

Forensics

Question 1: (14 points)

Blood is a common substance analyzed in many forensics cases. Since it is a complex biological fluid, there are many aspects of blood which can be analyzed and used to elucidate new information. Several chemical properties of blood allow forensics investigators to search for clues.

- a. One common way to analyze blood stain is to use luminol with H_2O_2 . This method was first developed by German criminologist Walter Specht in 1937.
- i. In the presence of blood, luminol and H_2O_2 react to produce the excited form of 3-aminophthalate, which releases the energy by emitting a photon with an energy of $4.50 \times 10^{-19} \text{ J}$. What is the wavelength (**in nm**) of the photon that is given off? (2 points)

$$\lambda = \frac{h * c}{E} = \frac{(6.626 \times 10^{-34} \text{ Js}) \left(\frac{3.0 \times 10^8 \text{ m}}{\text{s}} \right)}{(4.50 \times 10^{-19} \text{ J})} = 442 \text{ nm}$$

+1 point if students use the wavelength equation above.

+1 point for correct answer with correct units in nm.

- ii. What is the color of the photon emitted, according to your answer from part a? (1 point)

Blue, or indigo, or purple/violet

+1 point if students answer with any of these colors.

- iii. Based on the information given above, is ΔH positive, negative, or zero for the reaction between luminol and H_2O_2 ? Explain (1-2 sentences). (2 points)

It is negative because energy is released in the form of light.

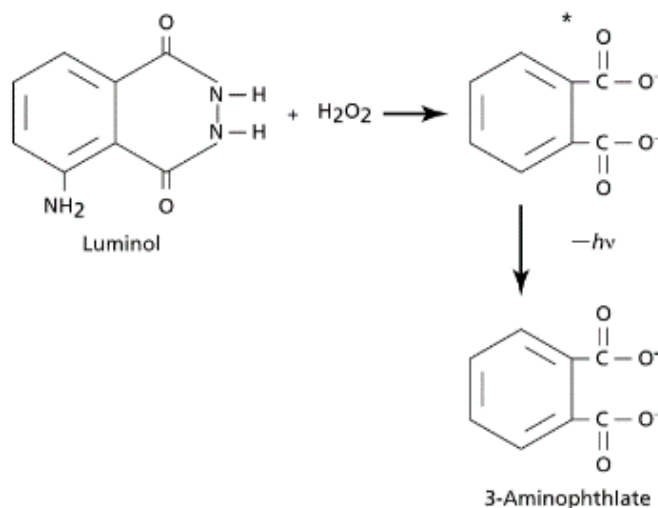
Aside: More specifically, the energy released by the reaction, instead of being released as heat, is used to excite the electrons in the product, which is what leads to chemiluminescence. However, students are not required to state this.

+1 point for saying that ΔH is negative

+1 point for correct reasoning (energy is released as light – must specify light for credit; alternatively, accept a more detailed explanation that corresponds to the note above)

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- b. Below is the mechanism of the reaction between the luminol reagent and hydrogen peroxide:



- i. What is the byproduct of this reaction? (1 point)

Nitrogen gas or N₂

+1 point for correct answer.

- ii. Is ΔS positive, negative, or zero for this reaction and why? (2 points)

ΔS is positive for this reaction due to the liberation of nitrogen.

+1 point for identifying that ΔS is positive

+1 point for the reasoning that a gas (nitrogen) is released

- iii. Based on your answers to part a.iii (ΔH) and part b.ii (ΔS), is this reaction spontaneous at all temperatures, low temperatures only, high temperatures only, or not spontaneous at any temperature? Use an equation to explain why. (3 points)

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

Since the enthalpy of reaction is negative, and the entropy of reaction is positive, both contribute to a negative Gibbs value. This means that the reaction will be spontaneous at ALL temperatures.

+2 points for “spontaneous at all temperatures”

+1 point for identifying that a positive entropy and negative enthalpy results in a negative ΔG

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- iv. The only reactants listed for the chemiluminescence reaction are luminol and hydrogen peroxide. However, this mixture will only luminesce when it comes into contact with traces of blood when sprayed at a crime scene. What do you predict is the role of blood in this reaction? Is your answer to part iii consistent with this prediction? **Explain (1-2 sentences). (3 points)**

The blood is acting as a **catalyst**. This is consistent because, if the reaction is spontaneous, then the reason why luminol and hydrogen peroxide doesn't luminescence normally must be because the rate is too slow (or a similar explanation)

+1 point for mentioning the blood is a catalyst

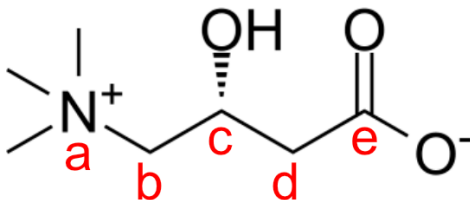
+2 points if the written explanation is sufficient in mentioning kinetic limitations be the reasons for this phenomenon, and not thermodynamics.

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Question #2: (18 points)

You are called as part of a forensic investigation team when a group of town locals report a nearby factory for illegally dumping waste products into the stream that runs through town and into a lake. Using your knowledge of chemistry, you must analyze samples taken from the stream and lake to determine whether or not the factory has been polluting the stream.

- a. One of the compounds produced by the factory is L-carnitine (molar mass = 161.2 g/mol), whose structure is shown below.



- i. Which letter(s) label chiral centers in the structure above? If there are none, say so. (2 point)

Only location C is a chiral center!

+2 points for correct answer. No partial credit given if any other location is mentioned as a chiral center.

