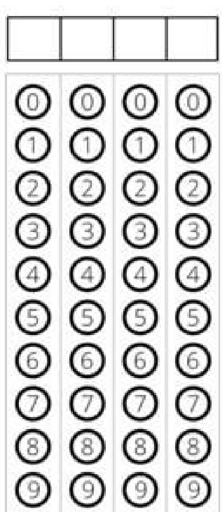
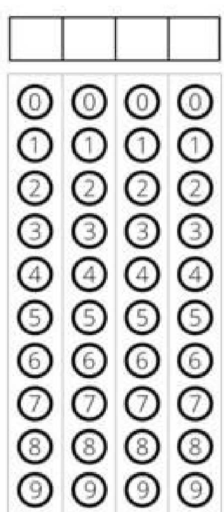
CHEMISTRY OF COOKING

WUCT 2018

A group of two students will work together on this exam. Many cooking techniques rely on chemistry in order to transform basic ingredients into delicious food. This exam will explore the reactions that food undergoes when it is being produced as well as the chemical properties of food itself. While the ability to cook will not be required to successfully complete this exam, we would love to hear any recipes you may have. Cheating will NOT be tolerated.

Student 1 ID	Student 2 ID
	

Team: ______________________________

Team ID: ___________________________

Student 1: __________________________

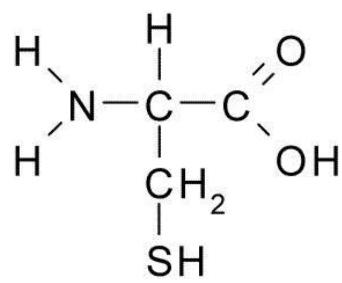
Student 2: __________________________

COOKING

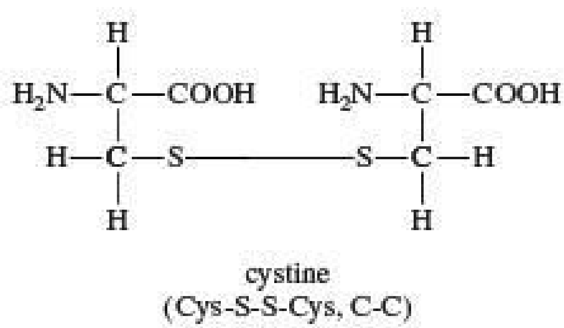
Question 1

To make the simplest of breads, one only needs four main ingredients: flour, water, yeast, and salt. The processes that lead to the production of bread, however, can be quite interesting.

a. One such process is the formation of gluten from the proteins glutenin and gliadin. When flour is mixed with water, glutenin and gliadin proteins dissolve and bond together due to strong bonding between the sulfur atoms on the cysteine amino acid (shown below) that is present in each of the two proteins.



i. (3 points) Using the chemical structure of the cysteine amino acid above, draw how two of these molecules would bond.



ii. (1 point) The strong disulfide interactions in gluten are what give dough its elastic and stretchy characteristics. The formation of the disulfide bond is represented in the reaction $2RSH \rightleftharpoons R_2S_2 + 2\ H^+ + 2e^-$. What kind of reaction is this?

Oxidation

COOKING

iii. (2 points) Since the pH of bread dough is normally between 4 and 5, the above reaction can be paired with the reduction of oxygen in acidic solution so that there is no net loss of electrons. Write this reduction half reaction and the combined balanced reaction.

$O^2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$4RSH + O_2 \rightarrow 2H_2O + 2R_2S_2$

iv. (3 points) The standard reduction potential of oxygen in acidic solution is +1.23V. The cell potential for the reaction $2RSH \rightleftharpoons R_2S_2 + 2H^+ + 2e^-$ is estimated to be about +0.08 V. Find the ΔG° for the reaction at 298 K.

ΔG° = -(4 mol)(96500 C/mol)(1.31 V) = 505,660 J = 505.66 kJ

v. (3 points) How does dissolving salt tighten the bonds between gluten in acidic bread dough?

Dough typically has a low pH, meaning that some of the gluten proteins will be positively charged and repel each other. When salt is added, it will dissolve and some of the Cl- ions will bond to positively charged amino acids on gluten, neutralizing the charges and allowing the gluten proteins to bind more closely and make a more stable dough.

