

October 2007 Teacher's Guide

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About the Guide

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

Student Questions

Serendipitous Chemistry

- 1. What is the origin of the word "Vaseline", the commercial product marketed by Robert Chesebrough?
- 2. How does Vaseline prevent the development of infection in body wounds?
- 3. Where in nature is nylon found?
- 4. What is the practical value of carbon and silicon (both in the same chemical family) being able to form four single bonds?
- 5. Why are carbon-carbon bonds preferred over silicon-silicon bonds in polymers?
- 6. What is a polymer?
- 7. What is the difference between silicone and silicon?
- 8. Why are some artificial sweeteners not used in baking?

Linus Pauling, American Hero

- 1. At what institution of higher learning did Pauling earn his PhD degree?
- 2. What tools did Pauling use to "unravel the structure of proteins"?
- 3. Pauling and others discovered that the change of shape of blood cells in sickle cell anemia was due to a change in the cell's DNA. What was the significance of this discovery?
- 4. What determines whether the process of protein denaturation will be reversible?
- 5. Comment on the following statement: "Pauling had always been an advocate for peace."
- 6. What, specifically, was Pauling's main concern about atomic bombs: e.g., the sheer magnitude of the destruction, the large amounts of heat given off in the explosion, something else entirely?
- 7. What were the consequences of his anti-nuclear, anti-war stance?
- 8. Who was the Linus Pauling Institute named for?
- 9. To what areas of human endeavor did Pauling contribute significantly?

What's That Stuff? Pencils and Pencil Lead

- 1. Name the town in England near which the first significant pure deposit of graphite was discovered.
- 2. Name the chemist who identified graphite as an allotrope of carbon.
- 3. The "lead" in a pencil is actually a mixture of graphite and what other material?
- 4. What is the name given to the metal ring that holds the eraser on a pencil?
- 5. Wood from what kind of trees is used to make most modern pencils?
- 6. In the United States a pencil made with very hard lead would be marked with what number?

Percy Julian: Rising Above Racism

- 1. Name the three colleges/universities from which Julian earned his three degrees.
- 2. What chemical element is found in all alkaloid compounds?

- 3. Name the African bean from which physostigmine is extracted.
- 4. Describe how glaucoma causes blindness.
- 5. Which industrial company hired Julian in 1935, and what did they make?
- 6. Steroids typically have how many carbon rings?
- 7. Compound S is a precursor chemical to what important treatment for arthritis?

Tantalum, Congo, and Your Cell Phone

- 1. What other elements besides tantalum are present in coltan?
- 2. What element combines with tantalum at the surface of a piece of tantalum metal?
- 3. What cell phone component is tantalum used to make?
- 4. Why does aluminum resist corrosion well?
- 5. In what countries (other than Congo) is coltan found?
- 6. In a capacitor, what kind of charge builds up on the plate with excess electrons?
- 7. What do we call the insulating material between the two plates of a capacitor?

Answers to Student Questions

Serendipitous Chemistry

1. What is the origin of the word "Vaseline", the commercial product marketed by Robert Chesebrough?

The word "Vaseline" is a combination of the German word "wasser" and the Greek word "elain" (oil).

- 2. How does Vaseline prevent the development of infection in body wounds? Vaseline prevents the development of infection in wounds by forming a barrier between the wound and the air, preventing the growth of bacteria that are oxygen-dependent. It also retains moisture which is particularly important in the healing of burns.
- 3. Where in nature is nylon found? Nylon is not found in nature—it is a manufactured product, a synthetic polymer.
- 4. What is the practical value of carbon and silicon (both in the same chemical family) being able to form four single bonds? Being able to form bonds means that large chains of molecules, polymers, can be formed with many additional atoms or groups attached to the sides of the chains. Single molecules as large as automobile tires are possible!
- 5. Why are carbon-carbon bonds preferred over silicon-silicon bonds in polymers? Carbon-carbon bonds are stronger (check bond energies) than silicon-silicon bonds, therefore not as easily broken (less reactive) compared with the more reactive bonds of silicon.

What is a polymer?

A polymer (which means "of many parts") is a long molecule formed from atoms linked or bonded into a continuous chain.

- 6. What is the difference between silicone and silicon? Silicone is a carbon compound (polymer) that contains the element silicon.
- 7. Why are some artificial sweeteners not used in baking? Sweeteners like Aspartame cannot be used in baking because the heat will cause the molecule to decompose or break apart. Acid conditions will have the same effect.

Linus Pauling, American Hero

- 1. At what institution of higher learning did Pauling earn his PhD degree? Pauling earned his doctorate at the California Institute of Technology, CalTech.
- 2. What tools did Pauling use to "unravel the structure of proteins"? Pauling used his own diagrams and models, the rules he had established ("Pauling's rules"), and x-ray crystallography to determine protein structures.
- 3. Pauling and others discovered that the change of shape of blood cells in sickle cell anemia was due to a change in the cell's DNA. What was the significance of this discovery?

The discovery that cellular shape changes were due to mutation of DNA was the first demonstration that protein changes were associated with human disease.

4. What determines whether the process of protein denaturation will be reversible? The denaturation process will not be reversible if the bond being broken is the strong peptide bond; the process can be reversed if the bond being broken is the weaker hydrogen bond.

5. Comment on the following statement: "Pauling had always been an advocate for peace."

Pauling did not originally advocate for peace. According to the article, before the beginning of World War II, Pauling had advocated going to war against the Axis powers. It was only after the use of the atomic bombs on Japan that he questioned the right of the government to inflict that much damage on another country and began his quest for peace in earnest.

6. What, specifically, was Pauling's main concern about atomic bombs: e.g., the sheer magnitude of the destruction, the large amounts of heat given off in the explosion, something else entirely?

Pauling's major concern was with atmospheric fallout of nuclear radiation left over after the bomb exploded. He feared large numbers of babies would be born with birth defects as a result of above-ground nuclear explosions.

- 7. What were the consequences of his anti-nuclear, anti-war stance? The FBI investigated Pauling for possible ties to Communism; he was repeatedly denied the issuance of a passport; he lost grants for research; he was denied security clearance; and he was fired from a consulting job with a pharmaceutical firm.
- 8. Who was the Linus Pauling Institute named for? The Linus Pauling Institute was named for Linus Pauling [No trick question here!]
- 9. To what areas of human endeavor did Pauling contribute significantly? Pauling contributed significantly to the areas of chemistry, molecular chemistry, biochemistry, and humanitarianism.

What's That Stuff? Pencils and Pencil Lead

1. Name the town in England near which the first significant pure deposit of graphite was discovered.

Graphite was discovered in Borrowdale.

- 2. Name the chemist who identified graphite as an allotrope of carbon. Carl Scheele first identified graphite as an allotrope of carbon.
- 3. The "lead" in a pencil is actually a mixture of graphite and what other material? *Clay is the other ingredient in a pencil, besides graphite.*
- 4. What is the name given to the metal ring that holds the eraser on a pencil? The ring that holds the eraser on a pencil is called a ferrule.
- 5. Wood from what kind of trees is used to make most modern pencils? Incense cedar trees are the source for the wood in most modern pencils.
- 6. In the United States a pencil made with very hard lead would be marked with what number?

Number 4 pencils in the US are very hard lead pencils.

Percy Julian: Rising Above Racism

- 1. Name the three colleges/universities from which Julian earned his three degrees. Julian earned his degrees at DePauw University (bachelors), Harvard University (masters), and the University of Vienna (Ph.D.)
- 2. What chemical element is found in all alkaloid compounds? *Nitrogen is found in all alkaloid compounds.*
- 3. Name the African bean from which physostigmine is extracted. *Physostigmine is extracted from the Calabar bean.*
- 4. **Describe how glaucoma causes blindness.** *Glaucoma causes blindness by building up pressure inside the eye.*

- 5. Which industrial company hired Julian in 1935, and what did they make? *Glidden hired Julian. The company makes paints and chemicals.*
- 6. **Steroids typically have how many carbon rings?** *Steroids typically have four carbon rings.*
- 7. Compound S is a precursor chemical to what important treatment for arthritis? Cortisol is the product prepared from Compound S. Cortisol is used to treat arthritis.

Tantalum, Congo, and Your Cell Phone

- 1. What other elements besides tantalum are present in coltan? *Niobium, iron, manganese, and oxygen*
- 2. What element combines with tantalum at the surface of a piece of tantalum metal? Oxygen combines with tantalum at its surface.
- 3. What cell phone component is tantalum used to make? Tantalum is used to make capacitors for cell phones.
- 4. Why does aluminum resist corrosion well? Aluminum oxidizes rapidly, and a piece of aluminum quickly develops a layer of aluminum oxide on its surface that protects the metal inside from further oxidation.
- 5. In what countries (other than Congo) is coltan found? Coltan is also found in Australia, Brazil, and Canada.
- 6. In a capacitor, what kind of charge builds up on the plate with excess electrons? Negative charge builds up on the plate with excess electrons, because electrons have negative charges.
- 7. What do we call the insulating material between the two plates of a capacitor? The name for the insulating material between the plates of the capacitor is a <u>dielectric</u>.

ChemMatters Puzzle: CHEMISTRY SYLLABISM

No, not chemistry symbols ... syllables ! We give below clues to twelve chemical **names** (elements, groups, people), and a box containing **all** the syllables that make up those terms. You can cross them out as you solve a clue. The number of syllables in the name is given in parentheses.

As an additional help, the <u>first</u> letters of each of the 12 terms reading down generate the name of a famous chemist. Other letters, marked by an asterisk, read down to identify the concept he/she is famous for (and our puzzle theme !)

The SYLLABLES (in alphabetical order): BI BIG CU DI E EL ES EX FUR GEN GEN H LIE MENT MER NI NI O OX RA RY SUL TI THERM TRI TRO UM UM UM UM Y	ER TER
CLUES: 1. Box 72 in the periodic table (3)	
2. Collection of atoms all with same number of protons (3)	
3. Some bacteria are able to "fix" this (3)	
4. The radioactive Group 2 metal (3)	<u>*</u>
5. The first element to have a $4d^1$ electron (3)	<u>-</u>
6. Liquid that's 13.6 times denser than water (3)	*
7. The important element in all acids, says Lavoisier (3	
8. An element with several allotropic forms (2)	<u>-</u> -
9. A process in which Δ H is negative in sign (4)	^
10. Founder of the influential "Annalen der Chemie"(2)	*
11. Ethyl propanoate, for example (2)	*
12. First element to complete its 4f subshell (4)	*

*

Answers to CHEMISTRY SYLLABISM

- 1. Hafnium
- 2. Element
- 3. Nitrogen
- 4. Radium
- 5. Yttrium
- 6. Mercury
- 7. Oxygen
- 8. Sulfur
- 9. Exothermic
- 10. Liebig
- 11.Ester
- 12. Ytterbium

The designated letters spell out HENRY MOSELEY

The concept for which he is famous is the ATOMIC NUMBER.

Moseley used his X-ray studies in 1913-14 to assign each element a unique integer, its atomic number. It was soon shown to be related to the proton number in each atom's nucleus. Moseley was tragically killed in 1915, fighting at Gallipoli during World War I.

A few notes:

Clue 5: Although Yttrium is in period 5, the subshell that it initiates is the 4d, not 5d.

Clue 12: Although Ytterbium's position is the 13^{th} Lanthanide, its electron configuration has been determined to be [Xe] $4f^{14}4d^05s^2$. Most of the lanthanides have a $5d^1$ electron in the ground state.

Clue 7: Lavoisier was a great chemist, but on this matter, he was simply wrong ! Many acids do contain oxygen, but not all. Modern definitions stress the importance of Hydrogen (as H^+ ... a proton) as the key element

Clue 10: Justus von Liebig in the middle of the 19th century was a key researcher in Organic Chemistry, inventor (the Liebig condenser), author, publisher (as in the clue), and educator. Many college instructors in Chemistry today can trace their educational "lineage" back to Liebig through his many students.

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	Percy Julian	Linus Pauling, American Hero	Tantalum, Congo, and Your Cell Phone	Accidental Chemistry	Pencils and Pencil Lead	Question From the Classroom
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 interaction of energy & matter.			~			
Life Science Standard C: of matter, energy, and organization in living systems.		~				
Science and Technology Standard E: about science and technology.	~	~	~	~	~	~
Science in Personal and Social Perspectives Standard F: of personal and community health.	~			~	~	
Science in Personal and Social Perspectives Standard F: about natural resources.	~		~	~	~	
Science in Personal and Social Perspectives Standard F: 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

Me	Text	Statement
		1. Science proofs and math proofs are similar.
		2. Performing experiments may alter the original conditions.
		3. Measurements may be made with absolute certainty.
		4. Scientists prefer to go with the simplest explanation that explains their observations.

Serendipitous Chemistry

Ме	Text	Statement
		1. The petroleum material that Vaseline comes from is colorless.
		2. Vaseline, also known as petroleum jelly, does not burn.
		3. Silicones are very stable polymers with silicon-oxygen bonds as well as
		organic groups.
		4. Cille Dutte has no prostical use other than for ortentainment
		4. Silly Putty has no practical use, other than for entertainment.
		5. Artificial sweeteners have been discovered by violating lab safety rules.
		6. Aspartame may be safely used in cooking.
		7. Fewer than 10 everyday products were discovered through serendipity.

Linus Pauling, American Hero

Me	Text	Statement
		1. Pauling won two Nobel Prizes for chemistry.
		2. Pauling excelled in chemistry as a high school student.
		3. Pauling's work changed how we understand chemical bonds.
		4. Pauling used experimental data to investigate bonding.
		5. The most electronegative element is sodium.
		6. The alpha helix structure of proteins is held in a spiral by covalent bonds.
		7. Pauling was the first scientist to demonstrate that changes in the shape of
		just one protein is related to human disease .
		8. Pauling worked to stop nuclear bomb testing because he was concerned
		about the health consequences of radioactive fallout.

What's That Stuff? Pencils & Pencil Lead

Me	Text	Statement
		1. Pencil lead contains about 10% lead, so if a piece gets stuck in your finger it should be removed.
		2. Graphite is a form of carbon.
		3. The original pencils were wrapped with string.
		4. The hotter the lead is heated, the softer the pencil lead becomes.
		5. Most of the world's pencils are made with red cedar.
		6. One of the purest graphite deposits known is near Ticonderoga, New York.
		7. A line drawn by a pencil will conduct electricity.

Percy Julian: Rising Above Racism

Ме	Text	Statement
		1. Julian was valedictorian of his class at DePauw University.
		2. Julian earned his Ph.D. from Harvard University.
		3. Alkaloids such as caffeine and nicotine are nitrogen-containing organic
		compounds found mostly in plants.
		4. Julian decided to synthesize physostigmine because his wife suggested it.
		5. When synthesizing a new chemical, the melting point is used to determine if
		the synthesis is correct.
		6. Julian discovered the steroid stigmasterol in crystals that formed in a batch of soybean oil that had been contaminated with water.
		Soybean on that had been containinated with water.
		7. Julian discovered how to synthesize cortisol from soybeans.
		8. Julian died before being recognized for his achievements.

Tantalum, Congo, and Your Cell Phone

Me	Text	Statement
		1. Although more than ³ ⁄ ₄ of the world's coltan (a mineral containing tantalum) is in Congo, most of the world's coltan used in cell phones comes from Australia.
		2. Capacitors store electrical energy quickly, then release it slowly.
		3. The insulators in capacitors cause electrons to build up on the negative plate.
		4. Tantalum metal conducts electricity, but tantalum oxide does not.
		5. Capacitors can store more electrical charge if the negative and positive plates are far apart.
		6. Most cell phone manufacturers have found an alternative to using tantalum in their capacitors.
		7. Because coltan was smuggled out of Congo by foreign invaders and rebel armies who used the money to buy weapons, coltan from Congo was called "blood tantalum."

Reading Strategies

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

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

Serendipitous Chemistry

As you read, complete the chart describing the common products that were discovered accidentally.

Торіс	Vaseline	Silly Putty	Artificial Sweeteners
W но developed the product?			
Wнy was the discovery considered serendipitous?			
WHEN was it discovered and/ or marketed?			
W нат is it made from?			
How is it produced?			

Linus Pauling, American Hero

As you read, list **at least 5 details** regarding Pauling's contributions in each of the following areas.

Bonding Protein Structure Nuclear Test Ban Treaty	
Protein Structure	Bonding
	Protein Structure
Nuclear Test Ban Treaty	r Toteni Structure
Nuclear Test Ban Treaty	
	Nuclear Test Dan Treat
	Nuclear lest Ban Treaty

What's That Stuff? Pencils and Pencil Lead

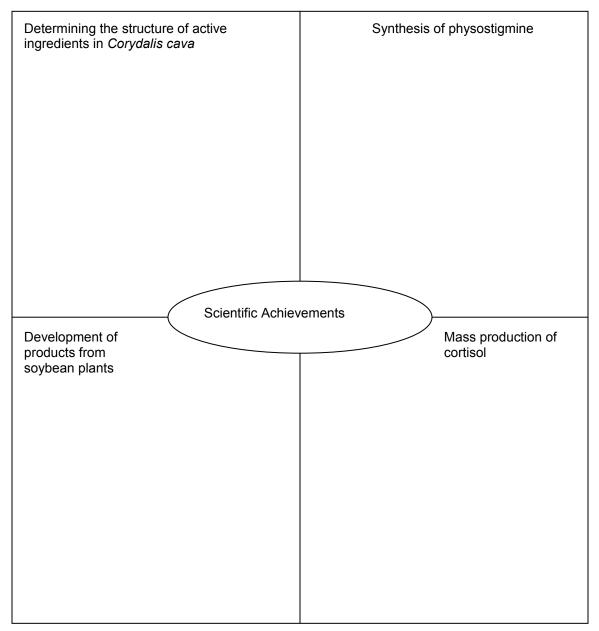
Pencil part	When was this developed?	What is it made from?
Lead		
Ferrule		
Pencil		
Colored pencils		

Percy Julian: Rising Above Racism

As you read, complete the two tasks below.

