2024 WUCT: Chemystery

This exam consists of 7 questions and is worth 100 points. You will complete this exam as a team of two. You will have 1 hour to take the exam. The only allowed resources for this exam are a calculator and the provided equation sheet. You may NOT use any other notes or books. 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 the blank scratch page at the end of the exam. Make sure to clearly indicate in the problem's designated space where the rest of your work can be found. Any work anywhere other than the exam or the scratch page will not be graded. Dark pencil or pen is preferred.

In this exam, you have been assigned to investigate Ms. Kim S. Tree's tragic murder. You will apply a wide range of chemistry topics and concepts to solve the murder mystery. Each question covers one potential suspect. The final question brings everything together to single out one true cause of death and assess potential treatment. Best of luck, Detective!

Problem #1: ***(10 points)***

Ms. Kim S. Tree has an estranged son, Spectromeh. A prolific writer, he was written out of the will for not following in his mother's footsteps. He came to the birthday party messy with ink from work and gave his mother a birthday card. Was this a true olive branch or a gift of death? To find out, you decide to test the ink samples collected from Spectromeh. He claims that he only uses the purest of inks, and while the formula is secret, it is only made of two compounds. To test this claim, you use chromatography.

a. The components of chromatography include a mobile phase which runs through a stationary phase, resulting in the separation of substances. First, you try thin layer chromatography (TLC). TLC separates substances by what property? ***(1 point)***

It separates based on the relative polarity of substances (+1pt).

b. If Spectromeh's claims are true what do you expect to see on the plate? ***(1 point)***

We expect to see two spots (+1pt) on the plate if the substances are separable by TLC.

c. For TLC plates, the retention factor or R_f value can be calculated by the following equation:

$$R_f = \frac{distance\ traveled\ by\ sample}{distance\ traveled\ by\ solvent}$$

Conceptually what does an R_f value of 1 mean and is the result useful? Why or why not? ***(3 points)***

An R_f value of 1 means the sample traveled the same distance as the solvent (+1pt). This is not a useful result (+1pt) as it does not provide insight into whether the sample could be separated by polarity (+1pt).

d. Initially you use a 1:1 ratio of hexane (nonpolar organic solvent) to ethyl acetate (polar solvent) and get an R_f value of 0. Which solvent should you increase to get a greater R_f value? Describe how this change works. ***(2 points)***

You should increase the **ethyl acetate** concentration (+1pt). Adding more of the polar solvent will **increase the strength of the interactions** between the sample and the mobile phase, carrying it farther (+1pt).

e. You record the following data:

Full length of the plate: 10.0 cm
Distance to the start line: 1.0 cm
Distance to first sample dot: 6.0 cm
Distance to second sample dot: 4.5 cm
Distance to solvent front: 9.0 cm

All distances are measured from the plate bottom. If these notes describe all of the observed results,

i. Give the R_f values of all observed sample dots. ***(2 points)***

R_f = (6.0 cm - 1.0 cm) / (9.0 cm - 1.0 cm) = **0.625** (+1pt)
R_f = (4.5 cm - 1.0 cm) / (9.0 cm - 1.0 cm) = **0.4375** (+1pt)

ii. Are they consistent with Spectromeh's claims? ***(1 point)***

Yes (+1pt)

<u>Problem #2</u>: *(14 points)*
At one point in the night, Kim ran into her ex-business partner and shared a piece of cake with them. You need to investigate the ingredients in the cake for poisonous substances. You crumble the cake into tiny pieces and find that you can use neodymium magnets to extract an unknown metal substance from the cake. To figure out the identity of this metal, you first conduct a couple of experiments to build up a reference table:

a. You plunge a 645 g piece of aluminum into 375 g of water. The temperature of the water increases from 26°C to 87°C. If the original temperature of the aluminum piece was 251°C, what must the heat capacity of aluminum be in J/gC? c_{water}= 4.18 J/g°C ***(3 points)***

$-q_{Fe} = q_{water}$
$-m_{Al}c_{Al}\Delta T_{Al} = m_{water}c_{water}\Delta T_{water}$
+1 point for setting up equality

$-(645g)(c_{Fe})(87°C-251°C) = (375g)(4.18\ J/gC)(87°C-26°C)$
+1 point for plugging in numbers

$c_{Fe} = 0.904\ J/gC$
+1 point for correct final answer

b. You run two identical experiments with three other metal pieces. The table below summarizes your findings.

Metal	Mass (g) of Metal	c_s (J/g°C)	Mass (g) of water	T_i (°C) of water	T_f (°C) of water
Al	645	0.904	375	26	87
Fe	645	0.449	375	26	87
Cu	645	<0.449	375	26	87
Pb	645	0.129	375	26	87

Given the above information, which metal, aluminum or iron, would have the higher initial temperature? Account for the differences in initial temperature in the two experiments. Justify your reasoning. ***(2 points)***

Iron (+1) needs to be heated to a hotter temperature than aluminum because it cannot store as much energy as heat per gram of metal. This relationship is seen in the heat capacity values of each iron and aluminum (+1).

c. How are the values of c_s in the table related to molar heat capacity (c_m)? Please show a calculation to support your answer. ***(2 points)***

0.449J/g°C * 55.845g/mol = 25.07J/mol°C +1 point for showing a calculation
Related by the molar mass +1 point for mentioning molar mass

d. Now you move on to testing your cake sample. When you run the magnet along the cake sample, you are actually able to collect metal fillings along the magnet. Excited by this result, you immediately weigh the collected fillings to be 1.12 g. This time, you add the collected fillings into exactly 0.1 mol of boiling water (100°C). If the water's temperature drops to 95°C, what is the identity of the metal? Using your general knowledge, is it poisonous? *Assume that the metal is at room temperature, or 20°C, at the beginning of your experiment.* ***(1 point)***

$-q_{\text{unknown metal}} = q_{\text{water}}$
$-m_{\text{unknown metal}}c_{\text{unknown metal}}\Delta T_{\text{unknown metal}} = m_{\text{water}}c_{\text{water}}\Delta T_{\text{water}}$
$-(1.12\text{ g})(c_{\text{unknown metal}})(95°C-20°C) = (0.1\text{ mol})(18.01528\text{ g/mol})(4.18\text{ J/gC})(95°C-100°C)$
$c_{\text{unknown metal}} = 0.449\text{ J/gC}$

