shown that crude oil contained a kerosene fraction, oilmen saw that crude oil had a very bright future (no pun intended). It wasn't long before the entire area of Pennsylvania where the oil seeps occurred became dotted with oil wells, some only feet apart. Entire towns grew up around the oil wells, much as did boom towns during the Gold Rush of the wild west. Pennsylvania produced thousands of barrels of crude oil a day during this era. At that time, oil production exceeded demand and the price of oil plummeted from \$2.00 a barrel when Drake first began drilling to \$.10 a barrel. Many drilling ventures experienced bankruptcy as a result. Eventually demand caught up with production and Pennsylvania was the center of world oil production up until the Texas oil boom in 1901.

At the time of Drake's first well, there was little or no use for the gasoline fraction, and that was often burned off. It only took a few years until the advent of the internal combustion engine, however, before the gasoline fraction became the most desired (and expensive) fraction of the crude oil. And with the advent of the electric light, and with kerosene facing a decreasing demand as a lamp fuel, the kerosene fraction of crude could now be turned into even more gasoline to satisfy our automobile fuel needs.

For more information on the Drake oil well, see <u>http://www.drilshop.com/hallfame/drakewel.html</u>, or visit the Drake Well Museum at <u>http://www.drakewell.org/index.htm</u>.

A barrel of crude oil contains 42 gallons. The origin of this volume goes back to the early days of crude oil discovery, extraction, and transport in Pennsylvania. Oil drillers used old wine barrels to carry the crude to market, either by wagon or boat. Those barrels originally held 48 gallons of wine, but when the oil men transported the crude by wagon or boat, some oil inevitably leaked out in transport, so the dealers who received the oil at the end of the trip only paid for 42 gallons of oil, to allow for some spillage during the trip. Eventually, oil men only put 42 gallons in the barrel in the first place, hence the 42-gallon barrel.

More on Crude Oil

Crude oil differs greatly in composition dependent on its place of origin. "Light", "heavy", "sweet", and "sour" are all terms applied to crude oil. Light crude has low viscosity, while heavy crude is very viscous. Sweet crude has low sulfur content, while sour crude contains more sulfur. Colors range from yellow to orange to green to black. Light, sweet crude is usually the petroleum of choice because it contains larger percentages of the more desirable lower molecular weight hydrocarbons, so it requires less processing (cracking), and because it contains less sulfur, so distilling this crude ejects less pollution into the atmosphere.

Geologic conditions in the past help to determine the content of crude. In the Middle East, crude contains more straight chain hydrocarbons, while crude from Nigeria is mainly aromatics and cyclic hydrocarbons. Mexican crude can contain up to 5% sulfur, while Pennsylvania crude contains less than 0.1% sulfur. Web site sources can be found in the **Websites for Additional Information** section, "More on Crude Oil".

More on the Petronius Oil Drilling Rig and Oil Field

The Petronius oil field is found about 130 miles southeast of New Orleans in the Gulf of Mexico. The field produces about 60,000 barrels of crude a day from 17 wells. The height of the drilling rig is 1870 feet, 1734 feet of which is underwater. It is the tallest structure built by man (if you include underwater structures). It is a compliant tower, which means that its structure can rise and fall with waves, currents and winds. The mooring legs and templates were constructed in 1997, and the North module (4,000 tons) of the "topsides" – the main decking construction – was constructed elsewhere and towed out and put in place as one unit in 1998. The South module (3700 tons and \$70 million) was being put in place by a crane when one of the supporting cables snapped and it toppled into the gulf to the sea bottom. A second South module was constructed and put in place within a year of the first attempt, and drilling and production began in 2000. For more details on the project, as well as photos that give one an idea of the magnitude of scale of the project, see http://www.offshoretechnology.com/projects/petronius/.

More on Oil Refining

The products of the fractional distillation process were sufficient for the times shortly after the invention and manufacture of the "horseless carriage", but the gasoline fraction produced from straight distillation did not provide a high enough octane rating for the engines with higher compression ratios that were developed later. Race cars, in particular, needed a better fuel. Eugene Houdry, a French chemist who also enjoyed racing, developed a catalytic cracking process that took higher molecular weight hydrocarbon molecules (like xylene or naphthalene) and broke them down into smaller molecules (like octane), using an aluminosilicate catalyst, Fuller's Earth. The catalyst is an abundant clay, so it is economical to use.

Houdry had worked with another Frenchman, E.A. Prudhomme to develop a catalytic cracking process to produce gasoline from lignite, a brown coal that is further decomposed than peat, but not as much as bituminous coal. Their process had been shown to be successful but, in 1929 and with the financial support of the French government, the process was found not to be economically feasible. A 60-ton per day pilot plant they had built was closed down the same year it opened.

But Houdry used what he learned from that process and applied it to crude oil. Here his process worked very well, and the products were far superior to those produced solely from distillation of crude. The molecules of his product weren't just smaller than their source material – they were more highly branched also. It was the extra branching of these alkanes that made them slower burning in engines, thereby providing the higher octane rating. The availability of a new fuel with higher octane rating meant that automobile manufactures could now focus on building engines with greater compression ratios that could take advantage of the higher octane rating available through Houdry's process – and they succeeded.

Houdry joined ranks with Sun Oil Company, and by 1937, he had a refinery online that was processing 15,000 barrels of crude a day. He had developed a way to clean and regenerate the catalyst quickly, without the need to add additional catalyst, which made the process very inexpensive to operate. The plant produced almost 50% gasoline from the crude it processed, compared to 25% for most other refineries, and the gasoline it did produce was higher octane than the other refineries, as well.

One of the unexpected benefits of Houdry's process came with the beginning of World War II. The Houdry process was able to produce 100-octane gasoline. In the high compression engines of airplanes, the 100-octane gasoline was just what they needed. The Allied forces had available to them the gasoline produced by Houdry's process, while the Axis forces did not. That meant that our airplanes were far superior to those of the enemy, both in speed (10% better) and lifting power (25% better). This gave us superiority in the skies. Houdry's catalytic cracking refinery provided 90% of the gasoline used by Allied aircraft in the first two years of the war.

Yet another benefit of the Houdry process was a by-product of his catalytic cracking process – butadiene. In another article in this issue, "Retiring Old Tires", discussion centers around SBR rubber, styrene-butadiene rubber. The butadiene part of that polymer came from Houdry's relatively new process. So he not only provided gasoline for the war effort, but one of the essential ingredients for the rubber used to make tires for the Allied war machine, as well.

Seventy years later, catalytic cracking is still being used to produce gasoline for the world's automobiles. Even today, more than half of the gasoline produced in the U.S. is made by the catalytic cracking process.

In 1956, Houdry was granted a U.S. patent for a generic automobile catalytic converter to reduce overall airborne emissions from automobile exhaust. Today catalytic converters are standard equipment on automobiles sold in the U.S.

Much of the material above was taken from the American Chemical Society's National Historic Chemical Landmarks web site at

http://acswebcontent.acs.org/landmarks/landmarks/hdr/hdr process.html.

More on Fractional Distillation

The diagram below shows the various fractions of crude oil (in the center column of text in the diagram) coming off a fractionating tower at various temperatures (in the left column of text in the diagram). The fractions are then sent for further processing, as shown on the right side of the diagram. (The illustration was taken from www.eia.doe.gov.)



More on gasoline

The diagram below shows the relative amounts of end-use products that are typically made from a barrel of crude oil (in gallons).



Illustrations taken from www.eia.doe.gov

The "Other Distillates" fraction can be further processed during the summer months (when consumers are not heating their homes) to produce extra gasoline (for increased driving during the warm months.

If students are interested in seeing how a 4-cylinder engine works, you can show them an animated visual of the complete combustion cycle at <u>http://www.carbibles.com/fourstrokeanimation.mov</u>.
Connections to Chemistry Concepts

- 1. **Distillation** Refineries use this process to separate most major fractions of crude oil from one another. The focus for chemistry class is boiling point as it relates to intermolecular forces.
- Intermolecular attractions Boiling points of organic molecules relate directly to their size and surface area in contact with other molecules.
 a. London dispersion forces (van der Waals forces) These explain why nonpolar molecules have attractions for each other.
- 3. **Organic chemistry** The chemistry of petroleum is virtually all organic chemistry.
- Catalysis Cracking of larger hydrocarbons into more useful, smaller molecules is done primarily through the use of catalysts to lower the boiling point of the mixture. Unification of smaller molecules into larger ones also involves the use of catalysts.
- 5. **Structural formulas** Organic chemistry gives us a chance to show students the varied structures of various hydrocarbon molecules.
- 6. **Types of reactions** Combustion is one of the 5 major types of reactions students study in chemistry.
- 7. Thermochemistry and heats of combustion The major use of petroleum is as a fuel. Why not stress petroleum as the source of these fuels as we use their data to calculate heats of combustion?
- 8. Acids and bases the protons that produce the carbocations, discussed in the alkylation process in the article, are hydrogen ions donated from sulfuric or hydrofluoric acid catalysts.

Possible Student Misconceptions

- 1. "Crude oil is the stuff you buy in a can to put in your car engine." Crude oil is a mixture of hundreds of different hydrocarbon molecules. Engine oil is only a small portion of what's in crude oil and a very specific small part at that.
- 2. "Distilling gasoline gives us all the gas we need for fuel for our cars." The actual amount of gasoline (octane) found directly in crude oil is not sufficient for our needs. That amount must be supplemented by cracking, unification and alteration.
- 3. "We're paying way too much for our gasoline in the U.S., now that prices have gone up!" We're certainly paying more than we did two or more years ago, but that's primarily because the cost of crude oil has increased so dramatically in that same time period. Actually, despite the recent price increases, the cost of gasoline in the United States is still way less than in other countries around the world. Drivers in most European countries are paying anywhere from \$4.00 to \$6.50 a gallon for gasoline (although they purchase it by

the liter), while drivers in the Middle East (oil-producing countries) are paying from 60 – 90 cents a gallon, and Venezuelan drivers are paying only 12 cents a gallon!. Venezuela has a very large supply of oil reserves, and the government of Venezuela controls oil production in that country and is subsidizing the cost of gasoline for its citizens.

- 4. "The only thing petroleum is good for is to burn it." As mentioned in the article, many of our everyday products are made with petrochemicals, materials developed from petroleum. If we continue to burn our global supply of petroleum, we won't have it for making other materials, such as plastics, pharmaceuticals and electronics parts. Teachers may want to look at the American Chemical Society's chemistry textbook, Chemistry in the Community, for a chapter on the choices involved in using petroleum, to build or to burn.
- 5. "Crude oil is composed only of alkanes, saturated hydrocarbons." Crude oil is composed primarily of alkanes, but unsaturated hydrocarbons also can be found in crude oil. It also contains alkenes, alkynes and aromatic hydrocarbons.

Demonstrations and Lessons

- 1. Use molecular models to construct various alkanes for students to compare when discussing the separation of fractions of crude oil based on relative boiling points.
- 2. Do a heat of combustion lab using several hydrocarbon fuels, instead of just measuring the heat of combustion of a burning candle. For example, use propane, butane, and kerosene as fuels. 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.
- 3. NSTA's Scope, Sequence and Coordination has a short series of investigations on Oils and plastics, # 957 in their sequence, which deals with hydrocarbons, organic macromolecules and plastics. One of the activities (plus an assessment piece) deals with the viscosity of oils. The teacher version can be found at <u>http://dev.nsta.org/ssc/pdf/v4-0957t.pdf</u>. The student version is at <u>http://dev.nsta.org/ssc/pdf/v4-0957s.pdf</u>. The detaiols of the concepts behind the topics is at <u>http://dev.nsta.org/ssc/moreinfo.asp?id=957</u>. The student version seems to give only rudimentary directions. You might have to flesh them out yourself.
- 4. "An Environmentally Friendly Oil Spill Experiment" is available from Environment Canada from their website: <u>http://www.ec.gc.ca/ee-ue/default.asp?lang=en&n=6AEDF280</u>. The experiment is fairly open-ended and, if taken alone, it may appear to be geared for middle school students. However, it is part of a package of 6 "chapters" about oil spills, and the rest of the material appears to be aimed at high school. The experiment requires a lot of materials, although they are all readily available. You can find the entire package, called "Oil, Water, and Chocolate Mousse", at <u>http://www.ec.gc.ca/ee-ue/default.asp?lang=En&n=28D123C0-1</u>. The *ChemMatters* article doesn't focus on oil spills, but it is a reality of life.
- 5. Several lessons center around a Thirteen/WNET production, "Extreme Oil". The video can be purchased from PBS online. The first lesson is "Exploring the History of Oil", and the second is "Exploring the Science of Oil". Perhaps a cooperative lesson with a social studies teacher could make this even more interesting. The first lesson takes students on a tour through time to show how

oil has affected societies, and the second takes them on a virtual tour from a drill site, through a pipeline, to the processing plant. Here's the teacher's site: <u>http://www.pbs.org/wnet/extremeoil/teachers/index.html</u>. This is a 3 DVD set, priced at \$59.95 from PBS at <u>http://www.shoppbs.org/searchHandler/index.jsp?searchId=20015493751&keyw</u> <u>ords=Extreme+Oil&y=1&x=22</u>. Maybe you can get your librarian to order it for you!