1. Make a chronological list of significant events in Julian's life. Include dates if they are given in the reading.

2. Complete the chart describing *how* Julian accomplished the work described, and the *significance* of what he did.



Tantalum, Congo, and Your Cell Phone

As you read, list the elements (with their symbols), compounds (with their formulas), and minerals (with their constituents) mentioned in the article. You should be able to find at least 7 elements, 3 compounds, and 2 minerals.

Elements	Compounds	Minerals

In the chart below, compare and contrast negative and positive electrodes. In the top part, list their differences, using bullets. List their similarities in the bottom box.

Negative Electrode	Desitive Electrode		
Negative Electrode	Positive Electrode		
Similarities			

Serendipitous Chemistry

Background Information

More on Petroleum Distillation.

Vaseline is what remains after distillation of the various liquid components of petroleum, which is a mixture. Robert Chesebrough patented the process which included the filtering of the viscous substance through bone black, a carbon powder. The process of distillation of petroleum to produce, among other things, kerosene (or paraffin oil) for lamps was developed in 1849 by a Canadian geologist, Dr. Abraham Gesner. It was this process that Chesebrough took advantage of to first produce kerosene which he sold (it is not clear from the various references if Chesebrough was actually into the distillation of whale oil, including that of sperm whales. Other than sperm whales, whale oil comes from the rendering of whale blubber, not distillation. Sperm whales yielded oil from an organ in the "nose" area of its head. If the oil was exposed to the air, it would solidify enough to be used for smokeless candles, considered the finest quality ever produced)

But the distillation process, particularly utilizing vacuum, was used by Chesebrough to produce his Vaseline product, a substance that remained after the various liquids were evaporated from the petroleum at their different boiling points. Whereas Chesebrough followed the route of producing the Vaseline through distillation, a man named John D. Rockefeller decided in 1865 to stick with producing kerosene from petroleum distillation, partnering with a Samuel Adams who owned a Cleveland refinery. A network of kerosene distilleries were established that eventually came to be known as Standard Oil. By the end of the 19th C., kerosene had dropped in price from 59 cents/gallon in 1865 to 7 cents in 1895. This put whale oil out of the competition (it was still 40 cents a gallon in 1896). One technology replaced another. And so it continued with Thomas Edison's incandescent light bulb of 1879 eventually displacing kerosene lamps!

More on Rubber and Silicone

Contrary to the author's statement that at the end of World War II no suitable rubber substitute had been found, in reality, rubber equivalents were developed before the war began (1930s) primarily in Germany. It was this basic formulation that was eventually used by DuPont, through the work of Wallace Carothers (of nylon fame) in the 1930s to develop the synthetic rubber product called Neoprene. Another product developed by the chemist Waldo Semon at BF Goodrich was based on the polymerization of butadiene (Polybutadiene or BR). By 1943, another polymer developed under Semon combined styrene and butadiene And this formulation, known as "GR-S" or SBR, remains the basic synthetic (non-latex rubber) rubber material to this day.

Historically, the first synthesis of rubber was done in 1900 with the polymerization of 2,3dimethylbutadiene. The rubber was called methyl rubber and was commercialized in 1909 by Bayer in Germany. Although Germany continued to use more natural rubber (obtained from the USA) than synthetic, they were forced to go back to the methyl rubber because of the Great War of 1916 which cut supplies from the USA.

The Russians in 1910 developed a polymer from the 1,4-butadiene to give butadiene rubber (BR) but there was no commercial pressure to develop it as in Germany. Later in Switzerland (patented, 1932), were developed so-called Thiokol rubbers made from ethylene polysulphide (referred to as GR-P rubber in the USA). IG Farben in Germany extended the research of Bayer to develop the polybutadiene rubber which was called Buna S (styrene butadiene rubber, SBR, or GR-S in America) and Buna-N (butadiene acrylonitrile rubber, NBR

or GR-A). Because of joint research operations of IG Farben and the Standard Oil (remember John D. Rockefeller and kerosene distillation plants?), Standard Oil eventually held the US patents for all the Buna rubbers. As a result, the American synthetic rubber industry took off, displacing natural rubber at the beginning of World War II.

At this point in time, natural rubber is still a special product in demand, with more than 6 million tons produced annually in the USA (versus more than 10 million tons of synthetic rubber produced annually). Related to this demand are the ongoing efforts to develop a chemically and physically viable method for recycling rubber, both natural and synthetic. At the same time, given the present state of global warming and our dependence on petroleum as the source of raw materials for rubber synthesis, the use of natural rubber (from rubber tree latex) means that the trees, which are a renewable resource, are absorbing carbon dioxide through photosynthesis.

More on Silicone

The development of silicone compounds, in contrast with the serendipity of silly putty, is an excellent case study in rational chemical research. It is also an interesting story in that two different companies and some of their chemists at Corning Glass and General Electric initially cooperated in trying to solve a problem associated with producing an insulation for wires that could withstand high temperatures (in the range of 200 ° C) without deterioration or destruction of the insulation material. These wires were part of the electrification of the railroads using electric engines manufactured by General Electric.

Corning chemists were working on the problem, initially using asbestos that was good to 155 °C. But this material over time became brittle and failed. The next thing was the use of glass fiber (think fiber glass insulation developed by Corning) which could be impregnated with resins which were good to 155 °C, But again, the phenols in the glass failed over time. So what could replace the carbon-based phenols? The Corning chemist, Dr. James Hyde thought through the needs for a new and different insulation. And one chemical possibility was a carbon-silicon combination that was both flexible and could tolerate the higher operating temperatures.

Eventually Hyde worked out a synthesis reaction that produced a so-called ethyldichlorosilane that was applied to glass fibers as a fluid, then heated to high temperatures, producing a hardened rubbery mass that was flexible. The material met the high temperature tolerances needed for the electric wire and motor insulation. However, the process was uneconomical. It required too many steps, involved too many expensive chemicals that could not be reused, and the percent yield was too low. This is when the General Electric chemists visited Corning chemists, on invitation, for professional consultation, so to speak.

One GE chemist, Dr. Winton Patnode, recognized the chemistry utilizing siliconcontaining compounds and agreed it was the right direction for making a good insulation material. Returning to GE, Patnode consulted with an inorganic(!) chemist, Dr. Eugene Rochow about the issue. His thinking sorted through all the chemistry issue involving the use of carbonmetal bonding, avoiding oxygen but using silicon from the metalloid group. The alkyls of carbon and silicon are thermally stable and do not react with water or air in the 200-300 °C range. His compound would be simply a methyl-silicone (silicon with oxygen) network. Unfortunately, there was nothing in the literature to suggest how the synthesis would be done! In a series of experiments, Rochow first repeated Patnode's synthesis reactions. Then he devised some simpler procedures that produced the necessary intermediate, a tricholorosilane, which was needed to produce the methylated compound of trichorosilane. It was this compound that was the intermediate.

In his devised procedure methyl chloride and some hydrogen chloride passed over silicon (with some copper) at high temperature. The residue that resulted was a liquid. Then Rochow treated the liquid with water which produced a clear resinous substance that he

believed was the sought after methyl silicone. The chemistry seems to be that the hydrogen chloride etched the copper-silicon surface and the copper acted as a catalyst for the silicon to react with the methyl chloride, producing the intermediate. Adding water produced the methyl silicone. The synthesis was a one step process in contrast with Hyde's multi-step synthesis. In contrast with silly putty, here was a combination of rational planning, experimentation accompanied by careful observation. An interesting aside is the fact that GE and Corning got into a patent battle over the silicone-making process. Through the courts, GE won the battle.

More on Artificial Sweeteners

Artificial sweeteners are good examples of the effort to design molecules with a specific physical structure (and shape). In recent years it has become apparent that the receptor areas for detecting sweetness on the tongue operate in part because a molecule will fit within what is known as a "triangle of sweetness", a specific three point area of contact between the molecule and the receptor surface. The actual receptor site has not been isolated though taste bud structures in the tongue have been known for a long time. (see ChemMatters article, "Artificial Sweeteners", Feb. 1998, p.4). A general description of a sweet-tasting substance has been proposed by two of the pioneers in relating structure to sweet taste, Robert S. Shallenberger and Terry E. ACree of Cornell University. All sweet molecules have a common feature known as a glycophore. This glycophore will have one or more atoms that have available electrons located near a hydrogen atom that is attached to a relatively electronegative atom. Other investigators have added additional characteristics including an L-shaped molecule with positively and negatively charged regions on the upright part of the L and a hydrophobic region on the other end, the base of the L.

(www.college.hmco.com/chemistry/intro/zumdahl/intro_chemistry/5e/students/protected/focus/c h11_3pdf-)

Additional research information suggests that on the tongue, the primary receptor for sweetness is a specific protein dubbed T1r3. This protein "…has a well-defined pocket where smaller molecules can enter and possibly bind. Binding depends on a good fit of molecular shape and the presence of groups that interact chemically to stabilize binding" (<u>www.sciam.com/print_version.cfm?articleID=ooo7F523-93F</u>). The fact that artificial sweeteners are sweeter than sucrose (for the amount used) is directly related to the fact that artificial sweeteners more strongly bind to the tongue receptors than sucrose, remaining there for a longer period of time. The additional fact is that artificial sweeteners have few or no calories. Saccharin has no calories because it passes through the digestive system without being absorbed into the blood system and to body cells. Therefore it is not metabolized. Aspartame (NutraSweet[™]) is metabolized into methanol (potentially toxic but not in the normal amounts produced) and two amino acids, phenylalanine and aspartic acid. Further metabolism of these products does yield some calories but far fewer than from the amount of sucrose needed to produce the same amount of sweetness.

A very complete description of the various artificial sweeteners including research on safety and limits to usage (baking vs. beverages, etc) is found at the Food and Drug Administration's website (www.fda.gov/fdac/features/2006/406_sweeteners.html)

The tongue with its taste receptor cells bundled together to form a taste bud detects several categories of taste sensation- salt, sour, sweet, bitter and umami which refers to the taste associated amino acids from meat and cheese. These regions are very specific and can be mapped very easily using swabs saturated with a given liquid that produces one of the five taste sensations listed. (This makes for a good student activity). There is a threshold for tasting these different substances and it varies considerably. The average threshold for tasting "salt" is 0.01 M; for sour, 0.0009M; sweet, 0.01M; bitter, 0.00008M; umami, 0.0007M.

Connections to Chemistry Concepts

- 1. **Distillation**—This method of separation of a liquid mixture depends on the fact that individual pure substances in the mixture have different boiling points. Separation begins when the temperature of the mixture reaches that of the first pure substance with the lowest boiling point, with other substances separating out in order from lowest to highest boiling point. Separation of various organic compounds in petroleum is done in tall distillation towers. In the case of whale oil, whale fat (blubber) is cooked as any other meat, with the oil separating out from the rest of the watery mix because of its insolubility and different density. However, the oil is not separated from the blubber by distillation.
- 2. **Organic compound**—Any chemical that contains carbon (excepting carbon dioxide). Because of the bonding based on the carbon atom, organic compounds have an infinite number of configurations with important "functional" groups attached. The size of organic compounds is wide ranging. It is thought that a truck tire of synthetic or natural rubber, a polymer, is a single molecule!
- 3. **Viscosity**—Defined as resistance to flow, the viscosity of a liquid is determined by molecular structure and resulting intermolecular forces that are possible through polarity. In organic compounds, hydrogen bonding is common, particularly involving the hydroxyl group (-OH). Differences in viscosity between organic alcohols, such as glycerol and 1-propanol (both three carbon alcohols), are produced by the number of –OH groups, with propanol, the least viscous, having only one hydroxyl group and glycerol, with three hydroxyls, being the most viscous of the several three carbon alcohols possible.
- 4. **Calorie**—Because of the potential energy associated with chemical bonds, changes in the arrangement of atoms within a new compound formed will change the potential energy of the new bonds. Breaking bonds always requires an input of energy (endothermic) and making bonds releasing some energy (exothermic). In the case of sugar metabolism, the reaction between sucrose and oxygen will form carbon dioxide and water. The resultant energy changes in the bonds broken (reactants) and formed (carbon dioxide and water) produce a net energy change that is exothermic. In animal cell metabolism this net release of energy is efficiently channeled into other chemical compounds as potential energy rather than as thermal energy as in the case of simple burning of an organic compound such as oil or wood.
- 5. **Amino Acids**—An organic acid which contains the functional amine group (-NH₂) as well as the carboxyl group (-COOH) and is fundamental to the various structures of living organisms. Amino acids are linked together through the carboxyl and amine groups (a peptide bond) to form very long chains that are known as polypeptides and/or proteins. Through hydrogen bonding between various points on the polypeptide, various shapes of a molecule can be produced which are specific enough to provide "identification" within living systems (think enzymes, pharmaceuticals, allergens, antibodies, DNA, among other things).
- 6. **pH**—The numerical range of acidity through alkalinity is important to the structural integrity of molecules such as the artificial sweeteners. Some molecules can by hydrolyzed in an acidic environment which would break down the sweetener's structure and would no longer function as a flavoring for foods.
- 7. **Cross-links**—In polymer-like materials including thermal plastics and proteins, linkage between several chains of atoms can be produced through covalent bonding of atoms such as sulfur between the chains, as in the vulcanization of rubber, producing a rather hard material.

Possible Student Misconceptions

- 1. **"Petroleum is a single, pure substance."** Petroleum is a mixture of many different carbon-containing compounds which are separated out from each other using distillation which depends on differences in boiling points for the various compounds in the mixture.
- 2. **"All polymers are synthetic."** *Polymers are both synthetic and natural.* Some examples of natural polymers include silk, cotton, starch, glycogen, polypeptides or proteins, cellulose and hair.
- 3. **"The sweet taste of various substances is due to the chemical composition of the molecule, as in sucrose, ordinary table sugar."** Sweet taste is dependent on the physical arrangement of the atoms in a molecule producing a particular shape that interacts with the nervous system through receptors on the tongue. It isn't due just to the presence a particular collection of atoms.

Demonstrations and Lessons

- The production of Vaseline as well as other petroleum fractions, such as kerosene, involves the process of distillation. It is a basic process for separation of mixtures, utilizing the fact that pure substances in a mixture have different boiling points (for liquids) Either as a demonstration or as a lab exercise, distillation can be used to separate a simple solution of ink and water, or a more interesting mixture of isopropyl alcohol and water. Testing the products of separation involves taking advantage of other characteristic products, including density, flammability, and boiling point. The setup for the distillation of the isopropyl alcohol solution can be found at <u>www.chemheritage.org</u> website. Go to <u>http://www.chemheritage.org/EducationalServices/pharm/antibiot/activity/ distil.htm</u>.
- Another demonstration that can be done is the synthesis of the polymer, nylon. Be aware that this demonstration requires that you handle the chemicals safely and with good ventilation. Instructions for this demo can be found at <u>http://science.csustan.edu/Stkrm/Recipes/Recipes-Nylon.htm</u>.
- Silly putty can be approximated with a well known recipe involving white glue and boric acid or starch to make "gluep". The recipe for this activity can be found at <u>http://www.epilogsys.com/scoutingweb/subpages/slimeSP.htm</u> and <u>http://chemistry.about.com/od/everydaychemistry/a/sillyputty_2.htm</u>.
- 4. A latex rubber ball can be made by students. Directions for this lab activity can be found at www.chymist.com/Rubber.pdf
- 5. Myriad polymer projects, including the Silly Putty, can be found at the following site: <u>http://www.grc.nasa.gov/WWW/K-12/Summer_Training/Magnificat/Polymer_Project.html</u>

Student Projects

 Students could research the evidence originally used to determine whether various sweeteners are safe or potentially dangerous to human health. Because the government agency, the Food and Drug Agency (FDA) is involved with determining the safety of food products, is politics involved with the scientific evaluations or are criticisms of the safety of various food and drug substances based on poor science, no science, religion—or what? A debate or student presentations could be made in class. The FDA website and specific food and drug product safety can be found at: <u>http://www.cfsan.fda.gov/</u>. Another useful website that provides some scientific information about artificial sweeteners and cancer risk can be found at:

http://www.cancer.gov/cancertopics/factsheet/Risk/artificial-sweeteners.

- 2. Students could map their tongues to determine the specific locations of the taste buds for sweet, sour, bitter, salty, umami. Solutions of sugar (0.1 M), lemon juice, unsweetened baking cocoa, salt (0.1M), and glutamic acid (0.1 M) are applied with cotton swabs to different locations on the tongue. Are there distinct locations? You might also try making solutions of various artificial sweeteners along with sucrose, first using a fixed mass of the artificial sweeteners per 100 cc that is detectable when applied with a swab. Then use the same mass of sucrose and compare the intensity of the sweet sensation. Reference for the mapping of the tongue can be found at: http://pbskids.org/zoom/activities/sci/tonguemap.html. There is a debate about the idea that there are specific zones on the tongue for each of the taste sensations. This could prove to be a good student research project.
- 3. Rubber from the latex of rubber trees is a topic that could be investigated by students. There is the history behind countries like Britain and Holland who maintained plantations in Southeast Asia when these countries were empires with colonies that supplied raw materials of all kinds. Rubber plantations are still in production but as national enterprises, not part of a colonial empire. The maintenance of rubber trees, the collecting and processing of the latex raw material involves basic physical and chemical principles. What is the difference between latex (natural) rubber and synthetic rubber? How is each processed into the final product of either a soft or hard rubber material? Some useful references for this research include: <u>http://www.bouncingballs.com/chemistry_tech_conservation/latexprocess.htm</u> and <u>http://www.bouncingballs.com/serendipity/pictale.htm</u>

Anticipating Student Questions

- 1. **"What is the difference between silicon and silicone?"** Silicon is the element which is considered a metalloid since it has some characteristics of a metal (conducts electricity, is shiny) and a non-metal (not ductile or malleable). Silicone is a carbon-containing compound that has silicon as part of the structure. Its characteristics are much different from silicon alone including the fact that it is soft and pliable.
- 2. "What makes rubber 'bouncy'?" Natural rubber consists of polymeric chains that are joined in a loose (random) network. There is room for these chains or strands to move. When a deforming force or stress is applied to the rubber, as in bouncing a ball against a hard surface, the chains of the polymer undergo bond rotation and the chains elongate. Because the chains are linked to each other, they cannot come apart. The energy of deformation is given up as the elastic material returns to the previous disorganized state. You can actually detect these changes in potential energy by taking a rubber band and stretch it across the area above your upper lip. Note any change in temperature (should become cooler as energy of stretching goes into organizing the loose polymer strands.) Keeping the rubber band touching the areas above your upper lip, allow the rubber band to suddenly go back to the slack position. Because the polymer strands become more disorganized, the potential energy of the previously stretched band is given up, and the rubber band should feel a bit warmer.