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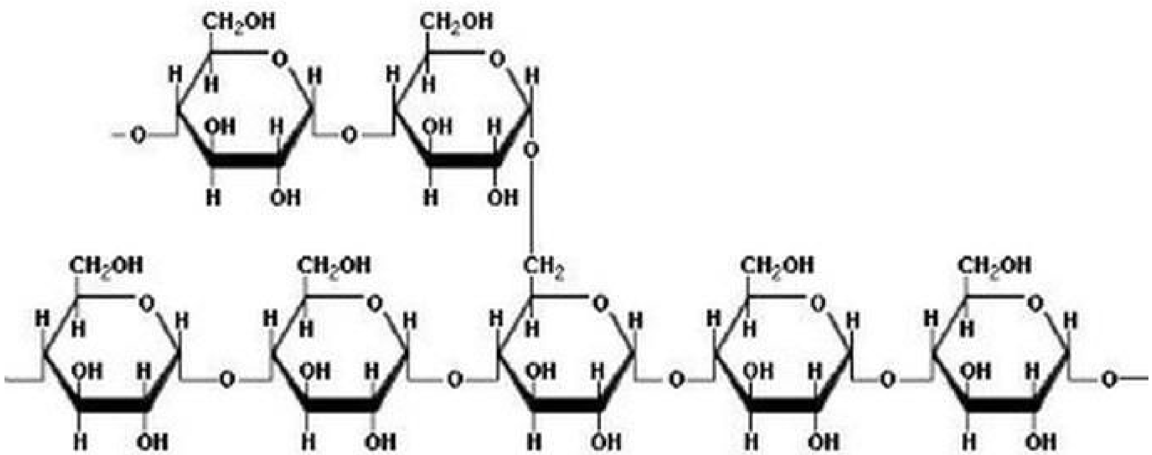
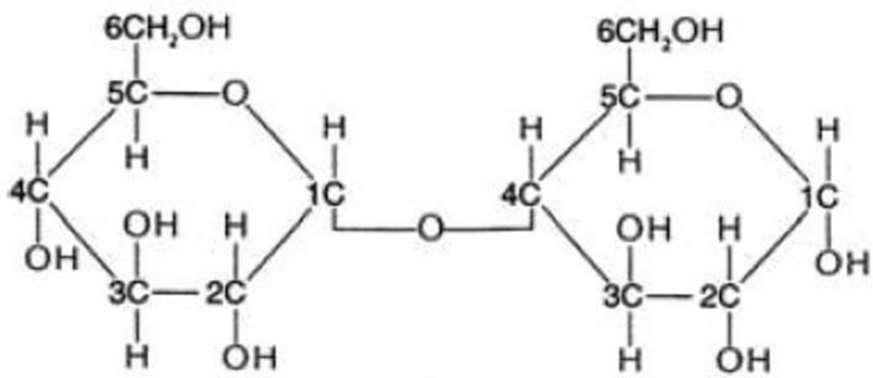
b. Yeast requires sugar to undergo fermentation, but flour contains very little of it. Instead, yeast uses maltose that is produced when the breakdown of starch is catalyzed by enzymes present in flour, most notably amylase. Yeast will then use maltase to break down maltose into glucose, a sugar useable for fermentation.

   i. (3 points) Part of a starch chain and a molecule of maltose are shown below. Propose what amylase does molecularly to produces maltose from a starch chain (i.e., what bonds are broken and formed).





Maltose

Amylase catalyzes a reaction between starch and water, adding a hydrogen atom to a connecting oxygen and then adding an OH to the other side. This causes a maltose molecule to break off with a hydroxyl group on each side of the separation. (Starch is hydrolyzed).

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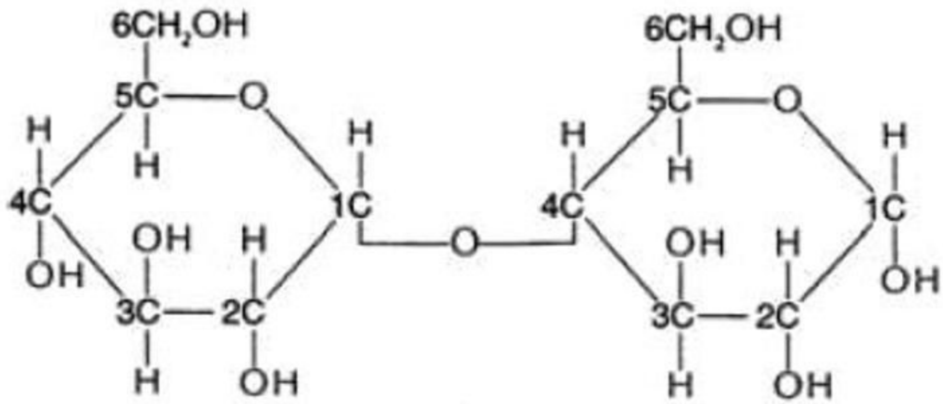
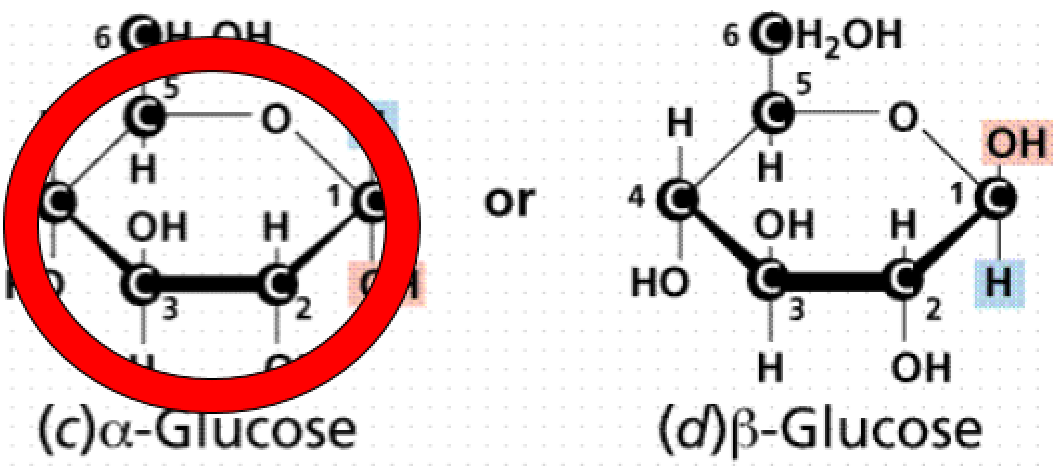
(2 points) Glucose has two isomers, α-glucose and β-glucose, shown below. When the above maltose is broken down into glucose, circle the resulting glucose isomer. For convenience, the maltose is reproduced below.



