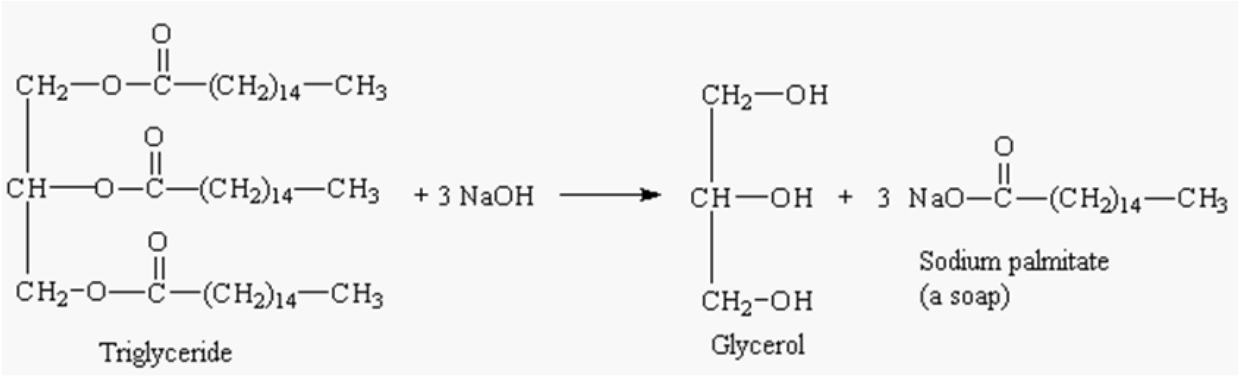
2022 WUCT: Chemistry of Cosmetics

This exam consists of 6 questions and is worth 100 points. You will work together with a partner to answer the questions. You will have 1 hour to take the exam, followed by 10 minutes of upload time during which you cannot make changes to your exam. The only allowed resources for this exam are a calculator and the provided equation sheet. You may NOT use any other notes, books, or websites (other than Gradescope and HopIn). You must show your work and box your final answer to receive credit for a problem. NOTE: If you get the answer to an early part of a question incorrect but later use that answer for a subsequent part of the question, you can still earn full credit for those subsequent parts. Please write your answer in the designated space on the answer sheet. If you need additional space for a problem, you may use scratch paper, but make sure to clearly indicate in the problem's designated space where the rest of your work can be found. Dark pencil or pen is preferred so that your writing clearly shows on your submitted document in Gradescope.

<u>Problem #1</u>: ***(16 points)***

Soap is made by reacting fat with a strong base, as shown below. This process is known as saponification, and this experiment can easily be done in a laboratory. 20 grams of commercially available animal fat was fully dissolved in 100 mL of ethanol. To this mixture, 30 mL of 6M NaOH solution was added. The mixture was heated in a microwave until all of the fat was fully dissolved. 20 mL of water was added afterwards and left to cool. The cooled mixture was then poured into a beaker with 100 mL of 0.2% NaCl solution. The solution was filtered in order to separate the soap from the glycerol that was formed.



a) Calculate how many carbon atoms are in 20 grams of triglyceride. The molar mass of triglyceride is 808.3 g/mol. ***(3 points)***

b) Identify the limiting reagent in the reaction. ***(4 points)***

c) Calculate the molar mass of sodium palmitate with the correct units. ***(2 points)***

d) You go through the procedure and obtain 5 grams of soap. Calculate the theoretical yield and the percent yield. ***(4 points)***

e) Imagine that you used a hot plate instead of a microwave to fully dissolve all of the fat. The fat was fully dissolved after running the microwave with a power rating of 50 kJ/min for 5 minutes. When using the hot plate with a power rating of 70 kJ/min, the fat was fully dissolved after 3 minutes. Is it more efficient to use the microwave or the hot plate to perform the experiment? In other words, which method would save more energy? Explain your answer. ***(3 points)***

