2022 WUCT: Team Exam

This exam consists of 7 questions and is worth 100 points. You will work together as a team to answer the questions. HINT: It is recommended that you split up the questions so that you have time to finish the exam. You will have 1 hour to take the exam, followed by 15 minutes of upload time during which you cannot make changes to your exam. The only allowed resources for this exam are a calculator and the provided equation sheet. You may NOT use any other notes, books, or websites (other than Gradescope and HopIn). You must show your work and box your final answer to receive credit for a problem. NOTE: If you get the answer to an early part of a question incorrect but later use that answer for a subsequent part of the question, you can still earn full credit for those subsequent parts. Please write your answer in the designated space on the answer sheet. If you need additional space for a problem, you may use scratch paper, but make sure to clearly indicate in the problem's designated space where the rest of your work can be found. Dark pencil or pen is preferred so that your writing clearly shows on your submitted document in Gradescope.

Problem #1: ***(15 points)***

Selective precipitation is a very helpful laboratory technique for separating a mixture containing multiple ions. This process uses the common ion effect and a difference in relative solubilities to precipitate out one solid at a time, thereby removing a certain ion of interest from the solution. Whether you are interested in the solid that precipitates out or the solution left over, selective precipitation requires a careful reflection of which ions are going where. This problem guides you through what such a thought process might look like.

You are given 150.0 mL of an aqueous mixture of 1.5 M sodium sulfate (Na_2SO_4) and 1.25 M sodium chloride (NaCl). You slowly add a 0.025 M aqueous solution of silver nitrate ($AgNO_3$), using a buret so that only one drop at a time comes out. Assume that one drop is equivalent to 0.05 mL and that the volume remains approximately 150.0 mL for each part of this problem. The mixture quickly becomes opaque. Use the information in the table below to answer the following questions.

Salt	K_{SP}	Molecular Weight
Silver sulfate	1.4×10^{-5}	311.80 g/mol
Silver chloride	1.8×10^{-10}	143.32 g/mol

a) Why does the solution become opaque? ***(1 point)***

b) Write the two reactions that have the solubility product constants given in the table above. Be sure to include phases. ***(2 points)***

c) What is the first salt that precipitates out of solution? ***(2 points)***

d) Consider the original mixture of sodium sulfate and sodium chloride. If the ion of interest is the one that precipitates, what is your ion of interest? ***(1 point)***

e) How many drops of the silver nitrate solution are needed for the second salt to begin precipitating? ***(2 points)***

f) How many grams of the first precipitate can you collect before the second salt precipitates? Assume that the volume remains at a constant 150.0 mL even after drops of the silver nitrate solution are added. ***(3 points)***

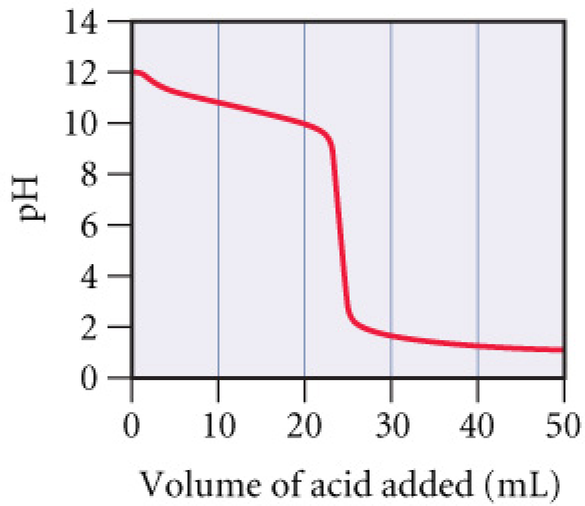
g) What mass percent of the ion of interest listed in part (d) are you able to remove from the aqueous solution? ***(2 points)***

h) Do you think this is an effective way to separate out the ion of interest from the mixture? Why or why not? ***(2 points)***