Maltose



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Cirlce the α-Glucose

DO NOT WRITE BELOW THIS LINE

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ii. (3 points) Experiments conducted at 300K show that $\Delta S° = 38.27\ J \cdot mol^{-1}$ and $\Delta H° = -4.02\ kJ \cdot mol^{-1}$ for the enzymatic breakdown of maltose. What is the equilibrium constant, K, for this reaction?

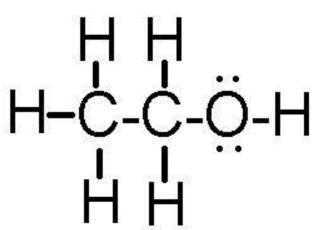
G° = H° – TΔS° = -15500 J/mol
G° = -RTlnK ln K = 6.21
K = 497.7 (Allow answers between 490-510 due to rounding)

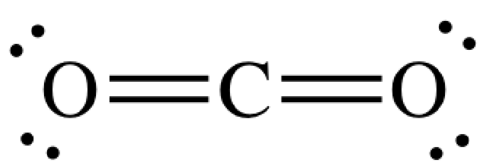
c. Ethanol fermentation by yeast is what gives bread much of its texture and shape, as the gas produced by fermentation is what allows bread to rise.

i. (1 point) Balance the reaction for ethanol fermentation shown below.

$C_6H_{12}O_6 \rightarrow \underline{2}\ C_2H_5OH + \underline{2}\ CO_2$

ii. (2 points) Draw Lewis dot structures for the two products of the reaction.





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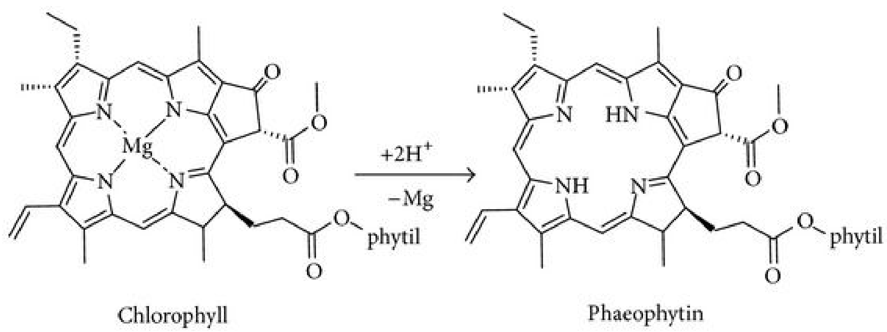
Question 2

Broccoli soup is a healthy and delicious dish that can be served alongside many other appetizers to start off a great meal.

a. Simmering broccoli in chicken broth is the first step in making broccoli soup. This process reduces broccoli's chlorophyll-a content (a pigment that gives vegetables their green color) because the heat and slightly acidic chicken broth catalyzes the conversion of chlorophyll-a to pheophytin-a, causing the green color to fade. The structures of chlorophyll-a and pheophytin-a are shown on the following page.



i. (2 points) Explain why chicken broth is a better solvent for this reaction than water. Your answer should include an acidity argument based on the molecules shown above.

As chicken broth is a mostly aqueous solution, its increased acidity will allow for more formation of pheophytin from chlorophyll. Pheophytin will then hydrogen bond with the water present in broth, allowing chlorophyll to have a greater solubility in chicken broth than pure water.

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ii. (4 points) No one wants a brown-colored broccoli soup, so you decide you will only cook the broccoli until 25% of the chlorophyll-a is converted to pheophytin-a. You need to cook 4 cups of broccoli, which contains a total of 80 mg of chlorophyll. Treat the mixture of broccoli and chicken broth as a 2 L homogenous solution. Chlorophyll-a has a molar mass of 893.51 g. The rate constant, k, for this reaction is 0.06 min^{-1} and the reaction follows first order kinetics. How long should the broccoli simmer in the chicken broth?