- 3. **"What is the chemical difference between natural (latex) rubber and synthetic rubber?"** Since both rubber types are polymers, the difference comes from the building unit or monomer. In the case of natural rubber the primary monomer is known as 2methyl-1,3 butadiene (a 4-carbon structure with double bonds). Synthetic rubber can be made from a number of different monomers, depending on the characteristics needed in the rubber. In fact, the earliest synthetic rubbers were made from almost the exact same monomer as in natural rubber except that it had two methyl groups attached to the butadiene. Other synthetic rubbers use the butadiene-based monomer but add other groups and elements including nitrogen, silicon, and chlorine.
- 4. "If you consume an artificial sweetener, which is a chemical substance, why isn't it a source of calories within the body?" The key point is that the chemical has to go through a chemical reaction to make available the calories if it is an exothermic reaction. In body metabolism, the products that result from chemically changing something like sugar contain bond energies that are later available as a caloric or energy source. Two particular molecules of this type include ATP and glycogen. For the sweeteners, Saccharin, Sucralose, and Acesulfame-K, the molecules are never metabolized in the body. They are excreted unchanged. They still produces the sweet taste on the tongue but this does not involve a metabolic change—it is some kind of physical/chemical interaction with the nervous system through specialized receptors.

References

A reference that all teachers might consider is the Sourcebook 2.1 from the ChemSource Project. It is available from ACS at the following address: <u>http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=education%5Ccurriculum</u>%5Cteachres.html.

The unit on Polymers is particularly useful. It includes a wealth of teaching ideas including diagrams, lab exercises and their preparation, problem solving, background information for both teacher and student, along with the less obvious, such as cartoons, humor, and crossword puzzles. The four-volume set covers all the topics that a teacher could possibly cover in one year.

Websites for Additional Information

More sites on Natural and Synthetic Rubber

Teacher's Guide for ChemMatters, October 2005, p.4 <u>http://chemistry.org/education/chemmatters.html</u>—Also check an article on the whys and how of super balls by Robert Becker in the same issue of ChemMatters, but this has to be accessed as a back issue on the CD available from ACS. <u>http://acswebapplications.acs.org/portaltools/shopper/productDetail.cfm?prod_cd=1-CMCD3</u>

<u>http://www.chymist.com/rubber.pdf</u> includes background information on the molecular structure of natural rubber as well as the lab exercise in making a latex ball.

MacroGalleria as part of the very useful Polymer Science Learning Center at the Univ. of S. Mississippi, contains several web pages on polymer structure including useful diagrams for cross linkage in vulcanized rubber as well as other molecules. <u>http://www.psic.ws/macrog/xlink.htm</u>. For information on polybutadiene in synthetic rubber, <u>http://www.psic.ws/macrogcss/pb.html</u>. For polyisoprene, <u>http://www.psic.ws/macrogcss/isoprene.html</u>.

The Polymer Ambassadors web site at <u>www.polymerambassadors.org</u> has an activity for making Gluep, the non-silicon analog to silly putty, along with a plethora of other polymer activities.

<u>http://www.infoplease.com/ce6/sci/A0869822.html</u> for basic information on natural rubber as well as <u>http://www.bouncing-balls.com/timeline/naturaloname.htm</u>. and <u>http://www.bouncing-balls.com/chemistry_tech_conservation/latexprocess.htm</u>.

In the same "Bouncing Balls" series above are a number of other very good reference articles on the history of synthetic rubber, as well as extensive biographies of several important chemists involved, including Waldo Semon and Wallace Carothers.

Check <u>http://www.bouncing-balls.com/timeline/synthetiics.htm</u>. as well as information on vulcanizing at <u>http://www.bouncing-balls.com/chemistry_tech_conservation/vulcanization.htm</u>.

Good visual descriptions of cross-linkage in the vulcanizing process as well as historical and chemical descriptions of the process can be found at <u>http://en.wikipedia.org/w/index.php?</u> <u>title=Vulcanization&rpintable=yes</u>.

More sites on Silicone

The development of the process to synthesize silicone is a very interesting story that is presented very well in terms of the people and the chemistry behind the development of the product that was originally needed as an insulator for high temperature applications. The reference for this story is found at <u>http://science.kennesaw.edu/~mhermes/silicon/sil6cone.htm</u>, sections 4-6.

There are articles in the ChemMatters CD archives on Silly Putty. They are, April, 1986, p.15; Feb. 1998, p. 10, 12. http://acswebapplications.acs.org/portaltools/shopper/productDetail.cfm?prod_cd=1-CMCD3

A reference that includes both the standard recipe for making silly Putty but more important, a diagram of the bonding in the molecule is found at <u>http://chemistry.lsu.edu/webpub/</u><u>demo-2-silly-putty.pdf</u>

At the American Chemical Society site, there is another description of Silly Putty with some additional human interest tales. The article can be found at: <u>http://pubs.acs.org/cen/today/print/7848scit3.html</u>.

If you want to know the actual chemical composition of Silly Putty along with some student antics, it can be found at http://merlin.alfred.edu/muller/FormerPhysWorld/PhysWorld/Project5/sillyputty.group4.htm

A complete article on Silly Putty with some useful molecular structures and references can be found on the ChemMatters Archive CD, April 1986, p.15-17.

This is the website for the story about Vaseline as used in the *ChemMatters* article, "Accidental Chemistry", <u>http://www.damninteresting.com/?p=424</u>

More sites on Artificial Sweeteners

The molecular structures of Saccharin, Sodium cyclamate and Aspartame can be found at <u>http://www.elmhurst.edu/~chm/vchembook/549receptor.html</u>.

Articles from the ChemMatters CD Archives can be found for artificial sweeteners for Feb. 1988, p.4-8. This includes a good description of the so-called "Triangle of Sweetness" with good diagrams and molecular structures. The CD can be purchased at the following website: http://acswebapplications.acs.org/portaltools/shopper/productDetail.cfm?prod_cd=1-CMCD3

The work of a scientist in the field of carbohydrates, with good background chemistry about carbohydrates as well as how this particular chemist goes about problem-solving that has a very human dimension to it can be found at the National Institutes of Health website, <u>http://publications.nigms.nih.gov/findings/oct04/sweet.html</u>.

The physiology of taste is an interesting topic that links chemicals with the taste receptors of the neurological system and the interaction of various combinations of chemicals on the tongue. Go to the following:

http://www.vivo.colostate.edu/hbooks/pathphys/digestion/pregastric/taste.htm

The FDA's website on artificial sweeteners reviews the various health concerns for artificial sweeteners and the data that "alleviates" those concerns. The site is <u>http://www.fda.gov/fdac/features/2006/406_sweeteners.html</u>.

More on Whales and Whale Oil

A modern day article attempts to make the case that the development of petroleum industry in the 19th century saved the whales because the distillation product, kerosene, replaced whale oil. Whether or not that is really a compelling argument, (given the fact that in the 20th century we were trying to save the whale because it was still hunted, albeit for meat!) the article has a good bit of historical information related to the sociological and economical side of 19th century whaling. It makes good reading, particularly for students who may be deficient in the history of that period of American industry. Go to http://www.littletechshoppe.com/ns1625/gesner.html.

An article on sperm whales can be found on the ChemMatters Archive CD; Oct. 1988, p.4-7. It includes some good molecular structures for comparing sperm whale oil with that of other whales. The Archive CD can be purchased at http://acswebapplications.acs.org/portaltools/shopper/productDetail.cfm?prod_cd=1-CMCD3.

Linus Pauling, American Hero

Background Information

More on the history of Pauling's chemical bond theory

Pauling's understanding of bonding was based on the concept of "hooks and eyes", the prevailing theory of bonding when he was an undergraduate at Oregon Agricultural College. Atoms bonded according to the number of hooks that it had to connect to other atoms, and the number of eyes it had to allow other atoms to attach to it. A bond was thus one hook attached to one eye. Further research on the nature of the chemical bond was done by his scientific "hero", Gilbert N. Lewis, and Irving Langmuir, both of General Electric. They had proposed the idea of octets of electrons, and they had generalized that atoms were most stable with 8 electrons around their nucleus. This allowed chemists to account for the number of bonds and bond formation. Pauling used this idea, but to him this was not very satisfactory as it merely described the existence of bonds, it did nothing to explain why bonds formed in the first place. He sought a deeper understanding.

For that, he traveled to Europe where research was being done that focused on quantum physics. He studied quantum physics, learning from the original discoverers – Schrodinger, Heisenberg, Pauli and Somerfeld. Heisenberg developed a purely mathematical expression that described the atom. For physicists, accustomed to describing nature solely with mathematical expressions, this was great; for chemists like Pauling, accustomed to visualizing atoms, it was less than satisfactory. He needed more. He discovered Schrodinger's newly-developed wave mechanical model of the atom and found what he'd been looking for. This model described the newly discovered properties of atoms in terms of standing waves. This was much more palatable to chemists. Eventually, Heisenberg's and Schrodinger's equations came together into what we now know as quantum mechanics.

Pauling's work at CalTech directly followed from his doctoral work – the study of molecular structures via x-ray crystallography. By using paper models of molecules and their x-ray photos, he was able to elucidate structures of molecules that other chemists could not.

Back in Europe, two German physicists, Heitler and London, had developed the calculations needed to show the bond energy and bond distance between two hydrogen atoms, based on quantum mechanics. Unfortunately, the mathematics of these calculations required huge amounts of time to calculate. With today's computers, it would be relatively easy to do, but without them, the calculations were almost impossible.

After many attempts, Pauling, by making certain assumptions, was finally able to simplify the calculations needed. Then he astounded the world by announcing that he had succeeded in using quantum mechanical calculations to explain the tetrahedral bonding of carbon, a much more difficult task than the calculations for the hydrogen-hydrogen bond. His calculations worked for bond angle and bond length. This was a giant step toward the general acceptance of quantum mechanics by chemists worldwide, as carbon was the most important element to all of organic chemistry and had not been readily understood by old theories of bonding. He theorized the existence of hybridized orbitals in the carbon atom, and in other atoms, as well. He continued these calculations to develop similar results for many more complex molecules.

Pauling was not alone in his work on quantum mechanics. The two Germans, Heitler and London, had continued to study chemical bonds, as did John Slater, of MIT. Slater actually published his work before Pauling. It contained findings that overlapped (and corroborated) Pauling's, but the two agreed to maintain friendly competition. Their theory of the chemical bond came to be known as the HLSP, for Heitler, London, Slater and Pauling. Eventually it became known simply as the valence bond theory.

In what seemed to be a very different approach, Hund (of Hund's rule fame) and Robert Mullikan of Harvard espoused that the electrons in a bond are not shared directly between the two atoms, as valence bond theory does, but rather are shared across the entire surface of the molecule. This came to be known as molecular orbital theory, and at first seemed to be directly opposed to valence bond theory. Eventually it came to be seen that both theories led to the same end, and which one was chosen depended upon which was easier to use, and which gave better results for the specific situation.

The valence bond theory flourished under Pauling's teachings (and publishing), while Mulliken's molecular orbital theory remained somewhat obscure. Years later, chemists would take up his theory, refine it, and make it popular and useful, just like valence bond theory.

A missing piece to the puzzle was still the difference between ionic bonds and covalent bonds, and whether a bond had to be either one or the other. Pauling eventually showed that quantum mechanics was compatible with the idea of ionic bonds, covalent bonds, and everything in between. The concept of resonance helped Pauling to link the two extremes of bond types.

The concept of electronegativity followed naturally as an attempt to determine which of the atoms in an ionic bond had the greater pull on the electrons in the bond. Electronegativity was the part of his bond theory that was the least related to quantum mechanics, and since it was almost non-mathematical, it was the easiest to understand and the most readily accepted by his peers.

Pauling presented his bond theory in a series of 7 major papers, "The Nature of the Chemical Bond, Parts I-VII, over the span of several years. The series of papers covered the bonding in almost all compounds, from very simple binary compounds to very complex organic molecules, including resonance, non-octet molecules, double and triple bonds, and conjugated systems. It was a very inclusive theory and it was embraced by most chemists in the years that followed.

More on electronegativity

Even though the Pauling scale of electronegativity is the most widely known and used scale in high school chemistry, according to Wikipedia

(<u>http://en.wikipedia.org/wiki/Electronegativity</u>), there are at least 5 different ways to calculate electronegativity. The Pauling equation that relates the electronegativity difference between the two atoms in a bond is given by the following equation:

$$\chi_{A} - \chi_{B} = (eV)^{-1/2} \, \P E_{d}(AB) - [E_{d}(AA) + E_{d}(BB)]$$

The term $(\chi_A - \chi_B)$ represents the electronegativity difference between atoms A and B, respectively; E_d represents the bond dissociation energy (in electron Volts) for each pair of atoms, AB, AA and BB. The term $(eV)^{-1/2}$ exists merely to produce a dimensionless number. Pauling originally chose hydrogen as a reference, and with the dissociation energies then available, the calculation resulted in hydrogen being assigned the value of 2.1. Later improvements in thermodynamic data involving bond energies changed hydrogen's electronegativity to 2.2.

More on Pauling—DNA

Although the article discusses Pauling's work on the chemical bond and the chemical structure of proteins, it does not (due to limitations of length) discuss his role in the discovery of the chemical structure of DNA. Pauling was right in the thick of the investigation of the structure of DNA, and it was perhaps only because of his concentration on the study of protein structures

that he was not the first to discover the structure of DNA. X-ray crystallography was the method of choice for discerning molecular structures at the time, and Pauling was an expert at it. That alone gave him an advantage. Add to that the fact that he was studying hydrogen bonding in proteins that gave rise to the alpha-helical structure, and DNA is a small (OK, maybe not so small) step beyond proteins. The OSU Pauling web site gives a very interesting recounting of the research to find the structure of DNA at "The Race for DNA", at

<u>http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/dna/index.html</u>. Watson and Crick weren't the only scientists trying to find the elusive structure.

More on Pauling—Vitamin C

Linus Pauling is best known in scientific circles for his research and publication involving the nature of the chemical bond. He was then able to apply this knowledge to the search for the chemical structures of proteins. For these accomplishments he was awarded the Nobel Prize in Chemistry in 1954.

In political circles, Dr. Pauling is best known and remembered for his promoting of peace during the Cold War with Russia. He repeatedly marched in rallies to promote peace and force the government to stop the testing of its nuclear arsenal. He was able to rally many famous, influential scientists to his cause, resulting in the petition mentioned in the article.

But in health circles, Dr. Pauling is better known for his promoting of vitamin C as the cure for the common cold, and even cancer. He believed so strongly in its benefits that he himself took mega-doses of the vitamin throughout his life, and he advocated that the American people do likewise. His promotion of and research into the effects of vitamin C on human health is one area that is controversial to this day.

As a two-time winner of the Nobel Prize, Pauling exerted great influence on the scientific world and the general public as well. His research and his strong belief in the curative effects of vitamin C led him to publish three books, mostly directed to the general public, on the subject. The influence of a world-renowned scientist should not be overestimated. Many people (one of the present TG editors included) believed Pauling and took those "prescribed" mega-doses of vitamin C, expecting that eventually Pauling would be proved to be right.

Through his Linus Pauling Institute at the University of Oregon, he initiated testing of vitamin C in mice to determine its effects. Because Pauling directed much research on vitamin C onsite at the Institute, it has an entire section of its web site devoted to vitamin C and its positive effects on all manner of human health issues, from scurvy to cancer, from lead toxicity to heart disease. You can find this information at

<u>http://lpi.oregonstate.edu/infocenter/vitamins/vitaminC/</u>. When published results from scientific tests, for example, from the Mayo Clinic, differed from Pauling's findings, they cite "...significant methodological differences between the Mayo Clinic and Pauling's studies..." In this case, the methodological difference was how the vitamin was administered, orally or intravenously.

Pauling also studied the results of other researchers in the field. Unfortunately, the results did not bear out his expectations. Even today, test results involving large numbers of human subjects have shown that, at best, vitamin C merely reduces slightly the severity and/or duration of the common cold, and does not prevent it. And other studies have shown that vitamin C actually may exacerbate the growth of cancerous cells.

Despite these findings, Pauling continued to cling to his beliefs and to try to convince others that his hypothesis was correct. According to the source listed below, he even went so far as to ask the then-president and one of the principle researchers of the Institute, Arthur Robinson, to resign after the researcher's tests indicated that high doses of vitamin C might actually have been responsible for higher than normal incidences of skin cancer in their test mice. After Robinson left, Pauling then destroyed the research results, according to this site. A later lawsuit by Robinson (1983) against the Institute resulted in an out-of-court settlement for more than a half-million dollars awarded to Robinson by the Institute.

The above information (and more) on Pauling's dealings with vitamin C can be found in the article, "The Dark Side of Dr. Pauling's Legacy" at

<u>http://www.quackwatch.com/01QuackeryRelatedTopics/pauling.html</u>. Check out the "Web sites for Additional Information" section at the end of this TG for more sites on this controversy.

More on the chemical bond from past issues of ChemMatters on the ChemMatters CD

"Permanent Waves" in the ChemMatters April 1993 edition, page 8 talks about the role of chemical bonds in the structure of hair and in making waves.

"Mystery Matters: Blood Markers" in the ChemMatters April 1992 issue, page 4 discusses chemical bonds in proteins in the blood, vis a vis a wound victim.

In the ChemMatters December 1984 issue, page 4, the topic of chemical bonds in the proteins of eggs is discussed in "Egg Cookery".