 Although the chemical reaction below is not related to any hydrocarbon cracking process, you can present a catalyzed reaction to students using cobalt(II) chloride, Rochelle's salt, and hydrogen peroxide. Two sources of this demonstration/lesson can be found at the Chemical Heritage Foundation site, http://www.chemheritage.org/EducationalServices/pharm/tg/antibiot/demos/cataly .http://www.chemheritage.org/EducationalServices/pharm/tg/antibiot/demos/cataly
 .http://www.flinnsci.com/Documents/demoPDFs/Chemistry/CF0255.01.pdf.

nup.//www.ninnsci.com/Documents/demoPDFs/Chemistry/CF0255.0

Student Projects

- 2. Students can research the Strategic Petroleum Reserve and report to classmates. (President Bush tapped into the SPR to help minimize the effects of the drastic price increases on gasoline in recent years.)
- Students could initiate a school-wide project to save energy. An example of this is the Green Schools Program from the Alliance to Save Energy. The project is a K-12 program. You can find out more at <u>www.ase.org/greenschools</u>.
- 4. Students can form teams to teach elementary and middle school students about unbiased energy information. An initial contact might be: <u>www.oogeep.org/EdMaterials/default.htm</u>. This is the Ohio Oil and Gas Energy Education Program. They provide free materials, although the project is focused on the state of Ohio. Still, it is a place to get information about how to start the program in your own area. Perhaps your own state already has such a program.
- 5. Students can research the price of gasoline around the country and around the world and report to classmates.
- 6. Students can research the various components of crude oil to determine molecular formulas of these hydrocarbons. It would be a good introduction to organic chemistry for those students who have had none and a good review for those who have already been introduced to the topic.

Anticipating Student Questions

- 1. "If there are saturated hydrocarbons, are there unsaturated ones, too?" Yes, there are other types of hydrocarbons in crude oil. Alkenes (hydrocarbons with double bonded carbon atoms), cycloalkanes (saturated hydrocarbons linked in cyclic molecules), alkynes (hydrocarbons with carbon-carbon triple bonds, arenes (cyclic molecules with double-bonded carbon-carbon links), and dienes (molecules with two double bonds).
- 2. "Why can't petroleum chemists just change all of the crude oil into gasoline? That would keep prices down." For starters, some molecules in crude oil are too large or too complex to be broken down into gasoline. In

addition, we need those other fractions of crude oil for other purposes; e.g., diesel oil for trucks, buses, trains and boats; home heating oil to keep us warm in winter; crude bottoms for asphalt for roads; volatile compounds for solvents; petrochemicals for medicines and plastics; etc.

- 3. "If 87 octane gasoline is good for my car engine, isn't 89 or 91 octane even better?" Not necessarily cars are designed to use a specific grade of gasoline, usually the lowest that will work in that car to prevent knocking and pinging to keep the price down for driving the car. If you use a higher grade than recommended, it can cause the engines of older cars to overheat, and newer cars have sensors that detect higher octane fuel and retard the timing of the combustion so that fuel economy actually decreases. It also costs more per gallon to use the higher octane rated gasoline.
- 4. "Are the protons referred to in the alkylation process in this article related to the protons in the acids we studied?" Yes, they are the very same hydrogen ions donated by acids. So the alkenes (double-bonded hydrocarbons) could be considered Brönsted-Lowry bases, since they accept protons from the donor acid.

References

"The End of Cheap Oil." National Geographic, June 2004. written by Tim Appenzeller. The author investigates the global supply and demand of crude oil by visiting drilling and production sites, and interviews scientists and other experts.

The Prize by Daniel Yergin. This Pulitzer prize-winning non-fiction book details the history of the petroleum industry.

Websites for Additional Information

More on the Petronius Oil Field and Rig

<u>http://www.offshore-technology.com/projects/petronius/</u> from Offshore-Technology.com provides information about the Chevron/Texaco Petronius project. Specifications for the project can be found on the same web site at <u>http://www.offshore-technology.com/projects/petronius/specs.html</u>.

More on Crude Oil

For more information on Drake's first Pennsylvania oil well, visit the Paleontological Research Institution's site at <u>http://www.priweb.org/ed/pgws/history/pennsylvania/pennsylvania.html</u>. The site describes why Drake drilled in Titusville, and what the economic conditions were at the time. It also offers several photographs of other oil wells in the region at the time.

The Energy Information Administration published a 77-page book, entitled, "Petroleum: An Energy Profile 1999". The book gives a detailed description of the state of petroleum use worldwide, as of 1999, including extensive background about what petroleum is, where it comes from, how we get it, how we use it, and how long it will last. Charts and tables abound. It also discusses the U.S.'s Strategic Petroleum Reserve. Find it at

http://www.eia.doe.gov/pub/oil_gas/petroleum/analysis_publications/petroleum_profile_1 999/profile99v8.pdf

Chevron presents a short description of what crude oil is and how and where it developed at <u>http://www.chevron.com/products/learning_center/crude/</u>. The site also contains a few photos showing that crude oil found at different locations around the world appear dissimilar, ranging from the common black to yellow and greens.

Wikipedia has considerable data on global petroleum production/consumption, as well as basic information on its origin, history, and uses at <u>http://en.wikipedia.org/wiki/Petroleum</u>.

This site, <u>http://www.epa.gov/region6/6en/xp/lppapp6a.pdf</u>, is a 1988 appendix to an EPA document that provides several tables of information concerning the actual percentage composition of various types of crude oil, as well as a table for gasoline composition. Sulfur content in crude oil, for example, varies from 0.1% to 4.3%, with 1.1% being the average. The gasoline content may be different today, since the table is rather dated at 1988. MTBE, for example, is listed as 15% of gasoline content, but today, MTBE has been banned from use in gasoline.

The U.S. Strategic Petroleum Reserve Crude Oil Assay Manual, dated March 2002 and found at <u>http://www.spr.doe.gov/reports/docs/CrudeOilAssayManual.pdf</u>, contains an extensive analysis of each type of crude oil contained in the SPR. Each location of the oil stocks has its own assay. This site contains 34 pages of data on the composition of various crude oil stocks in the reserve. The contents are listed by the name of the compound (mostly, but not exclusively, IUPAC names). This site might be a good place to have students go to practice writing structural formulas from the names of organic compounds.

As oil's price goes up, returning to extract leftover oil from previously tapped wells becomes more lucrative. For a story on how chemistry is helping to extract that oil, see the November 20, 2006 *C&E News* article, "Back to the Well", at <u>http://pubs.acs.org/cen/coverstory/84/8447cover4.html</u>.

Check out this website for the theme song to the television version of "The Beverly Hillbillies". (The Clampetts struck it rich when they found oil bubbling from the ground in their backyard in the Appalachian mountains.) <u>http://www.sitcomsonline.com/thebeverlyhillbillies.html</u>. The song includes references to oil, "**black gold**" and **Texas tea**". Older teachers (like me) may remember the show, but younger teachers – and students certainly – will probably never have heard of it. Here are the lyrics, from the same site:

"The Ballad of Jed Clampett" by Paul Henning

Come and listen to a story about a man named Jed A poor mountaineer, barely kept his family fed, Then one day he was shootin at some food, And up through the ground came a bubblin crude.

Oil that is, black gold, Texas tea.

Well the first thing you know ol Jed's a millionaire, Kinfolk said "Jed move away from there" Said "Californy is the place you ought to be" So they loaded up the truck and moved to Beverly.

Hills, that is. Swimmin pools, movie stars.

More websites on Oil Refining

<u>http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html</u> This OSHA site gives good background material on the entire petroleum refining process. Although it focuses at least in part on the safety in the industry, it still gives good scientific content that teachers and students can use and understand, including a very detailed diagram of both the atmospheric and the vacuum distillation processes (and many diagrams of other processes not described in the CM article).

"How Stuff Works" has a good article on petroleum refining at <u>http://www.howstuffworks.com/oil-refining.htm</u>. It includes a discussion of crude oil, from wellhead to final product.

<u>http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html</u> This OSHA site gives good background material on the entire petroleum refining process. Although it focuses at least in part on the safety in the industry, it still gives good scientific content that teachers and students can use and understand, including a very detailed diagram of both the atmospheric and the vacuum distillation processes (and many diagrams of other processes not described in the CM article).

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A reform movement to stop refinery pollution exists. Check out the Refinery Reform Campaign's web site at <u>http://www.refineryreform.org/index.htm</u>.

More websites on Fractional Distillation and Fractions

<u>http://www.elmhurst.edu/~chm/onlcourse/chm110/outlines/distill.html</u> this site discusses energy needed to break bonds in fractional distillation, and shows illustration of petroleum distillation column (but some incorrect science here – "strands of spaghetti")

http://concise.britannica.com/ebc/art-1545 Britannica art – distillation column

<u>http://www.chemguide.co.uk/physical/phaseeqia/idealfract.html#top</u> this site presents a rather detailed account of the theory behind the process of fractional distillation. It is probably for teacher background only. It also allows you to backtrack in the site to other background pages to help you understand this one. At the end of this page is a diagram of one small part of the petroleum fractional distillation column in more detail, showing the openings and bubble caps in the column, and it gives a description of how the column works <u>http://library.thinkquest.org/C006295/course/loader.php?subject=course&location</u> <u>=petroleum_fractional_distillation.htm</u> You can find a somewhat animated diagram of the distillation tower here, along with a description of the fractions of crude oil at each level.

Wikipedia has a good diagram of a fractionating tower, although it is not specific to petroleum. You can find it at <u>http://en.wikipedia.org/wiki/Fractionating_column</u>. The site also contains a close-up of several of the collecting trays and bubble cap arrangements, and a description of the process.

<u>http://www.energymanagertraining.com/petrochemical/Fractional%20distillation.h</u> <u>tm</u>. This site provides an animated sequence of the fractional distillation process, showing each fraction coming off at its own level. The site is limited to descriptions of the fractions and the basic process, although they are very descriptive.

One fraction that did not get much attention in this article is the crude oil "bottoms", part of which is asphalt. Here's an article from the American Chemical Society's November 22, 1999 issue of the *Chemical and Engineering News*, in their ongoing series, "What's that Stuff?", entitled, "Asphalt": http://pubs.acs.org/cen/whatstuff/stuff/7747scit6.html.

Yet another "What's That Stuff?" *C&E News* article, March 13, 2006, covers "Motor Oil". Find it at <u>http://pubs.acs.org/cen/whatstuff/84/8411oil.html</u>.

One more "What's That Stuff?" *C&E News* article, February 21, 2005, talks about "Gasoline". It's at <u>http://pubs.acs.org/cen/whatstuff/stuff/8308gasoline.html</u>.

More websites on Teacher Information and Lesson Plans

The American Petroleum Institute (API) web site provides a program called, Adventures in Energy. It consists of a series of interactive screens that takes students through the entire process off providing petroleum to consumers, from searching for oil to processing to making useful products. The site, at <u>http://www.adventuresinenergy.org/</u>, is somewhat spotty. Some screens have a person speaking while the text of their talk appears written on the screen, and some screens have just the text. Animations are nice, but small so that processes like cracking or reforming or sulfur cleaning that are intended to represent the process at the molecular level, complete with audio cracks or pops, don't really show what is happening. Molecules of various fractions are represented as spheres of specific colors for each fraction, and that color scheme is used throughout the site, but the fractions and their defined colors are only shown on one slide, so they are easily forgotten later.

The above-mentioned site, "Adventures in Energy", is only one of many sections of the API site, "Classroom Energy!". The web site, at <u>http://www.classroom-energy.org/index.html</u>, also contains materials for K-12 teachers and students on many topics of energy, most of which is at the K-8 level. The site contains lesson plans and online activities, including games and puzzles for students.

A free CD containing all the materials on the API's "Classroom Energy!" web site can be ordered at <u>http://www.classroom-energy.org/free_material.html</u>.

"The Story of Oil and Natural Gas", at <u>http://www.api.org/story/</u>, is another API product. It highlights with narration and video clips the production of oil and natural gas from exploration, through production, transportation, refining, distribution, and finally to consumer products. While there isn't much chemistry in the presentation, a lot of the technology of oil and gas development is shown.

<u>http://www.energyquest.ca.gov/teachers_resources/lesson_plans.html</u> provides an extensive list of online teacher resources on the topic of energy.

Maybe there's a petroleum museum in your area that you could take your students to for a field trip. Here's a list of 23 museums throughout the United States: <u>http://www.api.org/classroom/museums/index.cfm</u>.

The "How Stuff Works" web site has several pertinent articles related to petroleum and gasoline: "How Gasoline Works":

<u>http://www.howstuffworks.com/gasoline.htm;</u> "How Oil Drilling Works": <u>http://www.howstuffworks.com/oil-drilling.htm;</u> and "How Oil Refining Works": <u>http://www.howstuffworks.com/oil-refining.htm</u>.

The February 2007 issue of *ChemMatters* (Volume 25, number 1) contains an article, "Chemistry on the Fast Track, The Science of NASCAR", on pages 5-7 and online at <u>http://acswebcontent.acs.org/education/chemmatters/CMatter0207.pdf</u>. The article discusses various aspects of NASCAR racing, including the fuel used and how the internal combustion engine works. It also includes information regarding octane number.

More information on the refining process and gasoline production can also be found in the *Teachers Guide* for the *ChemMatters* NASCAR article in the February, 2007 issue online at

http://acswebcontent.acs.org/education/chemmatters/ChemMatters 0207.doc. Check out pages 24-27 of the Teachers Guide, a Word document. It is also available as a pdf document at

http://acswebcontent.acs.org/education/chemmatters/ChemMatters_0207.pdf.

Retiring Old Tires

Background Information

More on Rubber and Polymers

Chemists call the various kinds of rubber, "elastomers." All types of commercially produced elastomers are polymers, materials made of molecules that contain thousands of atoms. More in-depth information about polymers can be found at *The Macrogalleria*, a website created by the University of Southern Mississippi, at <u>http://www.pslc.ws/mactest/maindir.htm</u>.