$\ln[A]_t - \ln[A]_0 = -kt$

Initial concentration: (80mg)(1g/1000mg)(1mol/893.51g)/2L = 4.48×10^{-5} M

Final concentration: 0.75(4.48×10^{-5}M) = 3.36×10^{-5} M

t = [ln(3.36×10^{-5}) - ln(4.48×10^{-5})]/0.06 = 4.79 minutes

b. The next step is to puree the broccoli and chicken broth in a blender with 2.09 horsepower (1560W) for 5 minutes.

i. (2 points) Is pureeing the broccoli an endothermic or exothermic process? Explain.

Pureeing broccoli involves breaking the bonds holding the molecules of broccoli together. Breaking bonds is an endothermic process.

ii. (4 points) Determine how much total energy, in Joules, is absorbed to break all the bonds holding broccoli cells together. Assume complete energy transfer from the blender to the broccoli. Recall $P = \frac{\Delta E}{\Delta t}$.

2.09 horsepower = 1560W

5 minutes = 300s

1560W(300s) = 468000J

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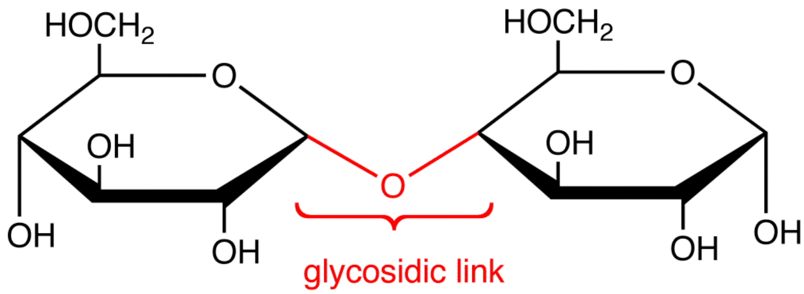
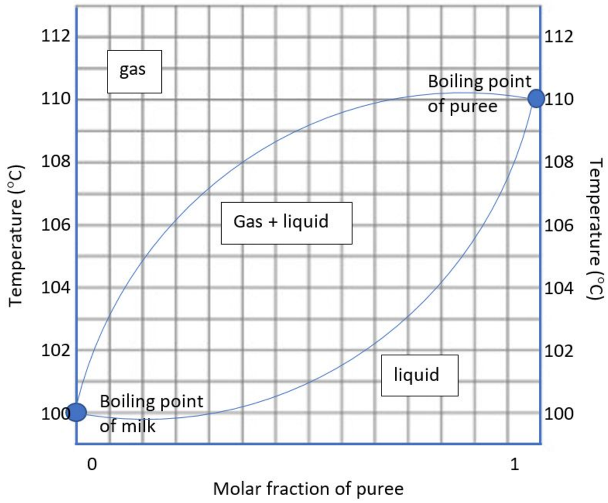
iii. (3 points) Pureeing the broccoli breaks apart the bonds holding broccoli cells together. The main types of bonds involved are hydrogen bonds and glycosidic linkages. A diagram of a glyosidic linkage is shown below. Does a hydrogen bond or a glyosidic linkage account for greater energy absorption? Explain with reference to bond dissociation energies. A picture of a glycosidic linkage and space to answer the question is provided below.



Glycosidic linkages are a type of polar covalent bond between carbon and oxygen. Hydrogen bonds are weak electrostatic interactions been hydrogens and electronegative atoms. Covalent bonds are stronger and have larger bond dissociation energies than hydrogen bonds, so breaking glycosidic linkages will require more energy than breaking hydrogen bonds.

COOKING

c. The third and final step in making broccoli soup is to combine the broccoli and chicken broth puree with milk and bring the mixture to a boil. Use the diagram below for questions ii through iv.



i. (2 points) Notice the values of a pure sample of milk (when the molar fraction of puree is zero) and of pure puree (when the molar fraction of puree is 1). Explain why the puree would have a higher boiling point than the milk.

Bonds holding the molecules of the puree closely together in liquid form are stronger than bonds holding together the molecules of milk. The stronger bonds require more kinetic energy, which is directly related to temperature, in order to break the bonds and enter a gaseous state, so the puree has a higher boiling point.

ii. (1 point) What is the boiling point of milk?

100 °C

iii. (1 point) What is the minimum temperature that a 1:1 mole fraction mixture of puree and milk would boil?

~101.5 °C

iv. (1 point) You decide to try out two different soups. One that with a 4:6 and one with a 6:4 ratio of milk to puree. Raising both soups to what single temperature would ensure both are boiling?

~100.5 °C.