- ii. Although L-carnitine is synthesized naturally in humans, L-carnitine supplements are often taken for several conditions or as part of certain diets. Naturally, a human body can produce around 193.44 μg per kilogram of body weight per day. However, up to 2,000 mg a day of L-carnitine is considered a safe dosage. Determine how many times more L-carnitine is delivered through a daily 2000-mg oral dosage compared to the amount synthesized endogenously. (2 points)

2.000g from pill

$$97\text{kg} * \frac{193.44 * 10^{-6}\text{g}}{1\text{kg}} = 0.0188\text{ grams}$$

$$\frac{2.000\text{g}}{0.0188\text{ grams}} = \mathbf{106.5\text{ times more}}$$

+2 points for correct final answer.

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b. D-carnitine, the enantiomer of L-carnitine, is highly toxic because it competes with L-carnitine for many binding sites.

- i. When screening the water samples, you look for the D isomer of carnitine to determine whether or not the company has been disposing of it illegally. You consider the following techniques: thin-layer chromatography with silica gel, simple distillation, and $^1\text{H-NMR}$ spectroscopy with CDCl_3 solvent. Which of these three techniques (list all that apply) could be used to separate and/or distinguish the two isomers? Explain your answer. (3 points)

Due to both of these being enantiomers and having identical properties, none of the methods above can be used to separate/distinguish them. They can only be separated by using something else that is chiral.

+1 point for “none of them”

+2 points for identifying that enantiomers have identical properties OR for identifying that they can only be separated via something else that is chiral

- ii. Since L-carnitine and D-carnitine are enantiomers of each other, they rotate the plane of polarized light in different directions. The optical rotation of pure L-carnitine is -31.3° , while the optical rotation of pure D-carnitine is $+31.3^\circ$. A racemic mixture of the two does not rotate the plane of polarized light (0° rotation). If you isolate a mixture of L-carnitine and D-carnitine from the stream and measure its optical rotation to be -29.8° , what percentage of the total carnitine in the stream is the D isomer? (2 points)

$$\text{Enantiomeric excess} = \frac{29.8}{31.3} = 0.952$$

$$x + (x + 0.952) = 1$$

$$x = \frac{0.048}{2} = 0.024 = 2.4\%$$

$$\text{Alternatively: } 31.3 - 29.8 = 1.5$$

$$\frac{1.5}{2 * 31.3} = 0.024 = 2.4\%$$

+2 points for correct final answer: 2.4%

NOTE: If an incorrect answer of 4.8% is given, then only 1 point will be awarded. 0 points if any other answer is given.

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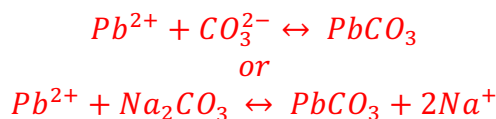
c. In addition to carnitine, you test the water for unsafe levels of lead. The limit of lead in drinkable water placed by the EPA is 15 μg per liter.

i. Convert the legal limit of lead to a molar concentration. (1 point)

$$\frac{15 * 10^{-6} g}{L} * \frac{1 mol}{207.2 g} = \frac{7.24 * 10^{-8} mol}{L}$$

+1 point for correct answer

ii. To determine how much lead is present in the water, you salt it out by adding sodium carbonate. Write a balanced net ionic equation showing the reaction that occurs when sodium carbonate is added to a solution of lead. (1 point)



+1 point for either of these reactions

iii. Assuming 1 L of solution, how many grams of sodium carbonate would you need to add to observe formation of precipitate if the concentration of lead is equal to the legal limit? The K_{sp} of lead(II) carbonate is $1.46 \cdot 10^{-13}$. Ignore the acid-base effects of the carbonate ion. (3 points)

Precipitate will form when $Q > K_{sp}$

$$1.46 * 10^{-13} < [Pb^{2+}][CO_3^{2-}]$$

$$\frac{1.46 * 10^{-13}}{[Pb^{2+}]} < [CO_3^{2-}]$$

$$\frac{1.46 * 10^{-13}}{7.24 * 10^{-8}} < [CO_3^{2-}]$$

$$2.02 * 10^{-6} < [CO_3^{2-}]$$

$$1L * \frac{2.02 * 10^{-6} mol CO_3}{L} * \frac{1 mol Na_2CO_3}{1 mol CO_3} * \frac{105.99 g Na_2CO_3}{1 mol Na_2CO_3}$$

$$= 2.14 * 10^{-4} g Na_2CO_3$$

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+1 point for substituting values into correct K_{sp} expression

+1 point for correct carbonate concentration

+1 point for correct final answer (2.14×10^{-4} g)

NOTE: If students present final answer with insufficient supporting work, **0 points** will be awarded.

- iv. You test a 1 L sample of water using this method and find that the concentration of lead is above the legal limit. The mass of sodium carbonate that you added before observing the formation of lead carbonate precipitate was (select one; no explanation required): **(1 point)**
- A. Less than your answer to part iii
 - B. Equal to your answer to part iii
 - C. Greater than your answer to part iii

+1 point for correct answer: A

- v. You take the factory managers to court for disposing illegally high amounts of lead in the water. During the trial, they argue that the lead levels are actually below the legal limit and that your conclusion is wrong because you ignored the acid-base effects of the carbonate ion in your calculation. Is their argument valid? Explain your reasoning. **(3 points)**

No, they are incorrect because the basicity of the carbonate would decrease the concentration of carbonate. This would in mean that the true lead concentration is even higher than the theoretical value we calculated.

+1 point for identifying that the factory managers are incorrect.

+1 point for identifying that the carbonate would decrease the concentration of carbonate.

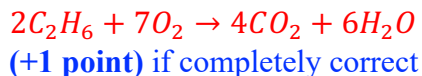
+1 point for identifying that the true lead concentration is even higher than what we calculated.

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Question 3: (27 points)

You are a forensic scientist called on to investigate your first case of arson. You first decide to review what you know about fires.

