**How do you make soap?**

**People have been making soap for at least 5000 years. A soap recipe was found on a Mesopotamian clay tablet dating from 2200 BCE. It is likely that the first soaps were made by accident when a cooking oil was dropped into ashes from a cooking fire. Since wood ashes are high in potassium hydroxide (potash), the strong base reacted with the fat (a triglyceride) to make a substance that would clean by encapsulating dirt. Soap was known across the ancient world, from the ancient Greeks, to Germanic tribes, and the Arabian peninsula. The word “soap” is derived from the Celtic “saipo,” and the Roman word “sapo.” What are the chemical components of soap? How is it made? What variables cause what outcomes in the final soap? You will explore the chemistry of soap, and link its properties to that of polymers.**

**Learning Objectives**: Upon completion of this exercise, you should be able to:

1. Identify the major functional groups found in soap and soapmaking
2. Explain how soap works at the molecular level
3. Draw balanced chemical reactions for the soapmaking process
4. Calculate various metrics for soap and relate them to the soap’s properties
5. Compare different ways of calculating the molecular weight of soap and polymers

**Terms You Should Know:** saponification, organic functional groups, molecular weight calculations, polymers

**Background Reading**: Atkins, Jones, & Laverman, Chapter 19, Sections 19.1, 19.2, 19.3, 19.5, 19.6; Chapter 20, Sections 20.2, 20.6, 20.7, Toolbox 20.1, 20.9, 20.10; Chapter 10, section 10.9,

Figure 3.9

**After Completing this Exercise, Textbook Problems You Should be Able to Answer**:

19.7, 19.9, 19.15, 19.29, 19.36, 19.39, 20.7, 20.19, 20.20, 20.29

**Assignments Related to this Unit**

**For Wednesday, November 4:**

Read this document.

 a) Verify that the two soaps made in class are overfatted. Turn in your work, clearly demonstrating how you arrived at your answer, at the beginning of the next class. The molecular weight to use for coconut oil and canola oils are 698 g/mol and 932 g/mol respectively. The recipe used 313 g of each oil, and 39.0 g (canola) or 53.0 g (coconut) of NaOH.

 b) draw a picture or cartoon that explains how soap works at the molecular level. Include several sentences of description.

All **exercises** in the text below are also copied on the last page. Feel free to word process your answers or print and then write them out on the page. Your answers will be due at the end of class. Work in teams of 3-5 students.

**Background Information**

*Organic nomenclature review.*

Organic chemistry is the chemistry of the carbon carbon bond. No other element binds to itself in as many different arrangement as carbon. As such, organic chemists use a shorthand notation to make it easier to see the overall structure. Butane, C4H10, is a linear hydrocarbon with the Lewis structure. However, carbon, with a steric number of 4, is tetrahedral, so a better representation of the structure is . Organic chemists do not write out all the hydrogen atoms in the Lewis structure because there are so many, and also do not indicate carbon atoms but instead use the vertices of a line drawing to indicate carbons. So, an organic chemist would write butane as . This is a much simpler drawing, but you have to remember that each carbon (a vertex or endpoint of the line) has 4 bonds, and if the atom is not listed, it is a hydrogen. Also, note that butane is considered a “straight chain” alkyl, even though it is not linear. Isobutane is a “branched chain” alkyl ; it has the same chemical formula but a different structure. You can also form rings to form cycloalkanes.

Common names are based on the carbon number as follows: 1 = methyl, 2 = ethyl, 3 = propyl, 4 = butyl, 5 = pentyl, 6 = hexyl, 7 = septyl, 8 = octyl, 9 = nonyl, 10 = decyl, 11 = undecyl, and 12 = dodecyl. The parent hydrocarbon, one with no other atoms attached, will have the –ane ending, as in methane, ethane, or propane. Many names are common names and do not follow this pattern! A generic alkyl group is called an “R” group, while a generic alkane would be RH.

One other class of organic molecules is an alkene. This is a species that contains a carbon-carbon double bond, C=C. The steric number about a carbon atom in such a structure is 3, and the structure will be trigonal planar. An example of an alkene is butene . This is actually 1-butene, because the C=C bond is at the end. The structure of 2-butene is . Remember that you can calculate the degree of unsaturation of an organic molecule by counting the number of carbons and hydrogens; a ring is a possible degree of unsaturation.

**Exercise 1: a) Draw all of the isomers of C5H12.**

**b) draw all of the isomers of C5H10.**

*Functional groups.*

Although organic chemistry is mostly concerned with C-C bonds, heteroatoms play an important role in organic chemistry. Heteroatoms are always drawn out, as are hydrogens attached to them. Organic nomenclature is a vast and complicated field. For soap making, we need to know about alcohols, carboxylic acids, and esters. One of the possible four carbon alcohols is 1-butanol , which is a solvent and fuel; the –ol ending indicates that it is an alcohol. The four vertices of the alkyl group remain, and an OH group is added to the end. Other common alcohols include the two-carbon ethanol (drinking alcohol)  and the 3-carbon isopropanol , found in hand sanitizer.

