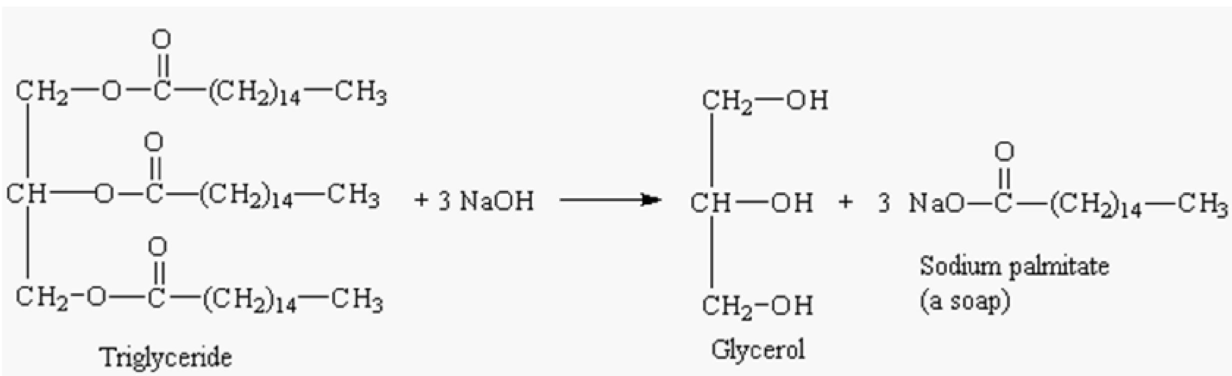
2022 WUCT: Chemistry of Cosmetics ANSWER KEY

<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)***

20 grams x $\frac{1\ mol}{808.3g}$ = 0.0247 mol triglyceride

0.0247 mol x $\frac{51\ mol\ C}{1\ mol\ triglyceride}$ = 1.26 mol C

1.26 mol C x $\frac{6.022 * 10^{23} atoms}{1\ mol}$ = 7.59 x 10^{23} atoms

+2 points for correct moles of carbon

+1 point for correct number of carbon atoms

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

Moles of triglyceride: 0.0247 mol of Triglyceride

Moles of NaOH: $\frac{6\ mol}{1L}$* 0.03 L = 0.18 mol of NaOH

Triglyceride: NaOH reacts in a 1:3 ratio → in order to react 0.0247 moles of triglyceride, only 0.0741 moles of NaOH are required

Thus, triglyceride is the limiting reagent.

+1 point for correct calculations of moles of triglyceride

+1 point for correct calculations of moles of NaOH

+2 points for identifying correct limiting reagent

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

Molar mass: 278.4g/mol

+2 points for correct molar mass calculating and correct units

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

1 mole of triglyceride will produce 3 moles of soap.

Thus, 0.0247 mol triglyceride will produce 0.0741 moles of soap.

Theoretical yield: 0.0741 moles * $\frac{278.4g}{1\ mol}$ = 20.629 grams

Percent yield: $\frac{Actual\ yield}{Theoretical\ yield}$ * 100 = $\frac{5\ grams}{20.629\ grams}$ * 100 = 24.24%

+1 point for identifying the correct ratio of triglyceride : soap (sodium palmitate)

+2 points for correct theoretical yield calculations

+1 point for correct percent yield calculation

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)***

Microwave: $\frac{50kJ}{min}$ * 5 min = 250 kJ required to fully dissolve the fat

Hot Plate: $\frac{70kJ}{min}$ * 3 min = 210 kJ required to fully dissolve the fat

The hot plate requires less energy to fully dissolve the same amount of fat so it is more efficient.

+1 point for correct energy calculations for microwave

+1 point for correct energy calculations for hot plate

+1 point for correctly identifying that the hot plate is more efficient

<u>Problem #2</u>: *(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	**ΔH˚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)***

Positive, the reaction goes from 1 moles of reactants to 2 moles of products and gaseous products are formed as a result of the reaction.

+1 point for correct answer

+1 point for correct reasoning

b) Determine the temperature in ˚C above which the reaction will be nonspontaneous.