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

You are given 89.5 mL of an aqueous solution containing an unknown amount of an unknown basic substance. To determine the identity and concentration of the base, you perform a titration using 25.0 mL of a 1.50 M hydrochloric acid (HCl) solution, a buret with a stopcock, a beaker, and the acid-base indicator Ethyl Red. Use this information to answer the following questions.

a) Below is a picture of the titration curve. Which of the following could the unknown substance be? Circle all correct answers. ***(3 points)***



   a. HCO_3^-
   b. S^{2-}
   c. HSO_4^-
   d. SO_4^{2-}
   e. OH^-
   f. H_3PO_4
   g. CN^-

b) Let's assume that the unknown basic substance is ammonia (NH_3). Write the complete ionic equation for the reaction taking place between the ammonia and the hydrochloric acid. ***(1 point)***

c) In your titration of the ammonia solution of unknown concentration and the 1.50 M hydrochloric acid solution, the equivalence point is reached after 25.0 mL of acid has been added. If the K_b of NH_3 is 1.80×10^{-5}, what is the pH of the equivalence point? ***(3 points)***

d) Ethyl Red is a weak acid that serves as an acid-base indicator. When Ethyl Red reacts with water, its pK_a is 5.4. As the pH increases, this indicator changes color from colorless to red. Would Ethyl Red serve as an appropriate indicator for this titration? Why or why not? ***(2 points)***

e) Instead of hydrochloric acid (HCl) solution, you accidentally use 1.50 M aqueous sodium hydroxide (NaOH) solution. Sketch what the curve of the new pH versus volume of base added would roughly look like. ***(2 points)***

f) You spot your mistake and are back to using the hydrochloric acid solution. But now, instead of using your unknown basic substance in this titration, you accidentally add the acid to 89.5 mL of sodium hydroxide (NaOH) solution of unknown concentration. When performing the titration, you still use the same acid-base indicator, Ethyl Red. Does this indicator tell you that the concentration is larger, smaller, or the same as the actual concentration of the sodium hydroxide aqueous solution? Be sure to justify your answer. ***(2 points)***

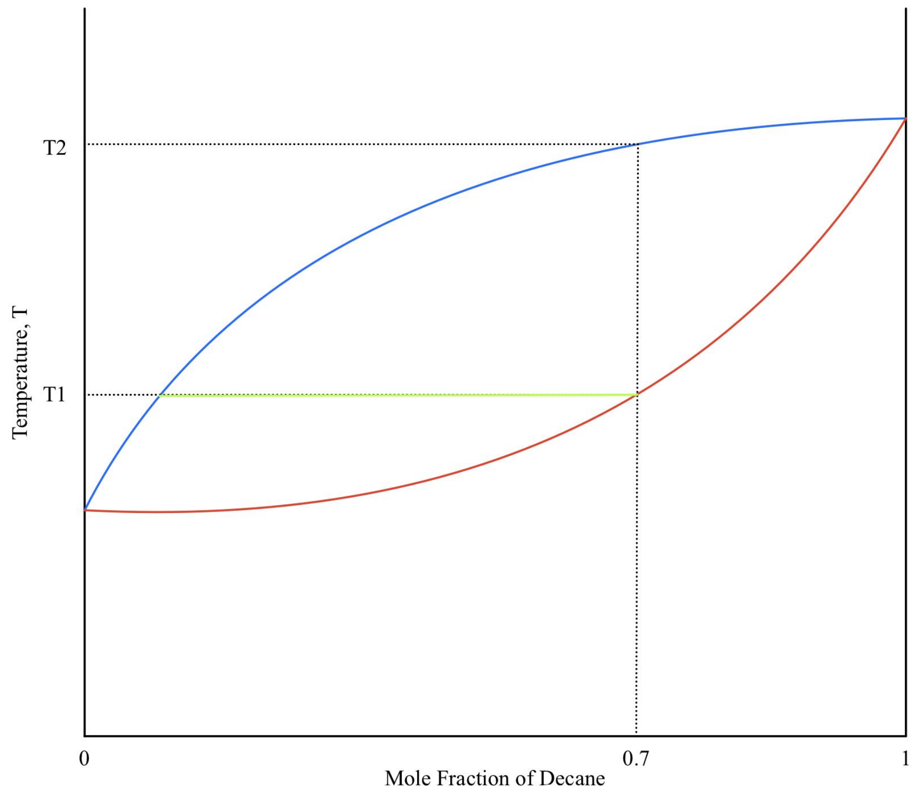
g) After reaching the correct equivalence point of the hydrochloric acid and sodium hydroxide solution titration, you then use this mixture as the titrant to determine the concentration of 89.5 mL of the same aqueous ammonia solution used above. Draw a sketch of the titration curve below. In your sketch, make sure to indicate the exact pH for any important points, including the initial pH and the final pH. ***(2 points)***