Problem #2: ***(12 points)***

Many beauty products, including face moisturizers, foundations, deodorants, conditioners, and body lotion, use formaldehyde as a preservative to prolong shelf life and prevent bacterial contamination. Formaldehyde, however, is a carcinogen, thus constant exposure to formaldehyde poses real health concerns. Fortunately, a study found that the amount of formaldehyde inhaled from the use of common beauty products is too minimal to pose a risk to human health. In industry, methanol (CH_3OH) with an addition of a catalyst is often used to make formaldehyde.

$$CH_3OH\,(l) \rightarrow CH_2O\,(g) + H_2\,(g)$$

Substance	$\Delta H^\circ f$ (kJ/mol)	S (J/K mol)
CH_3OH (l)	–239.1	127.2
CH_2O (g)	–108.7	218.8
H_2 (g)	0	130.6

Given the thermodynamic data under standard conditions (1 atm and 25°C) above, answer the following questions.

a) Will ΔS of the reaction be positive or negative? ***(2 points)***

b) Determine the temperature in °C above which the reaction will be nonspontaneous.
(4 points)

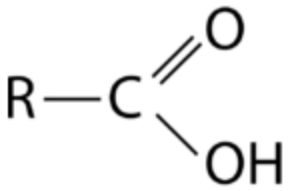
c) The equilibrium constant for the following reaction is 6.5×10^8 at 30°C. Calculate the value of ΔG for the reaction. ***(4 points)***

d) What does it mean when a chemical system has reached minimum free energy? Circle all correct answers. ***(2 points)***

a. The forward and the reverse reactions have stopped
b. The concentrations of the reactants and products are not changing
c. The rate of the reaction is at its maximum
d. The temperature is at absolute temperature
e. The system's entropy is at its minimum
f. The reaction is complete
g. The system has reached equilibrium
h. The rate of product formation is faster than the rate of reactant formation

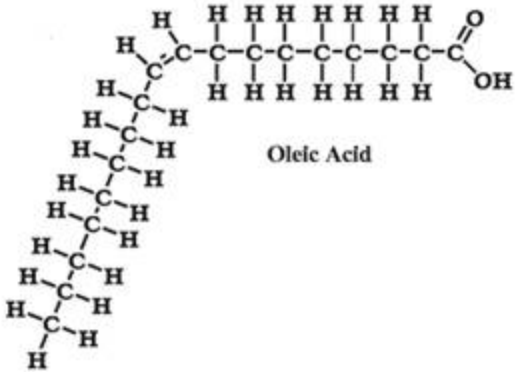
Problem #3: ***(15 points)***

Lipstick is composed of many waxes, fats, and oils. To produce a glossier lipstick, more oils are added, which help create that shinier appearance. One such oil used in lipsticks is olive oil. Although its makeup varies, olive oil consists mostly of oleic acid, along with smaller portions of other acids, such as palmitic acid and linoleic acid. These acids belong to a class of compounds known as fatty acids, which are chains of carbon and hydrogen atoms with a carboxylic acid group (shown below) at one end, where R represents the hydrocarbon chain.



carboxylic acid

Oleic acid is a colorless and odorless chemical. Its structure is shown below.

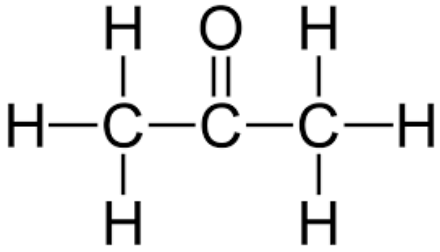


In this question, we will examine the physical and chemical properties of oleic acid, and fatty acids in general, that comprise the chemical foundation of lipstick.

a) Where is the molecular dipole of this compound and why? Please describe the specific areas in the molecule where electron density will be highest and lowest. ***(3 points)***

b) When oleic acid is placed into water, it is so slightly soluble as to be considered insoluble. However, when it is added to acetone, it is very soluble. Why does this occur? ***(2 points)***

Acetone:



c) Oleic acid is a liquid at room temperature. Its boiling point is approximately 360℃ at a pressure of 1 atm.

