2022 WUCT: Medicine Topic Exam ANSWER KEY

Problem #1: ***(13 points)***

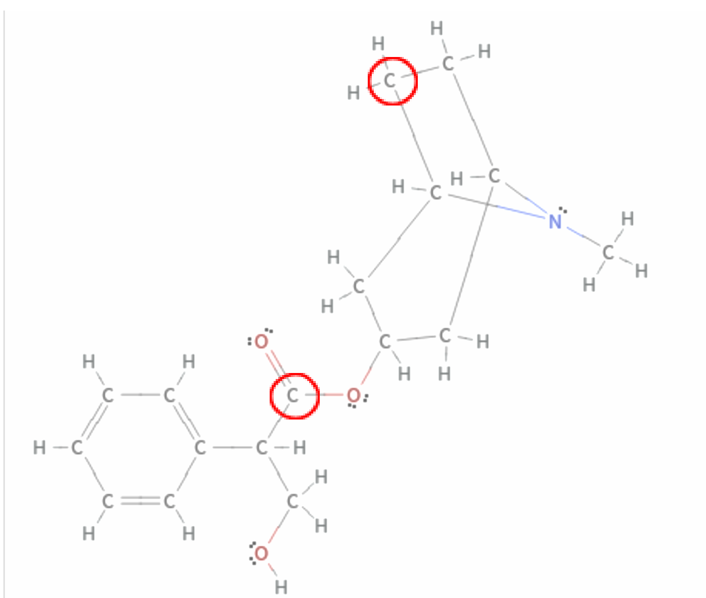
Atropine is commonly used as a medication to treat the symptoms of bradycardia, an abnormally low heart rate. The molecular formula of atropine is $C_{17}H_{23}NO_3$.

a) What is the molecular mass of $C_{17}H_{23}NO_3$? ***(2 points)***

Molecular mass = 17(12.01 g/mol) + 23(1.0079 g/mol) + 1(14.01 g/mol) + 3(15.999 g/mol) = 289.369 g/mol

+2 points for correct molar mass calculation

b) Shown below is the lewis structure of atropine. Write the correct hybridizations of the circled carbons. Also write how many hydroxyl groups are present in the molecule. ***(3 points)***



+1 point for labeling top carbon as sp^3 hybridized

+1 point for labeling bottom carbon as sp^2 hybridized

+1 point for stating there is 1 hydroxyl group in the molecule

c) Assume a researcher is conducting an experiment with the compound and has a step in the procedure that calls for the addition of 1.50 mL of a 3.0% by mass $C_{17}H_{23}NO_3$ solution. How many moles of $C_{17}H_{23}NO_3$ are added in this step? Since the concentration of $C_{17}H_{23}NO_3$ is quite low, you can assume that the density of the $C_{17}H_{23}NO_3$ solution is the same as water, 1.0 g/mL. Show your work below and round your answer to two decimal places. ***(4 points)***

1.50 mL $C_{17}H_{23}NO_3$ x (1.0 g $C_{17}H_{23}NO_3$ / 1.0 mL $C_{17}H_{23}NO_3$) = 1.50 g $C_{17}H_{23}NO_3$

1.50 g $C_{17}H_{23}NO_3$ x 0.03 = 0.045 g $C_{17}H_{23}NO_3$

0.045 g $C_{17}H_{23}NO_3$ x (1 mol $C_{17}H_{23}NO_3$ / 289.4 g $C_{17}H_{23}NO_3$) = 1.55 x 10^{-4} mol $C_{17}H_{23}NO_3$

+2 points for correct calculation of grams of $C_{17}H_{23}NO_3$
+2 points for correct final answer

d) In a second portion of the experiment, the researcher is working with the elements xenon and chlorine. Together, they form a neutral compound, $XeCl_n$, where n is a whole number integer. The mass of 7.0544 x 10^{20} molecules of $XeCl_n$ is 0.3199 g. Determine the whole number integer value of n. ***(4 points)***

Moles = (# molecules / N_A) = (7.0544 x 10^{20} molecules / 6.022 x 10^{23} molecules / mol) = 1.17 x 10^{-3} mol $XeCl_n$