- a. Fire is produced by a combustion reaction when a fuel reacts with oxygen.
- i. Write a balanced equation for the combustion of ethane (C_2H_6) with oxygen gas, using the smallest whole-number coefficients. (1 point)



- ii. Using the reaction in part i, calculate the molar heat of combustion of ethane (C_2H_6) using the bond energies provided below. (4 points)

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C—H	413	O—O	204
C—C	347	C=C	614
C—O	358	C=O	745
O—H	467	O=O	498

To find the total change in enthalpy, find the energy of bonds broken and subtract from the energy of bonds formed.

$$\begin{aligned}\Delta H_{\text{Comb}}^{\circ} &= (10(\text{C}-\text{H}) + 2(\text{C}-\text{C}) + 7(\text{O}=\text{O})) - (8(\text{C}=\text{O}) + 12(\text{O}-\text{H})) \\ \Delta H_{\text{Comb}}^{\circ} &= \left(10 \left(413 \frac{\text{kJ}}{\text{mol}} \right) + 2 \left(347 \frac{\text{kJ}}{\text{mol}} \right) + 7 \left(498 \frac{\text{kJ}}{\text{mol}} \right) \right) \\ &\quad - \left(8 \left(745 \frac{\text{kJ}}{\text{mol}} \right) + 12 \left(467 \frac{\text{kJ}}{\text{mol}} \right) \right) = -3,254 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

This is for 2 moles, so to find the heat of combustion for 1 mol, divide that result by two. This means that the molar heat of combustion is:

$$\Delta H_{\text{Comb,Molar}}^{\circ} = -1,627 \frac{\text{kJ}}{\text{mol}}$$

(+1 point) for correct overall process

(+1 point) for correctly solving for the two-molar heat of combustion -3,254 kJ/mol

(+2 points) for correct final answer

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- iii. You consult a chemistry databank and find that the experimental heat of combustion is -1560 kJ/mol. Assuming that the experimental value is correct, what is the relative error of your bond energy calculation? Explain why bond energy calculations do not always yield accurate enthalpy values (1-2 sentences). **(2 points)**

$$\text{Rel error} = \frac{1627 \frac{\text{kJ}}{\text{mol}} - 1560 \frac{\text{kJ}}{\text{mol}}}{1560 \frac{\text{kJ}}{\text{mol}}} = 4.3\%$$

The tabulated bond energies are an **average** energy across many different molecules and may not be representative of the particular bonds in a given reaction.

(+1 point) for correct relative error (4.3%)

(+1 point) for correctly stating that bond energy values are averages, **OR** bond energy values are not representative of the particular molecules in a reaction, or something in the same vein.

- b. You arrive at the scene of the case. One goal of your investigation is to identify the accelerant of the fire.
- i. An accelerant is defined as any substance that speeds up the development and escalation of a fire. This may sound like the definition of a catalyst, but some accelerants are not catalysts. What is the difference between an accelerant and a catalyst? **(1 point)**

An accelerant may be consumed in the reaction, but a catalyst is not.

(+1 point) for correct answer

- ii. The most common accelerants are hydrocarbon-based fuels. Two examples are butane (C₄H₁₀) and diesel (a mixture of saturated and aromatic hydrocarbons with an average ratio of C₁₂H₂₄). Using their molecular formulas, determine in the distillation of crude oil which of the two accelerants would be collected first and explain why. **(3 points)**

In distillation, the product with the lowest boiling point (highest volatility) would evaporate and be collected first. Compounds with lower intermolecular forces have lower boiling points, and butane, as it is smaller, has lower London dispersion forces than diesel. Thus, butane will have the lower boiling point, and thus be collected first.

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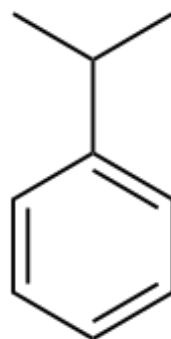
(+1 point) for mentioning that the molecule with the lower boiling point (higher volatility) would evaporate first (be the distillate).

(+1 point) for mentioning London dispersion forces effect on the molecule's relative.

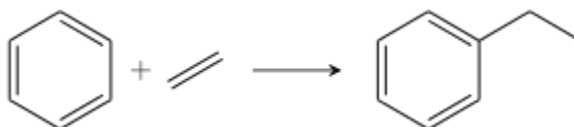
(+1 point) for mentioning that the butane would be collected first.

NOTE: If student simply states that the butane would be collected first, with no explanation, **0 points** will be awarded.

- iii. As mentioned before, diesel itself is a mixture of hydrocarbons, composed of roughly 75% alkane and 25% aromatic compounds such as naphthalenes and alkylbenzenes. Cumene, an alkylbenzene present in diesel, is shown below.



Cumene forms via a process known as electrophilic aromatic substitution, a process where an atom on an aromatic molecule is replaced by an electron pair-accepting molecule. An example of an electrophilic aromatic substitution is shown below.



Name and draw the reactants that are required to produce cumene using the same mechanism. (2 points)

Propylene and benzene



AND



OR



(+1 point) for properly naming both molecules

(+1 point) for properly drawing both molecules

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- iv. You begin to take samples of objects to scan for possible traces of uncombusted accelerants. Your supervisor tells you that because the fire was put out with water rather than a fire extinguisher, absorbent materials are most likely to still contain accelerant residue. Explain why this is the case when water is used to put out a fire. *(2 points)*

Accelerants are usually hydrocarbons, which are highly hydrophobic. When fire is extinguished with water, the accelerants will not be dissolved, and instead are pushed and sealed into absorbent material where they accumulate, shielded from evaporation.