Carboxylic acids have the ending –oic acid, so butanoic acid would be . This is a four carbon “straight chain,” but the terminal carbon has a =O and a -OH group on it. Since that carbon has used up its four bonds (one to carbon, 2 to the =O and 1 to the –O), it has no hydrogens attached to it. The deprotonated form would have an –oate ending, as in sodium butanoate.

Esters are formed from the combination of an alcohol and a carboxylic acid. They are named according to the name of the alcohol group and the name of the carboxylic acid. Esters are often fragrant; the major odor component of banana is isoamyl acetate (3-methylbut-1-yl ethanoate would be the name but the 3-methylbut-1-yl group has a common name of isoamyl and ethanoate has a common name of acetate as in acetic acid) . Ethyl acetate, , is a common solvent used in laboratories and nail polish remover.

The esters found in fats are called triglycerides. They are the triply esterified version of glycerol (a 3-carbon tri-alcohol). These naturally occurring substances are found in cell membranes and of course in fat deposits in your body. They are natures method of segregating cells and storing energy (fuel).

**Exercise 2:**

**Draw the following molecules: butyl propanoate, propyl butanoate, heptanol, dodecanoic acid**

*The chemical reactions of soap.*

The chemical reaction that occurs between a fat (a triglyceride) and NaOH (saponification) is as follows:



In consumer soapmaking, the soap is overfatted. This means that the NaOH is the limiting reagent, and an excess of fat is used. This prevents the caustic lye from coming into contact with skin, and this practice also allows the soap to leave behind oils to keep your skin soft. Different oils have different structures (different numbers of carbons and double bonds) and these can significantly affect the properties of the soap.

When ash leftover from burning wood is extracted with water, the main soluble species is potassium carbonate (K2CO3). When calcium oxide (CaO, quicklime), is dissolved in water, it is converted into “slaked lime,” otherwise known as calcium hydroxide (Ca(OH)2). Slaked lime reacts with the wood ash extract to form insoluble calcium carbonate, leaving soluble potassium hydroxide (KOH).

**Exercise 3: Draw balanced chemical reactions for the conversion of wood ash extract to KOH.**

**a) dissolving potassium carbonate**

**b) dissolving quicklime**

**c) reaction of slaked lime with wood ash extract**

KOH reacts exactly the same as NaOH in the saponification reaction, but the properties of the soap differ due to the larger size of K+ relative to Na+. For example, liquid soaps are made with potassium instead of sodium. Of course, modern soapmakers have access to both chemicals in high purity, allowing control over soap properties.

Oil components

Common cooking oils, such as corn, canola, coconut, and olive oil, are not pure compounds. They are extracted from their respective plants using a solvent, and removal of the solvent leaves behind the oil. Scientists use a similar extraction of plant oils from oranges using liquid carbon dioxide. The following figure lists some of the structural variety of the carboxylic acid groups found in natural fats. Most of the carboxylic acids are alkanes, though there are a few alkenes. Note that all naturally occurring double bonds in fats are “*cis”* double bonds, which means that the alkyl groups on either side of the double bond are both coming off of the same side. Some synthetic fats are hydrogenated (such as those found in margarine) and imperfect hydrogenation can lead to incorporation of “*trans*” double bonds which can not be processed by the body and therefore can lead to health problems.

**Exercise 4:**

**Why is canola oil a liquid at room temperature while coconut oil is a solid?**



Octanoic acid: C8H18O2

Lauric acid: C12H24O2

Myrstic acid: C14H28O2

Palmitic acid: C16H32O2

Linoleic acid: C18H32O2

Oleic acid: C18H34O2

Ricinoleic acid: C18H34O3

Stearic acid: C18H36O

Natural oil components:

***Canola Oil (wt %)***

*Oleic 61%*

*Linoleic 32%*

*Palmitic 4%*

*Stearic 3%*

***Coconut Oil (wt %)***

*Lauric 50%*

*Myristic 16%*

*Palmitic 9.5%*

*Octanoic 15%*

*Oleic 9.5%*

***Olive Oil (wt %)***

*Oleic 75%*

*Palmitic 13%*

*Linoleic 10%*

*Stearic 2%*

Iodine number in soaps with alkenes

Another metric that is often considered in soapmaking is the **Iodine Index.** Simply stated, *the lower* *the Iodine Index number, the harder the bar of soap.* It has to do with the degree of unsaturation (the number of double bonds). It is expressed as mass of iodine (grams) that reacts with 100 g of the oil. We saw bromonation of alkenes previously in this course.