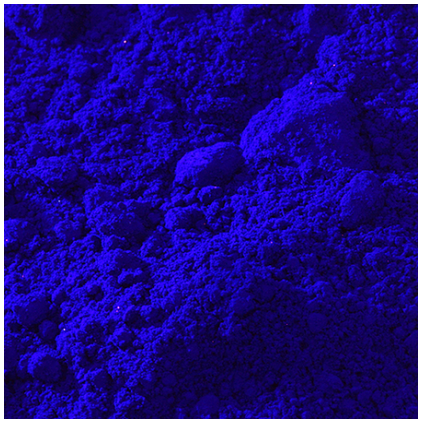
i) Why is its boiling point greater than that of water (100℃)? ***(2 points)***

ii) You are building a new manufacturing plant for lipstick in Denver, where the elevation is much higher than sea level. Your current plant operates at sea level with an atmospheric pressure of 1 atm and uses a temperature of 360℃ to cause boiling. Do you need to change your new plant's conditions in Denver? Why or why not? If so, how? ***(3 points)***

d) You are given 430 g solid oleic acid at -50℃ and you want to melt it and bring it to a temperature of 35℃ in order to use it to make a certain lipstick. Given the properties of oleic acid, how much energy (in kJ) will be required for this physical transformation? For this problem, assume a specific heat capacity of 3.256 J/g℃ for liquid oleic acid and 1.643 J/g℃ for solid oleic acid. ***(5 points)***
Heat of Vaporization: 83.8 kJ/mol
Heat of Combustion: -11.15 kJ/mol
Heat of Fusion: 39.6 kJ/mol
Melting Point: 13.4 ℃
Boiling Point: 360.0 ℃
Molecular Weight: 282.5 g/mol

Problem #4: ***(18 points)***

Eyeliner has been worn since the times of ancient Mesopotamia. In fact, heavily applied eyeliner is often seen on figures in art from ancient Egypt. In addition to its use as makeup, eyeliner was used as a form of eye protection against the sun. Pigments are a key ingredient in the production of eyeliners. Often, chemicals such as iron oxides, titanium dioxide, and Prussian blue are used to give eyeliners their characteristic colors. This question will focus on the chemistry of Prussian blue.



The dark blue Prussian blue pigment has the chemical formula $Fe(III)_4[Fe(II)(CN)_6]_3$. Prussian blue is produced from a white solid ferrous ferrocyanide salt reactant, of the form $Na_2Fe[Fe(CN)_6]$ or $K_2Fe[Fe(CN)_6]$. Adding sodium chlorate ($NaClO_3$) gives $Fe(III)_4[Fe(II)(CN)_6]_3$, or Prussian blue.

a) To make Prussian blue, a chemist takes $Na_2Fe[Fe(CN)_6]$ and produces $Fe_4[Fe(CN)_6]_3$. What is the oxidation state of each iron atom in these formulas? Place your answers on the lines directly under the iron atoms in the formulas below. ***(4 points)***

Reactant	Product
$Na_2Fe[Fe(CN)_6]$	$Fe_4[Fe(CN)_6]_3$
1st Fe: _____	1st Fe: _____
2nd Fe: _____	2nd Fe: _____

b) Given that sodium chlorate is added to the reactant to produce the product of Prussian blue, is sodium chlorate an oxidizing agent or reducing agent? Justify your answer. ***(2 points)***

c) Based on your answers to part (a), what atom/element in Prussian blue (the product) do you think is responsible for the dark blue color shown in the picture above? ***(2 points)***