In "Extremophiles—Life at the Edge", ChemMatters Vol. 17, No. 4 December 1999, the author discusses protein molecules that are not denatured, even at extreme temperatures. They have enzymes that keep working, even at high temperature. These they dubbed extremozymes.

Connections to Chemistry Concepts

- 1. **Chemical bonds**—Pauling developed the present-day ideas of chemical bonding.
- 2. **Quantum mechanics**—Quantum mechanics was used by Pauling to ascertain the nature of chemical bonds.
- 3. **Hybrid orbitals**—Pauling's applications of quantum mechanical equations to chemical bonds led him to the idea of hybridized orbitals to explain carbon's tetravalent bonding, rather than the divalent bonding that the physicists using the original wave mechanical equations believed should exist.
- 4. **Polar and nonpolar molecules**—Pauling's electronegativity scale is still used to predict the polar nature of bonds/molecules. The greater the difference between the atoms' abilities to draw electrons toward themselves (electronegativity), the more polar (ionic) the bond will be.
- 5. **Hydrogen bonding**—The structure of macromolecules is often due to hydrogen bonding.
- 6. **Electronegativity**—The concept of electronegativity is used to explain polarity in chemical bonds, as well as hydrogen bonding.
- 7. **Organic chemistry**—Proteins and DNA are organic molecules (albeit rather complex ones for first-year chemistry students).
- 8. **Biochemistry**—Hemoglobin, proteins and DNA are all biochemical entities.
- 9. **Proteins**—Denaturation of proteins is often demonstrated in biology classes.
- 10. **Analytical chemistry**—The structures of proteins and of DNA were determined using X-ray crystallographic photographs

Possible Student Misconceptions

- 1. "I remember Pauling—he's the guy who established the Pauling exclusion principle in quantum mechanics." No, that's the <u>Pauli</u> exclusion principle. (different guy—Wolfgang Pauli)
- 2. "So, those quantum mechanical electron orbitals are solid, just like the models my teacher showed me and the ones I saw in the textbook." Students may well think that

orbitals are real objects. Warn students that these are only models representing the plotted (3-dimensional) solutions to mathematical equations. Provide several analogies, like the fan blades appearing to make a full circle when a fan is turned on, or like the color- blending on a spinning top, to reinforce that what the student sees is not necessarily what is "real".

- 3. **"Chemical bonding is either ionic or covalent."** Actually, most bonds are not ionic or covalent, but a mix of both. There's no such thing as a 100% ionic bond, and the only 100% covalent bonds are those between like atoms; e.g., *F*₂, *O*₂, etc.
- 4. "Covalent bonds must be weaker than ionic bonds because substances held together by covalent bonds are generally gases or liquids at room temperature, while compounds held together by ionic bonds are solids and generally have high melting points." Students making statements like this are confusing intermolecular forces with intramolecular bonds. Intramolecular bonds are those holding atoms together within individual molecules (forces within molecules), while intermolecular forces are those attracting molecules to each other. Nitrogen is a gas because the attractive forces between molecules are relatively weak, while bonds between the atoms within a molecule are very strong. (Lightning is one of the only naturally occurring energy sources on earth that is strong enough to break apart a nitrogen molecule into free nitrogen atoms.)

Demonstrations and Lessons

 Flinn Scientific has an entire book on experiments in chemical bonding. It is one of their series of experiment books, Flinn ChemTopics Labs. Flinn sells the books, but you can access the preface page here:

http://www.flinnsci.com/Documents/ProductPDFs/ChemTopicLabs/vol %205/Chemical_Bonding_Preface.pdf. The book contains 11 labs, the titles of which can be seen on the materials list at http://www.flinnsci.com/Documents/ProductPDFs/ChemTopicLabs/vol %205/Master_Materials_Guide_vol5.pdf.

- 2. If you're looking for a complete teaching package on chemical bonding, here it is. *SourceBook* (See "References" section below for details) has a whole module devoted to the chemical bond, called "Chemical Bonding". You can find the module at http://dwb4.unl.edu/chem_source_pdf/BOND.pdf. After providing background material for the teacher on the various types of bonding, the module gives the central concepts that should be taught in the curriculum. Then it lists related concepts and skills and gives performance objectives for students. This is followed by "Activity 1: Physical Properties and Chemical Bonding in Solids", on pages 6-13. This lab is designed to help students distinguish between ionic and covalent bonds by investigating electrical conductivity of various substances in their solid, molten, and dissolved states. The student version provides all directions and safety concerns, and a student data sheet and student questions ("Implications and Applications"). The teacher version provides pre-lab discussion topics, a complete materials list, safety considerations, preparation needs, sample student data, discussion questions and answers, topics for post-laboratory discussion, and ideas for assessment. It is a very complete package.
- "Activity 2: Metals and Ionic Crystals", on pages 14-19 in the "Chemical Bonding" module of the *SourceBook* provides a lab activity for students to investigate the packing of atoms/ions. They build models of the 3 different packing arrangements in metals and ionic crystals. The source is the same site as number 2, above,

http://dwb4.unl.edu/chem_source_pdf/BOND.pdf.

- 4. "Demonstration 1: Electrical Conductivity of Solutions", on pages 19-21 of the "Chemical Bonding" module of the SourceBook, helps students see the difference between ionic and molecular substances. See source 2 or 3 above.
- 5. "Demonstration 3: Magnetic Analogy for Bonding Forces" on page 22, also from the "Chemical Bonding" module of *SourceBook*, uses magnets to represent the interplay between nuclei and electrons in the formation of a chemical bond. See source 2 or 3 above.
- 6. "Demonstration 4: Force at a Distance" on page 23, from "Chemical Bonding" in the *SourceBook*, uses a magnet model to illustrate how atoms might be initially drawn together as a precursor to forming a chemical bond.
- 7. Following the demonstrations in this module on chemical bonding, several other classroom activities are described. One is a discrepant event involving the graph of Pauling Fractional Ionic Character ("No Compound is 100% Ionic: A Group Activity" on pages 23-24), another deals with analogies involving the concept of resonance (pages 24-25).
- "Demonstration 1: Which Will Evaporate First?" is a demonstration involving intermolecular bonding. It can be found in another module of the *SourceBook*, "Condensed States" on page 18. This module is online at <u>http://dwb4.unl.edu/chem_source_pdf/COND.pdf</u>. The demonstration involves the evaporation rate of various alcohols and water from a blackboard.
- 9. You can find a student experiment that investigates the difference between thermoplastic and thermoset polymers in the "Polymer" module of the *SourceBook* at http://dwb4.unl.edu/chem_source_pdf/POLY.pdf. See "Activity 1: Thermoplastic and Thermoset Polymers" on pages 4-9. The results of this activity could be analogous to the bonding differences in denaturation of some proteins (that was cited in the article), depending upon whether one attempts to break primary chemical bonds or secondary intermolecular bonds
- Chromatography could also be used to show how the strengths of bonds differ and can be used to separate mixtures. "Demonstration 3: Separation of Chlorophyll Pigments by Paper Chromatography", pages 21-22 of the "Separations" module (<u>http://dwb4.unl.edu/chem_source_pdf/SEPN.pdf</u>) of the *SourceBook* is an example demonstration.
- 11. Distillation could also be used to show the difference in bond strength in compounds in a mixture.
- 12. This site <u>http://www.saskschools.ca/curr_content/chem20/ionicpds/physexpl.html</u> provides a data table of information re: ionic compounds and asks students a series of questions about the data.
- 13. Doing Chemistry offers an experiment, "Physical Properties and Chemical Bonding in Solids", similar to the one in number 2 above, testing ionic and molecular compounds via solubility and electrical conductivity. The site has the normal lab procedure, along with teacher notes, safety, etc., but it also has a video of the actual experiment being done, so that students could get most of the benefits of the lab without actually dealing with the chemicals involved. Or students who are absent and miss the lab can still see the video and still learn about the lab without actually doing the experiment. Access the site at http://dwb4.unl.edu/Chemistry/DoChem/DoChem037.html. This, too, is a very complete package of information about this experiment.

Student Projects

The first three projects below focus on increasing students' abilities to analyze scientific claims. This is one goal for preparing science-literate students/citizens.

- 1. Students might investigate the claims made by Pauling regarding vitamin C and the common cold and report their findings to the class.
- You might have students analyze the alleged relationship between vitamin C usage and the incidence of heart disease. They could begin by studying the graph and comments here: <u>http://www.vitamincfoundation.org/mortality.html</u>. (At the very least they could discuss the cause-and-effect relationship espoused on this page.)
- Have students visit the vitamin C Foundation web page, <u>http://www.vitamincfoundation.org/topten/</u>. The site gives 10 web sites that provide medical information to the public, and it states that these 10 have given misinformation relating to vitamin C. Ask students to analyze the misinformation and the attending "corrections" made by the site.
- 4. You might want to have students research and report their findings about the history of the theories behind chemical bonding.
- 5. Students might want to make their own analogies and demonstrate them in class for some of the terms used in chemical bonding; e.g., covalent and ionic, hybridization, resonance, and polarity. This may help other students better understand the material.

Anticipating Student Questions

- "Can you still buy chemistry sets?" Sure, chemistry sets are still available. They can be purchased from many different companies, including the following: <u>http://www.discoverthis.com/chemistry.html?gclid=CMTBrM_mk44CFSasGgoduj2cEw</u> and <u>http://www.discoverthis.com/chemistry.html?</u> <u>gclid=CMTBrM_mk44CFSasGgoduj2cEw</u>. The latter source even lists a Harry Potter Hogwarts chemistry set! You might also want to direct students (and their parents) to the following web site, which deals with what you should know <u>before</u> one buys a chemistry set: <u>http://chemistry.about.com/od/buyingadvice/bb/bybchemset.htm</u>.
 "Was Pauling the first scientist to study the nature of the chemical bond?" No,
- 2. **"Was Pauling the first scientist to study the nature of the chemical bond?"** No, many scientists in the past had wondered about or studied bonding in molecules, but until Pauling's time, there was no technology (e.g., x-ray crystallography, spectroscopy) to support those studies. That's why the hook-and-eye model hung around for so long.
- 3. **"Why does the author call Pauling an 'American Hero'?"** Pauling espoused anti-war views when it was not popular to do so (somewhat like today). He risked his fame, career, and possibly his life, for his beliefs.
- 4. **"Wasn't the hook-and-eye model of chemical bonding rather simple-minded for** scientists to believe?" In hindsight, the model seems overly simplistic, but students need to remember that scientists could only form theories (hypotheses, really) on the basis of the data they had on hand. Since no one could see atoms in bonds, no one could really determine the true nature of bonds. This model, which allowed chemists to visualize what was happening in a bond, was the best they had at the time. Even then, though, scientists recognized that it was not a very satisfactory explanation of bonding. That's one of the reasons Pauling pursued his studies of this enigma.
- 5. **"What are the symptoms of sickle cell anemia?"** The symptoms include anemia, fatigue, rapid heart rate, episodes of pain, and increased susceptibility to infection.
- 6. **"What's the big deal with the Nobel Prize, anyway?"** The Nobel Prize is arguably the most prestigious scientific award that any scientist can win. It signifies that the scientist is "at the top of his game". (You might tell students that it's analogous to the Oscars or Emmys in celebrity circles.)

References

The most extensive and authoritative web site on the life and work of Linus Pauling is found at the already oft-mentioned Oregon State University site. http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/index.html.

The NSF-funded project, ChemSource, has produced a compilation of teacher resources for teaching chemistry. Information about this 4-volume set, called SourceBook, is available from the American Chemical Society at http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html? DOC=education\curriculum\teachres.html. Cost is \$75.00. The material is also supposed to be available on CD. Thirty-six modules cover all the chapters of a normal chemistry curriculum, as well as specialty topics, like photochemistry and forensic chemistry. Each module contains teacher background material, labs (student and teacher versions, with safety duly noted), demos, history, analogies, humor, related materials and skills, objectives, key questions for students, concept maps, student misconceptions, teacher tips, and links to other topics and disciplines, and media resources. The latest version is version 2.1. Most of the work from the original volume, 1.0 (1994), is available online as pdf files at http://dwb4.unl.edu/chem source pdf/ChemSource.html. SourceBook contains a wealth of information that any/every chemistry teacher can use.

Websites for Additional Information

More sites on Pauling's life

A very brief biography of Pauling can be found on the Nobel Prize web site, at http://nobelprize.org/nobel_prizes/chemistry/laureates/1954/pauling-bio.html.

A more detailed biography of Pauling can be found on the Linus Pauling Institute web site, at http://lpi.oregonstate.edu/lpbio/lpbio2.html.

Oregon State University is the official keeper of Linus Pauling's memoirs and personal and professional documents. The university has documented all of its Pauling collection and has produced an extensive web site dedicated to Pauling's life and work. A section of the site provides an extensive timeline of Pauling's life juxtaposed against a timeline of world history. It gives a very interesting way of putting his life in perspective:

http://osulibrary.orst.edu/specialcollections/coll/pauling/timeline.html

More sites on the history of the chemical bond

Mark Leach's "Chemogenesis" web book has one section on chemical bonding: "A timeline of Structural History", located at http://www.metasynthesis.com/webbook/30 timeline/timeline.html. This site shows how the "biggies" of chemical history contributed to the understanding of the chemical bond. It includes links to online copies of many original historical works, compiled by Carmen Giunta, and it brings us right up to present-day bonding theory. Dr. Leach does tend to wax philosophical at times, but the site is a useful tool for teachers.

More sites on the nature of the chemical bond

Oregon State's web site also includes an entire section on Pauling's search for understanding of the chemical bond: <u>http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/index.html</u>,

All of Pauling's original 7 papers on the nature of the chemical bond can be found on Oregon State's web site at <u>http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/papers/index.html#1929p.1</u>.

In The August 13, 2007 edition of *Chemical and Engineering News on pp. 17-22*, you can find the cover story, "Molecules that Could Be", online at http://pubs.acs.org/cen/coverstory/85/8533cover.html. The story shows molecules that might exist, based on chemists' present understanding of bonding theory, but that have not yet been discovered. Disney isn't the only one who can have fantasyland.

More sites on vitamin C

An interview with Linus Pauling by Peter Chowka discusses Pauling's interest/belief in the benefits of vitamin C. It is Pauling's last interview before his death. You can find it at <u>http://members.aol.com/realmedia/pauling.html</u>.

The Vitamin C Foundation web site, <u>http://www.vitamincfoundation.org/</u>, cites numerous claims about the benefits of vitamin C in our daily lives. It is certainly not a balanced site, but students may want to investigate some of their claims.

Dr. Steve Barrett, webmaster of the "Quackwatch" site, is the source of most of the negative material cited at the beginning of this TG re: Pauling's recommendations of the health benefits of vitamin C. The article is at http://www.quackwatch.com/01QuackeryRelatedTopics/pauling.html. You can check out Dr. Barrett's credentials by clicking on his name at the top of this web page.

You can find another article about vitamin C's ineffectiveness on cancer on this page of Dr. Barrett's site: <u>http://www.quackwatch.org/01QuackeryRelatedTopics/Cancer/c.html</u>. Dr. Barrett cites specific studies and compares and contrasts Pauling's studies with those of other institutions.

More sites on Hemoglobin

Oregon State's site also includes a significant section on Pauling's studies involving hemoglobin in "It's in the Blood!": http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/blood/introduction.html

More sites on the history of the discovery of DNA

Once again, Oregon State's web site provides insight into the series of events that led to the discovery of DNA, in "the Race for DNA" at http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/dna/index.html.

The site even includes audio and video clips from Watson, Crick and Pauling on their contributions to the race: http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/dna/videos/index.html

More sites on electronegativity

Pauling's original paper published on the topic of electronegativity, "The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativities of Atoms", the fourth in his series of seven signature papers on the nature of the chemical bond, can be found at http://dbhs.wvusd.k12.ca.us/webdocs/Chem-History/Pauling-1932/Pauling-electroneg-1932.html, or at

http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/papers/1932p.11.html.

More sites on the Nobel Prize

The official Nobel Prize web site gives short biographies of all the winners of the Prize since its inception: <u>http://nobelprize.org/</u>. It also provides a biography of Alfred Nobel and the Prize.

Another Nobel Prize site, at <u>http://www.nobelprizes.com/</u>, provides an opportunity for readers to submit their own links to Nobel-related sites. Students need to be cautious about relying too heavily on these links as they don't seem to be peer-reviewed.

General Web References

http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/index.html.

What's That Stuff? Pencils and Pencil Lead

Background Information

More on Pencils

As the article describes, the earliest event that enabled pencil production on a large scale was the discovery of a huge graphite deposit at the Seathwaite Fell site near Borrowdale, Cumbria, England, in 1564. Local sheepherders used it for marking their flock. Chemistry was in its very early stages as a discipline, and the graphite was thought to be a form of lead. Originally it was used to line the molds for cannonball manufacture because of its refractory properties. Pencils were very much a secondary use, and it had to be smuggled out of the mines for use in pencil making. The soft graphite was originally wrapped in sheep skin or string to make a stable pencil.

Wooden housing made the pencil more popular, and for nearly two hundred years, graphite from the Borrowdale mines supplied pencils for England and the rest of Europe. As the Borrowdale deposit began to be depleted, manufacturers looked for other materials to mix with graphite to extend its lifetime. The article mentions Nicolas-Jacques Conté as the person in France who developed the powdered graphite-powdered clay-water mixture that replaced pure graphite by the late 1700's. Conté also found that he could vary the darkness of the pencil's markings by varying the ratio of graphite to clay in the mixture. At the time England and France were at war and pure graphite was not available to the French. Conté's method is still the basis for pencil manufacture today.

The world's second big graphite mine was discovered in the 1840's as Jean Pierre Alibert, searching originally for gold, found high quality graphite in Siberia along the Chinese border. Much of this was shipped to Germany where A. W. Faber Pencil Company was on its way to becoming one of the world's largest pencil manufacturers.