Molar mass = (mass / moles) = (0.3199 g / 1.17 x 10^{-3} mol) = 273.09 g/mol

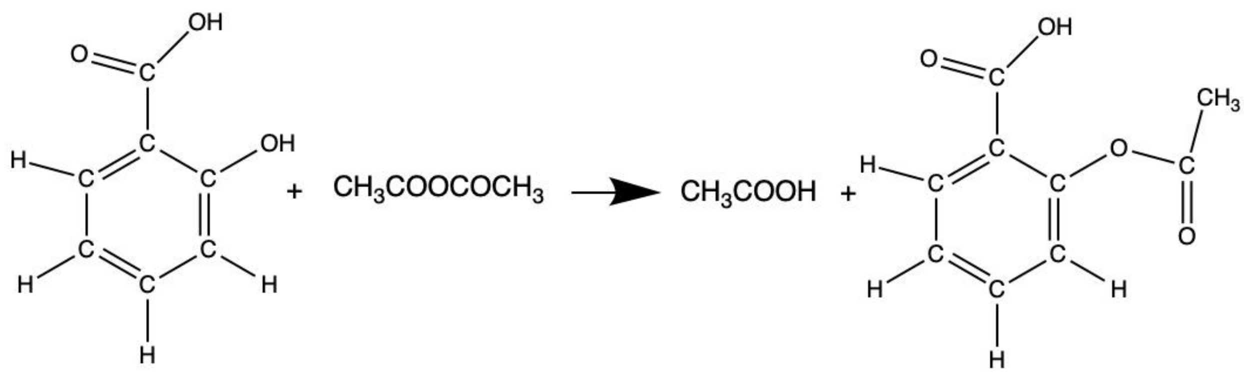
$XeCl_n$ has a molar mass of 273.09 g/mol

Therefore, n = 4.

+1 point for correct calculations of moles of $XeCl_n$
+1 point for correct calculations of molar mass of $XeCl_n$
+2 points for correct calculations of integer n = 4

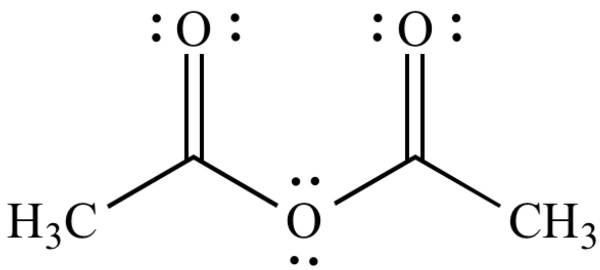
Problem #2: ***(15 points)***

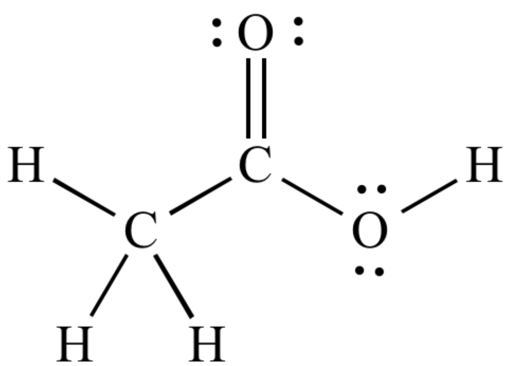
Aspirin is a common drug for relieving minor aches, pains, and fevers. The production of aspirin from raw materials can be divided into four separate reactions, the last of which is shown below:



Salicylic Acid   Acetic Anhydride   Acetic Acid   Aspirin

a) Draw the missing Lewis structures for acetic anhydride and acetic acid. ***(4 points)***