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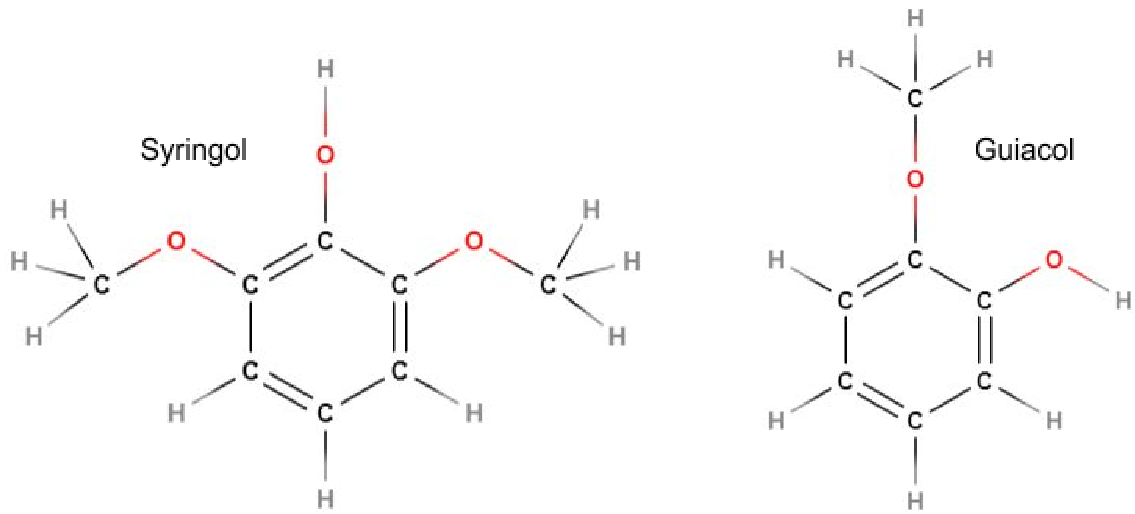
COOKING

Question 3

Many popular American foods, such as hot dogs and hamburgers, are best prepared on a grill. Though grilling is healthier than cooking or frying foods in fats and oils, there is also a risk of producing carcinogens. Let's take a closer look at the variety of chemicals and processes that are involved in grilling.

a. (2 points) Two of the main compounds that contribute to the signature taste and aroma of grilled meats are syringol and guiacol. Their structures are shown below.



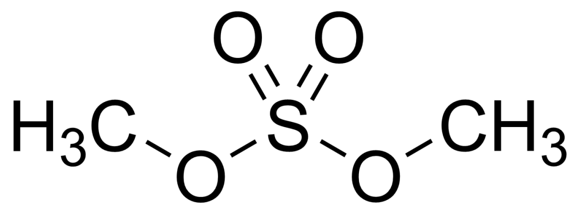
As grills can heat up to over 600 °F, Aaron decides to run an experiment to investigate the chemicals in his hamburger. It was found that guiacol boils at a relatively low temperature of 205 °C (400 °F), while syringol takes longer to boil, remaining liquid until up to 261 °C (502 °F). Why might this be the case?

Syringol contains more polar oxygen atoms, which increase its polarity in comparison to guiacol. As a result, the greater polarity of syringol allows it to have greater intermolecular forces than guiacol, imparting syringol the greater boiling point.

COOKING

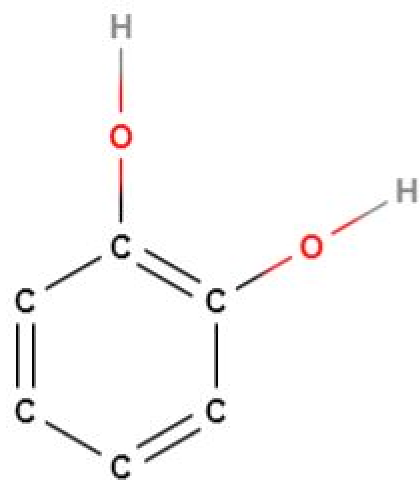
b. At work, Aaron wants to replicate the smoky flavor of grilled food but only has expensive chemistry equipment in his lab instead of a grill. He looks up a reaction online and finds that guiacol can be produced by reacting catechol with dimethyl sulfate.

i. (1 point) Given the Lewis dot structure of dimethyl sulfate below, what is the oxidation state of sulfur?



Oxidation state: +6

ii. (1 point) The structure of catechol is shown below.

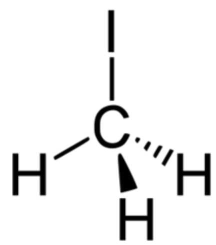


Circle a region of the compound that would react with dimethyl sulfate to form guiacol.

(Answer should circle one of the hydroxyl groups).

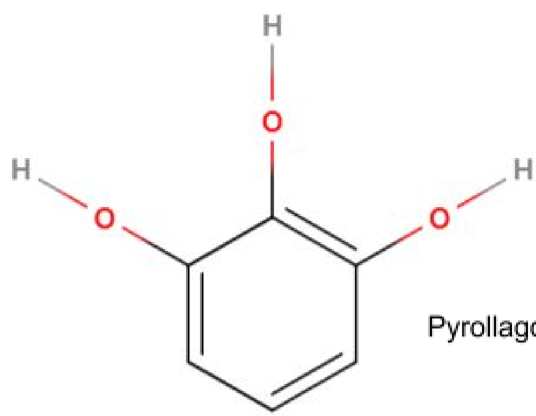
COOKING

iii. (2 point) Aaron does not have any dimethyl sulfate in his lab because of its extreme toxicity. He instead used methyl iodide to perform the same task and create the guiacol product from catechol. Given that the formula for methyl iodide is CH_3I, provide the hybridization of the central atom and a 3D VSEPR structure of the compound.