Unknown metal: iron +1 point for correct final answer

e. You had so much fun building up the table in b) that you decided to investigate the four metals further. The standard heat of formation of aluminum oxide is -1669.8 kJ/mol. The standard heat of formation of iron (III) oxide is 824.2 kJ/mol. Write and balance the corresponding two reactions. ***(2 points)***

$2\ Al_{(s)} + 3/2\ O_{2\,(g)} \rightarrow Al_2O_{3\,(s)}$ +1 point
$2\ Fe_{(s)} + 3/2\ O_{2\,(g)} \rightarrow Fe_2O_{3\,(s)}$ +1 point

f. The standard entropies of formation for aluminum oxide and iron (III) oxide are both negative. Without knowing the exact entropies, which formation reaction could occur spontaneously at room temperature? Justify your answer. ***(2 points)***

$\Delta G = \Delta H - T\Delta S$
For aluminum oxide: ΔH is negative, T is positive, ΔS is negative → ΔG could be positive or negative
For iron (III) oxide: ΔH is positive, T is positive, ΔS is negative → ΔG must be positive
+1 point for showing this sort of reasoning
Aluminum oxide +1 for correct final answer

g. Consider the following reaction: $2Al_2O_{3\,(s)} \rightarrow 4Al_{(s)} + 3O_{2\,(g)}$. Calculate the heat of reaction. ***(2 points)***

$\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$ = 0 - 2(-1669.8 kJ/mol) = 3339.6 kJ/mol

+1 point for setup

+1 point for correct final answer

Problem #3: ***(14 points)***

The next suspect on the list is Kim's butler, Francis Francium, who made the goulash for the party. The butler lays all the ingredients used to make the goulash out for your observation and, upon careful inspection, you notice that the salt container appears to be tampered with. To perform a few tests, you decide to take the tampered salt with you into Kim's study where you find a small chemistry lab equipped with a list of reagents and solutions. It's almost like Kim had expected her death upon her and was trying to lead you to who caused it.

a. Here is the list of reagents and solutions you found:

Compound Name	**Chemical Formula**	**K_{sp}**
Kensium cyanide	$Ks(CN)_2$	5.3×10^{-9}
Emilyum cyanide	$EmCN$	1.2×10^{-16}
Bismuth hydroxide	$BiOOH$	4.0×10^{-10}
Calcium fluoride	CaF_2	3.2×10^{-20}

Using your keen detective and chemistry skills, you begin by mixing the tampered salt with deionized water. You curiously find that precipitation occurs when 1.0×10^{-6} mol of the salt is added to 1 L of solution. Identify what the identity of the salt could be. Show your work. ***(6 points)***

$Ks(CN)_2$

$K_{sp} = x(2x)^2$

$5.3 \times 10^{-9} = 4x^3$

$x = 1.1 \times 10^{-3}$

$EmCN$

$K_{sp} = x^2$

$1.2 \times 10^{-16} = x^2$

$x = 1.1 \times 10^{-8}$

$BiOOH$

$K_{sp} = x^2$

$4.0 \times 10^{-10} = x^2$

$x = 2.0 \times 10^{-5}$

CaF_2

$K_{sp} = x(2x)^2$

$3.2 \times 10^{-20} = 4x^3$

$x = 2.0 \times 10^{-7}$

Since $x = 2.0 \times 10^{-7}$ for CaF_2 and $x = 1.1 \times 10^{-8}$ for $EmCN$, which is less than $1.0 \times 10^{-6}\ M$, the tampered salt could be either CaF_2 or $EmCN$.

+2 for properly balancing the Ksp to determine the molar solubilites
+2 for calculating the correct molar solubilities from the given Ksp
+2 for identifying **each** of the two salts that will precipitate out due to hypersaturation at this point

b. You find a notepad with instructions on an experiment that was being done, unrelated to the tampered salt you brought in. However, the person doing the experiment did not reveal what compound they were working with, instead using A to denote the cation and B to denote the anion. However, you find in their notes that they dissolved 8.9×10^{-5} g of the unknown salt in 150.3378 mL of carbon tetrachloride. What is the solubility of the unknown salt? Can you identify what salt he was using to experiment with? Hint: the molecular weight of the unknown salt was 29.66 g/mol. ***(4 points)***

$\frac{8.9\times10^{-5}\,g}{29.66\,g/mol} = 3.006756 \times 10^{-6}\ mol$

$\frac{3.006756\times10^{-6}\,mol}{0.1503378\,L} = 2.00 \times 10^{-5}\ M$

For EmCN, BiOOH: $K_{sp} = [A^+][B^-] = (2.00 \times 10^{-5}\ M)^2 = 4 \times 10^{-10}$

For $Ks(CN)_2$, CaF_2: $K_{sp} = [A^+][B^-] = (2.00 \times 10^{-5}\ M)\ (4.00 \times 10^{-5}\ M)^2 = 3.2 \times 10^{-14}$

The unknown salt was BiOOH.

+1 for the correct conversion to moles
+1 for the correct determination of solubility
+1 for the correct calculation of Ksp
+1 for identifying the correct molecule

c. Write the equation for the dissociation of AB in carbon tetrafluoride with the correct elemental symbols. ***(2 points)***

$BiOOH_{(s)} \rightleftharpoons Bi^{+}_{(aq)} + OOH^{-}_{(aq)}$

+1 for writing the correctly balanced chemical equation
+1 for including charges and phases

Alternate solutions to avoid double jeopardy:

$Ks(CN)_{2\,(s)} \rightleftharpoons Ks^{2+}_{(aq)} + 2CN^{-}_{(aq)}$

$EmCN_{(s)} \rightleftharpoons Em^{+}_{(aq)} + CN^{-}_{(aq)}$

$CaF_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2CN^{-}_{(aq)}$

d. You find that the tampered salt is soluble in water, alcohols, as well as in pyrimidine. Given this and the other parts of the question, which of the salts identified in (a) were most likely used? Hint: cyanide salts are soluble in aqueous and organic solvent. ***(1 point)***

EmCN +1 because CaF_2 is not soluble in organic solvent.

e. Write the dissociation equations corresponding to the salt you identified in (d). If you did not solve (d), write the dissociation equations for $AgCl$ and $PbCl_2$. Make sure to include phases and charges in your answer. ***(1 point)***

$EmCN_{(s)} \rightleftharpoons Em^{+}_{(aq)} + CN^{-}_{(aq)}$ +1 point

$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

Problem #4: ***(15 points)***
Next, you move on investigating Kim's husband, who Kim shared a drink with. You find the drink, which looks murky, and you recall that a drink stored too long could become poisonous.