By the beginning of the nineteenth century pencils were very popular around the world including in the United States. There were, however, no pencils being manufactured in the U. S. What's more, the War of 1812 shut down pencil imports from England. Of economic necessity, several U.S. entrepreneurs began to manufacture pencils (of lower quality) and several sources of graphite were discovered. Among the manufacturers were William Monroe in Massachusetts, Joseph Dixon in New Jersey and Eberhard Faber in New York City. Also among the early manufacturers was one John Thoreau who lived in Concord, Massachusetts. His brother-in-law, Charles Dunbar had found graphite deposits in New Hampshire. Thoreau's son, Henry David, eventually joined his father, and in the 1820's found the same formula that Conté has used for mixing graphite with clay for the filler for the pencil. It is fairly certain that the younger Thoreau—of Walden Pond fame—made the discovery independent of Conté (even though it was some years later) since the methods of pencil manufacture in Europe were closely guarded secrets.

After the Civil war, four major companies dominated pencil manufacture in the United States—Eagle Pencil Company, Eberhard Faber (brother of the German Faber and an immigrant to the US), the American Lead Pencil Company, and Joseph Dixon Crucible Company.

Joseph Dixon, originally from Massachusetts, experimented as a youth with pencil making. He saw the potential of pencils even though his company was founded to make graphite crucibles for making steel. In 1847 he moved his company to Jersey City, NJ. Three years later he received patents for the use of graphite crucibles in pottery and steel. The

company's now famous Dixon Ticonderoga pencils were named for the fort in New York which played a prominent role in the French and Indian War and the Revolutionary War.

By the 1870's over 20,000,000 pencils were purchased per year in the US. By 1912, the figure had grown in the US to be 750,000,000, while world wide the figure was at two billion. The article says that the current U.S. production is 2.8 billion.

More on Mechanical Pencils

Mechanical pencils trace their origin to England in the early 1800's, but following the rising popularity of wooden pencils around the turn of the twentieth century, there were two attempts to make mechanical pencils. Hayakawa Tokuji, the founder of Sharp, invented a mechanical pencil in 1915 and obtained a U.S. patent in 1926. The Eversharp pencil was developed by Charles R. Keeran, of Illinois. This was the first popular mechanical pencil, primarily because it had a large "lead" capacity and an easy-to-use propelling system. Keeran obtained his patent in 1915. Eversharp standardized the "lead" size at 1.2 mm. The "lead" was supplied by the Dixon Company.

More on Allotropes

Allotropes are different forms of the same element that result from a different arrangement of its atoms. Common examples are oxygen (O2 and O3), phosphorus (white, red, black and yellow) and carbon. The allotropes of carbon are diamonds, graphite, fullerenes and carbon nanotubes. 44Amorphous carbon is another well known allotrope of carbon and is the name used for coal, soot and other carbon compounds that are neither graphite nor diamond.

Which allotrope depends on the carbon bonding. Diamonds are the result of sp^3 bonding while the other allotropes are the result of carbon sp^2 bonding.

Graphite and diamonds are always referenced in chemistry textbooks, but buckyballs and carbon nanotubes may get less discussion because of their recent discovery—by Smalley, Kroto and Curl in 1985.

To view an interactive page on the structure of graphite, diamond and buckminsterfullerenes, see <u>http://www.creative-chemistry.org.uk/molecules/carbon.htm</u>

This web site is a complete classroom unit of study on the allotropes of carbon http://www.nsec.northwestern.edu/Curriculum%20Projects/Carbon%20Allotropes.pdf

For a web based module on the allotropes of carbon, go to

http://www.chemsoc.org/ExemplarChem/entries/2003/bristol_shanley/carbonallotropes/

Other common elements that exist in allotropic forms are phosphorus, sulfur and carbon. Like carbon, the differences in the allotropes can be accounted for by the arrangement of atoms.

Phosphorus—Red phosphorus is a crystalline powder with four atoms of the element arranged in a pyramid. It is stable in air, but still very reactive. It is used in strike-anywhere matches, since the heat generated by friction can ignite the allotrope. In black phosphorus, the atoms are arranged in a puckered sheet, somewhat like graphite. It is very unreactive. Compared to the other two, it has a higher boiling point and melting point. White (or yellow) phosphorus is a waxy solid at room temperature. It is very flammable in air. It is stored under water for this reason. It has a garlic-like odor. **Oxygen**—Molecular oxygen, O2, is made up of two oxygen atoms per molecule, and has the properties students know about. Ozone has three oxygen atoms per molecule and has an acrid odor. Ozone can be formed from oxygen by passing an electric charge through the oxygen. It can be detected in the air after a lightning storm. In very small concentrations it causes breathing problems in humans. So oxygen near the surface of the earth is a pollutant. Ozone higher in the atmosphere has the ability to absorb UV radiation from the sun and acts a protector for the earth.

Sulfur—Based on crystal structure it is possible to identify at least four allotropes of sulfur. Solid sulfur consists of molecules containing eight sulfur atoms joined in a ring, S_8 . Such molecules can pack to form more than one crystal. The most stable form of sulfur consists of orthorhombic crystals. If orthorhombic sulfur is heated to liquid and then cooled, the second solid allotrope of sulfur, long needle-like monoclinic crystals, are formed. They will slowly revert to orthorhombic form over time. Both forms are composed of S_8 molecules.

In the liquid phase the allotrope is called lambda sulfur, which is a low viscosity liquid that is soluble in nonpolar solvents. If it is heated more strongly the S8 rings break apart to form long sulfur chains called mu sulfur. Mu sulfur is not readily soluble in common solvents and is a very viscous liquid.

More on Graphite

An allotrope of carbon, graphite is usually found as veins, lenses, pockets and in thin layered deposits. It is found often with feldspar, mica, or quartz as impurities. There was no graphite produced in the United States in 2006. Imports came primarily from China, 42%; Mexico, 30%; Canada, 18%; Brazil, 6%; and other, 4%. Much of the graphite in use today is produced synthetically from petroleum coke, the tar residue after crude oil refining.

Physical properties

Density: 1.9 - 2.3 g/mL (compared to diamond at 3.50) Hardness : 1 - 2 Moh's scale m.p. = 3652-3697 °C(sublimes) Specific heat = 0.17 cal/g-°C Heat of refractoriness (resistance to heat)—up to 3000°C in an inert atmosphere Flammability- burns in oxygen at temperatures between 620°C to 720° C.

The crystal structure of graphite is made up of carbon atoms bound covalently to nearby carbon atoms at a distance of about 141.8 pm to form hexagon rings. These rings form sheets of graphite which are loosely bound to each other by weak van der Waals forces.

To see the crystal structure in a variety of forms, see the Naval Reserve Laboratory Center for Computational Materials Science site at <u>http://cst-</u> <u>www.nrl.navy.mil/lattice/struk/a9.html</u>

Uses: According to the United States Geological Service, the major uses of natural graphite in 2006 were refractory (high heat) applications, 27%; brake linings, 15%; and batteries, foundry operations, and lubricants, 8%.

The uses depend on the type of graphite produced: flake, lumpy (crystalline) or amorphous. Flake graphite has low electrical resistivity and so is used in making electrodes and batteries. The flake form is also used to make graphite crucibles by combining the graphite with clay and sand at high temperatures. Such crucibles are used to melt non-ferrous metals like brass and aluminum.

Both amorphous and crystalline graphite are used in lubricants because of their low coefficient of friction. The graphite is suspended in oil to form the lubricant. Amorphous graphite is also the form of choice in pencil manufacture because it is best at leaving residue on paper. The finer the graphite powder, the darker the streak.

In addition to its use in pencils, graphite is used to make battery electrodes, in composites where strength is important (tennis racquets, golf clubs) helicopter blades, artificial heart valves, lubricants, and as a nuclear power plant moderator.

Again, according to the USGS, "Advances in thermal technology and acidleaching techniques that enable the production of higher purity graphite powders are likely to lead to development of new applications for graphite in high-technology fields. Such innovative refining techniques have enabled the use of improved graphite in carbon-graphite composites, electronics, foils, friction materials, and special lubricant applications. Flexible graphite product lines, such as graphoil (a thin graphite cloth), probably will be the fastest growing market. Large-scale fuel-cell applications are being developed that could consume as much graphite as all other uses combined."

These uses are interesting because they highlight other properties of graphite. Synthetic carbon can be made into fibers, which are both strong and heat resistant. So this form can be used in places like brake shoes, electric motors and in heat-resistant products. Expandable graphite finds uses in fire-resistant structures like fire doors. When the graphite is heated, it expands and reduces the spread of the fire.

Graphite is related to a class of carbon allotropes called fullerenes, which include carbon nanotubes and the more familiar Buckyballs. Carbon nanotubes are used where strength is important, in products like fishing rods, golf clubs, bike frames. These materials are often referred to as composites.

Hardness: The "hardness" of pencils is determined by the ratio of graphite to clay in the mixture. In the United States, a numbering system is used with 1 representing a soft mixture and a 4 being a hard mixture. In Europe letters are used instead of numbers, with B designating soft lead and H meaning hard lead. The common grades are:

U.S.	Europe	Graphite %	Clay %	Wax %
#1	В	71	23	5
#2	HB	68	26	5
#2½	F	66	28	5
#3	Н	63	31	5
#4	2H	60	34	5

Graphite Production: The article describes one method of producing pencil "lead," the extrusion method in which the graphite and wax mixture is forced through a mold to form long rods. There is a second method in which the mixture is poured into a *billet press*. A metal rod then exerts pressure on the confined mixture to form a solid cylinder called a "billet." The billet can then be sent through the extrusion process.

More on Carl Scheele and Graphite

The article notes that Carl Scheele discovered that what at the time was called black lead was actually graphite, an allotrope of carbon. Scheele also discovered oxygen a year or two prior to Priestley and also discovered chlorine. The oxygen discovery was incidental to the experiments that Scheele was famous for, and since he did not describe or name the new gas, Priestley got credit. Scheele's described the gas as "fire-air" because it supported combustion, but because he believed in the phlogiston theory, dominant at the time, he did not think he had discovered a totally new gas. You might want to note to students that Scheele tended to taste chemicals, an unsafe practice at best. His symptoms prior to his death at the early age of 43 were like those of mercury poisoning.

Scheele was actually what we would today call a pharmaceutical chemist. In the middle of the eighteen century, a pharmacist and a chemist were synonymous. In the 1600's Robert Boyle suggested that carbon was an element, and Lavoisier affirmed that it was as he identified diamonds as a form of carbon in 1772. Nine year later, Scheele was able to show that graphite is a form of carbon by reacting it with nitric acid to produce carbonic acid and that graphite produced the same amount of carbon dioxide as an equal mass of carbon, thus confirming that graphite is carbon.

Connections to Chemistry Concepts

- 1. **Carbon Chemistry**—Graphite is not usually discussed when carbon chemistry is covered in the classroom. This article highlights and important use of this form of carbon
- 2. **Allotropes**—Different forms of elements may not be the most important chemical concept, but it is a chance to relate the properties of a substance with its chemical structure.
- 3. **Applied Chemistry**—The uses of graphite in pencils and elsewhere, is an opportunity to discuss with your class how chemicals are used in society and the processes involved in converting a raw material like graphite into useful products.

Possible Student Misconceptions

- 1. **"So if I chew on a pencil, can I get lead poisoning?"** Only if the yellow paint on the pencil is lead-based paint (which it isn't—at least in the US). The "lead" isn't lead, but graphite. The article describes the most frequent misconception about pencils—that the substances that makes the mark is actually the element lead. The article also describes in great detail the historical reason why the term "lead" has continued to be used even though a graphite-clay mixture is used as the marking material in a pencil.
- 2. **"Diamonds are related to this graphite stuff in my pencil??** If you have not covered allotropes when your students read this article, they might not be aware that graphite is a form of carbon and related to diamonds. *See "More on Allotropes".*

Demonstrations and Lessons

- 1. The Mineral Information Institute has a set of activities that allow students to investigate the materials that make up a pencil. <u>http://www.mii.org/pdfs/every/pencil.pdf</u>
- 2. For a complete unit on the allotropes of carbon, including activities, see http://www.nsec.northwestern.edu/Curriculum%20Projects/Carbon%20Allotropes.pdf.
- 3. For several activities about graphite, see <u>http://invsee.asu.edu/nmodules/Carbonmod/penwrite.html</u>
- 4. See for more resources http://www.pencils.com/index.html

Student Projects

- 1. Assign each student to bring to class a certain number of pencils. Each pencil must have a unique property (hardness, traditional vs. mechanical, etc.). Make marks on paper with each and compare.
- 2. Ask students who are taking art to bring in drawing pencils and charcoal and explain their uses.
- 3. Assign students to research varieties of pencils not discussed in the article, like colored pencils.
- 4. Assign students to do "rubbings" using pencils of varying hardness and compare the results.

Anticipating Student Questions

- 1. "You mean there is no lead in lead pencils?" The article explains this completely.
- 2. Few students, like most people, know how a pencil is made. This is a chance to discuss with students the science and technology behind the processes that transform natural resources into consumer products. It is also an opportunity to talk about finite resources. The graphite mines at Borrowdale are examples of finite resources running out. The more popular pencils became throughout England and the rest of Europe, the faster the graphite at Borrowdale was depleted. This was in part what created the need for the Frenchman Conté to find a way to extend graphite supplies in France—that and the fact that England and France were at war and graphite was embargoed.

References

Petroski, Henry. The Pencil: A History of Design and Circumstance, Knopf, 1992.

Fischler, George. Fountain Pens and Pencils. Schiffer Publishing, 1990.

Thomson, Ruth. Making Pencils. Franklin Watts, 1987.

Websites for Additional Information

For a complete unit on the allotropes of carbon, including activities, see <u>http://www.nsec.northwestern.edu/Curriculum%20Projects/Carbon%20Allotropes.pdf</u>.

For a web based module on the allotropes of carbon, go to <u>http://www.chemsoc.org/ExemplarChem/entries/2003/bristol_shanley/carbonallotropes/</u>.

You can view the Nobel Prize web site on the discovery of buckminsterfullerenes at <u>http://nobelprize.org/nobel_prizes/chemistry/laureates/1996/press.html</u>.

For more on carbon orbital hybridization and the structure of graphite, see <u>http://www.coe.drexel.edu/ret/personalsites/2005/Weerasooriya/lesson.html</u>

For more on pencil production, see the Faber-Castell site at http://www.faber-castell.de/docs/index- news_asp_id~14978_domid~1010_sp~E_addlastid~0_m1~14376_m2~14404_m3~14918_m4~ 14978_suma~.htm

For more on how pencils are made, see <u>http://www.acme-china.com/pencil%20making.htm</u> or <u>https://www.dixonusa.com/index.cfm/fuseaction=Ticonderoga.made</u>

For a history of mechanical pencils, see <u>http://www.vintagepens.com/Eversharp_history.htm</u>

For classroom activities on allotropes see <u>http://www.ccmr.cornell.edu/education/modules/documents/Allotropes.pdf</u>

Percy Julian: Rising Above Racism

Background Information

More on Percy Julian

The article describes many of Julian's chemical accomplishments. You might also want to note to students that chemists are always influenced by the society in which they live, and that they often themselves influence the society. By setting the Julian story in its historical context, you can integrate Julian's experiences with racism with his chemical achievements.

The Chemical Heritage Foundation (<u>www.chemheritage.org</u>) has produced a web site that provides some insights into the American history as seen through Julian's life. Some excerpts from the Chemical Heritage Foundation web site:

On his early life:

"Percy Lavon Julian was born in Montgomery, Alabama, on 11 April 1899. Although he was born on the cusp of the 20th century, the early part of his life was shaped by the events of the 19th century. He was African American—the grandson of slaves—growing up at a time when post–Civil War Reconstruction (the attempt to give African Americans political rights) was long past and Jim Crow segregation was practiced in Alabama and most other parts of the country. In fact, segregation had been ruled completely legal just three years before Julian's birth, in the U.S. Supreme Court case *Plessy v. Ferguson*.

"Legal segregation was only one of the obstacles faced by any ambitious African American. It was reinforced by general attitudes that can only be described as racist. Many white Americans believed that African Americans were not smart enough to handle the "higher reasoning" required to be a scientist, or lawyer, or businessman. These attitudes were sometimes backed up by scientists, who tried to prove that racism was justified. Even when individual African Americans showed great promise, white Americans justified excluding them from opportunities on the basis of the supposed weaknesses of "their race." In fact, showing too much ability or ambition might make someone a target of white reaction. The Ku Klux Klan emerged at the end of the 19th century; part of its purpose was to intimidate those people who resisted segregation."

His college experience:

"DePauw University changed Julian's life. He later recalled: "On my first day in College, I remember walking in and a white fellow stuck out his hand and said 'How are you?—Welcome!' I had never shaken hands with a white boy before and did not know whether I should or not.

"By the time he graduated with a B.A. in chemistry in 1920, Julian was valedictorian of his class and was elected to Phi Beta Kappa, the national honor society. His success inspired his brothers and sisters to enroll in and graduate from DePauw too, and for his parents to move to Greencastle, Indiana. But what could Julian do next? Some of his white classmates had been awarded fellowships to study for a master's or Ph.D. at other universities. But Julian got nothing. He finally got a job as a chemistry instructor at Fisk University, a college for African Americans in Nashville, Tennessee.

"Back in a segregated environment, Julian redoubled his enthusiasm for chemistry. He wrote a whole new series of lectures on organic chemistry. He gave copies of the lectures to his old professor at DePauw, William Blanchard, who praised them highly. Julian got Blanchard's support for the next step in his progress as a scientist: a fellowship to study at Harvard University. He wanted to study with Edward P. Kohler, one of the top experts in organic chemistry."

Finding a career in chemistry:

Unfortunately for Julian, the fame he derived from his synthesis of physostigmine was not enough to guarantee him a professorship at DePauw. Julian married Anna Johnson, a Ph.D. in social work from the University of Pennsylvania, not long after he published his papers in 1935, so he now had to be concerned about making a living for his family. Blanchard tried to get him a teaching appointment, since the money that had allowed him all of the free research time was running out. But the board of trustees of the University refused, saying it was still not considered appropriate for an African American to be teaching white students. No other white college or university was prepared to accept an African American professor either.