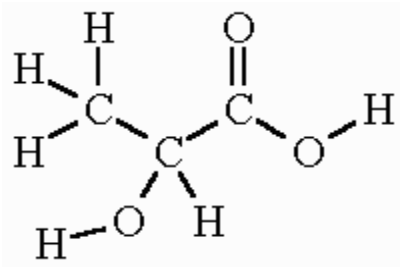
d) The blue color of Prussian blue is caused when light of just the right wavelength to remove an electron from the iron (II) cation and transfer it to an iron (III) cation is absorbed. The absorbed light appears as a reddish-orange color. If the frequency of the absorbed light is 4.409×10^{8} MHz and all of the absorbed light is assumed to transfer to the electron, what is the velocity of the electron wave-particle that leaves the iron (II) cation? ***(4 points)***

e) What are the quantum numbers of the electron that leaves the iron (II) cation for the iron (III) cation? There may be multiple correct answers. ***(2 points)***

f) What is the energy of the orbital from which the electron leaves? Give your answer in Joules. ***(4 points)***

Problem #5: *(22 points)*

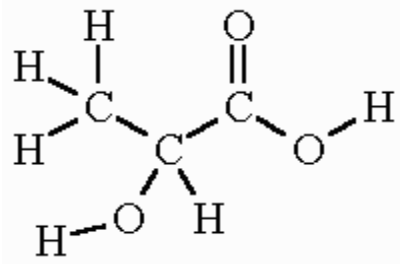
One ingredient often seen in skin care cosmetics is lactic acid. In fact, in ancient Egypt, Cleopatra bathed in milk, which contains lactic acid, in the hopes that her skin would look younger. Lactic acid helps to exfoliate the skin, fade out hyperpigmented spots, and regulate the pH of many cosmetic products. The structural formula of lactic acid is shown below.



This question explores the properties of lactic acid.

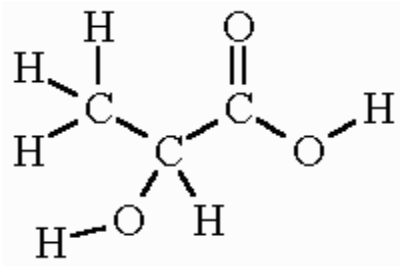
a) Lactic acid is sometimes used in shampoos, shower gels, and facial washes. One of the main chemicals in these products is water. Is lactic acid soluble in water? Why or why not? ***(2 points)***

b) On the structure below, label the hybridized or non-hybridized orbitals that participate in bonding for each atom. ***(2 points)***



c) As its name indicates, lactic acid is a bronsted-lowry acid.

i) On the structure below, circle which proton(s) are most likely to be the acidic protons. ***(2 points)***



ii) Of all the protons shown above, which proton is the most acidic and why? ***(2 points)***

d) Rank the relative acidities of the below acids in water, going from least acidic on the left to most acidic on the right. If there are any ties, indicate them with an equal sign (=). ***(2 points)***

HCl, CH_3COOH, HBr, H_2O, H_3O^+, NH_3, lactic acid

e) At 20℃, the pKa of lactic acid is 3.86.

i) What is the acid dissociation constant of lactic acid? ***(2 points)***

ii) Write the balanced chemical reaction below that has this equilibrium constant, drawing out Lewis structures for lactic acid and any similar structures. Be sure to label which compounds are acids and which are bases. Include any important resonance structures. ***(4 points)***

iii) Which side of the reaction, if any, is favored in this reaction? Justify your answer. ***(2 points)***

f) This reaction is allowed to run at 20℃ and reaches equilibrium. Afterwards, some changes are imposed and the reaction is allowed to re-establish equilibrium. Describe which way the reaction goes, to the right or to the left, to reach equilibrium again. Be sure to explain your reasoning in 1-2 sentences.