Because of bacterial metabolism, amino acids in a drink would be turned into ammonia, which in turn undergoes a complex conversion into nitrate. The following reactions take place on the cytoplasmic membrane of nitrifying bacteria.

$$NH_3 + O_2 + 2H^+ + 2e^- \rightarrow NH_2OH + H_2O$$

$$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^-$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

a. Write out the balanced equation for the whole reaction from ammonia to nitrate. ***(1 point)***

$NH_3 + O_2 + H_2O \rightarrow NO_3^- + 5H^+ + 4e^-$

b. Although nitrate isn't toxic, it will be reduced back to nitrite in the human body, which is a highly toxic substance. Without prompt medical treatment, ingesting 2.6 g sodium nitrite is lethal to an adult. You decide to test the concentration of nitrate in the drink.

You centrifuge the drink to remove all suspended solids and take a 2 mL sample from the supernatant. Nitrate levels can be determined using iodometry, where iodide is oxidized by nitrate under the reaction $6I^- + 2NO_3^- + 8H^+ \rightarrow 3I_2 + 2NO + 4H_2O$. One of the products, elemental iodine, is then titrated with the strong reductant thiosulfate in the following reaction: $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$, where starch is used as the indicator.

What is the typical sign that the endpoint has been reached? ***(1 point)***

Color change

c. If 1 mL of 1 M KI solution was added, and 2.35 mL of 0.10 M standard thiosulfate solution was used to reach the endpoint, what was the concentration of NO_3^- in your sample? You knew that Ms. Tree only took a ~100 mL gulp at the drink. Assuming NO_3^- is reduced to NO_2^- according to a 1:1 ratio in the human body, is the NO_3^- in that gulp fatal? Show all necessary work. ***(3 points)***

Multiply equation two by 3: $3I_2 + 6S_2O_3^{2-} \rightarrow 3S_4O_6^{2-} + 6I^-$
Add it to equation one: $2NO_3^- + 6S_2O_3^{2-} + 8H^+ \rightarrow 3S_4O_6^{2-} + 2NO + 4H_2O$
$n(S_2O_3^{2-})=2.35*10^{-3}*0.1=2.35*10^{-4}$ mol → $n(NO_3^-) = ⅓*n(S_2O_3^{2-}) = 7.83*10^{-5}$ mol
$[NO_3^-] = 7.83*10^{-5}/(2*10^{-3}) = 0.039$ M +1 point

$n(NO_2^-) = n(NO_3^-) = 100*10^{-3}*0.0392 = 3.92*10^{-3}$ mol

$m(NO_2^-) = 3.92*10^{-3}*(14+16*2) = 0.18$g (0.17g-0.19g all acceptable)
OR $n(NaNO_2)$ = 2.6g/(23+14+16*2g/mol) = 0.0377 mol to be fatal
+1 point for work

NOT FATAL +1 point

d. Which of the following are likely problems with iodometry? Choose all correct answers. (Hint: assume the facts given are true. False statements will arise from the second clause of each answer choice) ***(2 points)***
   i. Elemental iodine readily sublimes, making the result lower than the actual nitrate level.
   ii. Interference of other oxidants, which makes the result higher than the actual nitrate level.
   iii. Disproportionation of thiosulfate in acidic solution, which makes the result higher than the actual nitrate level.
   iv. Some iodine is further oxidized to iodate, making the result lower than the actual nitrate level.

ii and iii.
i: no effect; iv: no effect (this reaction is essentially an electron transfer from thiosulfate to nitrate. Form of iodine does not affect titration. $4IO_3^- + 3S_2O_3^{2-} + 3H_2O \rightarrow 4I^- + 6SO_4^{2-} + 6H^+$; $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$. IO_3^- is always first reduced to I_2.)

(2pt max for all correct, +1 for some combination of correct/incorrect, 0 for fully incorrect)

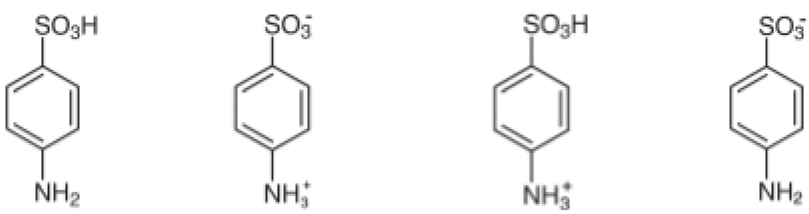
e. An alternative nitrate test with higher specificity is the sulphanilic acid method, where nitrate is reduced back to nitrite for quantitation. You decide to perform this test to make sure you didn't do anything wrong with iodometry. You take another 2 mL sample of the drink.

   This test takes place in an acidic environment. Therefore, you add 2 mL of 2 M CH_3COOH to the sample. What is the concentration of CH_3COOH molecules in the final solution? Show all your work. (Hint: assume acetic acid establishes an acid base equilibrium. K_a for acetic acid is 1.8×10^{-5}) ***(2 points)***

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$[CH_3COO^-] + [CH_3COOH]$ = 2mol/L*2mL/4mL=1M
$[CH_3COO^-] / [CH_3COOH] = K_a / [H^+] = 3.59*10^{-3}$ (1pt for correct relationships)

$[CH_3COOH] = 1 / (1 + 3.59*10^{-3}) = 0.996$ (1pt)

f. Sulfanilic acid (molecule S1, structure shown below) has curious properties. It is amphiprotic, meaning it acts both as an acid and a base. For our purposes, we'll assume it's a weak base and strong acid in water.