(4 points)

$\Delta G = 0 = \Delta H - T\Delta S$

$\Delta H = [0 + -108.7] - [-239.1] = 130.4$ kJ/mol

$\Delta S = [130.6 + 218.8] - [127.2] = 222.2$ J/K mol

$T = \Delta H / \Delta S = [130.4$ kJ/mol$] / [0.2222$ kJ/K mol$] = 586.87$K = **313.72˚C**

+1 point for using $\Delta G = H - T\Delta S$ equation

+2 points for correct temperature calculation

+1 point for correct conversion to Celcius

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

ΔG = -RT ln K = - 8.314 J / mol * K * 303.15*K * ln (6.5 x 10^8) = 51144.95 J/mol = 51.145 kJ/mol

+1 point for using ΔG = -RT ln K equation

+2 points for correct answer

+1 point for conversion of units to kJ/mol

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

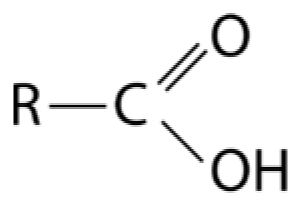
a. The forward and the reverse reactions have stopped
b. The concentrations of the reactants and products are not changing
c. The rate of the reaction is at its maximum
d. The temperature is at absolute temperature
e. The system's entropy is at its minimum
f. The reaction is complete
g. The system has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

+1 point for each correct answer (total of 2 points)

-1 point for extra answers circled or correct answers that are not circled

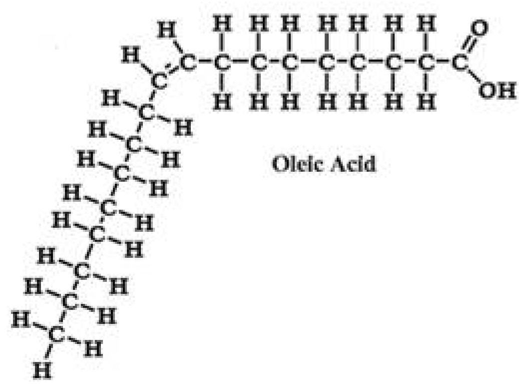
<u>Problem #3</u>: *(15 points)*

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)***

Electron density lowest at the other end of the hydrocarbon chain

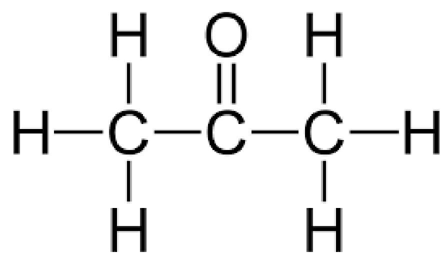
Oxygen is much more electronegative than C and H and will pull the electrons more towards it, producing a partial negative charge by the oxygen atoms. Carbon and hydrogen have similar electronegativities, and their electron density will be pulled over to the carboxylic acid group, generating a partial positive charge at the end opposite the carboxylic acid group. Thus, the molecular dipole points from the hydrocarbon end to the carboxylic acid end of the molecule.

+1 point for stating that electron density highest by carboxylic acid group (-COOH)

+2 points for correct justification

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:



+1 point for stating the following: Although oleic acid has a molecular dipole and has the potential to hydrogen bond, the majority of the molecule consists of a nonpolar hydrocarbon chain. Because of this chain, oleic acid is insoluble in the polar water molecules.

+1 point for stating the following: Acetone does have a polar C=O carbonyl group but the compound is less polar and consists of more nonpolar C-H bonds than water. Since "like dissolves like," this more nonpolar solvent can dissolve better the more nonpolar oleic acid.

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)***

Water can form hydrogen bonds, which gives it strong intermolecular attractions. However, here in addition to the potential for hydrogen bonding, it is mainly the fact that the molecule is so large and thus has such strong London Dispersion Forces that contributes to its significantly higher boiling point.

+2 points for correct justification

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)***

Yes, you need to change the new plant's conditions in Denver. Since the atmospheric pressure is less, the boiling point temperature will be less because boiling point occurs when the vapor pressure equals the atmospheric pressure. A lower temperature can be used.