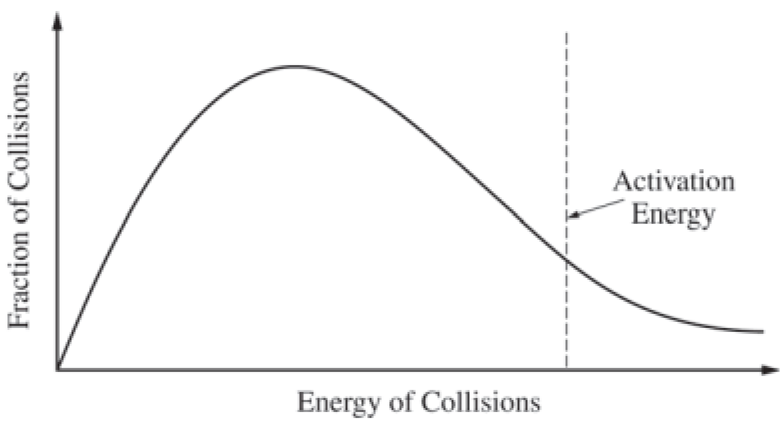




+2 points for each correct Lewis structure (total 4 points)

b) What is the hybridization of each of the two carbon atoms in acetic acid? ***(2 points)***
sp3 and sp2
+1 point for each correct answer (total 2 points)

c) The graph below shows a distribution for the collision energies of reactant molecules at room temperature. Heat is commonly applied to the starting materials to facilitate solvation and speed up the reaction. Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules when they are heated to a higher temperature. ***(2 points)***



A broader curve that is shifted to the right with the same total area under the curve
+2 points for correctly drawn curve

d) Given the following standard enthalpies of formation, predict which species, salicylic acid or aspirin, will increase in concentration following the temperature change described in part (c). Justify your answer. ***(3 points)***

Compound	**ΔH°f (kJ/mol)**
Salicylic acid	-585
Acetic anhydride	-625
Acetic acid	-484
Aspirin	-140

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

ΔH° = (-484+-140) - (-585+-625) = +586kJ/mol
Endothermic, increase temperature, reaction shifts right, aspirin will increase in concentration.
+1 point for calculating ΔH°
+2 points for correct interpretation

e) Predict which side of the reaction is favored at *equilibrium*. Include a discussion of the standard entropy of the reaction based on the number of reactants consumed and products formed. ***(2 points)***

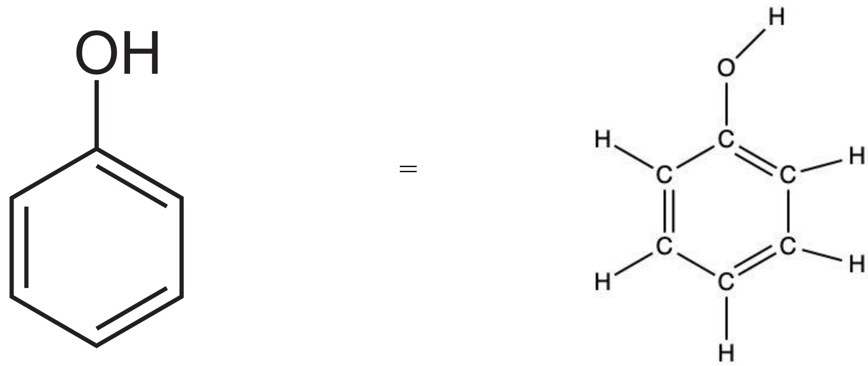
The number of reactant molecules are the same as the number of product molecules so ΔS°f is around 0 and ΔG° is positive; therefore, reactants are favored
+1 point for correct answer
+1 point for correct justification

f) In a different reaction, acetic anhydride can combine with H_2O to form acetic acid. This reaction favors the formation of products. Explain how the equilibrium constant, K, of this reaction compares to that of the original reaction. ***(2 points)***

If reactants are favored, then it has a positive ΔG° and K is less than 1
If products are favored, then it has a negative ΔG°, and K is greater than 1
Therefore, original reaction has smaller K than the new reaction
+1 point for correct answer
+1 point for correct justification

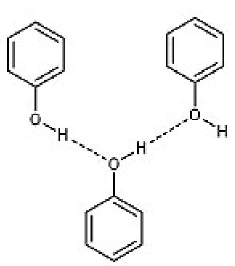
Problem #3: ***(12 points)***

Over 60% of FDA approved small molecule drugs contain at least one aromatic ring motif. Below is an example, phenol (molecular formula: C_6H_6O). Phenol is used to relieve pain and irritation caused by sore throat, sore mouth, or canker sores. One of the reasons behind this application is the stability the ring provides, allowing the drug to bind better to biological molecules.