So what could Julian do besides teach and do research in an academic laboratory? Physostigmine was not the only organic compound that had business uses. Some DePauw students who had worked in Julian's laboratory brought his name to the attention of the Institute of Paper, a business group dedicated to improving the paper industry. The head of the Institute thought Julian's research skills would be perfect for the industry and offered him a position as research scientist. But that offer was taken back when it was discovered that the home town of the Institute of Paper Chemistry, Appleton, Wisconsin, had a law forbidding African Americans from spending the night in town. Jim Crow laws were not found solely in the states of the old Confederacy.

Julian did finally find a place in industry, however. The Glidden Paint Company had a division dedicated to finding uses for soy beans. A company vice president, W. J. O'Brian, decided that Julian's research skills could make the Soya Division a major moneymaker for the company, so he appointed him director of the division in 1936."

The role of race:

"After World War II, U.S. society began to confront some of the symptoms of segregation. In 1947 Jackie Robinson became the first African American to play major league baseball, breaking one important barrier. In 1948 President Harry Truman ordered the end of segregated units throughout the armed forces. In 1954 the Supreme Court undid their decision in *Plessy v. Ferguson* with *Brown v. Board of Education of Topeka, Kansas*, saying that forced segregation of schools was inherently unequal.

"Percy Julian had been breaking down barriers since before the war, so he became the focus of great attention in both the black and white communities as civil rights and desegregation became more potent issues. In 1946 one of the most widely circulated magazines in the United States, *Reader's Digest*, published a biography of Julian under the title "The Man Who Wouldn't Give Up." In 1947 he received the Spingarn Medal, the highest award for contributions to society from the National Association for the Advancement of Colored People (NAACP), the most prominent civil rights group in the

country. In that same year he received the first of many honorary degrees, recognizing his contributions to science, from his old home university, DePauw. He would eventually receive honorary degrees from 18 other universities. In 1950 he was named Chicagoan of the year by the Chicago Chamber of Commerce.

"But even with these markers of success, Julian still confronted obstacles. Shortly after his family moved to the Chicago suburb of Oak Park in 1950, arsonists attacked his house. There was another attack the next year. Fortunately, no one in the Julian family was hurt, and the majority of Julian's white neighbors expressed outrage at the attacks.

"At the same time, Julian was beginning to feel limited by his research for Glidden. Glidden was, after all, in the soybean business. Julian, on the other hand, was



The Percy Lavon Julian commemorative stamp was issued in January 1993 as part of the U.S. Postal Service's Black Heritage Series.

excited by the prospects of extracting and synthesizing other steroids from whatever natural source was most promising. In 1953 he left the Glidden Company on friendly terms to pursue his own research once again."

"... By the 1960s, Julian was an "elder statesman" in both the chemical industry and the African American community. He was an active supporter of civil rights for African Americans but was troubled by the more strident tone of younger people. He even got into disputes with his children about how rapidly and vocally African Americans should push for equality. Even though he participated in the NAACP Legal Defense and Education Fund in 1968, he was skeptical even of Martin Luther King's strategy of nonviolence and dismissive of radicals like Malcolm X and Eldridge Cleaver."

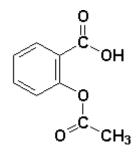
As the article describes, in 1993, Julian was also honored with this commemorative stamp.

More on Plant Chemistry

You can use this article to discuss with students how chemistry enables scientists to isolate, alter and synthesize chemicals that are found naturally in plants (and animals). Some of your students may already have heard about ethnobotany, the age-old practice of using plants medicinally. The mass media have recently covered attempts to find new pharmaceuticals in the rain forest of South America, for example. Percy Julian had a life-long interest in plants, and he spent much of his adult life isolating chemicals from plants (like *corydalis cava*, the calabar bean and soy beans), studying them and then modifying them to produce new substances.

You might want to provide some familiar examples of medicines that came originally from plants and are now produced synthetically:

Aspirin—Hippocrates (460-377 B.C.) noted that chewing the leaves of the weeping willow tree reduced pain, and this treatment was used extensively by the Greeks for pain and for reducing inflammation. Willow bark was also used by Africans and by Indians in North America for pain treatment. In the 1820's a compound named salicin was isolated from the willow bark, and later Karl Löwig in Germany treated salicin with acid to produce salicylic acid. Incidentally, an ester, methyl salicylate, was being used to treat muscle pain as oil of wintergreen. In the late 1800's researchers at Bayer added an acetyl group to the salicylic acid to make the familiar acetylsalicylic acid we know today as aspirin.



Aspirin structure

Digitalis—This compound is found naturally in purple foxglove, *digitalis purpurea*, which had been known for its medicinal uses since at least the Middle Ages. Digitalis was identified as the active ingredient in about 1775 by the Scottish physician William Withering, and in 1785 introduced it to medicine. The compound is dissolved and then recrystallized for use. Today, derivatives of digitalis are used to treat heart disease.

Diosgenin—This sapogenin steroidal compound is extracted from wild yams (Dioscorea) and is used to produce synthetic hormones used in birth control pills and fertility drugs. It is chemically very similar to cholesterol. Diosgenin provides about 50% of the raw

material for the manufacture of cortisone, progesterone, and many other steroid hormones. It is a white crystalline powder, very soluble in gasoline and ethanol and insoluble in water.

Anticancer Drugs—There are a number of drugs used to treat cancer which are derived from plants. Among them are:

- Rosy periwinkle (*Catharanthus roseus*)—used to treat leukemia and Hodgkin's Disease
- Mayapple—This plant contains podophyllotoxin, which is the starting material for producing the antitumor agent etoposide, used for the treatment of lung and testicular cancer.
- Pacific Yew(taxus brevifolia)—contains the compound taxol, used in the treatment of ovarian and breast cancer.

More on Alkaloids

As part of your discussion of plant chemistry, you could focus on plant alkaloids. The article describes Julian's interest in alkaloids, which are relatively stable nitrogen-containing compounds that are produced in plants from amino acids. Alkaloids are present in at least 15% of all flowering plants. Alkaloids have one of several common ring structures of which the nitrogen atom is a part. Such rings are called heterocyclic rings. One example is the indole ring structure, which appears at right. Molecular weights are usually in the range of 100-900 amu. They taste bitter and are generally present in pure form as white solids. They can be precipitated from solution with heavy metal iodides which produce a cream colored precipitate or by treatment with a base.

You can also use this discussion to explain the concept of "active ingredient." In plants that have been used for medicinal purposes for centuries, there is a specific chemical or set of chemicals that produce the desired effect. Alkaloids can be the active ingredient in plants like tobacco, chinchona, coffee and tea plants and cacao (see below). These active ingredients in natural products have been isolated, concentrated and used as medicine. Many of them have also been synthesized. For example, physostigmine, the substance that Julian famously synthesized, occurs naturally in the calabar plant.

In addition, the term is also used to describe the most important chemical in a manufactured product. Students can find the active ingredient on product labels. In general, it is important for chemistry students to understand that it is the chemical substances contained in natural or synthetic products that are responsible for the effect produced by the product. It is also important for students to understand the difference between the term "product" and the term "substance." For example, students should understand that caffeine is a chemical substance, and that it is the stimulant effect produced by the product we call coffee.

Corydalis cava—Julian likely reported that the principal alkaloid in *corydalis cava* was *corydaline*, which crystallizes as fine white needles, which melt at 135° C. It is odorless and tasteless in substance, but its alcoholic solution or the solutions of its salts are bitter. It is not soluble in water, but soluble with difficulty in alcohol.

More recent analysis has found the principal alkaloid in *corydalis cava* is bulbocapnine, which inhibits the reflex and motor activities of striated muscle. It has been used in the treatment of muscular tremors and vestibular nystagmus. Ruminants eating such plants suffer neurotoxic effects with agitation, convulsions, and sometimes death.

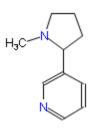
You can discuss several other examples of alkaloid substances that are familiar to students:

Caffeine—Caffeine ($C_8H_{10}N_4O_2$) is the common name for trimethylxanthine (systematic name is 1,3,7-trimethylxanthine or 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione). Caffeine is naturally produced by several plants, including coffee beans, guarana, yerba maté, cacao beans, and tea. For the plants, caffeine acts as a natural pesticide. It paralyzes and kills insects

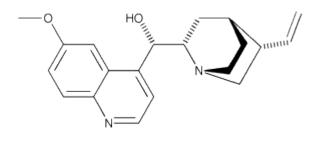
that attempt to feed on the plants. The molecule was first isolated by the German chemist Friedrich Ferdinand Runge in 1819.

When purified, caffeine is an intensely bitter white powder. It is added to colas and other soft drinks to impart a pleasing bitter note. It is also an addictive stimulant. One dose of caffeine ranges from about 75 mg to 250 mg. Tea is another common source of caffeine. Tea contains somewhat less caffeine per serving than coffee. Cola drinks also contain caffeine, about 25-50 mg per serving. "Energy" drinks, like Red Bull, often contain up to 400 mg of caffeine.

Nicotine—Nicotine in its pure form is a liquid alkaloid. Its formula is (C10H14N2) and its molecular weight is 162.23. Its properties include: density = 1.01 g/mL, m.p. = -79° C, b.p. = 247°C. It is hygroscopic. The liquid has a low vapor pressure, but the vapor burns at about 95°C. That means that most of the nicotine in a cigarette burns off, but sufficient amount is inhaled to produce the typical effects. The actual content of nicotine in tobacco can vary from 0.2% to 5%. It was first isolated from the plant in 1828, and it was first synthesized by A. Pictet and Crepieux in 1893.



Quinine—Natural quinine, once a major treatment for malaria, can be extracted from the bark of the Cinchona tree. The bark was ground into a fine powder and then mixed with water or alcohol. In the 1600's, South American Indians used Cinchona bark to treat fever without knowing that quinine was the active ingredient in the bark. By the mid-1600's the bark was being used to treat and prevent malaria. Quinine was not isolated from the bark until the early 1800's, however. In 1944, quinine was first synthesized by Robert Woodward and William Doering. Today it has been replaced by synthetic drugs such as chloroguine and mefloguine in the treatment of malaria.



Quinine structure

More on Soybeans

American farmers were just beginning to grow soybeans as a major crop in to early 1930's at about the time Percy Julian was hired as research director at Glidden. Glidden's research produced new uses for the crop and, in turn, spurred their growth.

Soybeans are grown primarily for their protein content, and secondarily for their oil. These two components make up about 60% of the weight of the bean with the rest being carbohydrate and ash. The oil is removed first, leaving the remaining solid to be processed into various products for human and animal use, including soy flour, soy protein and soy meal.

Extracted from the oil is a chemical called lecithin, a lubricant and emulsifier. The oil also yields vitamin E.



According to the USDA, the table below gives the complete chemical composition of soybeans. This table is another opportunity to discuss the chemicals in a natural product.

Nutrient	Units	Value per 100 grams	Number of Data Points	Std. Error
Proximates				
Water	g	69.05	6	2.776
Energy	kcal	122	0	
Energy	kj	510	0	
Protein	g	13.09	6	8.068
Total lipid (fat)	g	6.70	6	0.492
Ash	g	1.59	6	0.125
Carbohydrate, by difference	g	9.57	0	
Fiber, total dietary	g	1.1	0	
Minerals				
Calcium, Ca	mg	67	8	5.54
Iron, Fe	mg	2.10	8	0.391
Magnesium, Mg	mg	72	8	8.83
Phosphorus, P	mg	164	8	18.788
Potassium, K	mg	484	8	62.983
Sodium, Na	mg	14	8	1.347
Zinc, Zn	mg	1.17	8	0.163
Copper, Cu	mg	0.427	8	0.065
Manganese, Mn	mg	0.702	8	0.08
Selenium, Se	mcg	0.6	0	
Vitamins				
Vitamin C, total ascorbic acid	mg	15.3	8	1.744
Thiamin	mg	0.340	8	0.08
Riboflavin	mg	0.118	8	0.013
Niacin	mg	1.148	8	0.148
Pantothenic acid	mg	0.929	8	0.115
Vitamin B-6	mg	0.176	8	0.017
Folate, total	mcg	172	8	24.234
Folic acid	mcg	0	0	
Folate, food	mcg	172	8	24.234
Folate, DFE	mcg_DFE	172	0	
Vitamin B-12	mcg	0.00	0	
Vitamin A, IU	IU	11	2	
Vitamin A, RAE	mcg_RAE	1	2	
Retinol	mcg	0	0	
Lipids				

Fatty acids, total saturated	g	0.929	0	
14:0	g	0.007	1	
16:0	g	0.674	1	
18:0	g	0.249	1	
Fatty acids, total monounsaturated	g	1.518	0	
16:1 undifferentiated	g	0.013	1	
18:1 undifferentiated	g	1.492	1	
20:1	g	0.013	1	
Fatty acids, total polyunsaturated	g	3.783	0	
18:2 undifferentiated	g	3.338	1	
18:3 undifferentiated	g	0.445	1	
Cholesterol	mg	0	0	
Amino acids				
Tryptophan	g	0.159	0	
Threonine	g	0.503	0	
Isoleucine	g	0.580	0	
Leucine	g	0.938	0	
Lysine	g	0.752	0	
Methionine	g	0.138	0	
Cystine	g	0.157	0	
Phenylalanine	g	0.641	0	
Tyrosine	g	0.477	0	
Valine	g	0.620	0	
Arginine	g	0.905	0	
Histidine	g	0.348	0	
Alanine	g	0.549	0	
Aspartic acid	g	1.774	0	
Glutamic acid	g	1.966	0	
Glycine	g	0.503	0	
Proline	g	0.674	0	
Serine	g	0.651	0	

USDA National Nutrient Database for Standard Reference, Release 19 (2006)

Chemical derived from soybeans are used in many products such as margarine, salad dressings, and cooking oils, animal feeds, breads, cereals and snacks, margarine, salad dressings and cooking oils. For a chart listing many of the soybeans uses, see http://www.soystats.com/2000/useschart.htm

More on Chemical Synthesis

In chemistry, a synthesis is a type of reaction designed to produce a new chemical. In general chemistry courses the term "synthesis reaction" is to label reactions in which two elements combine to form a compound. In a sense all chemical reactions are synthesis

reactions because all chemical reactions have products that are different from the reactants or starting substances. But a synthesis reaction is one that chemists use to produce a specific desired chemical substance, often one that is a complex substance.

If a substance occurs in nature, we call it "natural" or "naturally-occurring." However, if the substance does not occur in nature, it is called a synthetic substance. There are also some chemicals that already exist in nature but are difficult to obtain so chemists might try to synthesize these chemicals too. So we can think about three kinds of chemicals: those that exist naturally and are abundant and readily available, those that exist in nature but are not easily obtained or are too expensive to obtain, and chemicals that do not exist in nature.

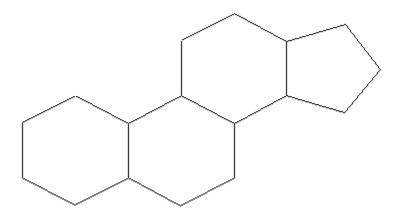
In Percy Julian's lab, for example, he was trying to synthesize physostigmine (or cortisone, etc.). Julian knew that physostigmine, a naturally occurring substance in small quantities, might be used to treat eye diseases like glaucoma and he wanted to synthesize the chemical so it would be widely available. He knew what product he wanted to end up with, and his mission was to find the right substances to start with as well as the best chemical reactions to use. Julian used a series of eleven synthesis reactions to produce the desired chemical product.

But physostigmine exists in nature. It is a natural product. Why would Julian want to synthesize physostigmine if it already existed in nature? Like many chemical substances, physostigmine exists in very small amounts as part of calabar beans. It is difficult to extract the physostigmine from the rest of the bean, and you get only a very small amount for your effort. Getting the substance from nature meant that it was very expensive. If a substance, like physostigmine, might benefit a lot of people, it has to be relatively inexpensive to produce. So, although physostigmine exists in nature, it is only present in the calabar bean in very small amounts and it is difficult to extract. Julian found a way to synthesize it and make it available to help a lot of people.

More on Steroids

The article refers to Julian's work on synthesizing steroids, and many students will associate the term "steroids" with anabolic steroids, simply because they have heard a lot about them. It is important that you take time to educate students about different types of steroids, because the popular press rarely makes the distinction. The term "steroid" is a catch-all term in magazines and newspapers, and students need to understand how the term is used popularly as opposed to how chemists use the term.

Steroids are a class of naturally occurring organic compounds that have the basic skeleton shown below. Most are fat soluble. In this structure there are three cyclohexane rings (six carbon atoms) and a cyclopentane ring. Chemical groups are often substituted, especially at C10 and C13. In the body steroids are derived from cholesterol, which is produced from squalene.



Examples of important steroids that students may already know include Vitamin D, cortisone, cholesterol and estrogen. In many cases the natural steroid compounds are modified and the derived synthetic compounds are used for medicinal purposes, legal or illegal.

Different atoms can be attached to the carbon atoms in the rings to make different steroid compounds, each with different properties. Change an atom here or there and you have turned an illegal performance-enhancing drug into a safe medicine for treating allergies.

Anabolic steroids are synthetic compounds derived from naturally occurring hormones, like testosterone, which are produced in the sex glands. Steroids used to treat allergies and asthma, on the other hand, are called corticosteroids because the natural substances are produced in the upper surface of the adrenal gland. Today both classes of chemicals are produced synthetically for medical use, and are available *legally* only by prescription.

Anabolic steroids enhance male characteristics (androgenic effect) and increase muscle mass (anabolic effect). These are the steroids used illegally by athletes. It is important to note that since anabolic steroids are hormones, they can have significant undesirable side-effects like risk for heart attack and stroke, liver cancer and acne. They can also trigger mood swings, depression and violent behavior. Anabolic steroids are sometimes referred to as androgens.

Percy Julian spent a lot of time tweaking steroids as described above. For example, he turned soybean steroids into cortisone. He also turned steroids from Mexican yams into sex hormones, paving the way for other scientists to invent the birth control pill. Later in his career, he looked into steroids that could be used as liquid crystals, materials that later scientists would use to make the liquid-crystal displays on every cell phone, calculator, and digital watch. In fact, modifying steroids was so important to his company that he put the four rings of the steroid chassis on his business cards and company stationery.