In a typical procedure, the fatty acid is treated with an excess of a solution of iodine monobromide (IBr) or iodine monochloride (ICl) in acetic acid. These are more reactive forms of iodine. Leftover unreacted iodine monobromide (or monochloride) is then allowed to react with potassium iodide, converting it to elemental iodine, whose concentration can be determined by titration with sodium thiosulfate. The net reaction then, shown for *cis*-2-pentenoic acid, is:

**Exercise 5:**

**a) Why would a bar of soap with a lower iodine index be harder?**

**b) Calculate the iodine number for canola, coconut, or olive oil. (only 1!)**

Molecular weight

What is the molecular weight of olive oil? Is that even an askable question? When we ask you to calculate the molecular weight of a substance, it has been of a pure substance. Olive oil is not a pure substance, so technically it does not have a molecular weight. However, it is made up of various components, each of which does have a molecular weight. We should be able to calculate some sort of average molecular weight.

Another field where molecular weights are tricky to define is in polymers. Polyethylene, polypropylene and polystyrene are three very common polymers made on a huge scale industrially. However, due to the way they are synthesized, each polymer chain does not have the exact same structure. One molecule might have 10,154 repeat units, while another might have 10,275. Polymer chemists have developed many methods for determining the molecular weight of a polymer.

The Number Average Molecular Weight, *Mn*

The number average molecular weight is not too difficult to understand. It is just the total weight of all the oil molecules in a sample, divided by the total number of oil molecules in a sample.

 Find total weight of each type of oil (NiMi)

 Total number of molecules (Ni)

 Mn = Total molecular weight of sample divided by number of molecules in the sample

 = (NiMi)/(Ni)

The Weight Average Molecular Weight, *Mw*

The weight average is a little more complicated. It's based on the fact that a bigger molecule contains more of the total mass of the oil sample than the smaller molecules do.

 First find the Weight Fraction of each type of molecule.

 Weight fraction of one type of molecule is weight of one type of molecule divided by total weight (WFi = NiMi/NiMi)

 The weight of that fraction is the weight fraction times the molecular weight of that component (Wi = (NiMi/NiMi)\*Mi = NiMi2/NiMi)

 The weight average is then the sum of all Wi values

**Exercise:**

**Lets do a simple example to show how these two calculations differ. What is the “average population” of the following four cities? What is the weighted average population?**

**To determine the weighted average, consider the fraction of people who live in each particular city as the ‘weight fraction’, and the population as the ‘molecular weight.’ This calculation highlights the difference between what the “average city” is, versus what the “average person” experiences. Explain that difference in a few sentences.**

city population

A 750,000

B 65,000

C 25,000

D 10,000

**In a similar manner, calculate the molecular weight of canola, olive, or coconut oil. Each team will calculate the number average of one oil, and the weight average of a second oil. You will compare your results to the rest of the class.**

Polymers

Distribution of molecular weights in a polymer sample (polyethylene, polypropylene, polystyrene) are expressed as the polydispersity index (PDI). Lower PDIs means a more uniform polymer. PDIs are always greater than 1; the Mw is always greater than the Mn.

In real life, molecular weights are often determined by osmometry, light scattering, sedimentation, viscosimetry, gel permeation (size exclusion) chromatography. Some of these techniques give Mw values directly, while others give Mn values directly. Neither is a *perfect* measure of the molecular weight, but each give a different characterization of the molecular weight distribution.

For more information about polymers and molecular weights, please see these websites:

http://www.chem.tamu.edu/class/majors/tutorialnotefiles/polymer.htm

<http://pslc.ws/macrog/average.htm>

<https://en.wikipedia.org/wiki/Molar_mass_distribution>

Members of your team (write legibly; work in teams of 3-5 students)

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Exercises:

1a) Draw all of the isomers of C5H12.

1b) draw all of the isomers of C5H10.

2) Draw the following molecules: butyl propanoate, propyl butanoate, heptanol, dodecanoic acid

3) Draw balanced chemical reactions for the conversion of wood ash extract to KOH.

a) dissolving potassium carbonate

b) dissolving quicklime

c) reaction of slaked lime with wood ash extract

4) Why is canola oil a liquid at room temperature while coconut oil is a solid?

5a) Why would a bar of soap with a lower iodine index be harder?

5b) Calculate iodine number for canola, coconut, or olive oil. (only 1!)

6a) Lets do a simple example to show how these two calculations differ. What is the “average population” of the following four cities? What is the weighted average population?

To determine the weighted average, consider the fraction of people who live in each particular city as the ‘weight fraction’, and the population as the ‘molecular weight.’ This calculation highlights the difference between what the “average city” is, versus what the “average person” experiences. Explain that difference in a few sentences.

city population

A 750,000

B 65,000

C 25,000

D 10,000

6b) In a similar manner, calculate the “MW” of canola, olive, and coconut oil. Each team will calculate the number average of one oil, and the weight average of a second oil. You will compare your results to the rest of the class.