The chemical structure of most polymers consists of a simple arrangement of atoms that repeats itself over and over again along the backbone chain of the polymer. This pattern is called a repeat unit. Polymer chains are made up of repeat units because they are formed by covalently joining together thousands of identical small molecules called *monomers*.



Figure 1: Polymerization of isoprene to make polyisoprene



Figure 2: Copolymerization of styrene and butadiene to make SBR rubber

The two most common polymers for making tire treads and sidewalls are natural rubber, or polyisoprene, and styrene-butadiene rubber, or SBR. Natural rubber is made from a monomer called *isoprene*, and the name of the polymer itself is *polyisoprene*. On the other hand, SBR is a *copolymer*, that is, a polymer made from two different monomers. SBR is made from about 75% butadiene and 25% styrene. The two different monomers join in no particular order, and the styrene-based repeat units are distributed statistically among the butadiene-based repeat units along the backbone chain. For this reason, SBR is called a *statistical copolymer*.



Figure 3: Statistical arrangement of styrene- and butadiene-derived repeat units in SBR rubber, where **B** is a butadiene-derived repeat unit and **S** is a styrene-derived repeat unit

Meanwhile, the inner linings of nearly all tires are made from synthetic elastomers based on polyisobutylene, because these polymers, called "butyl rubbers" have lower gas diffusion rates than most other elastomers. Silicones can also make very good elastomers, though they are rarely used to make tires. Polyurethane rubber hasn't traditionally been used to make tires, but experimental run-flat polyurethane tires have shown promise, and polyurethane tires could be in tire shops someday in the future.



Figure 4: Polymerization of isobutylene to make polyisobuytlene

A few aspects of polymer chemistry are particularly relevant to the topic of elastomers. Crosslinking is one of the most central. In most polymers, the molecules are shaped like long chains. In some materials, those polymer chains are joined together with covalent bonds so that all the polymer molecules in a sample combine into one giant molecular network. This is called crosslinking. Rubber latex is not crosslinked when it is harvested from rubber trees, but for most applications, it is crosslinked before being used. Pencil erasers and surgical gloves are among the few uses for uncrosslinked rubber.

Crosslinking prevents rubber from flowing when the weather gets warm. Crosslinking joins polymer chains together, limiting how much they can slide past each other. In vulcanized rubber, the chains are crosslinked just enough so that they can slide past each other to let the material stretch, but they can't slide past each other enough to allow the material to flow.

Since crosslinked polymers cannot be heated and reshaped (since a single molecule that large can't rightly melt or flow), objects made of crosslinked polymers like rubber must be molded before the chemical reactions that crosslink the polymer are carried out. The inability to re-mold crosslinked polymers makes them especially difficult to recycle, hence the problem of old tires described in the article.

Rubber is crosslinked using the chemistry of carbon-carbon double bonds. The repeat units of polyisoprene and SBR contain carbon-carbon double bonds. Sulfur can add across these double bonds in the polymer. A short chain of sulfur atoms can add across double bonds in two different polymer chains, thus joining the chains together. This is how crosslinking takes place. When rubber is crosslinked, the process is called "vulcanization." While Charles Goodyear reacted rubber latex with elemental sulfur when he first vulcanized rubber, today sulfur compounds are used to achieve the same effect.

Charles Goodyear also discovered that if he used relatively small amounts of sulfur to vulcanize rubber, he made a useful all-weather elastomer. When he used relatively large amounts of sulfur, he made a stiff, rigid material. This was used for many years for things we now make from rigid plastics, like hairbrush handles. What Goodyear didn't know was that more sulfur leads to more crosslinks between polymer chains, and less sulfur leads to fewer crosslinks between polymer chains. The more

crosslinks between chains there are, the harder it is for polymer molecules to slide past one another, and the more rigid the material becomes. Heavily crosslinked polymers are often used when stiff, rigid materials are needed. Epoxy resins, Bakelite, and Formica are all heavily crosslinked polymers. Materials like this are known as "thermoset resins."



Figure 5: Crosslinking of polyisoprene with sulfur

More on Rust, Thermochemistry, and Tire Fires

Tire fires are sometimes caused by something in the tires themselves, namely the steel belts that give the tire extra strength. Slowly, over time, the iron in the steel will combine with oxygen from the atmosphere to form iron oxide. This chemical reaction is exothermic, as oxidations usually are. The oxidation of iron is usually a kinetically slow reaction. (At least the reaction is slow when the pieces of iron are small and have relatively low surface-to-volume ratios. Powdered metals with lots of surface area oxidize much more quickly.) Since the reaction is slow, it releases heat slowly. This may not be a problem for a piece of iron lying in a mud puddle, where the heat can be dissipated into the surroundings much faster than it is generated. But when old discarded tires are piled up in high mounds, dissipating heat can be difficult. Steel belts in the tires deep at the bottom of the pile slowly rust, and slowly give off heat, but down there in the depths of the mound where breezes don't blow and air circulates poorly, the heat has nowhere to go. So over long periods of time, the heat slowly builds up, making the tires hot. Sometimes the tires get hot enough that they catch on fire.

The danger of fire isn't limited to piles of tires in landfills. In 1995, a highway in Washington State that had been built on top of roadbed made from ground up old tires caught fire. Rusting of the steel belts is thought to have ignited the blaze. Today, tire rubber is separated from its steel belts before it is used in roadbeds to prevent this sort of thing from happening again.

In addition to the toxic smoke and gases released by tire fires, the heat of the fire can cause rubber in the tires to break down into oils that seep into the ground and contaminate the soil and ground water. An average tire can produce over two gallons of oil.

More on Other Materials for Tire Cords

Steel is the first material that usually comes to mind when speaking of the cords used as belting in tires. Several different materials are used in cords in different parts of a tire. Polyester and nylon are often found in automobile tires. Puncture-resistant bicycle tires feature belts made from Kevlar[®]. All these materials are polymers, but they are not crosslinked when used in tire cords.

More on Thermoplastic Elastomers

Within the past twenty years or so a few kinds of rubber have been developed which can be recycled much more easily than most elastomers. These materials are called "thermoplastic elastomers" because they can be melted down and re-molded. Thermoplastic elastomers are not crosslinked, but rely on non-covalent interactions between polymer chains to bind them together as if they were crosslinked. One kind of thermoplastic elastomer is styrene-butadiene-styrene rubber, or SBS rubber. This material is a *block copolymer*. Unlike the repeat units in a statistical copolymer, the repeat units in a block copolymer are arranged in separate blocks. In SBS rubber, each polymer chain consists of three sections, two outer sections made from styrene monomers and a middle section made from butadiene monomers. Since the different chain blocks are actually immiscible in one another, the styrene blocks phase separate from the butadiene blocks.



Figure 6: A schematic showing the arrangement of blocks in a polymer molecule of SBS rubber

Clusters of styrene-based chain ends cluster together in clumps that serve to tie the rubbery butadiene-based blocks together, effectively crosslinking the polymer. However, the styrene-block clusters come apart when the material is heated, so the material can flow if it gets hot enough. This means you can heat and re-mold a piece of SBS rubber into new shapes, unlike covalently crosslinked elastomers.

More on the Cryogenic Method and the Glass Transition

The cryogenic method for separating rubber from steel and other cords in tires depends on liquid oxygen or supercooled air to cool tire rubber to low temperatures at which the material becomes brittle. This change in physical properties upon cooling is not a true freezing transition. Rubber does not crystallize upon cooling, and there is no observable heat of transition when rubber becomes hard and brittle at low temperature. Rather, rubber undergoes something called the *glass transition*. The glass transition is a change undergone by many polymers, and gets its name because when a polymer undergoes the glass transition it becomes like a glass: a brittle, amorphous solid. Every different polymer undergoes the glass transition at a different characteristic temperature called the *glass transition temperature*, or T_{g} . The glass transition is caused by the

change in molecular motion that happens when amorphous (non-crystalline) polymers are cooled. At temperatures above the T_g of a given polymer, the polymer molecules have enough energy to move about in place quite a bit, wiggling, twisting, and waving about. This is not translational motion, as the polymer tends to stay in one place while going about these gyrations. This motion makes a polymer sample flow easily under enough pressure, so that it can deform easily. But when the temperature drops below the T_g , the polymer chain stops moving. Once this motion stops, the polymer cannot accommodate stress as easily, so it becomes brittle. All elastomers have T_g 's below room temperature, while hard plastics have T_q 's that are above room temperature.

More on Drawbacks of Tire Derived Fuels

Tire derived fuels have an advantage over coal in that they don't produce appreciable amounts of nitrogen oxides as waste products. However, TDFs share with coal the drawbacks of producing carbon dioxide, a greenhouse gas, as well as solid particulate matter, which can cause respiratory ailments. Solid particulate matter consists of tiny particles which are smaller than the eye can see, but which are still in the solid phase rather than the gas phase. The solid particulate matter produced by coal and TDFs consists primarily of fine soot particles. In addition, environmental activists have raised concerns about heavy metals, chlorinated organic compounds, and other toxins in the emissions of TDFs.

More on Historical Perspectives

Rubber history is rich with stories of people as well as science. While it is wellknown how Charles Goodyear accidentally discovered vulcanization, it is less wellknown that he was a poor businessman, was swindled out of the rights to use his invention in Britain, died in poverty, and didn't even found the giant corporation that now bears his name. Still less known is how in the late 1800s British spies smuggled rubber seeds out of Brazil, the native home of the hevea tree, and used them to establish giant rubber plantations in what were then British colonies in Southeast Asia. International events continued to play a role in rubber science into the twentieth century. SBR was first developed in the U.S. during World War II as a replacement for natural rubber at a time when the Japanese occupied Malaysia and Indonesia, where most of the world's natural rubber is grown.

For more on these and many other stories from the history of rubber and its use in tires, visit *The Story of Rubber*, from the University of Southern Mississippi Polymer Science Learning Center and the Chemical Heritage Foundation: <u>http://www.pslc.ws/macrog/exp/rubber/menu.htm</u>.

Connections to Chemistry Concepts

Polymers — all commercial elastomers are polymeric. Many aspects of polymer chemistry, such as polymerization, crosslinking, and co-polymers can be introduced into a lesson about rubber.

Chemical reactions — Iron rusting in the steel belts of old tires is a chemical reaction - oxidation. In addition, polymerization and crosslinking are chemical reactions. Of course, the burning of tire rubber, whether in an accidental landfill fire, or in tire-derived fuel, is a chemical reaction (combustion).

Oxidation and reduction — The rusting of iron in steel belts is a redox process. **Thermochemistry** — rusting is an exothermic reaction, which can give off enough heat to start tire fires. **Separation** — Belt steel is separated from ground tire rubber using magnets. While this is not a true chemical separation, since the steel isn't dissolved in the rubber, the basis for the separation is a difference in properties between the rubber and the steel. Specifically, the two materials have different magnetic properties: steel is attracted to a magnet while rubber isn't. Though rubber and steel in tires don't constitute a chemical solution, property differences are the basis for all chemical separations. For example, difference in boiling point is the principle that makes distillation possible, and difference in solubility is the basis that makes separation by precipitation possible. In this light, the macroscopic separation of rubber from steel using magnets can be an illustrative model for understanding separations that take place at the unseen atomic-molecular level.

Surface area and reaction kinetics — Shredding of tires increases surface area and therefore increases the rate of reaction in the combustion of TDFs.

Possible Student Misconceptions

- 1. "All polymers are crosslinked." Many polymers exists as separate long chain like molecules that are not joined together in a crosslinked network. Natural rubber (polyisoprene) is not crosslinked when it is harvested from rubber trees (hevea brasiliensis), but must be vulcanized to crosslink it after being molded into a desired shape. Most forms of synthetic rubber are also synthesized without crosslinks and vulcanized after being molded.
- 2. "All rubber is the same material." Many different kinds of polymers are used as elastomers. Natural polyisoprene is just one example. Styrene-butadiene rubber, polybutadiene, silicones, and polyurethanes are just some of the many polymers used as elastomers.

Demonstrations and Lessons

- Crosslinking silicone rubber Silicone caulking is an elastomer that has been chemically designed to crosslink when it comes into contact with the air. Simply squeeze out some silicone caulk, and students can observe it change from a flowing material to a material that holds its shape as the crosslinking takes place within minutes. The chemical reaction releases acetic acid, and will produce a noticeable vinegar odor.
- 2. Crosslinked vs. uncrosslinked rubber You can easily demonstrate the difference in properties between uncrosslinked rubber latex (available at most arts and crafts stores) and crosslinked rubber (for example, pieces cut from an old bicycle tire tube.) Exposing both samples to temperature extremes using an ordinary freezer and a heat gun, you can show how crosslinked rubber keeps its properties at high and low temperatures much better than uncrosslinked rubber. In addition, you can also demonstrate how uncrosslinked rubber latex can dissolve in some organic solvents (like cyclohexane or tetrahydrofuran), while crosslinked rubber does not dissolve, but swells instead.

Suggestions for Student Projects

- 1. Many tire shops are involved in tire recycling, which is even required by law in some states. Students can investigate where old tires go in their communities by simply visiting tire shops and asking what they do with old tires.
- 2. Students or groups of students could each be assigned a different kind of rubber on which to prepare a report. The report could be in the form of a paper or a class presentation. Ask the students to pay special attention to information about the recycling of their particular elastomer.
- 3. Students could carry out a debate on the relative benefits and drawbacks of using tire derived fuels. Students may choose which position they would like to defend, or you might assign them a side to argue.