S1 S2 S3 S4

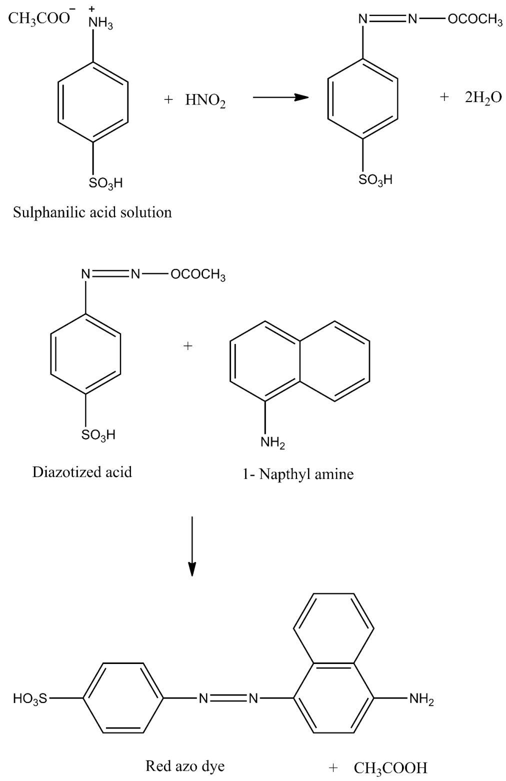
Which of the following shows the correct relationship between molecules and/or ions for a mixed solution of 1:1 molar sodium acetate (CH_3COONa) and sulfanilic acid? There is only one correct answer. (Hint: think about which species exist in solution) ***(1 point)***

i. $[CH_3COOH] + [H^+] = [OH^-] + [S4]$
ii. $[S2] + [CH_3COOH] + [H^+] = [OH^-]$
iii. $[S1] + [S2] + [S3] + [S4] = [CH_3COOH] + [CH_3COO^-]$
iv. $[Na^+] + [S2] + [H^+] = [OH^-] + [CH_3COO^-] + [S4]$

i

S1 and S3 do not exist in solution because $-SO_3H$ is a strong acid.
i: conservation of protons. Concentrations of H^+ and OH^- from water dissociation should be equal.
ii: conservation of protons; should be A
iii: conservation of matter: the sum of all forms of acetate and the sum of all forms of sulfanilic acid should have equal concentrations. $[S2] + [S4] = [CH_3COOH] + [CH_3COO^-]$
iv: conservation of charge. $[Na^+] + [H^+] = [OH^-] + [CH_3COO^-] + [S4]$

g. The whole process of the nitrate test is shown below. The concentration of red azo dye can be determined with spectrometry.



Which of the substances in the reaction could act as a catalyst? ***(1 point)***

CH_3COOH or CH_3COO^- or both

h. You run the sample on a spectrophotometer and measure a maximal absorbance of 0.028 at a wavelength of 495 nm. To translate absorbance data to concentration, a standard 0.10 M nitrate solution was used. You perform the exact same procedure on this standard solution and obtain a maximal absorbance of 0.067 at 495 nm. What is the concentration of nitrate in the sample? Show your work. ***(2 points)***

A = ebc (Beer's Law) so absorbance and concentration are directly proportional
0.067/0.10 = 0.028/C (+1 for showing work)
C=0.042 (+1 for correct final answer)

i. Which of the following are likely problems with the sulphanilic acid test? Choose all correct answers. (Hint: assume the facts given are true. False statements will arise from the second clause of each answer choice) ***(2 points)***

i. 1-naphthylamine breaks down under light, making the result lower than the actual nitrate level.
ii. Citric acid, which complexes with interfering ions, is not added, making the result higher than the actual nitrate level.
iii. Nitrite is undistinguished from nitrate, making the result (nitrate level) higher than the actual nitrate level.
iv. Nitrate partly breaks down in the standard solution, making the result lower than the actual nitrate level.

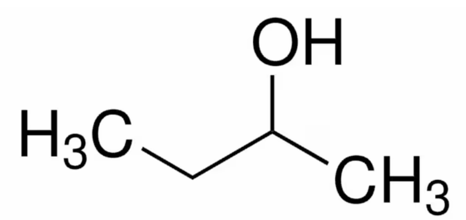
ii and iii
i: no effect. All reactants are over-added to ensure the completion of reaction.
iv: higher
(2pt max for all correct, +1 for some combination of correct/incorrect, 0 for fully incorrect)

<u>Problem #5</u>: *(14 points)*
In this problem, you will investigate the caregiver, who helped administer Kim's medicine that night. To do so, you first need to do some reading on an important organic chemistry topic: chirality.

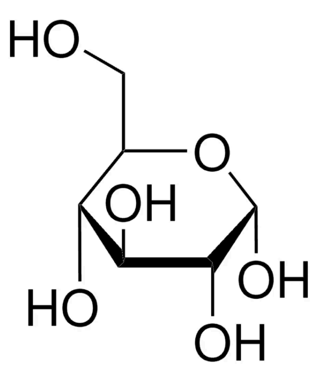
Chiral, a word meaning "hand" in Greek, is coined to express one important property of chemicals in organic chemistry: chirality.

Let's try to understand this term from its etymological (word-forming) origin. Picture your right hand's reflection in the mirror. Then, stack your left hand with your right hand, do your left hand and right hand overlap in the mirror? No, your left hand cannot fully overlap with the right hand. Your thumbs will pop out. The discrepancy embedded in our hands gives rise to the word "chirality". Chemists coined the case where mirror images cannot completely overlap as non-superimposable images. Otherwise they are superimposable. A molecule that possesses <u>non-superimposable mirror images</u> is known as a <u>chiral</u> compound. The two non-superimposable mirror images are also called enantiomers. On the other hand, one with <u>superimposable mirror images</u> is an <u>achiral</u> compound.