Problem #3: ***(11 points)***

A temperature-composition phase diagram is a two-dimensional map that shows which phase or phases are stable under a given set of conditions. In particular, pressure is held constant, while composition varies along the x-axis and temperature varies along the y-axis.

The temperature-composition phase diagram for an ideal mixture of octane (C_8H_{18}) and decane ($C_{10}H_{22}$) is pictured below. The blue line represents the condensation point curve, and the region above this line is the vapor phase. Conversely, the red line represents the boiling point curve, and the region below this line is the liquid phase. The region in between the two lines is the two-phase region.

Given this information, answer the following questions.



a) Which pure compound, octane or decane, has a higher boiling point? Please justify your answer using information from the diagram. ***(2 points)***

b) Which pure compound, octane or decane, is the more volatile compound? Please justify your answer. ***(2 points)***

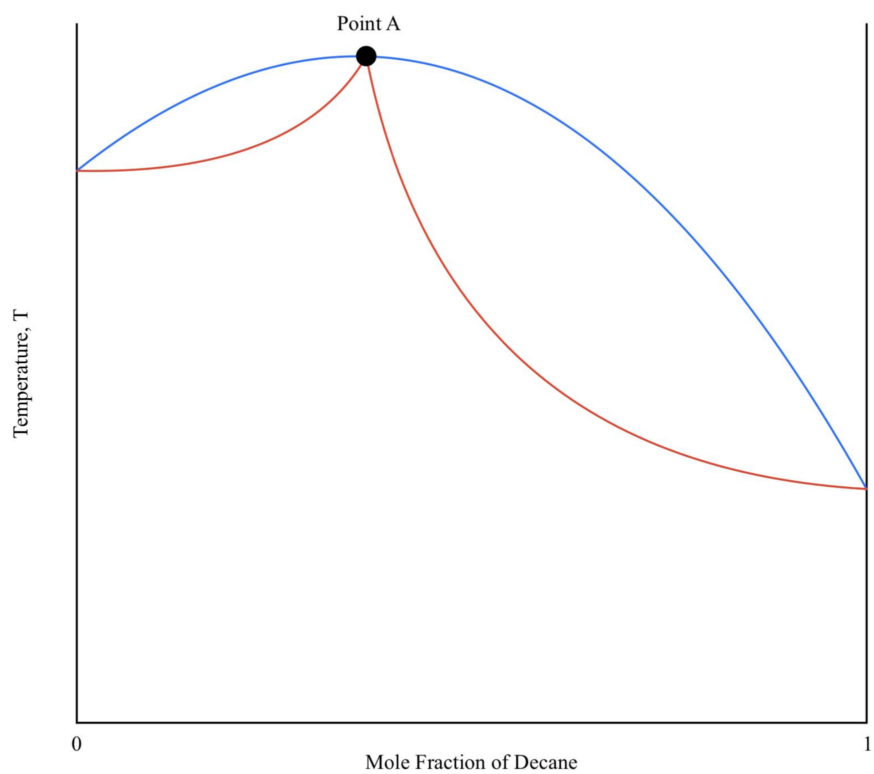
c) Assume you start with a mixture containing 0.7 mole fraction decane. How many grams of octane would you need to prepare this mixture from 15mL decane? Please show your work and report your answer to four significant figures. The densities for decane and octane are given below. ***(2 points)***
Density of decane = 0.726g/mL
Density of octane = 0.703g/mL

d) If the total vapor pressure of this mixture is 1.2atm, what is the partial vapor pressure of octane? ***(1 point)***