(+1 point) for mentioning the typical hydrophobic nature of the accelerants

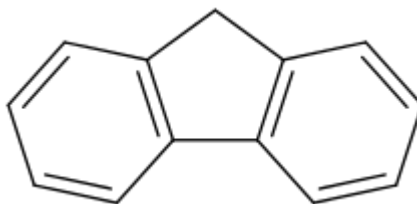
(+1 point) for mentioning that the accelerants do not dissolve in water

- v. In order to detect and identify accelerants, analytical techniques are used. One possible method is UV-visible spectroscopy, which is suited for compounds that absorb in the visible range, such as transition metal ions and highly conjugated compounds. Would butane or diesel be more clearly identified by a UV-vis spectrum? *(2 points)*

Diesel, as it contains significant amounts of aromatic hydrocarbons, which are conjugated organic molecules.

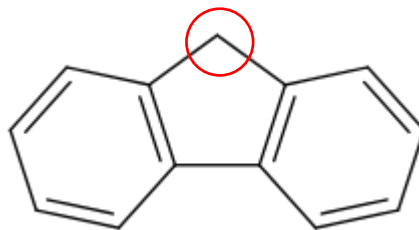
(+2 points) for indicating that diesel would be more clearly identified using UV-vis spectroscopy WITH an explanation, such as that this is due to the presence of **conjugated or aromatic** organic molecules.

- c. Some research has shown that the composition of soot may be dependent on the composition of the accelerant. The analysis of fire residue is often done through gas chromatography, and the specific combination of PAHs detected can sometimes be linked to corresponding accelerants. During analysis, one of the PAHs identified is shown below.



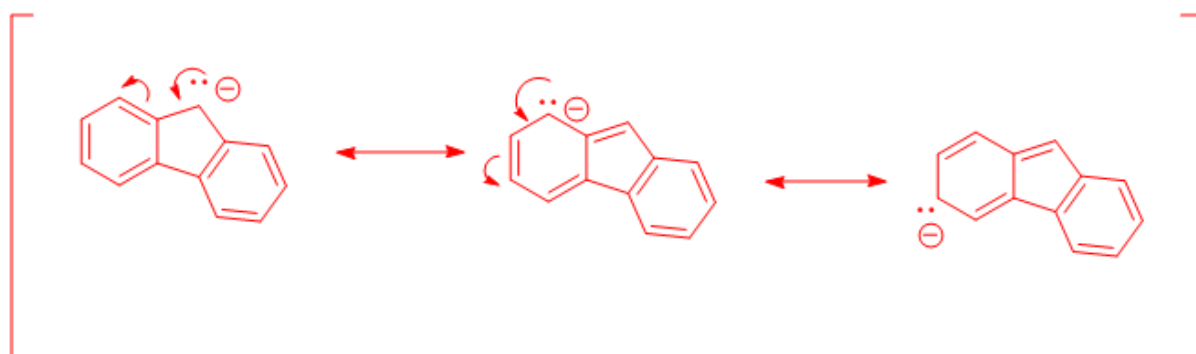
- i. Unlike many other PAHs, this one is known to be weakly acidic in certain solvents. Redraw the molecule on your answer sheet and circle the carbon(s) which is/are most likely to lose a hydrogen when the molecule is deprotonated. *(1 point)*

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(+1 point) for correct solution

- ii. Draw the conjugate base and two of its resonance structures to show why the carbon(s) you circled have the most acidic hydrogen(s). (3 points)



+1 point for correct conjugate base

+1 point for each correct resonance structure (including others not shown here)

Note #1: Electron arrows are not necessary for full credit and are included simply for instructional use.

Note #2: If students have correct bonding arrangements, but fail to include formal charge, then **0 points** will be awarded.

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- iii. To confirm the identity of this PAH, its acidity is tested in solution. When testing the acidity of this PAH, should you dissolve it in water, dimethyl sulfoxide (DMSO), or hexane? Explain your answer (1-2 sentences). **(3 points)**

It should be tested in DMSO. It cannot be tested in water because it is nonpolar and will not dissolve in water. It cannot be tested in hexane because hexane cannot accept a proton from acids.

+1 point for “DMSO”

+1 point for identifying that PAH will not dissolve in water

+1 point for identifying that hexane cannot accept a proton

The PAH signature of the soot was found to closely match that of soot produced from fires where the accelerant was nail polish remover, a material composed mainly of acetone. Acetone is known to be a highly volatile compound, which contributes to its ability to start fires. You believe that the fire may have started accidentally, when an open bottle of nail polish remover was left accidentally near a candle or countertop.

- iv. Acetone boils at 56.0 °C, requiring 31.3 kJ/mol of energy to transform from liquid to gas. From this data, calculate its vapor pressure (in atm) at 30.0 °C. **(3 points)**

Use the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\ln\left(\frac{P_2}{1 \text{ atm}}\right) = \frac{-31300 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{molK}}} \left(\frac{1}{303 \text{ K}} - \frac{1}{329 \text{ K}}\right)$$
$$P_2(\text{vapor pressure at } 30 \text{ }^\circ\text{C}) = 0.375 \text{ atm}$$

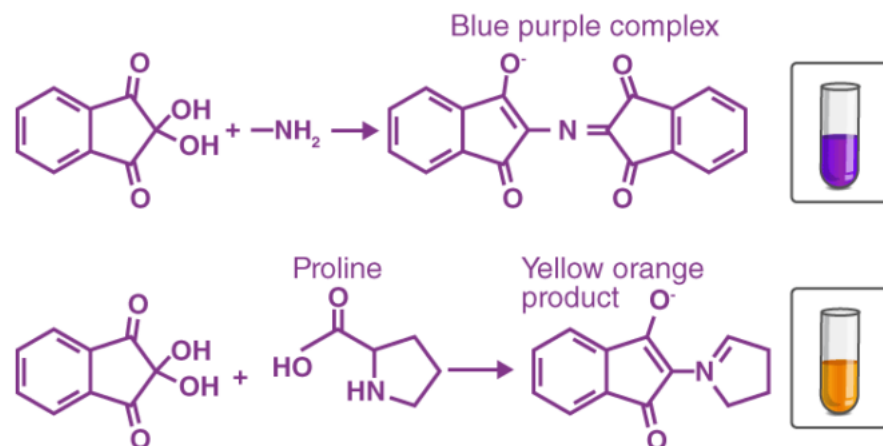
+1 point for using the Clausius-Clapeyron equation

+2 point for correct final answer **WITH** correct units.