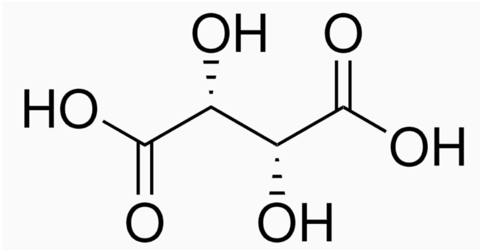
a. Identify the chirality of the following compounds (Note: solid wedge means bond pointing outward (toward you), and dashed line means bond pointing into the page). ***(4 points)***



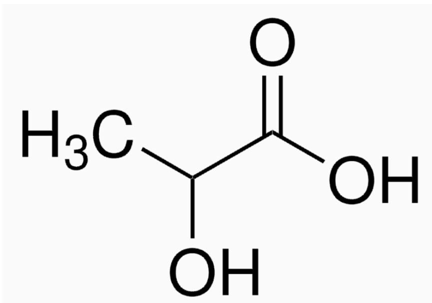
Chiral



Chiral



Achiral

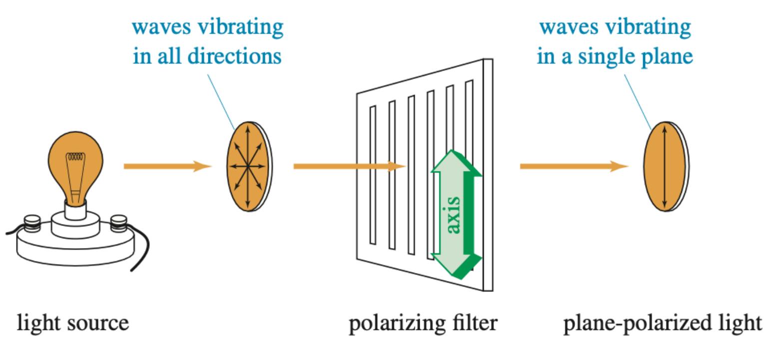


Chiral

(To grader, if correctly answered, 1 point is awarded for each compound. Otherwise, no point is awarded.)

b. Two enantiomers can have very different chemical properties. For example, thalidomide is a medicine used to cure morning sickness. Its enantiomer is a teratogen (chemicals causing abnormal fetal development).

Scientists developed a method to detect the composition of each enantiomer in a mixture. Different chiral products have different optical properties. Here is the apparatus:



As you may know, light is an electromagnetic wave pack that can be polarized by canceling waves going in other directions, leaving only one direction of the wave, as illustrated above.

Then, this polarized light will pass through a mixture, and behind the mixture, there will be a detector screen to see if the wave deviates from its original direction.

What should be the deflection angle of light if two enantiomers present in the same percentage? ***(1 point)***
Key: only 0 degrees will be accepted.

c. Given that the deflection angle is -2.4° for two enantiomers, and given that the optical activity of the right-hand form of this generic chemical is 4°. Calculate the enantiomeric excess in this sample. Enantiomeric excess is how much of one enantiomer present in the sample exceeds the other. (Hint: two enantiomers should have the same optical activity but in different orientations) ***(3 points)***
Solution: Two enantiomers should have the same optical activity but in different orientations.
So left-hand activity: -4 degree.
Set the proportion one enantiomer present in the sample is x, the other present in the sample will be 1-x. (Arbitrary, this solution set the right-handed form as x, could be the opposite.)
$4x+(-4)(1-x)=-2.4$
Solve and obtain $x=0.2$, $1-x=0.8$
E.E=(0.8-0.2)*100%=60%

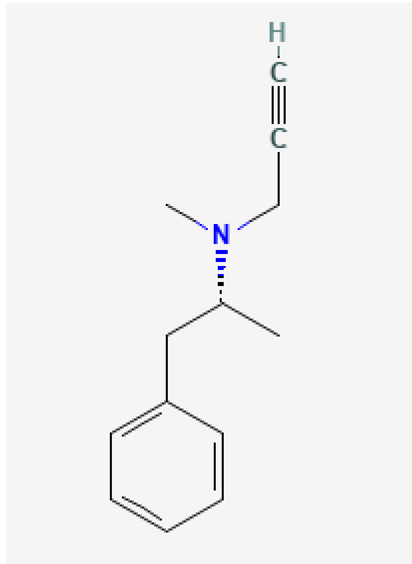
Rubric: +1 if the student correctly understands that two enantiomers have percentages that sum to 1.

+1 for correct set up of the equation, or other mechanism that could obtain the same answer.

+1 this final point will be awarded if one demonstrates correct understanding, set up correctly, and obtains the correct answer.

Now that we have practiced dealing with chirality, you can work on this part of the murder case:

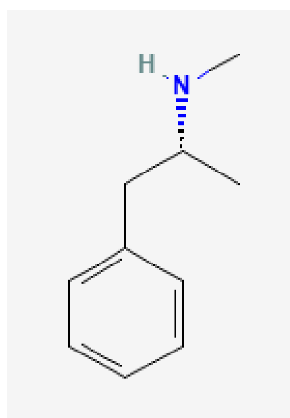
d. Mrs. Tree was diagnosed with Parkinson disease, her physician prescribed a medication known as Selegiline for treatment. The structure of this chemical is shown below.



This drug is usually prepared with hydrochloric acid. With that, comment on the solubility of the drug in water. ***(1 point)***

Soluble. (Insoluble is not acceptable as an answer.)

e. Methamphetamine, a drug that can be fatal if an excessive amount is consumed, is a chiral chemical. Selegiline hydrochloride can be metabolized to form one enantiomer of methamphetamine. Provided below is a structure of this methamphetamine enantiomer.



Could this enantiomer be distinguished from selegiline hydrochloride from solubility properties? Briefly explain your reasoning. ***(2 points)***

No.

Because according to like-dissolve-like principle, this structure contains a H-bond, which will easily interact with water molecules and readily dissolve in aqueous solvent. Since selegiline is soluble in water, these two compounds are not distinguishable based solely on solubility.

Rubric:
+1 if hydrogen bond is mentioned
+1 Another point can be awarded only when comparison is included in the explanation.

f. Fortunately, only the D-enantiomer of methamphetamine is fatal. The federal drug testing agency defined illicit prescription exposure as a specimen containing 20% D-methamphetamine.

When you are investigating the crime scene, you obtain a sample which contains the medication Kim is taking. You conduct the optical experiment mentioned previously. The resultant optical activity is 16.9°. The optical activity of D-methamphetamine is -18.5°.