Anticipating Student Questions

- 1. "Why can't rubber tires just be melted down and recycled like plastics?" The rubber in tires is crosslinked, and crosslinked polymers cannot be melted down because once crosslinked, a polymer sample becomes essentially a single huge molecule.
- 2. "Why can't you just put out a tire fire by pouring water on it?" Put simply, water doesn't work. Because of the shape of a tire, it's very hard for water from a fire hose to get into the depths of the burning pile of tires. Even if you could get water into the interior of a pile of tires, the oil released by the burning tires can catch fire as well, and water is not good for extinguishing oil fires. Think of a grease fire in a kitchen. Rather than using water, which can splatter the burning grease, such fires are best put out by smothering the flames with baking soda. Likewise, the preferred method for fighting tire fires is to smother the fire with dirt or sand.
- 3. "Why don't tires catch on fire when they're on a car?" The rusting of steel belts in tires is a slow process, so it releases heat very slowly. When a tire is on a car, the heat can easily be lost to the surrounding air. However, when tires are piled up in mounds or buried in landfills, it's hard for a tire to lose the heat because the pile of tires insulates the tires in the interior of the pile. Heat can't escape into the surrounding air as easily. With nowhere to go, the heat slowly builds up in a tire pile, possibly igniting a fire.
- 4. "If tire fires are so bad for the environment, why isn't it just as bad to burn tire derived fuels?" This question only has a partial answer, because the environmental impacts of burning TDFs is still a matter of some controversy. However, the main difference between tires burning in a landfill and tires burning in a furnace is that furnaces for burning coal, as well as those designed for burning TDFs are equipped with pollution control devices which reduce the amount of pollution that comes out of the furnace's smokestacks. The most common type of "scrubber" is called an electrostatic precipitator, and removes much of the solid particulate matter in coal and TDF emissions.
- 5. **"Why do TDFs burn better if the tires have been shredded?"** Shredding tires increases the amount of surface area of the particles of rubber that are being burned. Since combustion is the chemical combination of a substance with oxygen, combustion can only take place at the surface of a rubber particle, where the rubber comes into contact with oxygen from the air. The more surface

area the rubber has, the faster it will burn. Since smaller particles have more surface area per unit mass than larger particles, shredding the tires increases surface area. This consideration is important in many chemical reactions. For example, an aluminum pan does not burn, while powdered aluminum burns explosively. The reason is that powdered aluminum has more surface area, so oxidation takes place much more rapidly, rapidly enough to sustain combustion.

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"Experimental Road Smolders, Burns," Associated Press, February 1, 1996. http://www.metrokc.gov/procure/green/rubber.htm#12

White, Kathleen M. "Burning Roadbeds in Washington Could Wreak Havoc on Used Tire Chip Markets," *Recycling Times*. April 16, 1996. <u>http://www.metrokc.gov/procure/green/rubber.htm#13</u>

"Management of Scrap Tires: Tire Fires," United States Environmental Protection Agency. <u>http://www.epa.gov/garbage/tires/fires.htm</u>

Websites for Additional Information

The Macrogalleria — A broad tutorial on polymer chemistry, including information on specific polymers used in NASCAR racers, from the University of Southern Mississippi.

http://www.pslc.ws/mactest/maindir.htm

The Story of Rubber — The history and science of elastomers, natural and synthetic, from University of Southern Mississippi Polymer Science Learning Center and the Chemical Heritage Foundation. http://www.pslc.ws/macrog/exp/rubber/menu.htm

King County Environmental Purchasing Program: Tire-Rubber Material and Products — contains ample information of the uses for recycled rubber. http://www.metrokc.gov/procure/green/rubber.htm

Tire Makers Turn to Polyurethane — *Chemical & Engineering News*, September 10, 2001. http://pubs.acs.org/cen/topstory/7937/7937notw4.html

Tire Derived Fuel — from the United States Environmental Protection Agency. <u>http://www.epa.gov/garbage/tires/tdf.htm</u>

The Captivating Chemistry of Coins

Background Information

Money's history begins with the Chinese with their coinage (miniature tool money moldings rather than actual tools which were also used), guaranteed by the state sometime in the second millennium, BC. The ancient country of Lydia (a country in Asia Minor on the Aegean Sea between the 7th and 6th C. BC) was the birthplace of coined money. The early money was made from an amalgam of gold and silver called electrum. But the quality of these coins became high enough to represent a reliable symbol of purity (precious metals) and weight. Ionian Greece extended both the quality and the range of functions of coined money. As a result of using coins, markets were speeded up and vastly extended. It is thought that coins have been the most important form of money to date, a period of some 2700 years. ("Monetary Innovation in Historical Perspective", http:// www ex.ac.uk/ ~RDavies/arian/innovation.html).

Coins were minted by hand from various metals, in particular, those of inherent value such as gold and silver. This marked a transition from the earlier practice of using the weight of a metal as the legal tender. Before minting, there had to be mining. And nation states of the ancient world had to worry about reliable sources of these precious metals. Moving from expensive metals as money to a banking system in which legal tender could represent what was in reserve meant that coins could be made from less expensive metals. Not having to weigh coins to determine their value greatly speeded up everyday transactions!

Some notes on other types of money besides coins

The "minting" of coins by machinery rather than by handwork was proposed by Leonardo da Vinci in his designs of a water-powered mill driving seven hammers. Germans adopted this design to make fine coins called *"milled"*. The machine produced a milled edge that prevented people from "clipping" bits of precious metal as was done with hand-made coins. This machinery had its inspiration from Gutenberg's design of the famous printing press of 1440. The minting of coins rather than the printing of paper money was the result! Paper money was common in China back in AD 960, continuing in use for about 500 years. By 1450, the Chinese abandoned paper money because the quantity issued became so excessive that inflation and even hyperinflation resulted. But in Europe, paper money did not become common tender until the 17th Century.

Paper money had no intrinsic value compared with coins made from precious metals. So the paper money was backed by deposits of gold or silver – the paper money essentially being an exchange slip. This practice of using a paper "chit" slip or voucher was required during the Crusades when large sums of money had to be transferred from Europe to the Middle East in order to finance the military campaign. Warfare has had a long association with money and financial activities. An extensive treatise on the "Origins of Money and of Banking" can be found at http://www.ex.ac.uk/~RDavies/arian/origins.html

The Mint or Coinage Act of 1792 established in the United States regulations for the making of specified coin types, their physical and chemical composition, and the first Federal building (Philadelphia, the US Capital) in which the stamping of the coins was to be done. There is a very precise listing of coin characteristics as well as their names at <u>http://en.wikipedia.org/wiki/Coinage Act of 1792</u>. The term "dollar" (from the early German and Dutch word "daler" and the German "thaler") was established with this Act but as a coin, not paper currency as we know today. In 2000, the US Mint returned to the dollar coin issuing the Sacagawea dollar (followed by the Presidential dollar coin series in 2007). Sacagawea was the 15 year old Shoshone girl who became the crucial guide for the Lewis and Clark expedition in 1804. The history of Sacagawea's role in that expedition is documented at

http://www.usmint.gov/mint_programs/golden_dollar_coin/index.cfm?action=SacAbout

More on Alloys

Alloys of metals used for coins have a long history, going back to at least the Grecian times of the 7th century, BC. Using a pure metal such as silver or gold for coins lacks hardness. Adding other metals such as copper, zinc, manganese, nickel, or tin create complexes that are much harder. The transition metals are used for myriad alloys in the modern era. Bronze as an alloy dates back to 3500 BC. Copper is an abundant primary metal for coins going back to the Roman times in which copper was mined on the island of Cyprus, hence the name *cyprium* for copper, later shortened to Cuprum (Latin). Because copper can occur as a pure metal in nature (as well as in an ore) and because of its relatively low melting point compared with iron, copper was one of the earliest of metals to be used for tools and other artifacts. Addition of tin (and zinc) created the stronger alloy of bronze. It is still not clear from where the ancients in the Mediterranean region obtained their tin. An extensive listing of the elements and alloys used for coins can be found at http://www.tclayton.demon.co.uk/metal.html. A very interesting book (video available; check university libraries, particularly Penn State) on the history of metals can be found at http://www.amazon.com/Out-Fiery-Furnace-History-Mankind/dp/027100441X.

One of the early tests in European Middle Ages for the proper mix of metals in coins of gold or silver was a simple scratch test done on schist or quartz known as touchstones. The particular color trace left by the metal was used as a rough gauge of the purity of the coin's precious metal content.

More on Paper Money

As mentioned, paper money has its origins in China beginning about AD 960 (http://www.chinavista.com/experience/paper_make/paper_make.html). Paper itself is an interesting product which, when used for money, requires rather special characteristics, the most obvious being durability. The production of sheets of paper depend upon "glues" that often are inherent in the source material for the paper; i.e., wood and other cellulose products' molecules. This "glue" comes from the structure of the cellulose polymer (monomers of glucose) in which the cellulose, when placed in water, forms a slurry from broken bonds in the cellulose matrix. Highly polar water molecules hydrogen bond to the oxygen and hydrogen of the glucose in the cellulose fragments. When this slurry is collected, pressed and allowed to dry, the cellulose fibers regroup into a "mat" through rebonding of the cellulose fragments. (http://en.wikipedia.org/wiki/Papermaking), (http://hometown.aol.com/ppreble2/history2.html#chem)

Other sources of cellulose besides trees include flax (to make linen), cotton, and, more recently, hemp that has four times the amount of cellulose fiber per acre grown than trees. Hemp also has a renewable time frame of two years compared with 20 years or more for trees. Other chemistry issues associated with paper manufacture and usage include the use of bleach and caustic chemicals (sodium and potassium hydroxide) and the need to chemically "neutralize" these chemicals before being released into the environment, in particular, into rivers and other bodies of water. An extensive collection of information, including chemical, related to paper making is found at

http://practicalaction.org/docs/technical_information_service/papermaking.pdf

One of the more interesting "cellulotic" money materials was tobacco leaf, used in the England's American colony of Virginia because of a chronic shortage of official coins! The tobacco leaves, deposited in warehouses, were certified for quality and quantity. The value of the tobacco (rather than gold or silver deposits) was the guarantor of these certificates. In the modern era, paper money has become a high tech creation for the obvious reason of preventing counterfeiting. Again, counterfeiting has been around as long as money has been produced, either as coins or paper denominations. The Secret Service was originally established in 1865 to suppress counterfeiting! Secret Service responsibilities were broadened to include "detecting persons perpetrating frauds against the government." This appropriation resulted in investigations into the Ku Klux Klan, non-conforming distillers, smugglers, mail robbers, land frauds, and a number of other infractions against the federal laws!(See <u>http://www.treas.gov/usss/history.shtml</u>; <u>http://www.pbs.org/wgbh/nova/moolah/</u>.)

The present U.S. paper currency has a whole series of features that make counterfeiting very difficult. Obviously the use of electronic photocopiers by criminals is easily the most ineffective way to produce authentic looking bills! And here are some of the reasons:

- For a \$20 bill (and others as well), there is polymer security thread within the paper that has the words "USA TWENTY" printed on it. It also glows red under ultraviolet light. For \$10 bills, it glows yellow, and for \$5 bills, blue.
- Additional red and blue fibers are embedded throughout the paper.
- A watermark is embedded in the paper and can be seen when held up to the light. The watermark is of a president, depending on denomination, located on the front left side.
- The ink used for the serial number looks green when viewed straight on but appears black when viewed at an angle (called "color-shifting ink")
- The ink used for the rest of the printing contains a magnetic signature; a bill will be drawn toward an especially strong magnet, such as a neodymium magnet.
- The texture of the printing has several features difficult or impossible to duplicate. They include very clear, distinct and sharp saw tooth points on the Federal Reserve and Treasury seals. The same is true of the fine borderlines of the note. In addition, the portrait is lifelike and stands out distinctly from the background, not flat and lifeless as in counterfeits where the details merge into a background that is often dark and mottled.
- Microprinting is used for the words "The United States of America" that are hard to replicate because they are so small.

The paper used for U.S. currency is a cotton- and linen-fiber blend, with no starch-based sizing (the property that keeps ink from running) as in commercial paper. Hence, a simple iodine test would detect starch-sized paper because of a blue spot or line that would develop at the test site. And this is done as a quick check at banks. The bleach used in most wood pulp paper will fluoresce when exposed to UV light which is not true for the cotton/linen paper. (See

http://www.secretservice.gov/money_detect.shtml;

http://www.moneyfactory.gov/newmoney/)

Fluorescence is based upon the principle that an entire molecule capable of fluorescence, known as a fluorophore, upon absorbing light energy of a particular wavelength (as in the ultraviolet range) is raised to a higher energy level; subsequently the excited molecule loses some of that energy which is emitted at a different and longer wavelength (less energy than the original light source) as light detectable with the eye, though more sensitive instruments are used in the laboratory in which fluorophores are used a markers, particularly in biological analysis. Some special genes from microorganisms can be detected when they are caused to fluoresce. They are used as markers in a variety of biological applications. See

http://www.accessexcellence.org/TC/AP/LB6.html.

A very fine series of short videos, useful in the classroom, demonstrate the basic principles of fluorescence, at

http://probes.invitrogen.com/resources/education/tutorials/1Introduction/player.html

Connections to Chemistry Concepts

- 1. **Electromotive Series**—Copper-coated zinc pennies react with stomach acid while mainly copper pennies do not, because zinc is higher on the activity series of metals than copper. This can cause problems for children who swallow newer pennies.
- 2. **Oxidation-reduction reactions**—All the metals reacting with acids are redox reactions.
- 3. **Acids and Bases**—The stomach is acidic, the intestine is basic. That's why zinc pennies react much more slowly in the intestine than in the stomach.
- 4. **Ions, Aqueous Ionic Solutions**—Where does the metal go when the acid "eats" it away? Into solution as ions, of course.
- 5. **Metals and Metallic Properties**—The vending machines test coins based on metallic properties electrical conductivity, weight, ferromagnetism, diameter, rolling speed.
- 6. **Metallic Bonding** the properties of metals that include ductility, malleability, shininess (luster), high electrical and thermal conductivity are all due to the delocalized, mobile electrons that form non-directional bonds between the metal atoms.