Sp3

c. (3 points) In order to complete his recreation of the smoky grilled flavor, Aaron decides to add a small amount of syringol. However, syringol and a related compound, pyrollagol, are both kept in unlabeled bottles next to each other. In order to select the right chemical, Aaron decides to examine their solubilities in water. How will this help him identify syringol? The structure of pyrollagol and space to answer is provided below.



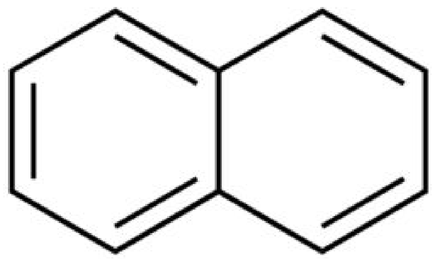
Pyrollagol

Syringol has carbons bound to the right and left oxygen atoms, while pyrollagol has hydrogens bound to all three oxygen atoms. This means that pyrollagol can form much more hydrogen bonds than syringol, giving pyrollagol a greater polarity and solubility in water, a polar solvent. Syringol, therefore, will be the less soluble compound.

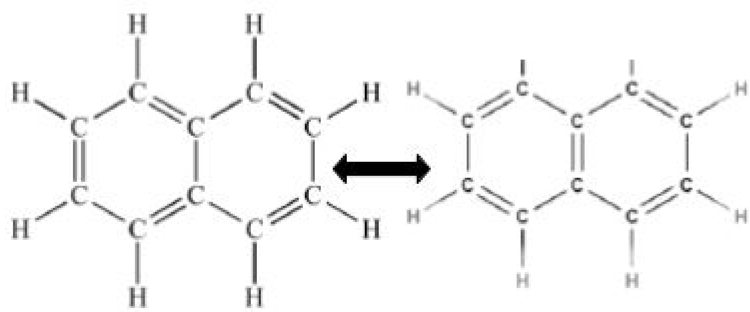
COOKING

d. Cooking with solid fuels, such as wood, leads to the production of carcinogens, including compounds like polycyclic aromatic hydrocarbons.

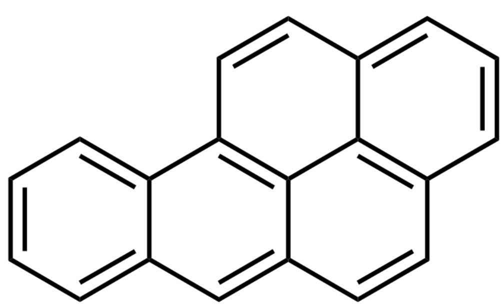
i. (2 points) A polycyclic aromatic hydrocarbon is a molecule composed entirely of multiple aromatic rings, most commonly benzene. They are known as hydrocarbons as these rings only contain two elements: hydrogen and carbon. The simplest known polycyclic aromatic hydrocarbon is naphthalene. Given the line structure and molecular formula below, draw Lewis structures of two resonance forms of naphthalene.



Naphthalene: $C_{10}H_8$



ii. (1 point) Shown below is the line structure of benzo(a)pyrene, the polycyclic aromatic hydrocarbon most commonly produced from combustion of foods. Use this structure to come up with the molecular formula of benzo(a)pyrene.



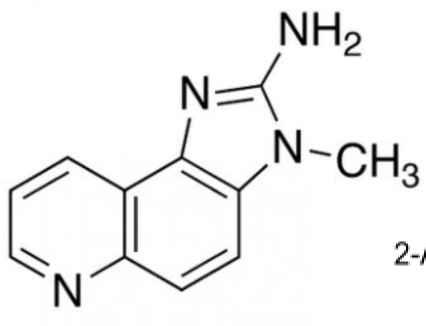
$C_{20}H_{12}$

COOKING

iii. (2 point) As benzo(a)pyrene is a hydrocarbon, it can be combusted to form water and carbon dioxide. Complete and balance the combustion reaction of benzo(a)pyrene. If you did not solve part ii, use $C_{18}H_{15}$ for the formula of the hydrocarbon.

$C_{20}H_{12} + 23O_2 \rightarrow 6H_2O + 20CO_2$
$2C_{18}H_{14} + 43O_2 \rightarrow 14H_2O + 36CO_2$

e. (3 points) Another group of carcinogenic compounds that can produced from grilling are heterocyclic amines. On well done grilled meats, these compounds can be found on the black crusty lines where the meat has touched the grill. Heterocyclic amines form when proteins and sugars in the meat react with the H_2O and CO_2 produced from combustion under high temperatures. An example of a heterocyclic amine is shown below.