More on Student Research

As the article describes, Julian returned with his Ph.D. in 1932 to DePauw as a Research Fellow. But he was also given the job of directing the lab work of DePauw's graduate and senior research. Julian expanded the research experience at DePauw, and his students' research papers were published in scientific journals, including the *Journal of the American Chemical Society*. In this way Julian provided an opportunity for university students to gain authentic research experience and the prestige of having their work published.

Much of the current research on science education recommends that even high school students be given authentic research experiences in order to learn first-hand how scientists do their work. There is also research that suggests that mentors contribute a great deal to students' career decisions. Using the Julian research example would allow you to incorporate research experiences for some or all of your students, either during class, after school or in the summer. Since class time is tight for many chemistry teachers, you might encourage students to do research for a school or local science fair. The latter two might be in the form of internships at chemistry-related companies in your area.

There are a number of journals that publish students' scientific research. Among them is the National Student Research Center, The Empiricist, and the Sci-Journal, which you can find on this page of resources <u>http://youth.net/nsrc/webs.html#anchor453011</u>. This page also has a list of competitions for student researchers. The Empiricist web site also has ideas for incorporating student research into your classes.

More on Minorities in Chemistry

Julian was the third African American to receive a Ph.D. in chemistry after St. Elmo Brady and Edward M. A. Chandler. **St. Elmo Brady (1884-1966)** St. Elmo Brady was born in 1884 in Louisville, Kentucky. At the age of 20 he left home to attend college at Fisk University in Nashville, Tennessee. At Fisk he was encouraged by his teacher Thomas Talley. When Brady graduated in1908, he took a job teaching at Tuskegee Institute in Alabama. After two years he went back to school, this time at the University of Illinois, where he earned a master's degree in 1914 and his Ph.D. in 1916, the first African-American to earn a Ph. D. in chemistry. Brady headed the chemistry department at Fisk University for 25 years until he retired in1952.

Edward Chandler (1887-) A native of Ocala, Florida, Edward Chandler went north to Washington, DC to attend college at Howard University. After graduation, he went to Clark University in Massachusetts where earned a master's degree. After that he went on to the University of Illinois, where he graduated with his Ph.D. in 1918. This made him the second African-American to earn a Ph.D. in chemistry, only two years after St. Elmo Brady had become the first, also at the University of Illinois. Chandler went on to spend his career working in the chemical industry, mostly inventing new synthetic dyes.

Two other important African-Americans of the time period are:

Ernest Everett Just (1883-1941) Ernest Everett Just was born in Charleston, South Carolina. His father and grandfather both died when Just was four years old. After Just finished elementary school, his mother moved the family north so her children could get better educations than they could have received in the segregated South. They settled in New Hampshire, where Just was a star student in high school, and then graduated with honors from Dartmouth College with a degree in biology in 1907. He went to work at Howard University, but managed to juggle teaching at Howard with doing research at Woods Hole Oceanographic Institute in Massachusetts, and studying for his Ph.D. He earned his doctorate from the University of Chicago in 1916.

Racism was always standing in the way of Just's career, so in 1929 he left the United States to work in Europe. He first worked in Italy, but then moved to Berlin in 1930. He worked at the Kaiser Wilhelm Institute in Berlin until 1933. That year, Adolf Hitler and the Nazis came to power in Germany. To escape the Nazis and their racist policies, Just left Germany and eventually settled in France, working at the University of Paris. He stayed in Paris even after World War II broke out in 1939. When the German army conquered Paris in 1940, Just was captured and held as a prisoner of war for a short time. After he was released to U.S. officials, he returned to Howard University. But by then he was too sick with cancer to teach classes. The cancer claimed Just's life in 1941, a little more than a year after he returned to the U.S.

George Washington Carver (1861-1943) George Washington Carver was a Julian contemporary. He was born a slave in Missouri as the Civil War was breaking out, but he was freed by the Emancipation Proclamation in 1863, and grew up in Arkansas where he and his mother lived on the farm of their former master. He studied agricultural science at Iowa State Agricultural College (Now Iowa State University). He earned his bachelor's degree in 1894 and a master's in 1896.

Around this time Booker T. Washington was founding a new school for African-Americans in Tuskegee, Alabama. Carver went to work at the new Tuskegee Institute. He was mainly interested in using chemistry to find ways to make life better for farmers in southeast Alabama where he lived. So he studied the soil there and found it was perfect for growing peanuts and sweet potatoes. Most farmers in Alabama and the rest of the South grew cotton, which is back-breaking work to pick, and makes soil infertile after a few years. Carver used chemistry to develop new products made from peanuts and sweet potatoes. For more on African-American chemists see <u>http://chemicalheritage.org/scialive/julian/activities/1c.html</u>

You can get a more current view of minorities in science and engineering from the National Science Board's *Science and Engineering Indicators, 2006:*

"With the exception of Asians/Pacific Islanders, racial and ethnic minorities represent only a small proportion of those employed in S&E occupations in the United States. Collectively, blacks, Hispanics, and other ethnic groups (the latter includes American Indians/Alaska Natives) constituted 24% of the total U.S. population, 13% of college graduates, and 10% of the college educated in S&E occupations.

"Although Asians/Pacific Islanders constitute only 5% of the U.S. population, they accounted for 7% of college graduates and 14% of those employed in S&E occupations in 2003. Although 82% of Asians/Pacific Islanders in S&E occupations were foreign born, native-born Asians/Pacific. Islanders are also more likely than their numbers to be employed in S&E." (Page 3-20)

"A longer view of changes in the sex and ethnic composition of the S&E workforce can be achieved by examining data on college-educated individuals in nonacademic S&E occupations from the 1980 Census, the 1990 Census, and the 2000 Census Public-Use Microdata Sample (PUMS) In 2000, the percentage of historically underrepresented groups in S&E occupations remained lower than the percentage of those groups in the total college- educated workforce:

- Women made up 24.7% of the S&E workforce and 48.6% of the college-degreed workforce.
- Blacks made up 6.9% of the S&E workforce and 7.4% of the collegedegreed workforce.
- Hispanics made up 3.2% of the S&E workforce and 4.3% of the college-degreed workforce.
 However, since 1980, share of S&E occupations has more than doubled for blacks (2.6% to 6.9%) and women (11.6% to 24.7%).
 Hispanic representation also increased between 1980 and 2000, albeit at a lower rate (2.0% to 3.2%). The percentage of foreign-born college graduates (including both U.S. and foreign degreed) in S&E jobs increased from 11.2% in 1980 to 19.3% in 2000." (Page 3-19)

More on Patents

Julian invented and patented more than 115 new chemical reactions. In fact, Julian spent most of his career looking for new ways to make compounds that already existed.

What is a patent? Why are patents so important? A patent is a legal document issued by a government. The U.S. government issues patents, and so do the governments of other countries. A patent is given to a person who invents something or a new way of doing something. The patent says that only the inventor can make the invention. It also says only the inventor can sell the invention. A patent is good for 20 years. After those 20 years, anyone can make or sell the invention.

From the ACS publication "What Every Chemist Should Know About Patents," (page 3): "... the following subject matter may be patented in the United States: a process, a machine, a manufacture (i.e., a manufactured product), or a composition of matter. In the chemical and allied fields, a patent may protect any of the following subject matter that falls into at least one of the categories cited above:

- a compound, which may be defined as a class of compounds or as a specific compound or group of specific compounds;
- a composition containing the compound;
- an article made from the compound or containing the compound;
- a process for preparing the compound; or
- a method of using the compound for a specific purpose (e.g., for curing a polymer system or for treating a medical condition)."

Julian's patents include those issued as part of his work at Glidden such as the recovery of sterols, producing vegetable protein, synthesizing a urea-protein complex, producing a waterproofing plastic from soybeans, methods of isolating vegetable protein, using proteins for paints, altering phospholipids to control the viscosity of chocolate, refining vegetable oils, a process for canning soybeans, a process for isolating soya protein and separating sterols from vegetable oils by hydration.

Patents in his later work include preparation of 3-amino-derivatives of steroids, a procedure for the preparation of progesterone, preparation of 17a-hydroxy-steroids, preparation of steroids of the C₁₉ series, preparation of cortisone, and a process for preparing Compound "S."

Connections to Chemistry Concepts

- 1. **Organic Chemistry**—Although this topic is often not covered in an introductory chemistry course, it might be covered by advanced classes or as independent study. Since Julian is an organic chemist, this article provides a point of contact to discuss what organic chemistry is and what organic chemists do. For a discussion of organic chemistry, see http://www.chemheritage.org/scialive/julian/activities/2b.html.
- 2. **Separations and Extractions**—These are two important processes for a natural products chemist, which Julian was. You can stress that most natural products are themselves mixtures, which must be separated into pure substances for them to be useful to chemists. You might connect the article to a discussion of separations or related lab work.
- 3. **Compounds vs. Products**—This is an important distinction for students. As consumers, we tend to think in terms of products, but chemists think in terms of the chemical substances that make up the products, natural or artificial. As an example, see "More on Soybeans", above for the long list of chemicals substances present in soybeans. This kind of discussion will allow you to make the point that "chemistry is everywhere."
- 4. **History**—Obviously this article is about the history of chemistry. It is important for students to understand that modern developments in chemistry are based on discoveries such as Julian's. It is also important for students to consider the interaction between scientists and the societies in which they live and work. Each influences the other.
- 5. **Product Development**—Student often do not have a grasp of where consumer products come from and how they are developed. The products that Julian developed from soybeans are good examples for students to study. You can make the point that chemistry is essential in the development of many consumer products and that chemical substances have many uses in our society.

Possible Student Misconceptions

- "Steroids—They're illegal, aren't they?" The article refers to steroids, and many students will equate that reference with anabolic steroids, simply because they have heard a lot about them, especially in baseball news. It is important that you take time to educate students about different types of steroids, because the popular press rarely makes the distinction. The term "steroid" is a catch-all term in magazines and newspapers, and students need to understand how the term is used popularly as opposed to how chemists use the term. (See "More on Steroids".)
- "Organic—That means 'no pesticides', right?" The term "organic" has come to mean one thing to the general public and something else to chemists. Introductory chemistry students will likely know the public meaning. In this article, however, "organic" refers to a specific branch of chemistry. For a discussion of the term see <u>http://www.chemheritage.org/</u> <u>scialive/julian/activities/2b.html</u>
- 3. "Plants don't contain chemicals...do they?" Unless your students have integrated their knowledge of biology with their chemistry, they will not think about plants as being made up of distinct chemical substances. The fact that Julian isolated many chemicals from plants provides you with an opportunity to discuss this. In the same way, many students also do not distinguish between a product and its ingredients, especially its active ingredients. Also, students often think of mixtures as if they were single substances. So, for example, many students think of milk as a single substance when it is, in fact, a mixture. By using the article to raise the issue of chemical compounds making up both plant systems and many commercial products you can highlight and correct these misconceptions.
- 4. **"We exploded hydrogen and oxygen in class once and made water. That's synthesis, right?"** General chemistry students may have learned several types of chemical reactions, including a general type called "synthesis" reactions (different textbooks may use different language). Used this way, the term "synthesis" has a narrow meaning. In chemistry the process of synthesizing a chemical substance typically involves many steps and requires complex processes. (See "More on Synthesis".)
- 5. "My idea of a scientist is a white guy with weird hair in a lab coat, right?" In the last few years, chemistry textbooks have tried to diversify the chemist role models they present to students. However, most students have the misconception that chemistry is a profession that has always been dominated by white Europeans. It is important to remind students that chemists come from diverse populations, and that currently the globalization of science industries requires that scientists from many countries and backgrounds be able to work together. This article allows you to introduce that discussion with students.

Demonstrations and Lessons

- 1. For a computer simulation of the synthesis process, see <u>http://www.chemheritage.org/scialive/julian/activities/3c.html</u>
- 2. For a computer simulation about identifying a substance by its melting point, see <u>http://www.chemheritage.org/scialive/julian/activities/5c.html</u>
- 3. You can illustrate the extraction process by having students extract the colors from plants (an activity that produces plant dyes). A possible procedure here <u>http://www.thebakken.org/</u>education/SciMathMN/plant-dyes/dyes1.htm or <u>http://www.chymist.com/Natural%20dyes.pdf</u>
- 4. You may be able to set up a lab activity that extracts caffeine from coffee or tea. Possible procedures:

http://departments.oxy.edu/tops/Caffeine/CAFFEINE-T.pdf

http://departments.oxy.edu/tops/Caffeine/caffreallife.htm http://www.everything2.com/index.pl?node_id=663575

- 5. If your students are capable and you have the required equipment and supplies, you could have students synthesize aspirin as an example of a true synthesis in chemistry. For a procedure see: <u>http://www.chemheritage.org/EducationalServices/pharm/asp/asp31.htm</u>
- 6. You can purchase a kit of soy activities for the classroom at <u>http://www.soybeansciencekit.com/lessons.html</u>
- 7. For several activities related to soy beans, including separating oil from protein and hydrolyzing the oil, see https://extension.usu.edu/aitc/teachers/pdf/lesson/spring99 soap.pdf
- 8. For a complete set of classroom activities relate to soybeans, suitable for grades 9-12, see <u>http://www.extension.iastate.edu/Publications/4H970.pdf</u>

Student Projects

1. You can assign each student or group of students different substances and ask them to determine if they are naturally occurring or synthetic. You can assign as many substances as you wish. Give each student or group of students URL's to begin their research. Here are samples:

Rubber http://en.wikipedia.org/wiki/Rubber Plastic http://www.plastics.org/s_plastics/index.asp Aspirin http://www.chemheritage.org/EducationalServices/pharm/asp/asp00.htm Ammonia http://www.bartleby.com/65/am/ammonia.html Cortisone http://www.medterms.com/script/main/art.asp?articlekey=6547 Nylon http://www.chemheritage.org/EducationalServices/nylon/nylon.html Gasoline http://science.howstuffworks.com/oil-refining.htm Sugar http://www.sucrose.com/lref.html Diamonds http://www.amnh.org/exhibitions/diamonds/ Steel http://www.historyforkids.org/learn/science/steel.htm

- You might purchase a copy of the NOVA special "Percy Julian: Forgotten Genius" and have students watch the video. It can be purchased at <u>http://www.pbs.org/wgbh/nova/julian/shop.html</u>. Or, some of your students may have recorded the program when it aired in 2007, and would be willing to share their recording.
- Student can access the DePauw University Archives web page at <u>http://www.depauw.edu/library/archives/percyjulian/chronology.asp</u> and either study original documents in the archive or listen to one of the audio recordings of addresses by Julian.
- 4. You could assign teams of students to research any of the diseases treated by medicines that Julian helped to develop. Alternately, you could assign students to research those medicines.
- 5. Students could be assigned to research the history of soy products and how soy products are in use today.
- 6. Encourage your high school students to follow the student research model developed by Julian at DePauw by entering science fairs, doing chemistry-related research projects and seeking out pre-college student internships.

Anticipating Student Questions

1. "Did Percy Julian really learn how to make the steroids I hear so much about—the ones that are bad for you?" See More on Steroids for a way to respond to this question.

- 2. "I thought racism was only in the South." The article provides several examples of racism outside the southern states. DePauw University in Indiana, for example, had very few African-American students when Julian entered in 1916, and his professors would not grant him a graduate fellowship based on his race. Just prior to his being hired at Glidden, he was denied a job at the Institute of Paper Chemistry in Appleton, Wisconsin, because the town—a sundown town—had a law prohibiting blacks from staying in the town overnight. When Julian moved to the affluent Chicago suburb of Oak Park, his houses was firebombed twice in 1950 and 1951.
- 3. "I thought you could only get a patent for a product or an object? How could Julian patent a chemical reaction?" See More on Patents.
- 4. "I thought segregation was illegal when Julian left DePauw? How could there be an 'African-American serving university' like Fisk?" Prior to the Civil War there were several colleges established to serve African-Americans. Among the earliest were Cheney University and Lincoln University in Pennsylvania. After the Civil War other colleges were established, often by African-Americans, to provide education for former slaves. This network became known as Historically Black Colleges and Universities (HBCU). Among the more well-known HBCU's are Morehouse College, Spelman College, Tuskegee University and Howard University. Julian taught at Fisk and Howard and also West Virginia State, another HBCU. Numerous web sites list all HBCU's.
- 5. **"Is physostigmine still used to treat glaucoma?"** No. Today doctors treat the disease by increasing the flow of aqueous humor out of the eye in order to reduce the intraocular pressure that characterizes glaucoma. Most often prescribed are beta-blocking drugs, alpha-andrenergic drugs, carbonic anhydrase inhibitors and mitotic drugs.

Websites for Additional Information

You can read a complete biography of Percy Julian, along with classroom activities illustrating his work, on the Chemical Heritage Foundation website at http://www.chemheritage.org/scialive/julian/teachers/narrative.html.

ACS Chemical Landmarks, see <u>http://acswebcontent.acs.org/landmarks/</u> and click on the "Medical Miracles" tab.

View the PBS NOVA website "Percy Julian: Forgotten Genius" <u>http://www.pbs.org/wgbh/nova/julian/</u>.

View the DePauw University Archives website on Julian at <u>http://www.depauw.edu/library/archives/percyjulian/chronology.asp</u> The site includes audio recordings of speeches given by Julian.

For an ACS publication on chemical patents, see http://www.chemistry.org/portal/resources/ACS/ACSContent/government/publications/Chem_patent2001.pdf

US Patent Office http://www.uspto.gov/

For a history of the Glidden Company, see <u>http://www.fundinguniverse.com/company-histories/The-Glidden-Company-Company-History.html</u>.

Your students can read another biographical memoir of Julian from the National Academy of Sciences series, by Bernhard Witkop, a long-time Julian associate <u>http://www.nap.edu/html/biomems/pjulian.html</u>.

For an online book on the chemistry and uses of soybeans see <u>http://books.google.com/books?</u> <u>id=Plmi4WfHos4C&dq=soybeans&printsec=frontcover&source=web&ots=Klims5EMyz&sig=w7I</u> DDbF7d5tj-MGOcCAs-akJe1s#PPP1,M1.