Possible Student Misconceptions

- 1. "Many consumer products contain the metals, sodium and potassium." The sodium and potassium are present as ions, part of a compound, not as the elements, Na and K, which are toxic atoms.
- 2. "All metals are magnetic." There are a limited number of metals that exhibit ferromagnetism which refers to the ability of a substance to become permanently magnetized by exposure to an external magnetic field. There is also the property called paramagnetism in which some transition metal <u>compounds</u> are attracted to a magnetic field.
- 3. "All metals are hard solids." Metals in elemental form vary considerably in their degree of hardness. Something like sodium and potassium can be cut with a knife, and mercury is a liquid. Gold and silver are quite malleable. Making metals harder is done through the addition of other elements, both metals and some non-metals such as carbon, forming mixtures or alloys.

Demonstrations and Lessons

- 1. Since metals are a major feature of money, there is lots of chemistry that can be done with students in the lab. In particular, consider the following:
 - Establish an activity series for selected metals using Cu, Mg, Zn, Fe, and Ag and the nitrate solutions of each metal (see standard lab manual); do microscale using well plates.
 - Determine properties of metals including reactivity with acids, bases, conductivity, magnetic properties, density, ductility, malleability, scratch resistance; compare with selected non-metal elements.
 - Students can brass-coat a penny by placing it in a hot, Zn(s)/ 3M NaOH mixture (see Chemistry in the Community [CHEMCOM] course, "Conserving Chemical Resources").
 - Students can see the chemistry of a penny by using a file to "nick" the edge of the penny, exposing the zinc under the copper surface, then placing it in HCI solution; observe bubbling (acid reacting with zinc but not the copper to produce a gas, hydrogen). Overnight reveals the thin copper shell without the zinc core.
 - Students could study electrolysis (and electroplating) using a solution of CuCl₂ in a U-tube, carbon electrodes (pencils will do, exposing the carbon on both ends of the pencil) in both ends of the U-tube, and a 9-volt battery with electrical leads. Production of chlorine gas will be noticeable.
 - Students could investigate the reactivity of some of the common acids on a selection of some of the common metals, including zinc, lead, aluminum, copper, iron, and magnesium. Relate the reactivity (or lack thereof) to Standard Reduction or Oxidation Potentials (electromotive series).
 - Students could do a qualitative activity in which copper metal reacts with nitric acid (micro scale; important color changes relate to the chemistry involved). A quantitative reaction could be done using a known mass of aluminum foil in a solution of copper nitrate. One of the products is solid copper for which the mass can be determined. Work out the mole ratios of the two metals and relate to the equation for the reaction.
- Students could make paper, using different sources of cellulose. There are several references that will prove useful; <u>http://www.gomez.org/papermaking.html</u> <u>http://www.tappi.org/paperu/welcome.htm</u> <u>http://www.paperonweb.com/pmake.htm</u>
- 3. Students could test the properties of paper. This includes first looking at different papers, including dollar bills, with a stereomicroscope. Excepting the bills, test the papers to see what effect a ballpoint pen, a gel pen, and a magic marker in terms of the paper's absorbency. Test the pH of the paper, using moist pH paper touched to each paper surface. Test the papers for the presence of starch using a standard iodine solution (4g. I₂ and 6 g KI in 100 ml water). Do strength tests for the different papers by first immersing the papers in water for a predetermined time, then suspend the individual strips using a paper clip on each end, then attaching progressively heavier weights until the paper comes apart.
- 4. Determine the various security properties of US currency bills as outlined earlier in the introduction (stereoscope examination, fluorescence with ultraviolet light, watermarks, etc).

Suggestions for Student Projects

- 1. Students could research some of the ores of the more common metals, their geographical origins as well as the chemical formulas of the various metal containing compounds found in the ore.
- 2. Students could research the various processes, chemical and physical, to extract the metals found in ores. Extraction methods include both the blast-furnace approach as well as electrolysis. There is a lot of chemistry here.
- 3. Students could research the history of paper and the various components of paper from around the world, including such things as linen and rice as well as tree pulp.
- 4. Students could research the chemistry behind corrosion, the preventive measures for corrosion, and the development of alloys that resist corrosion.
- 5. Students could research the use of lightweight metals, their composition, and the role of "additives". Consider for example the use of carbon, a non-metal, with such things as iron to produce high-strength steel. What is steel? What additives make steel into stainless steel?
- 6. Students could test for the different ionic forms of iron (Fe [II], Fe [III]) in a variety of sources. This includes vitamins, rust, plant food, raisins, cereal such as cream of wheat using the color changes that occur when either of the iron ions comes in contact with solutions of KMnO₄ and KSCN. An interesting aside is the fact that the cereal "Total" ^(R) contains solid iron particles rather than iron ions from compounds. This iron can easily be isolated by soaking the cereal in water in a beaker, stirring vigorously, and then applying a magnet to the side of the beaker to collect the iron filings.

Anticipating Student Questions

- 1. "Why is gold or silver more valuable than metals such as copper and iron?" Gold and silver are known as precious metals. These metals are scarce, but relatively easy to isolate from the background rock where they are found. They are shiny, and stay that way (except for silver's tarnishing). They are relatively soft (for metals), so they can be shaped into jewelry for adornment. And the shininess makes the jewelry obvious on the wearer great status symbols. For base metals, basically, the more difficult it is to find and process the metal from its ore, the more valuable it is. Prior to 1886. Aluminum was considered both precious and more expensive than gold because it was so difficult to produce from its ore, bauxite. Once the Hall process was developed, aluminum could be produced at a much lower cost, was more available and less expensive.
- 2. "Why is carbon, a non-metal, added to iron in the steel making process?" Carbon, with a covalent bonding capacity of four, can provide directional bonds between carbon atoms and metal atoms which are stronger than metal to metal bonds which are nondirectional (delocalized electrons). The property of malleability in iron is reduced as more carbon is added.
- 3. "How does heating remove a metal from its ore?" The metal in the ore is in the form of a compound, which means the metal in the compound is an ion rather than an atom. As such, the ion must be converted to an atom through the chemical process called reduction. Reduction of metal ions is most often

accomplished through heat and the presence of carbon in the form of coke or carbon monoxide gas. This heat-based process is known as pryrometallurgy.

4. "Why are metals shiny and non-metals are usually dull?" Shininess of metals (along with their other properties of good electrical and thermal conductivity, and malleability) is produced through the non-localized outer electrons of the metal atoms. These non-localized electrons, when struck by light, are able to move back and forth with the same frequency as the light. This oscillation of charged particles creates acceleration that results in radiation of electromagnetic radiation of the same frequency as the original light that struck the metal surface. Nonmetals have localized rather than non-localized electrons which are not free to interact with light in the same way as in the metal atoms.

References

1. The ACS book for teachers, "Science in a Technical World", @ 2000; ISBN 0-7176-3550-4; section on "Paper and Pulp Research", pp.299-382.

2. The CM article, "The Money Makers", cover story, Feb. 2003, p. 14.

Websites for Additional Information

http://neon.mems.cmu.edu/cramb/Processing/history.html- a short history of metals

<u>http://www.tclayton.demon.co.uk/metal.html</u> - this website provides a very extensive series of references and their details concerning metals used in coins and medals. All elements, alloys, and non-metal currency are linked.

<u>http://www.moneyfactory.gov/section.cfm/2-</u> website of the Bureau of Engraving and Printing; lots of good information about money

http://www.usmint.gov/- additional information on US money

<u>http://www.usmint.gov/mint_programs/golden_dollar_coin/index.cfm?flash=yes&a</u> <u>ction=SacAbout-</u> part of the US Mint site with the history of Sacagawea, the Shoshone guide, who is featured on the new dollar coin.

<u>http://www.treas.gov/usss/-</u> website of the Treasury Dept. and the Secret Service, with history and basics of protecting money from counterfeit.

<u>http://www.treas.gov/usss/know_your_money.shtml-</u> a good description of all the design considerations for US paper money to prevent counterfeiting.

<u>http://www.ex.ac.uk/%7ERDavies/arian/llyfr.html-</u> an extensive series of excerpts from a book on the History of Money by Glyn Davies; excellent reference.

<u>http://www.ex.ac.uk/%7ERDavies/arian/amser/chrono1.html-</u> specific details for the comparative chronology of money, from 9000BC on; excellent reference.

<u>http://pubs.acs.org/cen/80th/elements.html-</u> this website from the American Chemical Society features the periodic table. Included are extensive chemical descriptions of all the elements.

<u>http://www.fi.edu/pieces/knox/pressingon.htm-</u> a teacher-friendly website listing a variety of activities involving money, including information about one of the earliest coinmaking presses, still in use at the Franklin Institute in Philadelphia. There are also photos of the press. Additional resources, bibliography, and links

<u>http://www.pbs.org/wgbh/nova/teachers/programs/2314_moolah.html-</u> a NOVA website for teachers concerning classroom activities involving money, related to a NOVA program, "Secrets of Making Money".

http://pubs.acs.org/cen/news/85/i09/8509notw8.html-history-a historical detective story about silver usage in England's American colony of VA

<u>http://www.paperonweb.com/pmake.htm-</u> a reference on paper making that is very extensive, including the details of both commercial paper making, the history of the process, and activities and references for teachers.

http://www.gomez.org/papermaking.html- practical information on making paper

<u>http://practicalaction.org/docs/technical_information_service/papermaking.pdf</u> another practical commercial website that provides good information about the commercial paper making process along with the history of paper making.

<u>http://www.hqpapermaker.com/paper-history/-</u> another good website that links modern papermaking processes with papermaking traditions and processes in many other countries, again with history included.

A high school textbook on forensics that includes a good collection of lab activities dealing with testing for counterfeit money, paper character-istics, ink analysis using chromatography, and such is *"Forensic Science for High School"*, B. Deslich, J. Funkouser; Kendall Publishing Co, 2005; ISBN # 0-757501825-7

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The Death of Alexander Litvinenko

Background Information

More on the Unraveling Story

While the police were investigating the poisoning of Litvinenko in London, the Health Protection Agency (HPA) was responsible for the related issues of public health. Over the weeks that followed his exposure it became apparent that many different sites of contamination had occurred, indicating that a rather large amount of Po-210 had been used in the poisoning. This group (the HPA) issued daily updates on its website to quell any potential public panic, and they consulted with the local authorities to help them deal with handling of the local contamination sites.

At least fourteen sites in and around London were found to have Po-210 contamination, including four hotels and three hospitals. Contamination was also found on two British Airways airplanes, and traces of Po-210 were found at the British Embassy in Moscow, and in an apartment in Hamburg, Germany. You can find maps of these locations at the BBC website, at http://news.bbc.co.uk/2/hi/in_depth/6267373.stm.

Another article from the BBC, featuring the key players in the mystery, as well as their connections to the locations cited in the maps mentioned above, can be found at http://news.bbc.co.uk/2/hi/europe/6170249.stm.

More on the History of Polonium

Among polonium's first victims were its very discoverers. Marie and Pierre Curie first identified the substance in 1898. They had been studying pitchblende, an ore in which uranium is found. Happening across a sample of pitchblende that gave off much more radiation than one would expect for the amount of uranium present in the ore, they concluded that an unknown, extremely radioactive substance must be present in the material. The Curies succeeded in identifying a material that was 300 times as radioactive as uranium. They named their new element polonium after Marie's home country of Poland. A few months later, the two found a second element in pitchblende, and named it radium. To support their claims of discovery, and to fully characterize the new materials, the Curies had to isolate appreciable quantities of the two elements. This required refining down several tons of pitchblende ore to produce the chloride salts of the new elements in fractional-gram quantities.

Naming the element after Marie's homeland of Poland was an overtly political act. At the time Poland was not independent, but had been ruled by the tsars as part of the Russian empire for many years. Honoring Poland in the name of a new element was nothing short of a call for Polish independence, a thought which would have horrified Tsar Nicholas II, but which would be realized in 1918 following World War I and the Russian Revolution.

Not long after the discoveries of polonium and radium, Pierre purposefully gave himself radiation burns by holding radium salts close to his skin for ten hours time in order to study the effects of radiation on human health. Pierre soon began to show much more serious symptoms of radiation poisoning. His body became weak, and at times his legs shook too much for him to stand. Chronic pain plagued him as well. His death in a traffic accident in 1906 may have in fact spared him a more agonizing demise. Meanwhile, Marie also showed signs of exposure. The skin on her fingers showed visible cracks and scars. She caught colds often. Before Pierre's death, both Curies had suffered from constant fatigue. Most people just thought all this was the result of their hard work. No one suspected radiation could be so deadly. Needless to say, modern safety precautions for handling radioactive materials were not practiced in those days. Marie even kept a glowing vial of radium salts by her bedside at night. She eventually died of leukemia in 1934, most likely a result of her constant exposure to radioactive radium and polonium.

Marie Curie was not, however, the first person to die from exposure to polonium. That honor belongs to Nobus Yamada, a Japanese scientist. Yamada spent time in France working in Marie Curie's laboratory. The next year, after returning home, he died of illnesses related to his exposure to radioactive materials while in France.