Without making any calculations, you are able to rule out the possibility that methamphetamine is the true cause of death. Why? Briefly explain your reasoning. ***(3 points)***

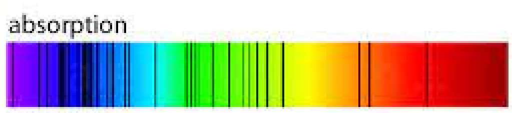
Sample Answer:
Both the l and d enantiomers should have the same optical activity (specific rotation.) And optical activity of a mixture containing equal proportion of both should be 0. Since the optical activity of this sample is 16.9 degree, this means the L-enantiomer occupies the major percentage, more than 80%. So D-enantiomer will present in less than 20%. This prescription is legal or has not gone through artificial manipulations.

Rubric:
+1 if the fact that L- and D- enantiomers possessed the same specific rotation is recognized.
+1 if one is able to deduct the fact that L-enantiomer occupies the major percentage.
+1 Conclusion and no redundant answer is given.

Problem #6: ***(18 points)***
The last suspect on the list is Kim's neighbor, Mrs. Curie. Mrs. Curie has an antique jewelry collection. Whenever she goes to a party, she likes to bring one of her most treasured possessions as a gift. When Mrs. Curie received the invitation to Kim's birthday party, she went to her jewelry display with a sly smile. She looked over each piece carefully before finally settling on a silver-gray ring, adorned with engravings of swirls. She placed it in a box, wrapped it up, and put a red bow on top. The night of the birthday party, she gave her gift personally to Kim, who excitedly opened it alone in her bedroom. You decide to see if the ring is made of any potentially toxic substances.

Because atoms have quantized energy levels, an atom is only able to absorb or emit certain frequencies of light. These emission or absorption spectra are unique for each element.

a. The first thing you do is take a light absorption spectrum of the substance composing the ring. Explain what the colors vs. black lines represent in the below spectrum. ***(2 points)***

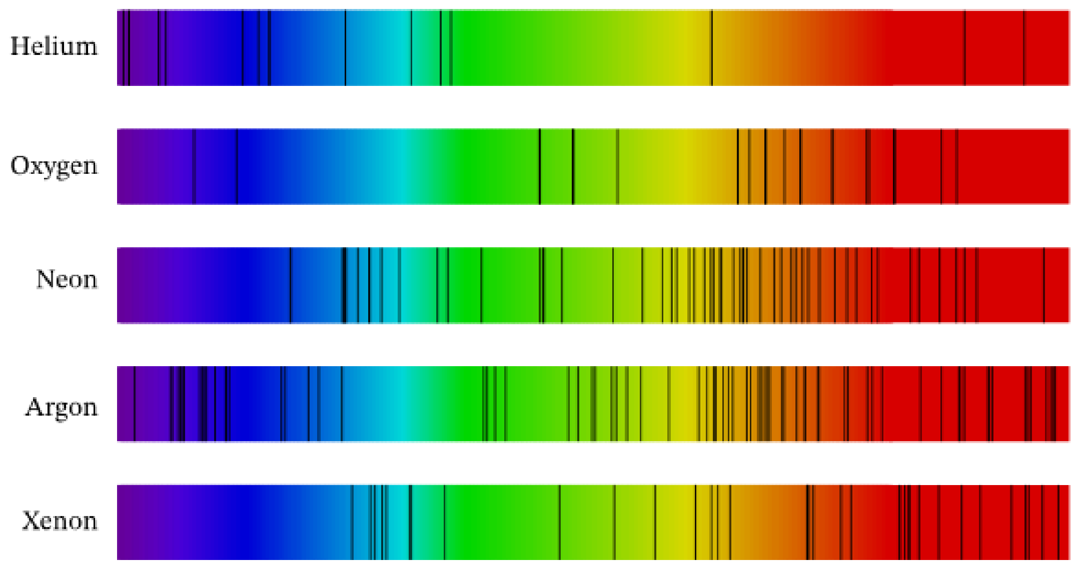


You shine light into the sample, and certain wavelengths/frequencies/energies are absorbed. The rest of the light goes through. The black lines represent the wavelengths/frequencies absorbed by the sample. +1 for explaining black lines as absorbed energies +1 for explaining colors as light that goes through

b. A table of the range of wavelengths that appear as each color of visible light is given below.

Color	**Wavelength (nm)**
Red	625 - 740
Orange	590 - 625
Yellow	565 - 590
Green	520 - 565
Cyan	500 - 520
Blue	435 - 500
Violet	380 - 435

When you take your absorption spectrum, you observe black lines at 486 nm, 512 nm, 525 nm, 543 nm, 561 nm, and 676 nm, among others. Using this information, which of the following elements can your mysterious substance most definitely not be? Rule out as many as you can. ***(3 points)***