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Question 4: (14 points)

Ninhydrin is a reagent used for fingerprint development. It reacts with the amines in amino acids left behind in fingerprint residue to produce a bright blue-purple product. However, ninhydrin also reacts with the amino acid proline to produce a different product that is orange-yellow instead.



- a. Explain why the product of ninhydrin and proline is orange-yellow, instead of blue-purple like the product formed by ninhydrin and other amino acids. Your answer should discuss molecular orbitals and the differences between the light absorbed by each of the two products. (6 points)

The blue-purple product absorbs orange or yellow light whereas the orange-yellow product absorbs blue or purple light (complementary colors). This means that the blue-purple product absorbs lower-energy (longer-wavelength) light than the orange-yellow product. Conjugation of p-orbitals decreases the HOMO/LUMO gap, thereby decreasing the energy of the light absorbed. The blue-purple complex has a larger array of conjugated p-orbitals than the orange-yellow product, which is why the blue-purple product has a smaller HOMO/LUMO gap and therefore absorbs lower-energy light.

+1 point for correctly identifying the colors absorbed by each product (complementary colors)

+1 point for correctly comparing the wavelength OR energy of the light absorbed by each product

+1 point for identifying that conjugation decreases the HOMO/LUMO gap

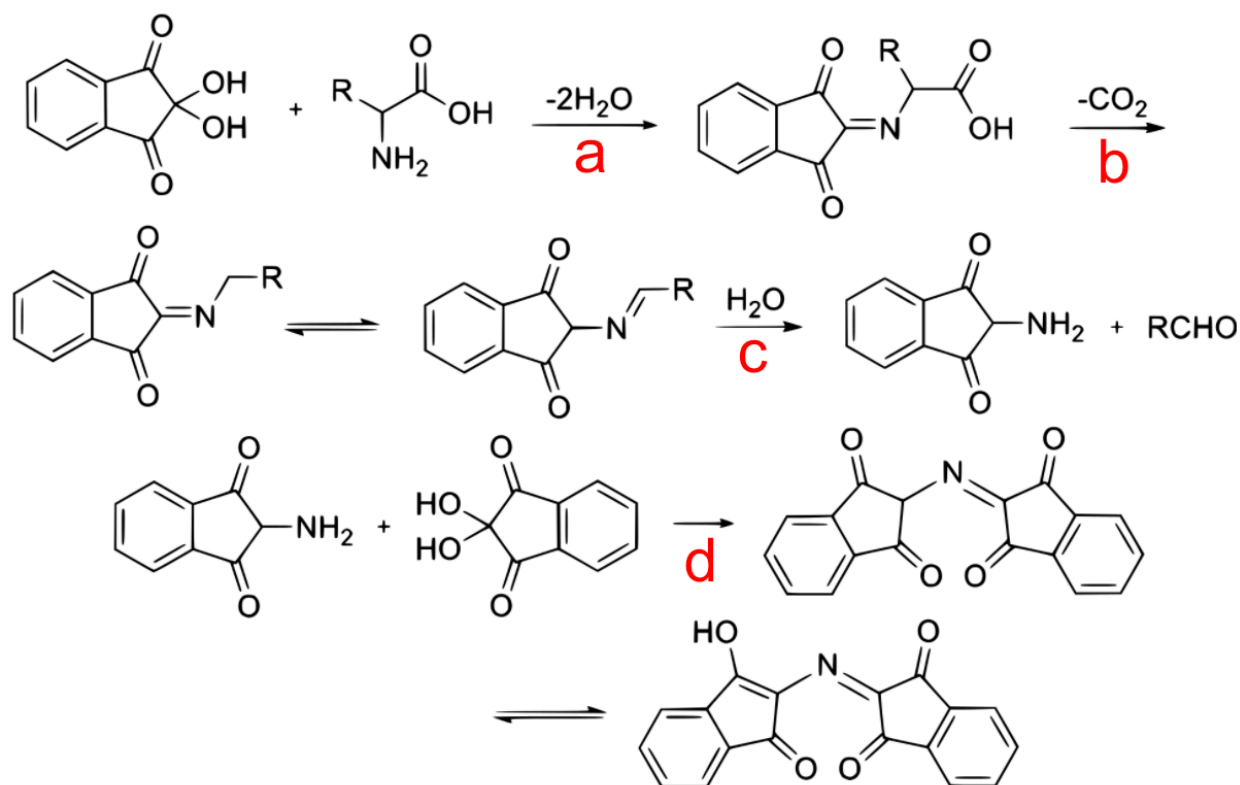
+1 point for identifying that conjugation decreases the energy / increases the wavelength of the light absorbed

+2 points for identifying that the blue-purple product is more conjugated than the orange-yellow product

- b. The following diagram shows the step-by-step reaction of ninhydrin with most amino acids to produce the blue-purple product. Four steps are labeled by a letter under the reaction arrow. Which step of the mechanism (a, b, c, or d) cannot proceed when ninhydrin reacts with proline? Use the structure of the orange-yellow product to

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justify how you know, and then propose an explanation for why the reaction with proline cannot undergo this step. (5 points)



The reaction cannot undergo step c. We know this because the orange-yellow product retains the carbon-nitrogen double bond of the intermediate right before step c. The reaction stops here because there is no lone pair available on the nitrogen atom in the reaction between ninhydrin and proline (nitrogen has four bonds).