The Curies probably unwittingly exposed their children to radiation from polonium and radium as well, bringing samples of the materials home in their pockets, and traces of radioactive materials lingered on their clothing and notebooks they took home from work with them. Their daughter Irène was often sick as a child. Irène would follow in her parents' footsteps and become a scientist. In the 1920s, she carried out her doctoral research on the α -emitting properties of polonium, using a sample of the material that her mother had isolated. Later, after marrying another scientist, Frédéric Joliot, the two would continue researching polonium together.

Since polonium is such a strong α -emitter, they used it as an α -source when studying how other nuclei behave when bombarded with α -particles. One of the most interesting phenomena they investigated was the radiation emitted by beryllium when bombarded with α -particles from polonium. They barely missed discovering that the radiation was in fact the neutral particle that physicists thought existed in the nuclei of atoms. It was rather a British team of James Chadwick and H. C. Webster who were first to discover the neutron. Even so, the French couple would use polonium to make another important discovery. Using polonium and beryllium as a neutron source, they bombarded aluminum with neutrons. Finding the radiation still present after the polonium had been removed, they realized they had created radioactive isotopes of aluminum. This was the first observation of artificially-induced radioactivity in a stable isotope. It was this discovery that earned Irène and Fred the Nobel Prize in Chemistry in 1935.

Amazingly, in light of modern knowledge of the dangers of radiation, Irène Joliot-Curie continued her work with polonium even while pregnant with her two children. Ellen Gleditch, another nuclear scientist, relates that once in the lab there was a serious polonium spill. Joliot-Curie ordered everyone else out of the lab for their safety while she cleaned up the spill herself. Historians have speculated that this exposure might have affected her health more than any other exposure she experienced during her career, and by the 1930s she came down with anemia and pleurisy. These may have been early signs of leukemia, which took her life in 1956. Her husband Fred followed her in 1958, succumbing to cirrhosis of the liver, also brought on by exposure to polonium.

All of these instances of exposure to polonium undoubtedly occurred because of inhalation of unseen particles of polonium in the air. Since polonium is an α -emitter, not a γ -emitter, its radiation can be stopped by skin, or by any closed container in which the polonium is kept. Polonium must be inhaled or ingested to do its damage (which is why Alexander Litvinenko's assassins could handle it with relatively little risk to themselves). In the cases of the early polonium scientists, inhalation is the most likely route of getting this radioactive substance into their bodies.

This was not the case with some medical patients who were exposed to polonium during World War II. Polonium-beryllium mixtures were used as neutron sources for initiating fission chain reactions in the atomic bombs used on Hiroshima and Nagasaki at the end of World War II. By now it was known that radioactive substances were dangerous. This had been made tragically clear in the case of the radium dial painters. An early use for radium was to make glow-in-the-dark clock dials. A paint containing radium compounds was used to make the numbers on the dials. In the 1920s, the young women employed to paint the dials often licked their brushes to give them a fine point. In doing so, they ingested radium. Many died from cancer.

When the Manhattan Project to develop atomic bombs was begun, project leaders knew radium's dangers, and they knew that more needed to be known about the dangers of other radioactive materials. In the project, more people than ever before would be working with the materials, and would be exposed to their radiation. A realistic understanding of the risks and safety measures that should be taken was necessary. Uranium and plutonium were used as fissile materials in the bombs, and poloniumberyllium mixtures were used as neutron sources to initiate chain reactions. A subgroup of the project was assigned to study the effects of these materials on human health. While accidents provided some of the subjects for study, in other cases terminally-ill cancer patients were injected with compounds of uranium, plutonium, and polonium.

The modern method for preparing polonium was also developed as part of the Manhattan Project. This method was first carried out in 1944 at a facility in Dayton, Ohio that would later become the U.S. Department of Energy's Mound Laboratory. The technique involves bombarding bismuth-209 with neutrons. A bismuth nucleus absorbs a neutron to become bismuth-210. Beta decay follows, turning the material into polonium-210.

$$^{209}\text{Bi} + n \rightarrow ^{210}\text{Bi} \rightarrow ^{210}\text{Po} + e^{-1}$$

This procedure is hardly trivial, nor are the chemical operations necessary to separate the polonium from the bismuth from which it was made. Making polonium is something that would be very difficult to do outside of a facility already especially designed for the purpose. Such facilities tend to be found only as part of nuclear weapons programs. This is one reason the Russian government is highly suspected of involvement in the death of Alexander Litvinenko.

Reference

Fröman, Nanny. "Marie and Pierre Curie and the Discovery of Polonium and Radium," from Nobelprize.org, official website of the Nobel Foundation. (Originally delivered as a lecture at the Royal Swedish Academy of Sciences in Stockholm, Sweden, on February 28, 1996.)

http://nobelprize.org/nobel_prizes/physics/articles/curie/

More on Nuclear Radiation

Nuclear radiation – that is, ionizing radiation emitted from nuclear decay reactions – can be broken down into essentially three types: alpha (α), beta (β), and gamma (γ) radiation. High-speed neutrons are another type of nuclear radiation, but their primary environment is within nuclear reactors, and (hopefully) our exposure to them is limited.

Alpha particles are composed of two protons and two neutrons – essentially helium nuclei, that is, helium atoms minus their electrons. These alpha particles are emitted as other nuclei decay. Because they are very massive particles (relative to the other two types of radiation), alpha particles are relatively slow-moving and have the least penetrating power through solid material of the three types. Their large positive charge causes them to interact with other atoms, causing the other atoms to lose electrons to the alpha particles, making the target atoms become ions. (This is what is meant by ionizing radiation.) Although they have a lot of energy, they are stopped by almost anything particulate. A piece of paper or the dead, outer layer of our skin cells can stop them. They only travel a few centimeters through the air before air molecules absorb their energy, so they offer us little harm, as long as they stay on the outside of our bodies. It is only when they enter our bodies that they cause cellular damage.

Beta particles are essentially electrons that have been emitted from nuclei in nuclear decay processes. They are very small and light relative to alpha particles, so they travel faster and have more penetrating power through solid material. They can penetrate the skin and can cause tissue damage, especially to the eyes. Even so, they can't penetrate very deeply, and they are therefore more dangerous when they are inhaled or ingested.

Gamma rays are not particles at all, but are photons of energy emitted in nuclear reactions, often emitted along with alpha or beta particles. Since gamma rays are massless particles with no charge, and they travel at the speed of light, they have the greatest energy and penetrating power of the three types of radiation. Gamma rays can travel right through the body and can do damage to any internal cells along their way. They are not directly ionizing radiation, but when they impact other atoms, those atoms absorb the energy and emit other particles that can then ionize other atoms around them.

More on How Radiation is Measured

There are 4 major terms to deal with when one speaks of radiation: strength or intensity of the particles being emitted, the energy of said radiation particles, the dose available from those particles, and equivalent dose, the effect that dose has on body tissue. The list below gives the basic units used for each of these terms, and the tables below that give equivalencies between conventional units and the more modern, more widely accepted SI units.

Intensity/Strength

1 becquerel = 1 radiation emission per second 1 Curie = 37 GBq = 37,000 MBq = 37,000,000 Bq 1 Bq = 37,000 pCi (1 pCi = 10^{-12} Ci)\

Energy of Radiation

1 J = 6,200 billion MeV

Dose

1 R produces approximately 1 rad of tissue dose

- 1 Gy = 100 rads
- 1 Gy = 1 J/kg of tissue

Equivalent Dose

1 Sv = 100 rem equivalent dose = absorbed dose x Radiation Weighting factor (W_R) Sv = Gy x W_R

Measure	Conventional Unit	SI Unit
Intensity/Strength	Curie (Ci)	Becquerel (Bq) (1 Bq = 1 emission event)
Energy of Radiation	electron-volt (eV)	Joule
Exposure to Radiation Present in Air	roentgen (R)	Gray (Gy)
Tissue (Absorbed) Dose	Radiation Absorbed Dose (rad)	Gray (Gy)
Equivalent Dose	roentgen equivalent, man (rem)	Sievert (Sv)

Type of Energy and Range	Radiation Weighting Factor (W _R)	
Gamma rays/X-rays	1	
Beta particles	1	
Neutrons		
< 10 keV	5	
> 10-100 keV	10	
> 100 keV to 2 MeV	20	
> 2 MeV to 20 MeV	10	
> 20 MeV	5	
Alpha particles	20	

As can be seen from the table above, alpha particles have a W_R of 20, indicating a greater damage effect once they have entered the body.

More on Radiation and Health Effects

The term "radiation" is used to describe the transmission of energy without the use of a material medium. Heat and light energy are forms of electromagnetic energy radiated by the sun, for example. However, the term is also used to describe the emissions of a radioactive substance, some of which is particulate and some, pure energy. The energy associated with radioactivity is significantly greater than the energy associated with most forms of electromagnetic energy. The energy of radioactive emissions is great enough to disturb electrons in substances exposed to it. That is, radioactive emissions can ionize, or remove electrons from, matter.

Humans are subjected to ionizing radiation constantly. It is low-level in intensity but ever-present. The usual term for this "sea" of radiation is background radiation. The major source of natural radiation for humans is radon. Another source is our own bodies in the form of radioactive isotopes of potassium (K-40) and carbon (C-14). Another source is cosmic radiation from space. We are protected from most of this by the atmosphere. Other sources are man made. For example, we receive low-level radiation each time we have an X-ray. On average, people living in the United States receive about 300-350 mrem of background radiation each year.

Exposure to higher levels of ionizing radiation is dangerous to human health. A radioactive substance emits either alpha particles, beta particles or energy in the form of gamma radiation, which is high energy radiation. All of these are dangerous to humans because they transfer their energy to biomolecules, thus changing their structure and damaging them. As molecules are damaged, cells die and tissue is destroyed.

Let's consider the case of humans being exposed to an external source of radiation. For example, students may have read John Hersey's book *Hiroshima*, which describes the effects of the atomic bomb on the people of that town. Some people were exposed to direct radiation in the form of beta or gamma radiation. But over a longer time period they were also exposed to the decay products of the nuclear reactions. These products are themselves radioactive atoms released in the atmosphere. Over time they may be inhaled or ingested or absorbed chemically in foods, which then may be ingested.

For another example, the event at the Three Mile Island nuclear power plant allowed radioactive iodine particles to escape into the air. The small iodine particles could be inhaled, and since the radioiodine is somewhat soluble in water, it may also be ingested in drinking water. In both case, then, the radioactive substance continues to emit ionizing radiation (beta radiation) inside the body. This is apparently what happened *intentionally* in Litvinenko case, but in his case the polonium emitted alpha radiation, a much more potent form of radiation in the body. When the radioactive species is contained within the body it is generally termed "contamination" rather than "exposure."

When cells are exposed to ionizing radiation, there are four possibilities:

- The radiation may pass through the cell without doing any damage
- The radiation may do minor damage which the cell can repair immediately
- The radiation may damage the cell nucleus so that the damage is passed on in cell division
- The radiation may kill the cell

In Litvinenko's case the radiation from the alpha particles released by the Po-210 killed his cells. The loss of those cells produced the symptoms described in the article.

How does ionizing radiation damage the body? First a few basics about the properties of the radiation: The three important variables for ionizing radiation are energy, ability to penetrate human tissue, and half life. The half-life of a radioactive isotope is the length of time required for half the original mass to undergo decay. Po-210 has a relatively short half-life of about 138 days. That means a large numbers of polonium atoms will give off their radiation in a short time period.

If we order the three basic forms of ionizing radiation according to mass, alpha particles are the most massive, beta particles next and then gamma radiation which has no mass. The order is reversed for ability to penetrate tissue. Alpha particles can be stopped or "shielded" by a layer of tissue paper or the layer of dead skin on the body. Beta particles can travel farther and can penetrate up to tens of millimeters into the skin. Gamma rays, similar to X-rays, can penetrate the human body easily.

Although the energy of ionizing radiation is in the same order as penetrating ability, that tells only part of the story, especially if the radioactive substance is *within the body*. If we measure the relative ability of each form of radiation to damage nearby tissue we find that beta and gamma radiation are about the same with a relative measure of 1, but alpha particles are 20 times more damaging. This relative measure is called the radiation weighting factor (W_R). The W_R is 1 for beta and gamma, but 20 for alpha. The article says that in absolute terms each alpha particle has 5.3 MeV of energy, more than 1 million times the energy needed to break a chemical bond. Since it

is believed that Litvinenko *ingested* Po-210, which undergoes alpha decay, each atom of decaying polonium in his body was capable of doing severe damage to the cells and tissue around it by changing the electrons in the bonds within biomolecules that make up cells. The change is caused by the release of energy when the alpha particle is absorbed and, therefore, stopped. Litvinenko's symptoms listed in the article are consistent with acute radiation poisoning.

According to the Hanford Health Information Network, which was established to study the effects of the release of radionuclides in the vicinity of the U. S. Department of Energy's nuclear weapons site in the state of Washington:

"Once a radionuclide is inside the body, some of it may enter the bloodstream. The chemical properties of the radionuclide determine how the body handles the radioactivity. The body does not recognize the difference between a radioactive and non-radioactive substance. For example, strontium-90 is chemically similar to calcium and the body utilizes strontium in the bone in much the same way it does calcium.

"When a radionuclide concentrates primarily in one organ, as when strontium concentrates in the bone, that organ receives a larger dose from the radioactive substance than do other organs or tissues. Other radionuclides, such as neptunium-239, which are not chemically similar to substances needed for the body's functioning, may also concentrate in different organs or tissues.

"Some radioactive substances do not concentrate in one organ, but are distributed throughout the body. Tritium, for example, is a form of hydrogen. Hydrogen is part of the water molecules present throughout the body, so tritium delivers a dose to all tissues.