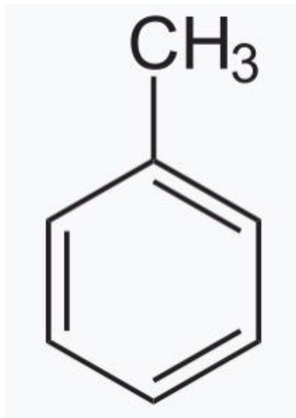
a) Explain the stability in terms of the bonding pattern of the ring. Note: There is a carbon atom everywhere there is a vertex. When the carbon atom has less than 4 bonds, it is assumed that the carbon atom is bonded to as many hydrogen atoms as needed to bring it to a total of 4 bonds. ***(3 points)***
Acceptable answers: resonance structure, conjugation of double bonds, no free rotation of bonds which leads to rigidity
+2 points for mentioning resonance structures due to conjugation of double bonds
+1 point for mentioning no free rotation of bonds lead to rigidity

b) Another important characteristic of phenol is that it can participate in hydrogen bonding. Draw at least three molecules of phenol with this intermolecular interaction, with relevant partial positive and negative charges. ***(4 points)***



+1 point for drawing 3 phenol molecules
+1 point for correct orientation of molecules
+2 points for correct charges (partial negative charge on oxygen and partial positive charge on hydrogen)

c) Structurally, a compound known as toluene looks very similar (see picture below). However, toluene has a different boiling point than phenol. Please identify which compound has the higher boiling point and explain. ***(3 points)***



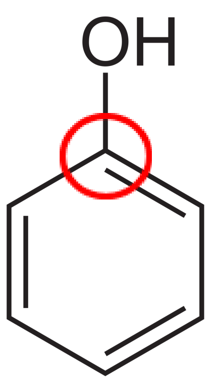
Phenol has a higher boiling point because hydrogen bonding is present in phenol while only LDFs are present in toluene.

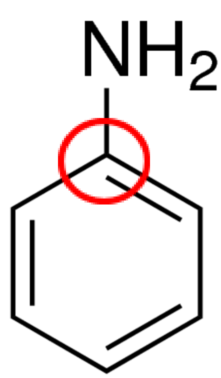
+1 point for stating phenol has higher boiling point

+1 point for indicating that hydrogen bonding is stronger in phenol

+1 point for stating toluene only has LDF

d) Please identify the geometries about the circled atom in both phenol and aniline. ***(2 points)***





+1 point each for stating that each carbon has trigonal planar geometry (2 points total)

<u>Problem #4</u>: *(13 points)*

Sulfuric acid, H_2SO_4, is a strong acid that is a common component in many chemotherapy drugs due to its ability to break down cancerous cell DNA. A researcher is working with sulfuric acid in a lab, configuring a set of experiments in an attempt to determine its quantity and concentration limits for an emerging chemotherapy drug. At 25˚C, the pH of a 25.0 mL sample of 0.15 *M* H_2SO_4 is 1.07. It reacts with water as shown in the equation below:

$$H_2SO_{4(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO_4^-{}_{(aq)}$$

a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Label which is the acid and which is the base. ***(2 points)***

$H_2SO_{4(aq)}$ and $HSO_4^-{}_{(aq)}$ or $H_2O_{(l)}$ and $H_3O^+_{(aq)}$

+2 points for identifying correct Brønsted-Lowry conjugate acid-base pair

b) Determine the K_a for sulfuric acid at 25˚C. Round your answer to three decimal places. ***(4 points)***

$[H_3O^+] = 10^{-pH} = 10^{-1.07} = 0.085$

$[HSO_4^-] = [H_3O^+]$

$K_a = [HSO_4^-][H_3O^+] / [H_2SO_4]$

$K_a = [0.085][0.085] / [0.15]$

$K_a = 0.048$

+1 point for correct $[H_3O^+]$ concentration

+1 point for correct Ka expression

+2 points for correct final answer

c) Read the statement below and determine if it is true or false. Justify your reasoning in 2-3 sentences. ***(2 points)***

If the pH of an acetic acid solution is the same as the pH of a sulfuric acid solution, then the molar concentration of the sulfuric acid solution must be less than the molar concentration of the acetic acid solution.