+1 point for identifying step c

+2 points for identifying the carbon-nitrogen double bond in the orange-yellow product

+2 points for identifying that the lone pair on the nitrogen is not available (also accept that nitrogen already has four bonds and cannot form any more)

c. Ninhydrin is the most preferred fingerprinting method for surfaces like paper and cardboard, which are made out of cellulose. On the other hand, techniques like dusting and cyanoacrylate are preferred for surfaces like glass, metal, and plastic. Explain why ninhydrin works well on surfaces like paper and cardboard but not on surfaces like glass, metal, and plastic. (3 points)

Cellulose and amino acids are both polar, so amino acids will be absorbed well by paper and cardboard but will not be absorbed well by nonpolar surfaces like glass, metal, and plastic.

+1 point for identifying that cellulose and amino acids are both polar

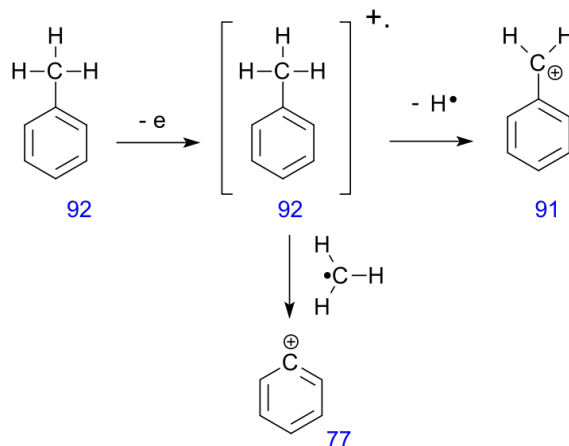
+1 point for identifying that cellulose will interact with / absorb amino acids well

+1 point for identifying that glass/metal/plastic are nonpolar

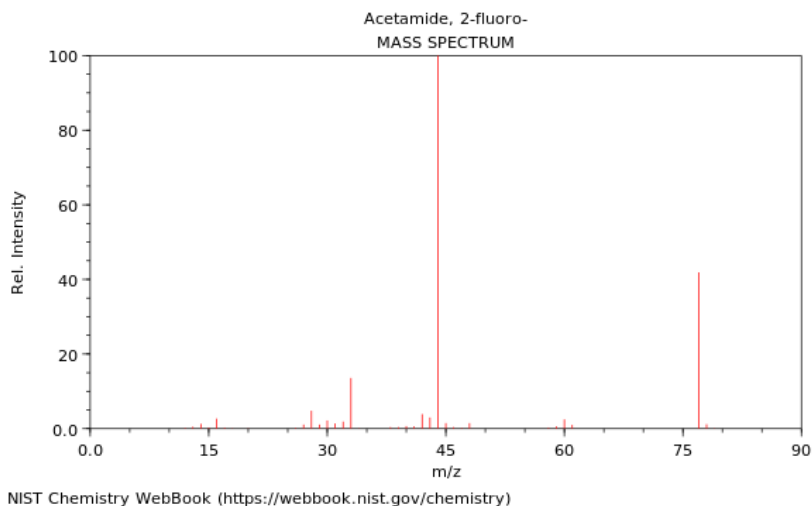
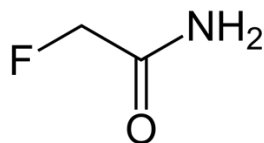
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Question 5: (18 points)

Forensic toxicologists use mass spectrometry to identify the presence and identity of poisonous substances at a scene. In mass spectrometry, the molecule is ionized to a high-energy radical cation, which then fragments via the breakage of a bond to produce two fragments: a radical species (which is not detected), and a singly charged cation whose mass (in amu) is measured by the spectrometer. Molecules can fragment in many different ways; an example is shown below (blue numbers indicate the mass of the fragment, in amu).



- a. One poison that can be used for crimes is fluoroacetamide. The structure and the mass spectrum of fluoroacetamide are given below.



The horizontal axis plots the mass-charge ratio, which we can assume to be equal to the atomic weight of the cationic fragment (in amu). The vertical axis plots the relative abundance of each fragment, or the likelihood at which that particular fragment is generated during fragmentation. The peak with the highest intensity is labeled the *base peak*.

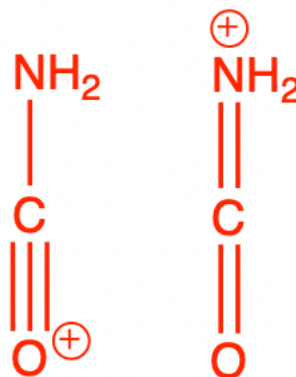
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Based on the molecular structure, draw the structure of the cationic fragment that is responsible for the high-intensity base peak. Then, draw two resonance structures of this fragment, and use these structures to explain why this peak has the highest intensity. (6 points)

Correct fragment:



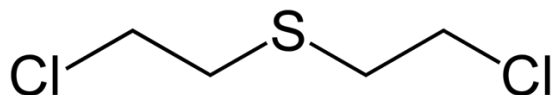
Correct resonance structures:



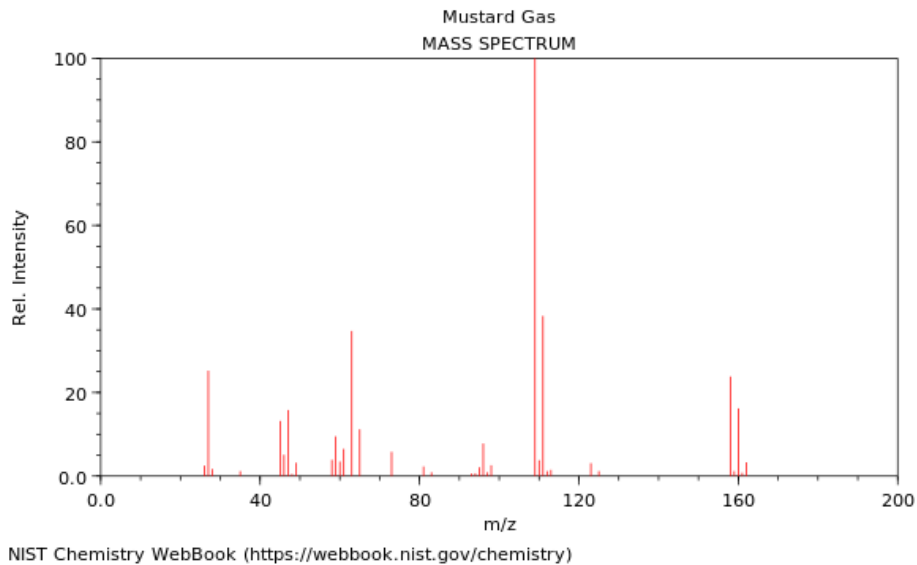
Resonance stabilizes the cation by spreading the positive charge across multiple atoms. The nitrogen and oxygen atoms donate electron density to stabilize the carbocation.

- +2 points for correct fragment (only +1 if positive charge on carbon is missing)
- +1 point for resonance structure with triple bond between C and O and positive charge on O
- +1 point for resonance structure with double bond between C and N and positive charge on N
- +1 point for saying that the cation is stabilized by resonance
- +1 point for saying that the cation is stabilized by electron-donating effects OR by the delocalization of the positive charge across multiple atoms

- b. Sulfur mustard is another toxic substance that was used as a chemical warfare agent in World War I. The structure and mass spectrum of sulfur mustard are given below.



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The molar mass of sulfur mustard is 159.08 g/mol. However, the mass spectrum shows three main peaks close to (but not equal to) $m/z = 159$.

- i. Based on the structure of sulfur mustard, explain why there are three main peaks at $m/z = 158$, $m/z = 160$, and $m/z = 162$ in the molecular peak region. What does each of these peaks correspond to? (4 points)

The reason for there being three peaks at this mass to charge ratio is that there are **two isotopes** of chlorine. Either both chlorines are the light isotope, one is the light isotope and one is the heavy isotope, or both are heavy isotopes.

+1 point for mentioning isotopes in any form.

+1 point for mentioning that it is the two isotopes of chlorine that cause the three peaks.

+2 points for mentioning the potential combinations of chlorines isotopes that cause the three peaks.

- ii. On the other hand, the base peak region only has two main peaks. Why is this? (1 point)

The fragment contains only one Cl atom.

+1 point for correct answer.

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c. Forensic toxicologists can also use mass spectrometry to identify the presence of toxic metals like arsenic, thallium, and lead, which have been used as homicidal poisons.

- i. How does the number of peaks in the mass spectrum for an atomic element compare to the mass spectrum for an organic compound, and why? (2 points)

There would be a fewer number of peaks because the atoms cannot fragment.

+1 point for mentioning fewer number of peaks

+1 point for mentioning that the atoms cannot fragment

- ii. What can the mass spectrum of an atomic element be used to identify and calculate? (2 points)

You can identify the **relative abundance** of isotopes. This can then be used to calculate the molecular weight or molar mass.

(must say abundance; just saying that you can identify different isotopes is not enough)

+1 point for stating relative abundance of isotopes (must say abundance; just saying that you can identify different isotopes is not enough for credit)

+1 point mentioning that we can use this information to calculate the average molecular weight / molar mass

- iii. Forensic toxicologists typically need to identify trace amounts of poisons in samples containing many other substances as well. The naturally occurring isotopes for arsenic, thallium, and lead are given below:

- Arsenic: ^{75}As (100%)
- Thallium: ^{203}Tl (29.5%), ^{205}Tl (70.5%)
- Lead: ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%), ^{208}Pb (52.4%)

Which of these toxic metals would be most difficult to conclusively detect using mass spectrometry in a sample containing many other substances, and why? (3 points)

Arsenic because it only has one isotope. As a result, its presence can easily be masked by another peak OR unlike thallium and lead, the identity cannot be confirmed by checking multiple peaks.

+1 point for indicating **arsenic** would be the most difficult metal to confirm using mass spec.

+1 point for indicating that this is because it has only one isotope.

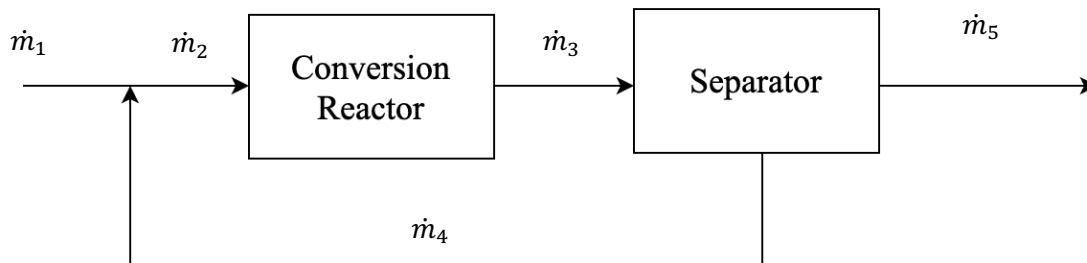
+1 point for indicating that this peak can be easily masked OR that the identity cannot be confirmed by checking multiple peaks

Forensics

Question 6: (9 points)

Recently a large explosion occurred at a large manufacturing plant resulting in fatalities. The explosion involved two reactor setups (one continuous shown in part a. and on batch shown in part b.) both experiencing temperatures above the volatile alkene product's ignition temperature. As a result of the explosion and loss of life, you are hired as an OSHA investigator to determine if it was faulty equipment or unsafe practices that was responsible for the explosion.