"The dose to different parts of the body is determined by a number of factors, including the amount of radioactivity present and its distribution, solubility in the bloodstream, and the type and energy of the emitted radiation. Once the radioactive substance is taken into the body, it will continue to give off radiation until either the radioactivity has decayed or the body has eliminated the substance through normal metabolism. Both of these processes occur simultaneously."

What kinds of cells are most vulnerable to ionizing radiation? In general, cells that divide at the highest rate are most vulnerable. So blood-forming tissue, reproductive organs, skins (and hair), bone and teeth, and some parts of the digestive system are most easily affected by ionizing radiation. The damage is caused when the energy of the radiation breaks chemical bonds and forms new chemical substances foreign to the body, produces free radicals or damages molecules that regulate and control important cell processes like cell division. If the damage is minor, cells can repair themselves, but at levels of energy involved in alpha particles, the damage is severe and cells die.

Biological damage from radiation falls into one of two categories—stochastic and non-stochastic, or acute damage. The effects suffered by Litvinenko were nonstochastic. That is, they were rather immediate and acute as a result of high level, shortterm exposure from the Po-210. Litvinenko died a mere 22 days after being contaminated. Stochastic damage is usually the result of long term, lower level exposure, and the effects, like cancer later in life or genetic mutations in future generations.

In order to be ingested, a water soluble compound of polonium, like polonium nitrate, would have to be produced and dissolved in water. The maximum safe amount of Po-210 in the body is about 7 picograms. The British Health Protection Agency (HPA) concluded that "polonium-210 ingestion of 1-3 GBq or more is likely to lead to death within a few weeks, assuming 10% absorption to blood (0.1 - 0.3 GBq). On reaching the

bloodstream, it would be rapidly deposited in major organs and tissues including the liver, kidneys and bone marrow. The intense alpha radiation within these tissues would result in massive destruction of living cells, leading to a rapid decline in health. Anyone receiving such doses would show symptoms of acute radiation sickness syndrome, and death would eventually result from multiple organ failure. Remedial medical treatment strategies are unlikely to be successful once significant amounts of polonium-210 have entered the blood stream and deposited in tissues, within a few hours of ingestion." <u>http://www.hpa.org.uk/hpa/news/articles/press_releases/2007/070306_polonium-210.htm</u> It should be noted here that about half of ingested polonium is excreted from the body in about 15 days. That is, the biological half life of Po-210 is about 15 days.

Radioactive contamination is not of itself contagious. People who were exposed to Litvinenko could not be contaminated as a result of the exposure. However, people exposed to Litvinenko's blood, urine or other body fluids could be contaminated. The HPA tested people who might have come in contact with Litvinenko or places where he had been with these typical results, as of March 15, 2007:

- "596 people had results 'below reporting level' below 30 millibecquerels (mBq) per day (natural levels of Po-210 in urine are typically in the range 5-15 mBq per day). It is therefore unlikely that any of these people had been exposed to Po-210
- "85 people had results above 30 mBq per day in their urine, but with a dose less than 1mSv indicating no public health risk, and no health concern to the individual, but probable contact with Po-210
- "35 people had results above 1 millisievert (mSv), but below 6mSv indicating no public health risk, and no health concern to the individual, but probable contact with Po-210
- "17 people had results above 6mSv which are not significant enough to cause any illness in the short term and any increased risk in the long term is likely to be very small."

More on the Medical Applications of Nuclear Radiation

Radioisotope	Half-Life	Uses
		Used as Tracers
Technetium-99m	6.01 h	Measure cardiac output; locate strokes, brain and bone tumors
Gallium-67	78.3 h	Diagnosis of Hodgkin's disease
Iron-59	44.5 d	Determine rate of red blood cell formation (contain iron); anemia assessment
Chromium-51	27.7 d	Determine blood volume and life span of red blood cells
Hydrogen-3	12.3 y	Determine volume of body's water; assess vitamin D use in body
Thallium-201	72.9 h	Cardiac assessment
lodine-123	13.3 h	Thyroid function diagnosis
		Used for Radiation Therapy
Cesium-137	30.1 y	Treat shallow tumors (external source)
Phosphorus-32	14.3 d	Treat leukemia, a bone cancer of the white blood cells (internal
		source)
lodine-131	8.0 d	Treat thyroid cancer (external source)
Cobalt-60	5.3 y	Treat shallow tumors (eternal source)
Yttrium-90	64.1 h	Treat pituitary gland cancer internally with ceramic beads

SELECTED MEDICAL RADIOISOTOPES

More on Polonium-210

Polonium-210 is a naturally-occurring radioactive isotope of polonium, element number 84. It is the product of uranium and thorium decay. Uranium ores contain only about 100 micrograms of polonium per ton. Polonium can be found naturally in tiny amounts in the soil (from U-238 decay) and the air (from the decay of Rn-222 gas), and in tobacco (primarily from atmospheric deposition onto the broad leaves). Every one of us has a very small amount of it in our body. At high doses, however, it can cause damage to tissue and organs. It is an alpha particle emitter, and since alpha particle have little penetrating ability, Po-210 poses no real threat externally. It is only when it is ingested, inhaled or injected that it poses a danger to us.

Po-210 is used in satellites as a heat producer to keep instruments from freezing up in the low temperatures of space. (Radioactive decay of Po-210 produces alpha particles, which are high energy particles that are stopped very quickly by anything in their direct path. The alpha particles' energy is quickly transformed to infrared energy in the receptor particles. This generates a lot of heat – 0.5 grams of the substance can produce temperatures up to 500°C inside its container. Unfortunately, Po-210's half-life of only 138 days means it cannot be used as a long-term source of energy for long space flights, and its use in this regard has been withdrawn.

Po-210 is also used as a static electricity eliminator in industrial settings, especially in photographic studios and textile mills. For this use it is packaged in minute quantities and is mixed with silver or another metal, and it is very difficult to isolate from these instruments. Its sale for industrial uses is regulated by the Nuclear Regulatory Commission (NRC) or a state agency. The NRC has evaluated the risk of the availability of these devices and other, small devices containing less than 0.1 μ Ci of radioactivity that are used to check or calibrate instrumentation, and it has made the following statement from a fact sheet on Po-210 it published: "At this time, the NRC has seen nothing to suggest that increased controls or security measures are required for polonium-210. The NRC constantly re-evaluates security needs for radioactive materials: should new information become available that suggests enhanced controls are needed, the agency will take appropriate action. December 19, 2006" (See the fact sheet at http://www.nrc.gov/reading-rm/doc-collections/fact-sheets/polonium.html.) The agency makes that statement based on the fact that all the Po-210 sources cited above would require extensive, expensive, and hazardous extraction processes and subsequent chemical reprocessing before the Po-210 would be in a form that would be likely to cause harm to others.

Polonium in its pure form is a metal, and is not soluble. To be dissolved into a drink, as is thought to be the case for Litvinenko, the polonium would have to be chemically processed into a soluble salt, probably polonium nitrate. A rather dated, but still useful, report from the National Academy of Sciences National Research Council, entitled, "The Radiochemistry of Polonium", one of a series called the "Nuclear Science Series", in 1961, offers a wealth of information about the chemistry of polonium. The report can be found at http://library.lanl.gov/cgi-bin/getfile?rc000006.pdf. This is an excerpt from that report.

Polonium metal is silvery gray in color, and is soft enough to be scratched readily. The metal reacts slowly with O_2 at room temperature, but rapidly at elevated temperatures. Therefore, the pure metal should be stored under vacuum or in an inert atmosphere. The intense radiation of curie level samples causes fluorescence in the surrounding gas and in glass or silica containers. In the dark, a quite spectacular blue-white glow is observed from curie level metallic samples or suspensions of insoluble Po compounds. The intense radiation of large samples of Po has a heating effect (27.4 cal/hr/curie – theoretical value),⁵ so that the temperature of the sample can be well above its surroundings. The

radiation also affects glass or silica containers, causing them to become dark and fragile(crazing).

As you can see from this reading, Po-210 as an element could not have been used to poison LItvinenko. Rather, the perpetrator would have had to have used a compound of polonium. The report lists the following compounds of polonium, in oxidation states ranging through -2., +2, +4, and +6:

Polonides (-2 ion) – Zn²⁺, Pb²⁺, Pt⁺, Ni²⁺, Ag⁺, Be²⁺, Ca²⁺, Na⁺, Hg²⁺, and Mg²⁺ Bivalent polonium (+2 ion) – Cl⁻, Br⁻, O²⁻, S²⁻ and SO₄²⁻ Trivalent polonium (+3 ion) – limited evidence, may be an unstable intermediate Tetravalent polonium (+4 ion) – Cl⁻, Br⁻, I⁻, O²⁻, S²⁻, O(OH)₂⁴⁻, NO₃⁻, SeO₄²⁻, and SO₄²⁻, as well as CO₃²⁻, CrO₄³⁻, and PO₄³⁻ Hexavalent polonium (+6 ion) – PoO₃

The article also reports that soluble salts of polonium include: PoF_2 , $PoCl_2$, $PoCl_4$, $PoBr_2$, $PoBr_4$, $Po(C_2H_3O_2)_2$, $Po(C_4H_4O_6)_2$, $PoSO_4$, $2PoO_2$ -SO₃ (basic polonium sulfate – probable structure), $2PoO_2$ -SeO₃, $Po(SO_4)_2$, and $Po(CN)_2$. (It is interesting to note that, although no mention is made in this report of $Po(NO_3)_2$ or $Po(NO_3)_4$ as soluble salts, many other citations on the web and in the literature cite those two compounds as being soluble.)

Connections to Chemistry Concepts

- 1. **Nuclear chemistry**—Connections here are obvious. The Litvinenko story is an excitingg (although somewhat morbid) way to link the theory to real life.
- 2. **Chemistry of elements**—This is a great chance to talk about polonium as a "regular" element, rather than merely focusing its radioactive aspects.
- 3. **Chemistry of the compounds of elements**—Too often students are warned of the dangers of the ingestion/inhalation, etc. of elements, when in reality it is the compounds of these elements that are really dangerous.
- 4. **Metabolic effects of nuclear radiation**—This is an opportunity to talk about nuclear radiation and its effects on the body based on a real-life case.
- 5. **Ionizing radiation**—You can present the major types of radiation alpha, beta, gamma, and neutron.
- 6. **Analysis/detection of radiation**—What tools do chemists use to detect this invisible energy?

Possible Student Misconceptions

- 1. **"Radiation is only used to harm people."** While the damaging effects of radiation grab all the headlines, many beneficial uses of radiation are made, especially in the area of medical applications (See "More on Medical Applications of Nuclear Radiation", above).
- 2. "All radiation is the same." Radiation comes primarily in 4 forms: alpha, beta, gamma, and neutron.
- 3. **"Radiation poisoning always causes cancer."** This is generally true for low doses of radiation that result in long-term degenerative cell growth, but in severe cases of

radiation poisoning like Litvinenko's, the radiation caused entire system failures resulting in death, way before cancers could even be detected.

- 4. **"Irradiated food is radioactive."** Although some foods have an extended shelf-life after radiation with gamma rays, irradiation only kills the microorganisms in the food. This process does not make food radioactive.
- 5. **"All radiation is man-made."** Most radiation to which humans are exposed is natural radiation from cosmic rays and from naturally occurring radioisotopes.
- 6. "Uranium used in nuclear bombs cannot be used as nuclear fuel in nuclear generating plants because it will produce a nuclear explosion." In fact, the isotope of uranium, ²³⁵U, used in bombs is the same as used in nuclear power plants because it is the only uranium isotope that is fissionable; i.e., can be split. Most uranium ore (90%) is ²³⁸U which is not fissionable. The uranium used in bombs is a much higher percentage of U-235 than that of nuclear power plants.
- 7. "If there's a malfunction in a nuclear power plant, the plant will explode like an atomic bomb." This can't happen because, as explained in #6, above, the fissionable material in the nuclear power plant is of a much lower concentration of U-235, so there is not enough there, at high enough concentration, to produce the explosion.
- 8. "If the half-life of a radioactive substance is 6 hours, all of it will decay in 12 hours." In 12 hours, half of the remaining half of the radioactive material will decay, meaning that ¼ of the original radioactive material remains. In mathematical terms, one would never reach 0. But in nuclear fact, eventually the last remaining reactive atom will undergo decay.

Demonstrations and Lessons

- 1. Students can detect radiation from radioactive sources:
- - outreach.phy.cam.ac.uk/camphy/cloudchamber/cloudchamber index.htm
- b. Detectable radiation is emitted from gas lantern mantels that are readily available from sporting goods stores. Detection is done using sunlight-sensitive paper available from science supply companies; one reliable source is *Educational Innovations*, www.teachersource.com; item #SPP-40. The mantels along with other objects that may or may not be radioactive (try a watch with luminescent dial, a low sodium salt that contains potassium, a smoke detector) can be placed in a light-tight drawer on top of a sheet of the sun-sensitive paper and left for various periods of time- 1 hour, 12 hours, 24 hours, 2 days. The paper, once exposed, is developed by immersing it in tap water. A light spot indicates exposure to radioactive material.
- c. A complete study of alpha, beta, and gamma radiation showing activity of various radiation sources, the effect of distance from and shielding of the radiation source can be done with Geiger counter equipment that your physics department may

possess. Otherwise, you may find equipment available from a local college or university. You can also contact the American Nuclear Society for possible loan of equipment (<u>www.ans.org/pi/edu/teachers/workshops/</u>). If you take their teacher workshop, they will give you Geiger counter equipment for free.