Sample Answer: True. Sulfuric acid is a strong acid and so it will ionize/dissociate fully. A smaller amount of moles of sulfuric acid is needed to produce the same concentration of H_3O^+ as an acetic acid solution, which will only partially ionize/dissociate)

+2 points for correctly choosing true and having a supporting claim. No partial credit. Students must correctly explain why the answer is true to get the point.

d) Assume a researcher wants to conduct a test to see if acetic acid is a valid substitute for sulfuric acid in the chemotherapy drug. In the process, he finds that creating a buffer and calculating its pH will reveal the effectiveness of the substitution. The researcher creates a buffer solution by dissolving 8.0 grams of sodium acetate in 160.0 mL of 1.2 M acetic acid. Assuming the researcher neglects any changes in volume from the sodium acetate, calculate the pH of the acetic acid/sodium acetate buffer solution. The K_a for acetic acid is 1.8×10^{-5}. Round to two decimal places. ***(5 points)***

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$
$[H_3O^+] = K_a[CH_3COOH_(]/[CH_3COO^-]$
(1.2 M CH_3COOH)(160.0 mL)(1 L/1000 mL) = 0.192 mol CH_3COOH
(8.0 g $NaCH_3COO$)(1 mol $NaCH_3COO$/82.0343 g) = 0.0975 mol $NaCH_3COO$
$[H_3O^+] = (1.8 \times 10^{-5})(0.192/0.0975) = 3.54 \times 10^{-5}$
pH = 4.45

+1 point for correct calculations of moles of CH_3COOH
+1 point for correct calculations of moles of $NaCH_3COO$
+1 point for correct calculations of $[H_3O^+]$
+2 points for correct final pH calculations

<u>Problem #5</u>: *(16 points)*

Imagine that it has been found that Atorvastatin, a commonly prescribed drug that is used to lower patients' cholesterol, actually has two differing existing chemical compositions each with their respective properties. Medical professionals deliberate about the effectiveness of the two drugs, known as Atorvastatin A and Atorvastatin B, and carry out research to analyze the effectiveness of each composition. Assume Atorvastatin A has a half life of 8 hours and Atorvastatin B has a half life of 6 hours.

a) Assuming that 1 g samples of both drugs are collected for experimentation, find the rate constant *k* of each. Round to the nearest thousandth. ***(5 points)***

   For Atorvastatin A:

   $K = \ln(2) / t_{1/2}$

   $K = 0.6391 / ⅓$ days

   $K = 2.079$

   For Atorvastatin B:

   $K = \ln(2) / t_{1/2}$

   $K = 0.6291 / ¼$ days

   $K = 2.773$

   +2 points for correct K rate of Atorvastatin A

   +2 points for correct K rate of Atorvastatin B

   +1 point for correct units (there are no units for rate constant)

b) Using the *k* rates constants calculated in part (a), how much of Atorvastatin A and Atorvastatin B will remain after one and a half days? Round to the nearest thousandth. ***(5 points)***

   For Atorvastatin A:

   $A_F = A_0 \cdot e^{-kt}$

   $A_F = 1 \cdot e^{-(2.079)(1.5)}$

   $A_F = 0.044$ grams

   For Atorvastatin B:

   $A_F = A_0 \cdot e^{-kt}$

   $A_F = 1 \cdot e^{-(2.773)(1.5)}$

   $A_F = 0.016$ grams

   +2 points for correct calculations of Atorvastatin A

   +2 points for correct calculations of Atorvastatin B

   +1 point for correct units

c) Doctors want to ensure that the Atorvastatin is out of the bloodstream as quickly as possible. As a result, they want to find which version of the drug takes the least amount of time to be cleared (1% remaining). In a written statement, identify which drug this is by finding the time it takes for each drug to be 99% cleared from the bloodstream. Round your answer to the nearest thousandth. ***(6 points)***

For Atorvastatin A:

$A_F = (0.01)\ (0.044 \text{ grams})$

$A_F = 4.419 \times 10^{-4} \text{ grams}$

$A_F = A_0 \cdot e^{-kt}$

$4.419 \times 10^{-4} = 1 \cdot e^{-(2.079)(t)}$

t = 3.715 days

For Atorvastatin B:

$A_F = (0.01)\ (0.016 \text{ grams})$

$A_F = 1.563 \times 10^{-4} \text{ grams}$

$A_F = A_0 \cdot e^{-kt}$

$1.563 \times 10^{-4} = 1 \cdot e^{-(2.773)(t)}$

t = 3.161 days

Atorvastatin B takes 3.161 days to be 99% cleared from the bloodstream while Atorvastatin A takes 3.715 days to be 99% cleared from the bloodstream. Therefore, Atorvastatin B should be chosen for patient use.

+2 points for correctly calculating the A_F values for both Atorvastatin A and B (must get both values to earn the point. If one or both are incorrect, the point is not given)

+ 2 points for correct t values for Atorvastatin A and B (1 point for Atorvastatin A and 1 point for Atorvastatin B

+ 2 points for correct written statement identifying Atorvastatin B as the favorable Atorvastatin type due to its shorter time to reach 1% of initial dose in the bloodstream.

<u>Problem #6</u>: *(15 points)*

Hearing aids are most commonly powered by silver oxide batteries. A silver-oxide battery uses silver (I) oxide as the cathode, zinc as the anode, plus an alkaline electrolyte, usually sodium hydroxide (NaOH) or potassium hydroxide (KOH).

a) Write the balanced half cell reactions that occur at each electrode. ***(2 points)***
Cathode $Ag^{+} + 1e^{-} \rightarrow Ag$
Anode $Zn \rightarrow Zn^{2+} + 2e^{-}$
+1 point for correct half cell reaction at cathode
+1 point for correct half cell reaction at anode

b) Using the information provided in the Table of Standard Reduction Potentials, determine whether this cell is a Galvanic cell. Please give evidence for your answer. ***(3 points)***
Cell potential (delta E^{o} cell) = 0.80V + -(-0.76V) = 1.56V
Positive cell potential = negative delta G = spontaneous reaction = Galvanic cell
+1 point for correct calculation of cell potential
+1 point for for connecting it to delta G and spontaneity
+1 point for correct final answer

c) In which direction do electrons flow? ***(2 points)***
Electrons flow from anode (Zn) to cathode (Ag^{+})
+2 points for correct answer

d) For nonstandard conditions (specifically, nonstandard molar concentrations), a version of the Nernst equation can be used to find Δε.

$\Delta\varepsilon = \Delta\varepsilon° - \frac{0.0257}{n}(\ln Q)$, where n is the number of moles of e- per mole of reaction

After the cell runs spontaneously for a certain period of time, the concentration of silver ions has decreased to 0.5 M, while the concentration of zinc ions has increased to 1.25 M. Assume the volume stays constant.

What is the cell potential at this point? It may be helpful to write out the overall electrochemical reaction. ***(4 points)***

$2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+}$

Δε = 1.56V - 0.0257/2 ln (1.25/(0.5)^2) = 1.54V

+1 point for correct n where n = 2
+1 point for plugging into equation
+2 points for correct final answer

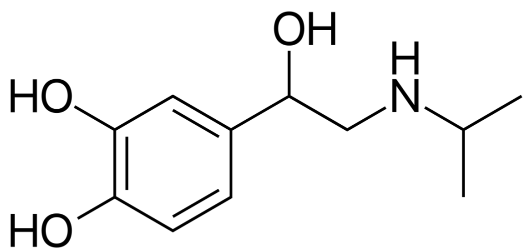
e) Calculate the solubility product constant, Ksp, of AgBr in pure water at 25°C. ***(4 points)***
AgBr (s) ⇌ Ag+ (aq) + Br- (aq)

For AgBr
Δε° = -0.80V + 0.07V = -0.73V
ln Ksp = nFΔε°/RT = (1mol)(96.5kcoul/mol)(-0.73V) / (8.314*10^-3kJ)(323.15K) = 26.220
Ksp = 4.10*10^-12