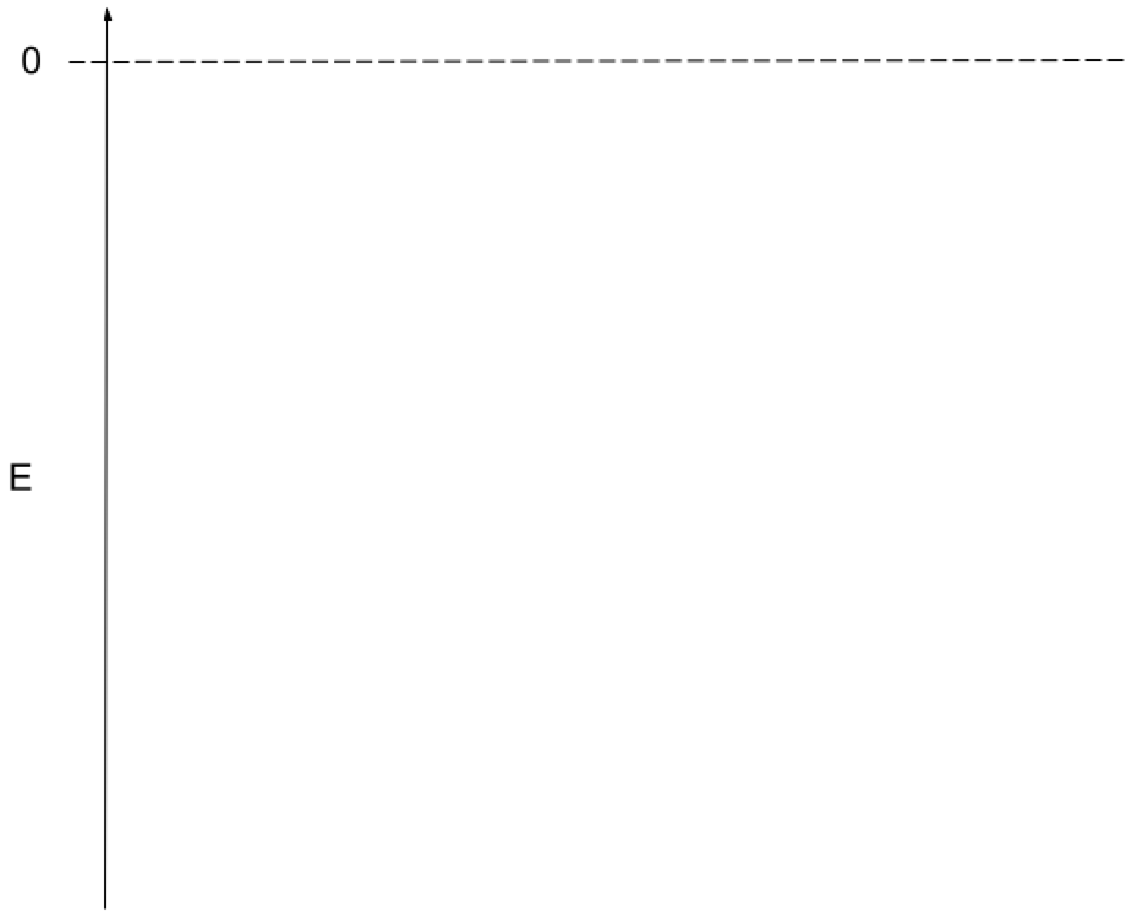
486 nm - blue
512 nm - cyan
525 nm - green
543 nm - green
561 nm - green
676 nm - red

Need at least 1 line in red, at least 3 lines in green, at least 1 line in cyan, and at least 1 line in blue

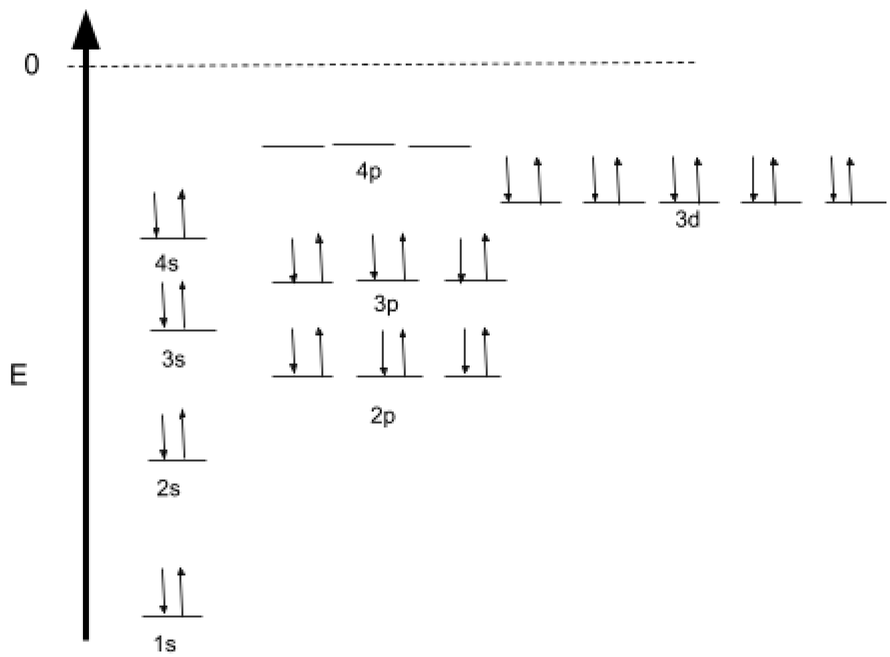
NOT Helium because only 2 lines in green
NOT Oxygen because 0 lines in cyan
NOT Argon because 0 lines in cyan
NOT Xenon because 0 lines in blue

Helium, Oxygen, Argon, Xenon +1 for each correct answer, but 3pt max

c. When you take and analyze your absorption spectrum, you discover that the mysterious substance on the ring is arsenic. On the axes below, draw an orbital filling diagram for an As^{3+} cation. ***(3 points)***



Answer:



+1 for correct number of electrons
+1 for correct use of orbitals
+1 for obeying orbital filling rules

d. Assume the arsenic orbitals have the energies shown in the table below. If you shine a light at a neutral arsenic atom that gives an excitation of a 2s electron to a 4p orbital, would this show up as a black line in the atomic absorption spectrum? Explain your answer in 1-2 sentences. ***(3 points)***

Orbital	Energy
1s	-60.78 eV
2s	-42.45 eV
2p	-29.36 eV
3s	-18.84 eV
3p	-9.65 eV
4s	-4.23 eV
4p	-2.86 eV
5s	-1.98 eV

2s: -42.45 eV

4p: -2.86 eV

$\Delta E = E(4p) - E(2s) = -2.86 - (-42.45) = 39.59\, eV$

$39.59\, eV \times \frac{1.6021773 \times 10^{-19} J}{1\, eV} = 6.3430199 \times 10^{-18} J$

+1 for calculating energy transition

$$E = h\nu = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{E} = \frac{(6.626076 \times 10^{-34} Js)(2.99792458 \times 10^{8}\, m/s)}{(6.3430199 \times 10^{-18} J)} = 3.131706415 \times 10^{-8} m$$

$3.131706415 \times 10^{-8} m \ * \frac{(1 \times 10^{9})\, nm}{1\, m} = 31.31706415\, nm$

31.3 nm

+1 for converting to wavelength

Visible light: 380-740 nm

No, because this excitation requires a wavelength of 31.3 nm. Visible light must fall between 380-740 nm, so this wavelength does not fall within this range.
+1 for explanation

e. You shine a light with a frequency of 1.50×10^{16} Hz at a neutral arsenic atom. Is this photon absorbed? ***(3 points)***