+1 point for correct answer (stating yes)

+1 point for correct justification

+1 point for stating that lower temperature can be used

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

q(solid to melting) = (430 g)(1.643 J/g℃)(13.4-(-50)℃) = 44791.466 J = 44.791466 kJ

(430 g oleic acid)(1 mol/282.5 g) = 1.52212389381 mol oleic acid = 1.522124 mol

q(melting the solid) = (39.6 kJ/mol)(1.522124 mol) = 60.2761104 kJ

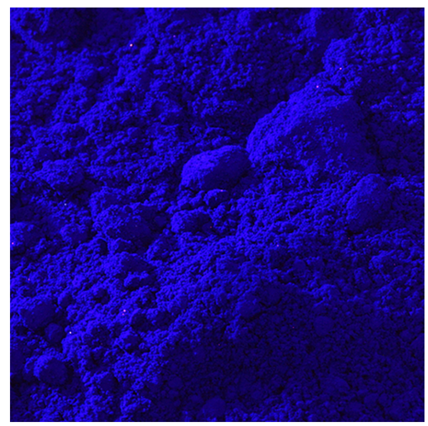
q(melting to 35) = (430 g)(3.256 J/g℃)(35-13.4℃) = 30241.728 J = 30.241728 kJ

q(total) = 44.791466 + 60.2761104 + 30.241728 kJ = 135.3093044 = 135.31 kJ

+1 point for correct q (solid to melting)
+1 point for correct q (melting the solid)
+1 point for correct q (melting to 35)
+2 points for correct q (total)

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: __+2___	1st Fe: __+3___
2nd Fe: __+2___	2nd Fe: __+2___

+1 point for each correct oxidation state (4 points total)

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)***

The Fe loses an electron to become oxidized from +2 to +3. Because this reagent is oxidized, the sodium chlorate must be reduced. It is causing the oxidation of the other reactant, so sodium chlorate is the **reducing agent.**

+1 point for correct answer

+1 point for correct justification

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)***

The **Fe atom (outside the brackets)** that goes from +2 to +3 oxidation state.

+2 points for correct answer

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)***

$c = \nu\lambda$

$$\lambda = \frac{c}{\nu} = \frac{2.99792458\times10^{8}\, m/s}{(4.409\times10^{14}\, Hz)} = 6.79955677 \times 10^{-7}\, m$$

$$\lambda = \frac{h}{mv}$$

$$v = \frac{h}{m\lambda} = \frac{(6.626076\times10^{-34}\, Js)}{(9.109390\times10^{-31}\, kg)(6.79955677\times10^{-7}\, m)} = 1069.76038904\, m/s$$

1.070 km/s

+1 point for correct wavelength calculation

+1 point for using correct velocity equation

+2 points for final correct answer

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)***

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

Fe^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Quantum numbers: n = 3, l = 2, m_l = any number between -2 and 2, $m_s = \pm \frac{1}{2}$

+2 points for correct quantum numbers

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

$$E_{n.l} =- 2.18 \times 10^{-18} J(\frac{z*^2}{n^2})$$

$$Z^* = 26 - 16 =+ 10$$

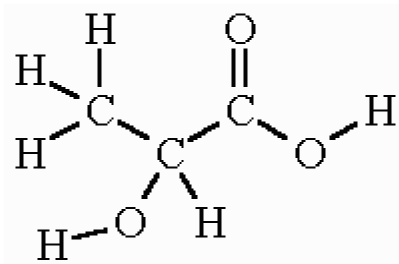
$$E_{3,2} = (- 2.18 \times 10^{-18} J)(\frac{10^2}{3^2}) =- 2.4222222 \times 10^{-17} J$$

$$- 2.42 \times 10^{-17} J$$

+1 point for using correct energy equation
+1 point for calculating correct Z effective
+2 points for correct final answer

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)***

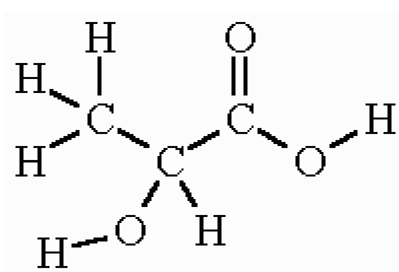
Lactic acid **is soluble** in water.

It contains two OH groups capable of hydrogen-bonding with water molecules. There is also a carbonyl group that can also participate in hydrogen bonding (?). An organic molecule is soluble in water if there is a hydrogen bonding group for every three hydrocarbon groups.