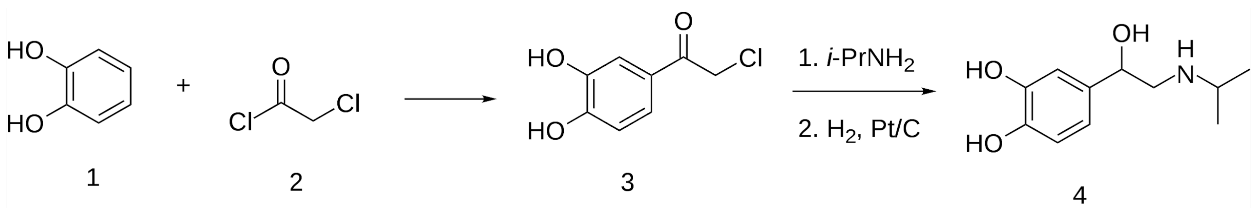
+1 point for correct calculation of Δε°
+1 point for correct plug in to Ksp equation
+2 points for correct final answer

Problem #7: ***(16 points)***

Isoprenaline, also known as isoproterenol, is an organic compound that can imitate the effects of the sympathetic nervous system. Isoprenaline is often used for treatment of various heart diseases, including bradycardia and heart block. It is also sometimes used to treat asthma. The molecular structure of isoprenaline is shown below.



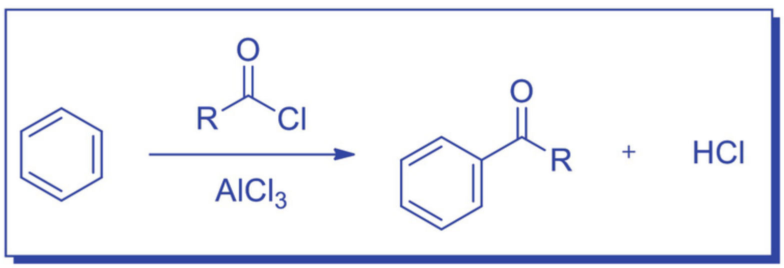
Isoprenaline is often made using a friedel-crafts acylation reaction, as shown below, between 1,2-dihydoxylbenzene (molecule #1) and chloroacetyl chloride (molecule #2) in the presence of an $AlCl_3$ catalyst. During the reaction, it forms an intermediate compound, 2-chloro-3′,4′-dihydroxyacetophenone (molecule #3), before becoming the final product, isoprenaline (molecule #4).