- a. First, you choose to investigate the continuous reactor system. This is the main reactor of the process for generating a highly volatile alkene compound through isomerization. A simplified diagram of the overall process is shown below:



This process involves isomerizing Alkene A from its trans chemical form (T) to its cis form (C). On the day of the explosion, the inlet feed was 100% T by mass and had a flow rate of 100 kg/hr. The outlet of the process a feed (\dot{m}_1) was 100% C by mass. The recycle stream (\dot{m}_4) was recorded as 20% C by mass and the reactor was estimated to achieves a 60% conversion by mass. Due to this process being exothermic, there were tight temperature controls which are known to have slow response times when the recycle mass stream is too large. The manufacturer of this system recommends that the total mass flow rate of the recycle stream not exceed 60 kg/hr in order to maintain tight control of the temperature of this process. Determine if these recommendations were violated given the operation conditions for the day of the explosion. (6 points)

First, we can do a basic mass balance for T:

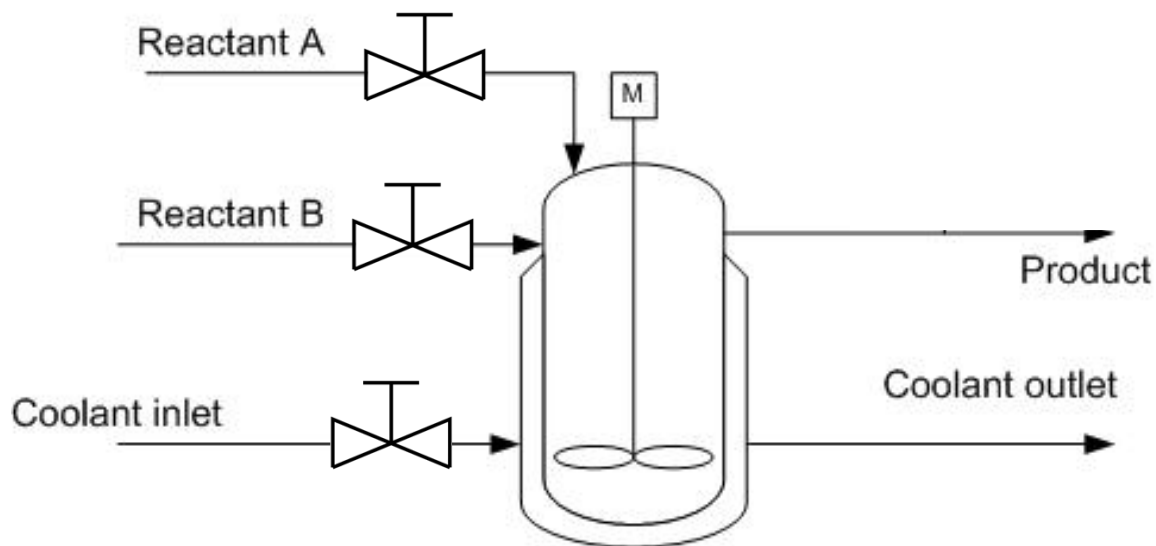
$$\begin{aligned} \dot{m}_{T,IN \text{ Reactor}}(0.6) &= \dot{m}_{C,OUT} = \dot{m}_5 \\ \dot{m}_5 &= \dot{m}_1 = 100 \frac{kg}{hr} \\ \dot{m}_{T,IN \text{ Reactor}} &= 166.66 \frac{kg}{hr} \\ \dot{m}_2 &= \dot{m}_1 + \dot{m}_4(0.8) \therefore \dot{m}_4 = \frac{\dot{m}_2 - \dot{m}_1}{0.8} = \frac{166.66 \frac{kg}{hr} - 100 \frac{kg}{hr}}{0.8} \\ \dot{m}_4 &= 83.3 \frac{kg}{hr} \end{aligned}$$

It is clear that the manufacturers recommendations were exceed by quite a large amount of 23.3 kg/hr! This definitely could be responsible for the explosion that occurred.

Forensics

- +2 points for the correct relationship between T into the reactor and C leaving the process.
- +1 point for correct T mass flow rate into the reactor
- +1 point for correct T mass balance between the \dot{m}_1 , \dot{m}_2 , and \dot{m}_4
- +1 point for correct final answer
- +1 point for brief explanation that mentions the manufacturers recommendations were exceeded.

- b. After following up on investigating the continuous reactor, you find that there were multiple valve failures for a batch process which was the ultimate cause of the explosion. Surprisingly, valve failures are quite common, and a key design idea is whether or not these valves fail in the open position (Fail-Open) or fail in the closed position (Fail-Closed). Looking at the schematic of the batch reactor below where streams A and B are reactant streams, and stream C is a cooling water stream, design each of these valves to be either Fail-Open or Fail-Closed and justify your answer. (3 points)



Immediately it is clear the **coolant inlet** should be **Fail-Open** because it is better to have too much cooling water to potentially suppress an exothermic reaction than the opposite.

For the reactant streams there are two main answers that will be accepted: The first is that **both reactant streams are Fail-Closed** because this would prevent any further reaction from taking place and stop the generation of energy. The second answer is that **one** of the two reactant streams (either of them is fine) will be **Fail-Open** while the **other** is **Fail-Closed**. This would both stop the reaction as well as potentially have more fluid to “cool” to reactor as we are adding in a fluid at a lower temperature.

- +1 point for indicating the cooling water should be Fail-Open with reasonable justification.
- +2 points for indicating the reactant streams as either combination presented above with a corresponding justification for this selection.