With soybeans moving into the biotechnology arena, there are many resources for you to use. One that presents both sides of the issues is <u>http://www.soybean.com/bseries.htm</u>.

The National Soybean Research Laboratory has many resources at <u>http://www.nsrl.uiuc.edu/aboutsoy/</u>.

General Web References

http://www.chemistry.org/portal/a/c/s/1/feature_tea.html? id=0207696a175c11d6e5ca4fd8fe800100

http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=minorityaffairs %5Cscholars.html

Tantalum, Congo, and Your Cell Phone

Background Information

More on the History of Democratic Republic of Congo

The so-called "coltan wars" were not the first time Congo's natural wealth has been its undoing. Sadly, this scenario has become a recurring theme in Congolese history. The first time it played out was in the late 1800s. While the western Atlantic coastal region of what is now the Democratic Republic of Congo was a source of captives for Portuguese slave traders as early as the 1500s, the region's climate, dense forests, and tropical diseases kept Europeans from colonizing Congo until the late 1800s. In 1885 King Leopold II of Belgium claimed Congo, not as a colony of Belgium, but as his own personal property. Leopold's rule was rapacious, even genocidal. He extracted wealth from Congo in the form of elephant ivory and rubber, paying little to anyone in Congo for these products. What's worse, enslaved Congolese men were forced to harvest the ivory and rubber. Working conditions were so brutal, and so many laborers died, that the country's population is thought to have dropped by half during Leopold's rule.

When the Belgian government took over administration of Congo from the king in 1908, conditions improved somewhat. Colonial rule was rather uneventful until Congo became independent in 1960. The new Congolese government was democratic but unstable, with civil war breaking out almost immediately. After a complicated power struggle, Joseph Mobutu came to power in a coup in 1965. He would rule the country as a dictator for 32 years.

A few years after coming to power, Mobutu changed his own name to Mobutu Sese Seko, and the name of his country to Zaire. Mobutu was the archetype of the rapacious thirdworld dictator, and the word "kleptocracy" may actually have been coined specifically to describe his rule. He let western mining companies extract Congo's mineral wealth for nearly nothing, asking only that they pay him personally enough to make himself incredibly wealthy. His opposition to communism and Soviet-allied states in Africa, like Angola, earned him U.S. support. All the while, Mobutu neglected the needs of his own people. Living conditions and infrastructure were allowed to deteriorate severely.

More on the Congolese Civil War

After the fall of the Soviet Union, the U.S. had little need to continue backing a megalomaniac like Mobutu. Without U.S. support, Mobutu lost his grip on power. In 1994, Rwandan army forces invaded eastern Zaire to flush out Hutu militia groups which had taken part in the Rwandan genocide against that country's ethnic Tutsis. Other nations entered the fray, either with their own troops or by supporting Congolese rebel armies. Finally, Mobutu was overthrown in 1997 by a rebel army led by Laurent Kabila. Zaire became Congo once again.

The regime change was very much a case of "meet the new boss, same as the old boss." As president, Kabila turned out to be as self-serving as Mobutu had been. What's more, many of Congo's neighbors had occupied parts of the country and were smuggling out mineral wealth, including coltan. Other parts of the country were controlled by rebel groups, some home-grown like the Mai Mai of eastern Congo, while others were supported by foreigners, like the Rwandan-backed Congolese Rally for Democracy or the Ugandan-backed Movement for the Liberation of Congo. These various groups fought each other for territory and control of mineral resources in a bloody civil war that claimed millions of lives.

Kabila had resisted any attempts at peace negotiation, but in 2001 he was assassinated by one of his own bodyguards. His son Joseph Kabila was named president. The younger

Kabila proved much more amenable to negotiations. A series of talks was orchestrated in large part by South African president Thabo Mbeki. In 2002, an agreement was reached to end the civil war. The nations of Angola, Zimbabwe, Uganda, and Rwanda agreed to withdraw their armies from Congo.

Even so, fighting simmered between Congolese rebel factions. Rwanda even reinvaded Congo in 2003, claiming to be chasing Hutu militias again. While such militias were ravaging eastern Congo, it is thought that the Rwandans were more interested in stealing coltan. In fact, the Rwandans did mine and smuggle coltan out of Congo in the areas they occupied, and were even reported to have been using prisoners as slave labor to mine coltan. Rwanda was soon forced to withdraw its armies under international pressure.

Joseph Kabila became a proper and elected president in 2006, but his government has not yet gained full control over the entire nation. As recently as July 2007, a faction of the Congolese army was in rebellion against the central government. An important aspect of this lack of stability is that coltan-mining, which is very important to the Congolese economy, has yet to resume. Unofficial boycotts of Congolese coltan remain in effect as long as there is no way to guarantee it is being mined in a manner that is fair to the Congolese people, and in a way that doesn't fan the remaining embers of the country's civil war. At the time of writing, Congo remains what it has long been: a nation devastated by its own natural wealth.

More on Tantalum

Tantalum is a transition metal, falling in the same group as vanadium in the periodic table. It has a very high melting point of 3017°C. Tantalum is nearly chemically inert aside from the oxidation that gives it the thin oxide coating that makes it valuable for use in capacitors. Hydrogen fluoride, acidic solutions containing fluoride ions, and sulfur trioxide are the only other agents that will react with tantalum, and even these agents only react at temperatures above 150°C.

Tantalum normally forms only one oxidation state, +5, which makes it unusual among transition metals. (Vanadium, for example, has oxidation states of +2, +3, +4, and +5.) However, tantalum compounds with tantalum in the +2 and +4 have been prepared.

Tantalum is a trace element, about as abundant as uranium in the earth's crust. However, unlike many trace elements, tantalum is not hard to get out of the ground. In Congo, the ore can often be found within feet of the surface, and separating the coltan is a simple matter because it is so much denser than the other materials it is found in. A Congolese miner with a shovel, a pick-ax, and a bucket can simply shovel the muddy ore out of the ground, and separate out the coltan by flushing the ore with lots of water.

Isolating tantalum from coltan is another matter entirely. The process is intensive in terms of energy needed and the reagents used. Part of the difficulty arises because coltan itself is difficult to decompose, and part of the difficulty arises from the fact that coltan contains both niobium and tantalum, and the two metals are hard to separate from each other.

In the refining process, coltan is first melted with alkali, and the resulting melt is treated with hydrofluoric acid. The result is a solution of niobium and tantalum salts. This solution is treated with methyl isobutyl ketone, which extracts the tantalum salts, leaving the niobium salts behind. The tantalum salts are then converted to tantalum oxide, which is then reduced with sodium or carbon to yield elemental tantalum metal.

Electrolytic methods are also used to isolate tantalum, but are not as commonly employed

Tantalum was first discovered in 1802 by Anders Ekeberg of Sweden. He gave the element its name because of the difficulty he had dissolving its oxide, a challenge he considered "tantalizing." For many years it was thought that tantalum and niobium (also called "columbium") were the same metal. In 1844 German chemist Heinrich Rose showed that tantalic acid and niobic acid were two distinct substances. This and similar studies on other analogous niobium and tantalum compounds established and therefore their parent metals were

distinct elements. It was Rose who gave the name "niobium " to the tantalum's companion metal, after Niobe, the daughter of Tantalus in Greek mythology. Pure tantalum was not isolated until 1903, by the Russian chemist Werner Bolton.

More on Capacitors

Capacitors in real electronic devices rarely look like the idealized schematic shown in the student article. The two plates are usually separated by a solid dielectric, often made of paper. The three-layered sandwich of anode, cathode, and dielectric is usually rolled up like a scroll, which is why the capacitors you might see inside a radio are cylindrical in shape. The ability of a capacitor to store electrical charge can be enormous. The capacitors inside a television set can store enough charge to electrocute a person, even when the TV isn't plugged in. Some uses for capacitors include protecting electrical circuitry from power surges, and storing computer data during lapses in electrical power.

Connections to Chemistry Concepts

- 1. **Oxidation**—Tantalum is good for making cell phone capacitors because of the thin layer of Ta2O5 that forms on any tantalum surface exposed to air. Similar oxidation is seen in everyday life in the behavior of aluminum, which also oxidizes easily, resulting in a thin oxide coating of any aluminum object that has been exposed to the air.
- 2. **Elements and Compounds**—Tantalum is found in nature as coltan, a complex oxide of tantalum, niobium, iron, and manganese.
- 3. **Electrolysis**—The refining of tantalum involves the electrolysis of complex fluorides of tantalum to produce the free element, which of course quickly oxidizes to form Ta₂O₅.
- 4. **Reduction**—Ta₂O₅ must be reduced to tantalum metal before it can be used to make cell phone capacitors.
- 5. **Transition Metals**—Tantalum is a *d*-block element, in the same group as vanadium. However, unlike many transition metals, tantalum has only one common oxidation state, 5+.
- 6. **The Periodic Table**—The related tantalum and niobium ores tantalite and columbite are usually found mixed together as coltan. Separating them is difficult because the two ores have very similar properties. This is because tantalum and niobium have very similar properties, being in the same column of the periodic table. In fact, the two were once thought to be a single element.
- 7. **Integrated Chemistry and Physics (IPC)**—The discussion of capacitors can involve a lot more physics than might be necessary in a traditional chemistry class, but in an IPC class the physics of capacitors could be explored more fully.

Possible Student Misconceptions

- 1. **"Tantalum metal is found in the ground in Congo."** In fact, tantalum compounds are found in Congo's soil, which must be chemically decomposed to produce elemental tantalum metal.
- 2. "A charged capacitor contains more electrons than an uncharged capacitor." When we charge a capacitor, all we do is move electrons from one metal plate in the capacitor to the other. The build-up of electrons on one plate is offset by the deficiency of electrons on the other. For this reason, some educators have expressed dissatisfaction with the normal way of describing capacitors as "storing charge" and prefer to speak of capacitors as storing energy.

- 3. **"Tantalum does not conduct electricity."** Tantalum metal conducts electricity very well. It is only the oxide coating, that is, tantalum(V) oxide, which does not conduct electricity.
- 4. **"Metals like aluminum and tantalum do not corrode."** Aluminum (and tantalum) appear stable to oxidation or other forms of corrosion. In fact, these metals corrode very readily. Aluminum oxidizes almost instantly when exposed to the air. However, the thin layer of aluminum oxide that forms on the surface of a piece of aluminum seals the metal inside from the air, protecting it from further oxidation. The same holds true for tantalum.

Demonstrations and Lessons

- Isolation of a metal by electrolysis—Electrolysis isn't the most common method for isolating tantalum, but it is used some. Tin can be isolated from SnCl₂ using the current of 9-volt batteries. A procedure is found in "Overhead Projector Demonstrations," *Journal of Chemical Education*, October 1987, vol. 64, no. 10, pp. 891–2. <u>http://jchemed.chem.wisc.edu/journal/Issues/1987/Oct/jceSubscriber/JCE1987p0891_2.pdf</u> (A subscription is required to view content online.)
- 2. **Capacitor charging and discharging**—For a general chemistry class, you might not need to demonstrate anything more than the ability of capacitors to store and release energy. The short video <u>Capacitor Charging and Discharging</u> from YouTube demonstrates this behavior of capacitors: <u>http://www.youtube.com/watch?v=OfL3QWJSCu0</u>
- 3. Leyden jar demonstrations—A Leyden jar is a very simple kind of capacitor, one that Benjamin Franklin used in many experiments. Homemade Leyden jars can be used to demonstrate some simple principles of capacitors, such as charging and discharging. A website with instructions for carrying out Leyden jar demonstrations is "Getting a Charge Out of Electrostatics," created by Donald Simanek at Lock Haven University of Pennsylvania.

http://www.lhup.edu/~dsimanek/scenario/e-stat.htm

4. **Other capacitor demonstrations**—The website "University of Washington Physics Department Lecture Demonstrations" gives short descriptions of several demonstrations involving capacitors on the page "Electrostatics." Complete procedures can be obtained by contacting the site's creators, at the e-mail address given on the page. These demonstrations might be especially useful for teaching integrated chemistry and physics (IPC).

http://www.phys.washington.edu/facilities/lectdemo/e_static.html

Student Projects

- Metal source reports—Assign each student a different metal and ask them to research and find out the chemical nature of the metal's ores, where geographically the ores are found, and how the ores are refined into metal. You may choose to ask your students to pay special attention to any issues of geopolitics or economics that relate to their assigned metal. (For example, you may ask the student assigned aluminum to consider why Jamaica is such a poor country despite producing most of the world's bauxite aluminum ore.) You may ask your students to present their findings as a written paper, a class presentation, a poster, or in some other medium.
- 2. **Other chemistry in cell phones**—Students could be assigned research projects on other aspects of the chemistry that goes on inside a cell phone. Other ideas: Working as individuals or in groups, students could research topics such as how lithium batteries work,

or how liquid crystal displays work. Again, you may choose to have your students present the results of their research as written reports, class presentations, or in some other format.

3. **Tantalum alternatives**—Students could research alternative technologies to tantalum capacitors, and report on their relative strengths and weaknesses.

Anticipating Student Questions

- 1. "Why can't we use some other metal other than tantalum to make cell phone capacitors?" Capacitors made from other metals would work just fine in cell phones, but they would be larger than tantalum capacitors. This means cell phones would be larger if they used some other metal in their capacitors. Tantalum capacitors can be made as small as they are because the oxide layer on the surface of a piece of tantalum is so thin, allowing the capacitor plates to be closer together than in any other metal, which in turn allows a tantalum capacitor to store more energy for its size than capacitors made of other metals.
- 2. **"How can I know if my cell phone contains Congolese tantalum?"** Since the industry boycott of Congolese coltan went into effect in the early part of this decade, unless your phone is very old, it is very unlikely that it contains tantalum from Congo.
- 3. "What keeps the electrons from jumping across the gap between the plates in a capacitor to complete the circuit?" In most capacitors, the dielectric keeps the electrons from jumping the gap. An electric current is the flow of electrons. A material that doesn't conduct electricity is a material that electrons have a hard time flowing through. So placing a material that does not conduct electricity (i.e. a dielectric) between the plates of the capacitor keeps the electrons from jumping the gap. If only air or a vacuum were between the plates, electrons could jump the gap if enough electrons were to build up on the negative plate. This would result in a big electrical spark.
- 4. **"Can a capacitor be used as a battery?"** A capacitor does act like a battery in that it provides electrical energy for doing useful work like lighting a camera flash, for example. However, capacitors usually discharge pretty quickly, so they aren't good for providing sustained electrical current over a long period of time. Capacitors wouldn't work very well for powering a flashlight, for example.

References

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"Tantalum", <u>Encyclopædia Britannica</u>. 2007. Encyclopædia Britannica Online. 13 Aug. 2007 <u>http://search.eb.com/eb/article-9071207</u>

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Traub, James, "The Congo Case," New York Times Magazine, July 3, 2005, p. 35

"Rwanda Denies Using Forced Labour," BBC News Online, March 22, 2001. This news story is concerned with reports that Rwandan army units were using Rwandan convicts as slave laborers in Congolese territory controlled by the Rwandan military during the Congolese civil war. <u>http://news.bbc.co.uk/2/hi/africa/1235293.stm</u>

Adam Hochschild, "The World; Chaos in Congo Suits Many Parties Just Fine," *New York Times*, April 20, 2003, Sec. 4 p. 3. This news story describes how certain parties benefited from the chaos in Congo because it made it easier to steal Congolese mineral wealth and other resources.

Websites for Additional Information

More sites on Coltan and Tantalum

Tantalum—This site provides all the basics on the element and its properties, from WebElements. http://www.webelements.com/webelements/elements/text/Ta/key.html

Tantalum Recovery by Liquid-Liquid Extraction—Alexander, Guy B. *Journal of Chemical Education*, March 1969, vol. 4, no. 3, p. 157. This article describes a commonly-used industrial procedure for refining tantalum metal from coltan ore. <u>http://www.jce.divched.org/Journal/Issues/1969/Mar/jceSubscriber/JCE1969p0157.pdf</u> (A subscription is required to view content online.)

Tantalum - Raw Materials and Processing—from the Tantalum-Niobium International Study Center. This site describes the sources and processing of coltan ores into tantalum metal.

http://www.tanb.org/tantalum1.html

More sites on Congo and the Congolese Civil War

Congo's Tragedy: The War the World Forgot—from Britain's *The Independent* newspaper. This story provides an in-depth account of the Congolese civil war. <u>http://news.independent.co.uk/world/africa/article362215.ece</u>

Congo, Democratic Republic of—CIA World Factbook. This site gives current facts and figures on Congo. https://www.cia.gov/cia/publications/factbook/geos/cg.html

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Coltan Mining in the Democratic Republic of Congo: How Tantalum-Using Industries Can Commit to the Reconstruction of the DRC—2003 report from Flora and Fauna International. This in-depth report describes how Congo's mineral resources can be exploited in a way which would benefit the Congolese people. <u>http://www.gesi.org/docs/FFI%20Coltan%20report.pdf</u>

More sites on Capacitors

How Capacitors Work—from HowStuffWorks. This site gives several pages of detailed but easy-to-follow descriptions of the inner workings of capacitors. <u>http://electronics.howstuffworks.com/capacitor.htm</u>

Capacitors—created by Tony van Roon, hosted by the University of Guelph. This site not only gives detailed nuts-and-bolts information about how real capacitors work, but also gives a historical perspective with lots of information on Leyden jars, a very early form of capacitor that was used extensively by Benjamin Franklin, among others. <u>http://www.uoguelph.ca/~antoon/gadgets/caps/caps.html</u>

Capacitor—from Basic Car Audio Electronics. This site provides background information on capacitors in general, as well as practical information about their use in audio electronic applications.

http://www.bcae1.com/capacitr.htm

More sites on Cell Phones

How Cell Phones Work—from HowStuffWorks. This site describes not only how the cell phone itself works, but also the cellular technology which allows millions of phone conversations to be carried on at any given moment using only a few microwave radio frequencies. http://electronics.howstuffworks.com/cell-phone.htm