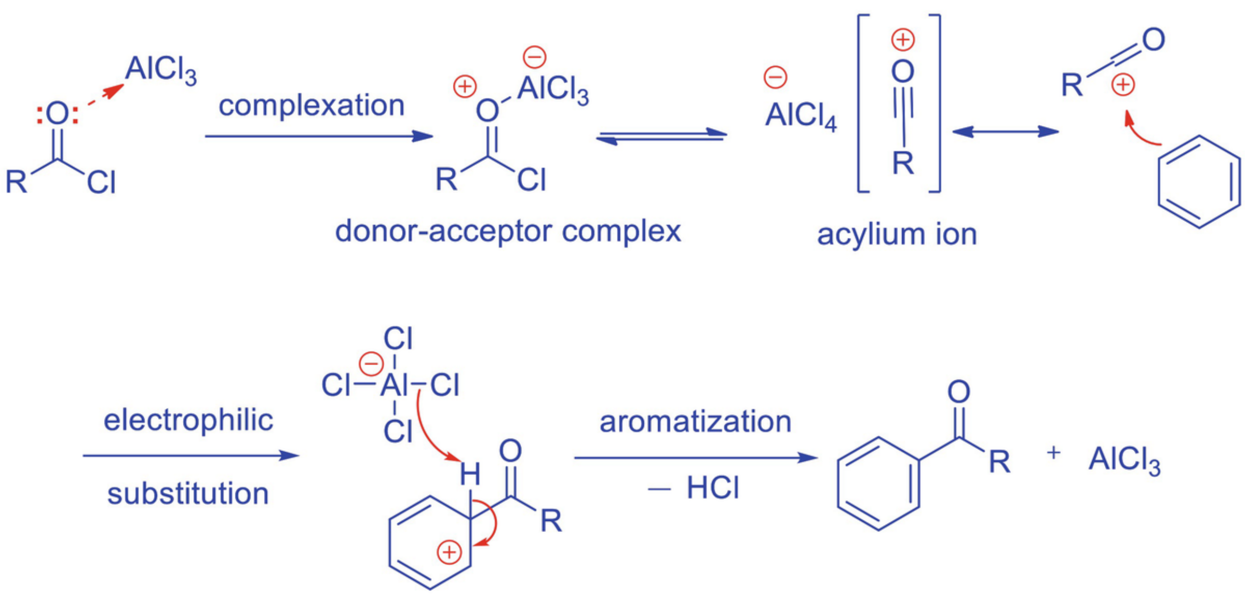


a) Write out the molecular formula for 1,2-dihydoxylbenzene (molecule #1) ***(2 points)***
   $C_6H_6O_2$
   +2 points for correct molecular formula

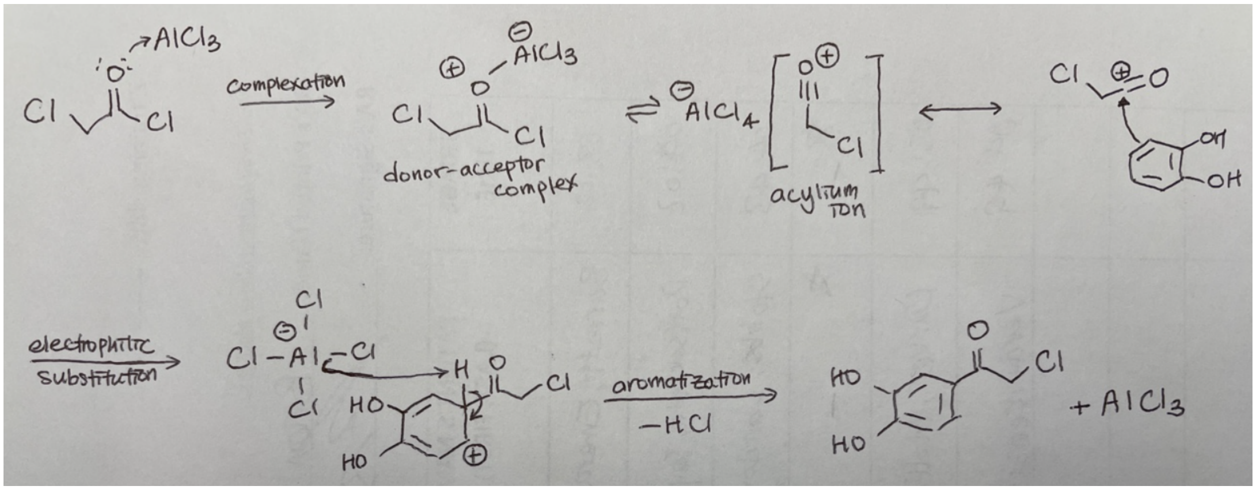
b) What is the empirical formula for 1,2-dihydoxylbenzene (molecule #1)? ***(2 points)***
C_3H_3O
+2 points for correct empirical formula

c) A friedel-crafts acylation reaction between 1,2-dihydoxylbenzene (molecule #1) and chloroacetyl chloride (molecule #2) in the presence of an $AlCl_3$ catalyst results in the formation of 2-chloro-3′,4′-dihydroxyacetophenone (molecule #3). The chemical mechanism behind a friedel-craft's acylation reaction between benzene and RCOCl in the presence of $AlCl_3$ catalyst is shown below. In the space below, show the entire mechanism of the reaction between 1,2-dihydoxylbenzene (molecule #1) and chloroacetyl chloride (molecule #2) in the presence of an $AlCl_3$ catalyst forming the intermediate compound, 2-chloro-3′,4′-dihydroxyacetophenone (molecule #3). ***(12 points)***





(space for answer for part c)



+2 points for replacing the -R group with -CH_3Cl group

+2 points for correct drawing up to the donor-acceptor complex

+2 points for correct drawing up to the acylium ion

+2 points for correct drawing up to before the electrophilic substitution step

+2 points for correct drawing up to after the electrophilic substitution step

+2 points for correct drawing up to after the aromatization step with the correct final products