2-Amino-3methylimidazo[4,5-f]quinoline

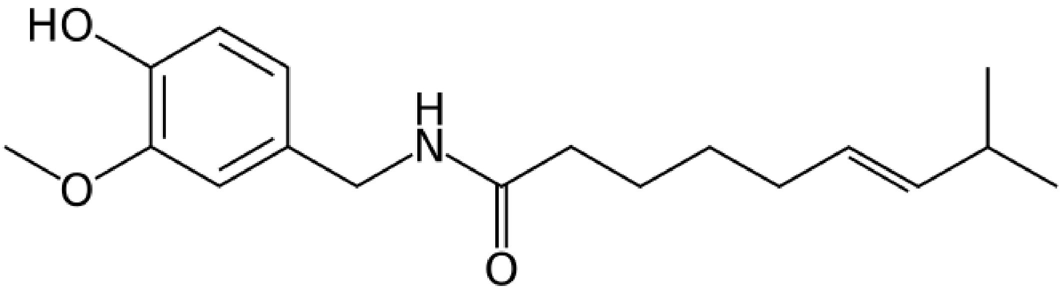
Several studies have shown that marinating meat before grilling it can actually significantly reduce the content of heterocyclic amine carcinogens (in addition to significantly enhancing flavor). Keeping in mind that marinades often contain high amounts of water-retaining starches and salts, propose one reason why this might be true.

The water-retaining compounds in the marinades are able to absorb water produced from combustion, preventing it from participating in the reaction that produces heterocyclic amines.

COOKING

Question 4

The substance that makes foods spicy is called capsaicin. Its molecular structure is given below. It binds to the vanilloid receptor subtype 1 (TRPV1), which sends a signal to the brain that results in the pain due to spiciness.



a. (3 points) Capsaicin is highly insoluble in water. Given the molecular structure of capsaicin, and explain why it is insoluble in water. Also, if you have just taken a bite out of a very spicy habanero pepper, would you expect drinking water to help relieve your pain? Explain your reasoning.

Capsaicin is a nonpolar, hydrophobic molecule, due to the long hydrocarbon chain and the absence of any charged groups. Since capsaicin is hydrophobic and insoluble in water, drinking water will not help relieve the pain in the long term. The capsaicin will remain bound to the tongue, since it does not dissolve in the drinking water.

b. (3 points) Milk is an excellent remedy for spiciness. Milk is an emulsion of fat globules, lactose (a type of sugar), and proteins. Approximately 80% of the proteins in milk are casein proteins, which aggregate to form structures called casein micelles. The casein proteins can sometimes behave like detergent molecules, by binding to hydrophobic molecules. Given this, why is milk such a good remedy?

Capsaicin is a nonpolar, hydrophobic molecule, due to the long hydrocarbon chain and the absence of any charged groups. The fat globules in milk will be able to dissolve free capsaicin and reduce spiciness by carrying away capsaicin from vanilloid receptors.

COOKING

c. (4 points) The solubility of capsaicin in water is just 0.0013 g / 100 mL, making it highly insoluble. A typical habanero pepper contains about 50 mg of capsaicin per gram of pepper. You eat a 9.5 g habanero, and 10% of the capsaicin is left in your mouth. With your mouth feeling like it's on fire, you drink 1 cup (236.6 ml) of water. How many mg of capsaicin is left in your mouth, assuming that water became saturated with capsaicin?

First calculate the capsaicin left in your mouth:
(50 mg capsaicin / g)(9.5 g)(0.10) = 47.5 mg
Capsaicin dissolved in the water:
(236.6 mL)(0.0013 g / 100 mL) = 0.0031 g = 3.1 mg
Capsaicin left: 47.5 mg – 3.1 mg = 44.4 mg

d. (5 points) Andy wants to make a habanero salsa. He doesn't want to make the salsa too spicy for his friends, so he wants the salsa to be exactly 0.08% capsaicin by weight. He wants to add tomatoes to 3 habaneros, which each weigh 7.9 g. How much tomato (in grams) should Andy add to create the salsa with just the right amount of heat?

Capsaicin in 3 Habaneros:

(3)(7.9 g)(50 mg / g) = 1185 mg = 1.185 g

Total weight of the salsa = 1.185 g / (0.08% / 100) = 1481.25 g

Calculate the weight of onion and tomato:

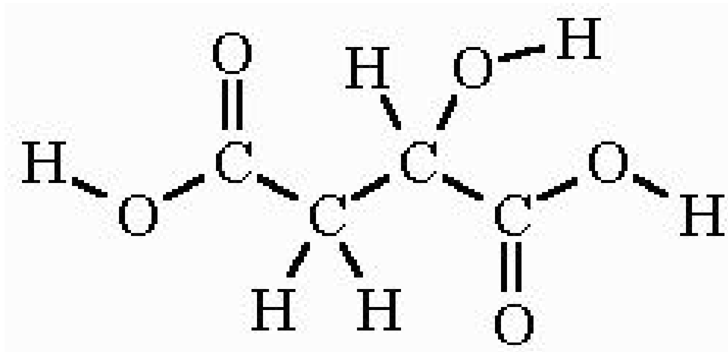
1481.25 g – 3(7.9 g) = 1457.55 g of onion and tomato

COOKING

Question 5

Cherries come in many different varieties, and each variety has its own culinary purpose.

a. The contributing chemical that produces the sour flavor in tart cherries, as well as many other fruits, is malic acid. Its structure is shown below.



i. (2 points) Draw a resonance structure of malic acid after it is doubly deprotonated. How many resonance structures will there be in total?