i) More lactic acid is added to the mixture. ***(1 point)***

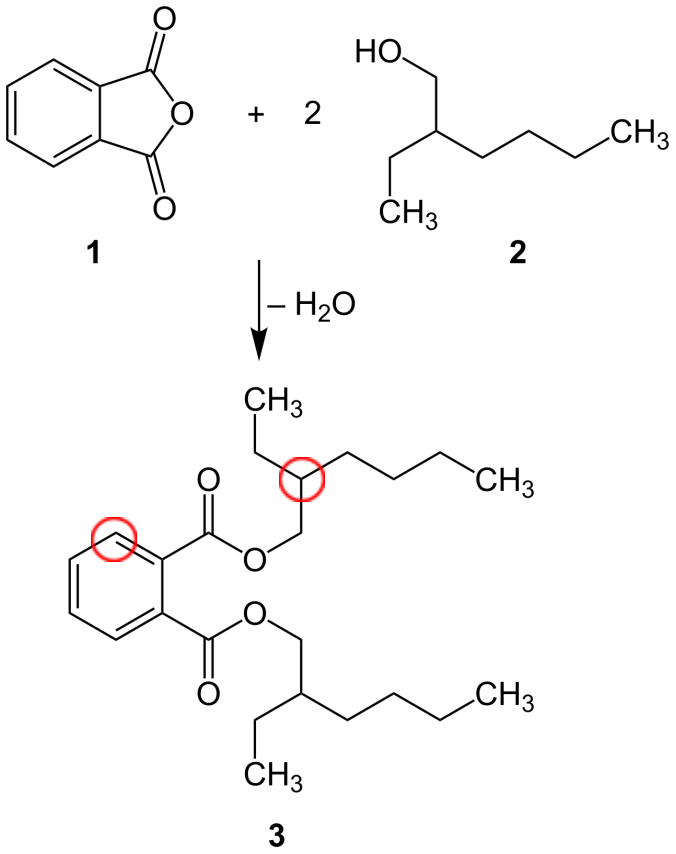
ii) A small amount of water is added to the mixture such that the volume is not significantly changed. ***(1 point)***

iii) Some solid graphite is added to the mixture. ***(1 point)***

iv) A significant amount of ice is added to the mixture. ***(1 point)***

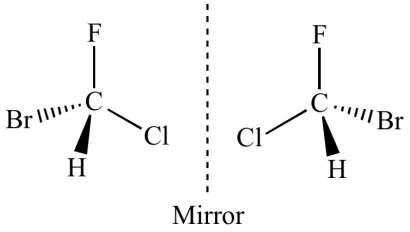
Problem #6: ***(17 points)***

Phthalates are commonly found in perfumes and added in order to help the scent last for a long time. However, phthalates may have harmful health effects. Some common health risks include cancer, endocrine disruption, human reproductive and developmental toxicity, as well as respiratory problems. The most common phthalate that is used in perfumes, DEHP (3), is usually mass produced in an industry that involves a reaction between phthalic anhydride (1) and 2-ethylhexanol (2). The vertices below represent carbon atoms. Any carbon with less than 4 bonds shown is assumed to be bonded to as many hydrogens as needed to reach a total of 4 bonds.



a) Write out the molecular formula of phthalic anhydride (1). ***(2 points)***

b) A chiral molecule is a compound that contains an asymmetric center and thus can occur in two non-super imposable mirror-image forms. Usually, a chiral carbon will have four nonidentical substituents. For example, bromochlorofluoromethane, as shown below, is a chiral compound with carbon with its chiral center. Is 2-ethylhexanol (2) a chiral molecule? Explain your reasoning. ***(3 points)***



c) Would you expect DEHP (3) to be hydrophobic or hydrophilic? Explain your reasoning. ***(3 points)***

d) What is the hybridization and geometry of labeled carbons (with red circles) on DEHP (3)? ***(4 points)***

e) The reaction between phthalic anhydride (1) and 2-ethylhexanol (2) can be described as a reaction between a nucleophile and an electrophile. A nucleophile is a compound that donates a pair of electrons to form a new covalent bond while an electrophile is a compound that accepts a pair of electrons to form a new covalent bond. For example, in the reaction shown below, the oxygen in the ROH acts as a nucleophile to attack the electrophilic carbon on the carbonyl group of the other molecule to form a new covalent bond. In the reaction between phthalic anhydride (1) and 2-ethylhexanol (2), determine which molecule acts as the nucleophile and the electrophile. Explain your reasoning. ***(5 points)***