+1 point for stating lactic acid is soluble in water

+1 point for correct justification

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



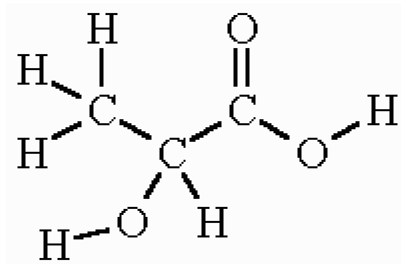
All Hs: 1s, **2 left Cs:** sp^3, **Rightmost C:** sp^2 and 2p,

Bottom 2 Os: sp^3, **Top O:** sp^2 and 2p

+2 points for correct hybridization for all atoms

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)***



The two hydrogens attached to oxygens.

+2 points for correct answer

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

The rightmost proton.

When the rightmost proton leaves, the conjugate base has two equivalent resonance forms, which stabilizes the negative charge. The more stable the conjugate base, the more acidic the proton is.

+1 point for indicating the rightmost proton

+1 point for correct justification

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

$NH_3 < H_2O < CH_3COOH < lactic\ acid < H_3O^+ = HBr = HCl$

+2 points for correct final answer

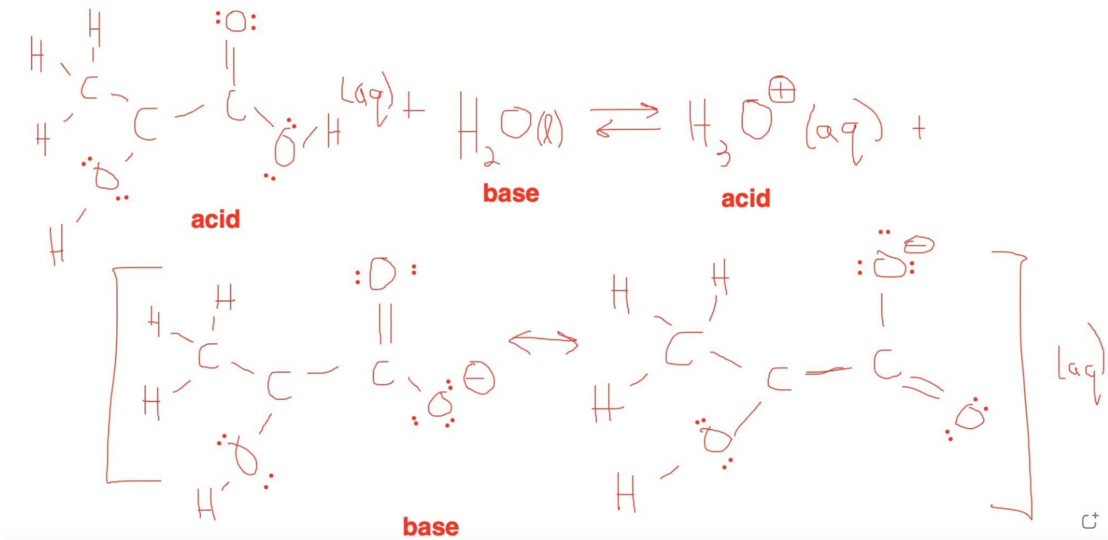
e) At 20℃, the pKa of lactic acid is 3.86.

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

$K_a = 10^{-3.86} = 1.38 \times 10^{-4}$

+2 points for correct final answer

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)***



+1 point for correct reactants and products

+1 point for correct labeling of acids and bases

+2 points for drawing equivalent resonance structures for lactate

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

Left/Reactant side is favored.

The acid dissociation constant is less than 1. At equilibrium, there are more reactants present than products.

+1 point for stating left/reactant side is favored

+1 point for correct justification

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)***

To the right.

Lactic acid is a reactant. Using Le Chatelier's principle, increasing the concentration of the reactant will cause the equilibrium to shift right to reach the same value for the equilibrium constant.

+1 point for correct answer and justification

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

No change.

Water is a liquid and does not appear in the equilibrium expression, unless the concentrations of the other reactants and products change. Since the volume is not changed, there is no change in the relative amounts of reactants and products.

+1 point for correct answer and justification

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

No change.

This solid does not appear in the chemical equation above and
does not affect any value in the equilibrium constant expression. Thus, the amounts of reactants
and products do not change.