The hydrogen atoms from each end will be removed from the molecule. On the resulting structure, the two carbons can form a single bond to either oxygen and an double bond with the remaining oxygen. As a result, 4 resonance structures are present of the doubly deprotonated acid.

ii. (1 point) What will the average charges of the doubled-bonded (carboxyl) oxygen atoms be after malic acid is doubly deprotonated?

-1/2

iii. (3 points) A student wants to make a cherry pie but doesn't have time to cook, so she decides to freeze the cherries (by freezing the water present in cherries) at -1.8 °C for tomorrow. If all of the malic acid in tart cherries is singly protonated and forms 1.45% of the mass of the cherry, by how many degrees Celsius does the freezing point of a 4 g cherry get decreased by malic acid? The water in the cherries has a molal freezing point depression constant of 1.86 °C · mol^{-1}.

0.058 g malic acid

133.08 g/mol malic acid 0.000436 mol malic acid

m = 0.109 mol/kg

$\Delta T = iK_fm$ = 2 (singly protonated) x 1.86 x 0.109 = 0.405 °C.

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b. The student decides to make a jam out of the cherries instead and thaws the cherries.

i. (3 points) The specific heat of a frozen cherry is 1.85 $J \cdot g^{-1} \cdot K^{-1}$, and 3.52 $J \cdot g^{-1} \cdot K^{-1}$ for a thawed cherry. The latent heat for the thawing process is 267 $J \cdot g^{-1}$. If 50.0 g of cherries are taken out of a freezer at -18 °C, how much energy is required to thaw the cherries to 25 °C? The freezing point of a cherry is -1.8 °C.

q = 16.2x1.85x50 + 267x50 + 26.8x3.52x50 = 19565.3 J

ii. (3 points) The student wants to quickly warm up the cherries so that she won't have to heat them for as much time. She puts the 50.0 g of cherries in an insulated bowl at 25 °C and pours in 0.5 kg of water at 99 °C. How much warmer will the cherries get? Assume that heat lost to the environment is negligible. Recall that the specific heat of water is 4.184 $J \cdot g^{-1} \cdot °C^{-1}$.

(50)(x - 25)(3.52) = (500)(99 – x)(4.184)

x = 93.26 °C

The cherries will increase in temperature by about 68.3 °C.

c. The student decides that the jam made from tart cherries is a little too sour, so she dilutes it with water.

i. (4 points) If the pH of 50 mL the original jam is 3.3, how much water should be added to increase the pH to 4.1?

$[H^+] = 10^{-3.3} = 5.01 \times 10^{-4}$

$[H^+] = 10^{-4.1} = 7.94 \times 10^{-5}$

$(5.01 \times 10^{-4})(50) = (7.94 \times 10^{-5})(x)$

x = 315.5

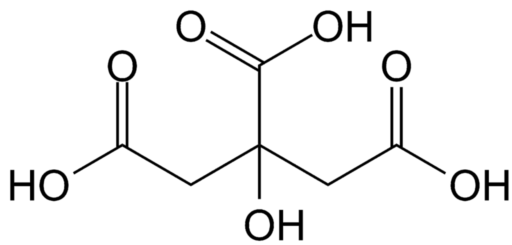
265.5 mL of water should be added to sufficiently dilute the jam.

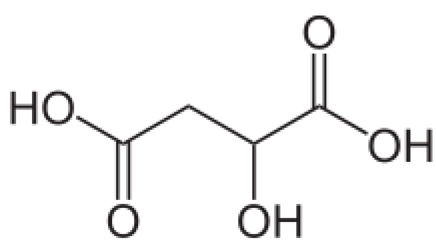
COOKING

ii. (5 points) The student wants to see if a pH of 4.1 is a good value of jam, so she performs a titration on 25.00 mL of store-bought jar of jam to find its pH to compare. If it takes 0.01287 mL of 0.25M NaOH to neutralize 25.00 mL of jam, what is the pH of the jam? The k_A of malic acid is 3.48 x 10^{-4}.

0.00001287 L x 0.25 mol/L = 3.22 x 10^{-6} mol
M = 0. 000129 mol/L
3.48 x 10-4 = x^2/(0.000129 – x)
x = 0.0001
The pH of the jam is 4.00 (accept anything within 0.2 of 4)

iii. (3 points) Another common acid present in fruits is citric acid. Fruits high in citric acid content tend to taste more sour than fruits containing malic acid, partially because citric acid is stronger than malic acid. Given the structures of the acids below and the knowledge that stronger acids have more stable conjugate bases, explain why this is the case.





Citric acid contains an additional COOH group compared to malic acid, which means that the electronegative oxygen atoms will help stabilize the conjugate base of citric acid more effectively by spreading the electron charge.