- 2. A modeling lab exercise dealing with the concept of isotopic masses (and its relationship to the average mass of an element) can be done using pennies. Two isotopes are represented by pre-1982 pennies and post-1982 pennies that have different average masses because of the difference in the zinc/copper content. Students can weigh two containers (film canisters if you can still find them), each with 10 pennies, either pre-1982 or post-1982. Record the mass of the 10 pennies of each type. (Students need to know the mass of the empty canister!). From this the students can get their average mass of a penny for each type. Next provide sealed canisters of 10 pennies, each with different ratios of pre- and post 1982 pennies. (Provide the mass of each empty canister since the students are not to open the canister). Have the students mass their assigned canister with penny mix. Explain the math for calculating the number of each type of penny present: TOTAL MASS of PENNIES= (*x* times the mass of pre-1982 pennies; 10-*x* = number of post-1982 pennies; 20-*x* = number of post-1982 pen
- 3. You can also model radioactive decay and half-life using pennies. Place 80 pennies in a shoe box or equivalent. Students turn all pennies heads-up, put lid on box and shake. Open the box and remove all pennies that have flipped to tails (represents decayed atoms). Record the number of tails removed. Close box and repeat the process three more times. This will complete four half-lives. Pooling class data, have students plot their individual data as well as the pooled class data on a graph number of half lives on the x axis, the number of UNDECAYED "atoms" on the y axis. Does the graph show the concept of what a "half-life" means in radioactive decay? Relate this graph to calculation problems involving half-lives of medical radioisotopes, calculating how much radioactive material remains in the body after various time periods after introducing the isotope into the body.
- 4. The chemistry program, Chemistry in the Community or ChemCom, has a very good unit on nuclear chemistry, complete with a variety of lab and paper activities along with problem solving exercises dealing with the dynamics of radiation, radioactive decay and half-life. (see the American Chemical Society website at http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=education%5Ccurricul_um%5Cchemcom.html) The textbook is published by W.H. Freeman with information about their materials at http://bcs.whfreeman.com/chemcom5e/default.asp?s=&n=&i=&v=&o=&ns=0&uid=0&rau=0 and http://www.whfreeman.com/chemcom/

Student Projects

 Students could research the various ways in which radiation is used in medicine, particularly in terms of radiation therapy; how does radiation kill a cancerous cell? What determines the choice of radioactive isotope when used as a tracer vs. radiation therapy? (Refer to chart of medical radioisotopes.) Why a half life of hours or days vs. years? A good reference for all things nuclear, including isotopes is found at <u>http://ie.lbl.gov/education/isotopes.htm</u> and <u>http://dbhs.wvusd.k12.ca.us/webdocs/Radioactivity/Radioactivity.html</u>
- 2. Students could research the practical application of carbon-14 half life to date archaeological artifacts. What other tracers can be used for dating material?
- 3. Students could research the uses of radioisotope tracers in agriculture, industry, and the environment. (See <u>www.chem.duke.edu/~jds/cruise_chem/nuclear/uses.html</u>.) One of the more controversial and misunderstood issues about radiation in the public sphere is the irradiation of various foods to extend their useful life by eliminating the major cause of food spoilage bacteria. This topic presents the student with the challenge to research the data to help separate fact from the fiction that has been created in the public mind.
- 4. Students could research the problem with radon gas in the home what is the source, what is the danger to human health, what are the techniques to ameliorate the source's effects (vs. eliminate)? References for radon are found at <u>www.epa.gov/radon, www.radon.com</u>, and www.cancer.gov/cancertopics/factsheet/Risk/radon
- 5. Students could research the issues surrounding nuclear power electricity generating plants. What is the basic principle for producing electricity when using uranium. What is the same and what is different for uranium production of electricity vs. coal, natural gas, oil, or hydro generation. What are the problems (environmental) with nuclear power generation? How do they compare with coal-, natural gas-, and oil-based electric generation? On what basis do societies choose a particular energy source for making electricity?

Anticipating Student Questions

1. "If uranium is used in atomic bombs as well as in nuclear reactors for electricity generation, why isn't there the danger of a nuclear explosion in the nuclear power generator?"

Both atomic bombs and nuclear reactors utilize the same uranium-235 isotope. But in a nuclear reactor, the splitting of the uranium-235 atoms with neutrons is done in small amounts (controlled or moderated by so-called control rods made of boron) where only 3% of the nuclear fuel is fissionable U-235. That is enough to sustain a chain reaction but not enough to produce a nuclear explosion. In an atomic bomb, the concentrated U-235 is made to split simultaneously through a type of compression reaction involving an initial non-nuclear explosion.

- 2. "If an element has both radioactive and non-radioactive isotopes, why don't these isotopes have different chemical properties?" Chemical properties associated with an element are determined by the proton number. Isotopes of the same element differ in mass because of the difference in numbers of neutrons, not protons, which are the same for all the isotopes of an element. Since all the isotopes have the same number of protons and therefore the same number of electrons, and since the chemistry of an element depends on its electron arrangement, all atoms of one element all have the same chemistry.
- 3. "What is the difference between ionizing and non-ionizing radiation?" Ionizing radiation occurs when high energy radiation as found in nuclear reactions and high energy electromagnetic radiation (X-rays, gamma rays) cause electrons to be ejected from molecules, creating highly reactive molecular fragments that can cause serious damage to living systems. Non-ionizing radiation does not form ions because the radiation is of lower energy. Examples of low energy radiation include ultraviolet and electromagnetic radiation in the visible range (= light!). Absorption of this radiation by molecules does excite electrons within the atoms of the molecules

but does not cause loss of the electrons to produce highly reactive molecular fragments.

- 4. "How can radiation be used to cure some forms of cancer when radiation itself can also cause some forms of cancer?" Some forms of radiation, such as X-rays, are classified as ionizing radiation (because of their high energy). Various molecules within a cell are ionized, producing reactive substances that can no longer function the way they normally do. One of the results is that the cell may lose control over cell division whereby the affected cells begin reproducing at an accelerated rate, which is considered to be a cancerous condition. To counter this condition, higher levels of ionizing radiation can be administered in which the damage to the nuclear components of the cancerous cell are extensive enough as to disrupt basic metabolic functions and the cell dies.
- 5. "If alpha radiation is produced by the most massive of particles, which means slower moving than beta particles, why is it considered to be more dangerous than beta or gamma radiation?"

Alpha particles can be stopped by a piece of cardboard, while beta particles and gamma radiation need heavier shielding. The issue concerns the ingestion of alphaproducing substances, such as gaseous radon, which come in direct contact with body cells such as those of the lung tissue at the alveolar level. Here the heavier alpha particles traveling very short distances can produce ionizing radiation effects on the nuclear material of the cell or important protein compounds such as enzymes, creating malfunctions in cell metabolism or permanent damage to the controlling functions of DNA. In addition, the decay products of radioactive radon include the heavy metals polonium, bismuth and lead, which remain in the body (not gaeous). They are also radioactive, producing additional alpha radiation.

References

Rayner-Canham, Marelene F. and Rayner-Canham, Geoffrey W. eds. *A Devotion to Their Science, Pioneer Women of Radioactivity*. Philadelphia: Chemical Heritage Foundation and Montreal and Kingston, Ontario: McGill-Queen's University Press, 1997.

A series of previous articles from *ChemMatters* can be obtained from back issues or the CD-based archives. They include:

- 1. "The Radium Girls—Dialing Up Trouble," ChemMatters, October, 1998, p. 13
- 2. "Radioactivity, It's a Natural," *ChemMatters*, April, 2000, p. 6. The article includes a chart for students to calculate their own background radiation Apr. 2000, p.6
- 3. Radiocarbon decay-Oct. 1985, p. 14
- 4. Dating techniques-Feb. 1989, p.12; Dec. 1994, p. 14; Feb. 1998, p.7 ; Feb. 2006, p.8
- 5. Labeling-Feb. 1994, p.12
- 6. Nuclear-based diagnosis, Dec. 1985, p.4 (use of Technetium)
- 7. Nuclear magnetic resonance- Feb. 1987, p.4
- 8. Nuclear power benefits- Dec. 1990, p.8
- 9. Isotopes- Francium, Dec. 1985, p.13; use in PET scans, Feb. 1994, p.12
- 10. Tritium- Oct. 1984, p.6
- 11. Uranium- Dec. 1994, p.14; enrichment, April 2005, p. 2
- 12. Irradiation of Food- Apr. 1999, p.16
- 13. "The Sun: Fusion at Work- Feb., 2007, p.8

Some of these articles and issues may be available online (2001 and more recent) at http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=education%5ccurriculu m%5cchemmatters%5cissue_arch.html. And while you're there, check out the Teacher Guides, also possibly available online (2001 and newer) at http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=education/curriculum/t gindex.html.

If you can't find them online, you can order a CD from ChemMatters that contains issues from 1983 -2003. A single CD only costs \$25.00, plus postage & handling. Order it online at

<u>http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=education\curriculum\c</u> <u>mprods.html</u>. Or purchase a site license for \$99.00, plus postage & handling and give all your students access to these great articles.

Websites for Additional Information

<u>http://www.nrc.gov/reactors/power.html-</u> an extensive website from the NRC on all aspects of nuclear reactors; useful for student research projects.

<u>http://science.howstuffworks.com/nuclear-power3.htm</u> - a complete reference site about the operation of nuclear power plants; useful for student research projects. Side bars have links to additional material on nuclear medicine, radiation, and how atomic bombs work with related issues.

More Websites on the Developing Story

The British Broadcasting Corporation (BBC) has extensively followed up on this story as it has developed. Check out a few of these pages on its web site: <u>http://news.bbc.co.uk/1/hi/uk/6180682.stm</u>. A number of articles from the BBC are available on this page, including the one in the next reference.

For maps of London and surrounding area where Po-210 has been detected, see <u>http://news.bbc.co.uk/2/hi/in_depth/6267373.stm</u>.

More Websites on the History of Polonium

Kaplan, Karen and Maugh, Thomas H. II. "Polonium's Quiet Trail of Death," *Los Angeles Times*, January 1, 2007. <u>http://www.latimes.com/news/science/la-sci-polonium1jan01,1,1525940.story?coll=la-news-science</u>

"The Manhattan Project: A New and Secret World of Human Experimentation," part of *Human Radiation Experiments* from the U.S. Department of Energy. http://hss.energy.gov/HealthSafety/ohre/roadmap/achre/intro_3.html

"Polonium," part of h2g2, from the BBC. http://www.bbc.co.uk/dna/h2g2/A18446204

More Websites on the Health Effects of Exposure to Nuclear Radiation

A good site to get the basics of radiation measurements is from the Canadian Centre for Occupational Safety and Health (CCOSH). This site gives definitions for all the basic units of radiation, from the strength of the radioactivity (measured in becquerels or Curies), to energy of radiation (measured in electron volts), to exposure (measured in roentgens, rads or gray). This can get very confusing, and this site explains the interrelationships among all these terms very concisely: <u>http://www.ccohs.ca/oshanswers/phys_agents/ionizing.html</u>

An extensive glossary of terms dealing with radiation can be found at the Centers for Disease Control and Prevention website, at http://www.bt.cdc.gov/radiation/glossary.asp.

An interactive graphic that shows the myriad sources and uses of radiation in our daily lives can be found at this EPA web page: <u>http://epa.gov/radtown/enter-</u><u>radtown.htm</u>. It depicts a "typical" town and shows all the different sites around and outside the town that contain potential radioactive sources.

A "Radiation Safety Program" PowerPoint presentation (120 slides) from the Safety and Environmental Protection Office of the Hong Kong University of Science and Technology deals with many aspects of radiation, including types of radiation, penetrating power, and terms and definitions of radiation measurements and effects is available at <u>http://www.ab.ust.hk/sepo/training/MC02v2/sld001.htm</u>. There are some typos and translation problems, and its focus is on radiation sources and emission apparatus, but it is a good overall source of radiation information.

For more on polonium' health effect, see <u>http://www.bt.cdc.gov/radiation/isotopes/polonium/ga.asp</u>.

Nuclear in the movies: <u>http://www.pbs.org/wgbh/pages/frontline/shows/reaction/interact/hollywood.html</u>

For more on biological effects of radiation see <u>http://www.ccnr.org/ceac_B.html#b.18</u>.

For a complete discussion of the biological effects of radiation from the National Academy of Sciences Press see <u>http://www.nap.edu/books/0309039959/html/</u>.

For more on the health effects of radiation see <u>http://www.epa.gov/radiation/understand/health_effects.htm#chemeffects</u>.

More Websites on Polonium

The International Atomic Energy Agency offers a fact sheet on polonium at <u>http://www.iaea.org/Publications/Factsheets/English/polonium210.html</u>. It describes the origins and uses of polonium, as well as its toxicity.

3Dchem.com offers information on polonium – the standard fare, plus a diagram showing its decay series, and a 3-dimensional arrangement of the atoms of polonium.

The Java applet interactive model can be moved around to see the 3-D effect. It also has a stereo effect, if you provide the 3-D glasses. Find it at http://www.3dchem.com/molecules.asp?ID=278#.

More Websites on Nuclear Chemistry

A good overview of nuclear radiation emissions can be found on the National Safety Council's website at <u>http://www.nsc.org/issues/rad/science.htm</u>. The information contained therein can be used by students or teachers.

Andy Darvill, a UK high school teacher, has made a website on radioactivity designed to help students meet the GCSE, the General Certificate of Secondary Education, taken by students in the 14-16 age range. The information is to accompany This site gives students a good background about radiation. It provides graphics, often animated, so the information is more visual. For example, it shows an animated comparison of the penetrating power of the three types of radiation. There are more pages available on the left side of the screen to learn more about sources and effects of radiation, as well as quizzes students can take to evaluate their understanding. Visit Darvill's site at http://home.clara.net/darvill/nucrad/index.htm.