+1 point for correct answer and justification

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

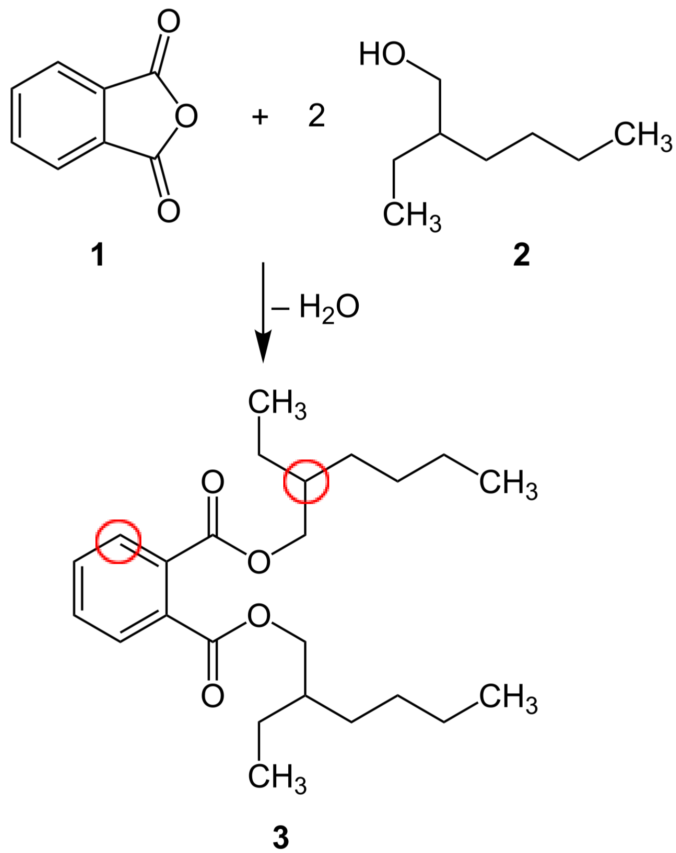
To the right.

At this temperature, the added ice melts to form water, which
increases the volume and decreases the concentration of hydronium ion, lactate ion, and lactic acid. Using the equation, $K_a = \frac{[H_3O^+]\ [lactate]}{[lactic\ acid]}$, reducing all of the concentrations by the same amount decreases the numerator more than the denominator, so the reaction must go to the right to reestablish equilibrium by Le Chatelier's principle.

+1 point for correct answer and justification

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.

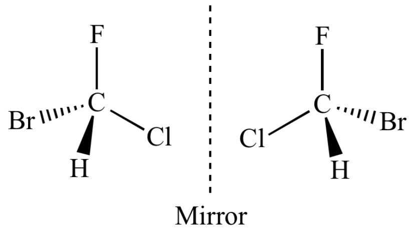


a) Write out the molecular formula of phthalic anhydride (1). ***(2 points)***

$C_8H_4O_3$

+2 points for correct molecular formula

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)***



2-ethylhexanol (2) a chiral molecule. The carbon in the center has 4 nonidentical substituents attached.

+1 point for correct answer

+2 points for correct reasoning

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

Hydrophobic, it has a large benzene ring with long hydrophobic side chains attached.

+1 point for correct answer

+2 points for correct reasoning

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

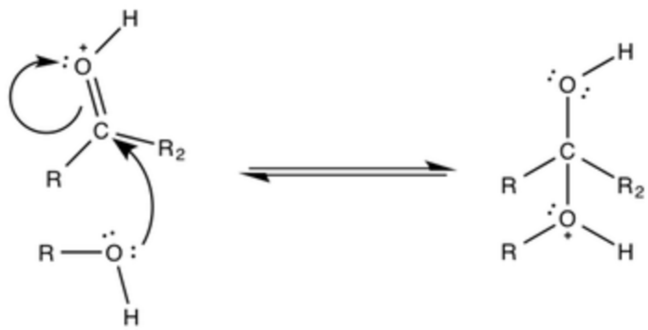
Carbon on the benzene ring: sp^2, trigonal planar

Carbon in the center: sp^3, tetrahedral

+1 point for each correct hybridization for the two carbons (total 2 points)

+1 point for each correct geometry for the two carbons (total 2 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)***



The phthalic anhydride is the electrophile while the 2-ethylhexanol is the nucleophile. The OH- hydroxyl group on the 2-ethylhexanol will act as the nucleophile and attack the carbonyl group on the phthalic anhydride.

+2 points for correctly identifying electrophile and nucleophile

+3 points for correct reasoning