$E = h\nu = (6.626076 \times 10^{-34} Js)(1.50 \times 10^{16} s^{-1}) = 9.939114 \times 10^{-18} J$

$E = 9.939114 \times 10^{-18} J \ * \frac{1\, eV}{1.6021773 \times 10^{-19} J} = 62.03504444\, eV$ +1 for showing work

Exciting an electron from 1s to 0 takes a minimum of 60.78 eV

This photon has more energy than is needed, so the arsenic atom will absorb the light and eject the electron. +1 for reasoning

Yes +1 for correct final answer

f. A light with a frequency of 2.83×10^{16} Hz is absorbed. What is the smallest possible deBroglie wavelength of the electron ejected from the neutral arsenic atom? ***(4 points)***

$\nu = 2.83 \times 10^{16} s^{-1}$

$KE = h\nu - \phi = 117.0394505\, eV - 2.86\, eV = 114.1794505\, eV \ * \frac{1.6021773 \times 10^{-19} J}{1\, eV}$

$= 1.82935724 \times 10^{-17} J$

+1 for calculating KE of ejected electron

$KE = (1/2)mv^2$

$2KE = mv^2$

$2(KE)(m) = m^2v^2$

$mv = \sqrt{2(KE)(m)}$

+1 for using KE equation

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

$\lambda = \frac{h}{\sqrt{2(KE)(m)}}$

$\lambda = \frac{(6.626076\times10^{-34} Js)}{\sqrt{2(1.82935724\times10^{-17} J)(9.109390\times10^{-31} kg)}}$ = 1.14775054 x 10^{-10} m

$1.14775054 \times 10^{-10} m * \frac{1\ nm}{1\times10^{-9} m} = 0.1147750539\ nm$

0.115 nm

+1 for using de Broglie wavelength equation

+1 for correct final answer

Problem #7: ***(15 points)***

a. To help you organize the information you have collected so far, which suspects can you eliminate? All of the suspects are listed below for your convenience. ***(1 point)***
   - Son (Spectromeh) *from Problem #1*
   - Ex-business partner *from Problem #2*
   - Butler (Francis Francium) *from Problem #3*
   - Wife *from Problem #4*
   - Caregiver *from Problem #5*
   - Neighbor (Ms. Curie) *from Problem #6*

+1 point automatically for answering this question, though below are the technically correct answers

Everyone except butler (Francis Francium) - cyanide, and neighbor (Ms. Curie) - arsenic

b. Activated charcoal is commonly given to patients to treat a variety of acute poisonings by absorbing the poison before the patient is induced to vomit it out. Given that activated charcoal works in part due to its negative charge, which of the following poisons would activated charcoal be useful for? ***(1 point)***
   - Cyanide
   - Arsenic +1 point for arsenic
   - Aspirin (acetylsalicylic acid is anionic in pH 7)
   - Ricin protein
   - Methamphetamine

c. You administer 50 g of activated charcoal to Kim, but her symptoms persist. Given what you know about activated charcoal, infer what must have been the poison Kim was given and explain why the activated charcoal did not work. ***(2 points)***

Activated charcoal did not work for acute cyanide poisoning because activated charcoal functions through its negative charge. Since cyanide is also negatively charged, activated charcoal would not bind and relieve the toxicity. +1 for referencing negative charge +1 for saying cyanide

d. Iron and cobalt can both react with cyanide to form coordination compounds. Consider the reactions below. Calculate ΔG for each reaction at a temperature of 25 °C. ***(2 points)***

$$Fe^{3+} + 6CN^{-} \rightarrow [Fe(CN)_6]^{3-}$$

$$\Delta H = -293.2\, kJ * mol^{-1}$$

$$\Delta S = 21.6\, J * K^{-1} mol^{-1}$$

$Co^{3+} + 6CN^{-} \rightarrow [Co(CN)_6]^{3-}$

$\Delta H \ = \ -302.4\, kJ * mol^{-1}$

$\Delta S \ = 20.4\, J * K^{-1} mol^{-1}$

$Fe: \Delta G \ = \Delta H \ - \ T\Delta S = \ -299.6\, kJ * mol^{-1}$

$Co: \Delta G \ = \Delta H \ - \ T\Delta S \ = \ -308.5\, kJ * mol^{-1}$

+2 points, +1 for each calculation

e. Which of the two reactions will have its equilibrium lying further to the right? If you did solve for (d), please provide a general conceptual answer to this question. ***(3 points)***

$Fe: \Delta G \ = - RT\, lnK$

$K \ = 3.07 * 10^{52}$

$Co: \Delta G \ = - RT\, lnK$

$K \ = 1.11 * 10^{54}$

Because $K_{Co} > K_{Fe}$, the formation reaction of the cobalt complex lies further to the right than the formation reaction for the iron complex.

+3 points - +1 from K calculation, +1 for reasoning that higher K means equilibrium is further to the right, +1 for choosing Co

f. Cyanide (CN^{-}) is known for its rapid and lethal poisoning effects. Cyanide mainly acts by inhibiting oxidative phosphorylation, a molecular mechanism that occurs on the inner membrane of the mitochondria during cellular respiration. This process uses oxygen to produce ATP which acts as an energy source for the cell by transporting electrons through different complexes on the membrane including the ferric ion rich cytochrome C oxidase (Complex IV). What is the mechanism that cyanide uses to be toxic? ***(3 points)***

By binding to (iron) ferric ions (Fe^{3+}) in cytochrome C oxidase (Complex IV) (+1), cyanide blocks the mitochondrial electron transport chain (+1) leading to ATP depletion (+1).

+3 points

g. In addition to activated charcoal, hydroxocobalamin, a chemical that contains a Co^{3+} center, can be administered therapeutically. Given what you know about hydroxocobalamin, explain why hydroxocobalamin does work on acute cyanide poisoning. ***(3 points)***

$Co^{3+} + 6CN^- \rightarrow [Co(CN)_6]^{3-}$ has a larger K than $Fe^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3-}$, it binds to cobalt better than it binds to iron. Since the mechanism CN- uses to be toxic is binding to the iron in cytochrome C, removing CN- away from ferric-ion rich cytochrome C by binding to hydroxocobalamin would treat its toxicity.

+3 points