At this mole fraction, one can draw what is known as a horizontal tie line (shown in green) in the two-phase region, intersecting the condensation point curve and boiling point curve. The point where the tie line crosses the boiling point curve corresponds to the mole fraction of decane in the liquid phase, while the point where the tie line crosses the condensation point curve corresponds to the mole fraction of decane in the vapor phase.

e) If the temperature of the mixture rises from T1 to T2, how do the compositions of the liquid and vapor change, respectively? ***(2 points)***

f) Below is another temperature-composition phase diagram, pertaining to a mixture of chloroform and acetone. Explain what is unique about the mixture in terms of its liquid and vapor phases represented by point A labeled in the diagram. ***(2 points)***



<u>Problem #4</u>: *(23 points)*

You are given solutions of the following salts: $AgCH_3CO_2$, $MgCl_2$, $Pb(NO_3)_2$, Na_2SO_4, $LiOH$, KBr, and CaF_2. This question will explore the solubility properties and reactions of these ionic compounds.

a) One of the solutions you are given contains a precipitate. Which of the above salts is in its precipitate form? ***(1 point)***

b) Since you are given all of these salt solutions, you decide to go ahead and mix them with each other to see what will happen. You do this methodically, mixing a little bit of a salt solution with each of the others in an array, as shown below. Label each box on your answer sheet to match the table below. Each box represents the mixing of the salt solutions listed in the column heading and row heading. In each box, write what you expect to observe: Precipitate (Ppt) or No Reaction (NR). If you believe one or more precipitates will form, write out the chemical formula of the precipitate(s).

For the salt listed in your response to part (a), cross out its corresponding row and column. You do not mix this precipitate with any other salt solution. ***(10 points)***

Salt Solution	$AgCH_3CO_2$	$MgCl_2$	$Pb(NO_3)_2$	Na_2SO_4	$LiOH$	KBr	CaF_2
$AgCH_3CO_2$							
$MgCl_2$							

$Pb(NO_3)_2$							
Na_2SO_4							
$LiOH$							
KBr							
CaF_2							

c) You are now given a new dissolved salt solution that contains one cation from one of the above salts and one anion from one of the above salts, but you are not told which cation or which anion. Your job is to figure out what the unknown salt solution is. First, you react your unknown with each of the solutions in the above table and record your results. For this problem, assume that mixing the unknown salt solution is able to dissociate the ions forming the precipitate so that the precipitate dissolves. These results are shown in the table below. ***(2 points)***

Salt Solution	Result After Mixing in Unknown
$AgCH_3CO_2$	Ppt
$MgCl_2$	NR
$Pb(NO_3)_2$	Ppt
Na_2SO_4	NR
$LiOH$	NR
KBr	NR
CaF_2	Ppt

What are all of the possible cations and possible anions that could compose this salt? ***(2 points)***

Cations: ____

Anions: ____

d) You then decide to take the pH of the unknown solution. You find that the pH is 7. Are there any cations or anions you can remove from your list of possible species? Or if there is only one possible combination of cation and anion, does this new information support that answer? Be sure to justify your answer. ***(2 points)***

e) To investigate the unknown solution further, you decide to conduct a flame test. A table of the characteristic colors of flame tests for various elements is given below.

Element	Flame Color
Li	red
Na	orange
K	purple
Rb	red
Cs	blue/violet
Ca	orange-red
Sr	red
Ba	green
Cu	blue-green
Pb	gray-white

A photograph of the result of the flame test is shown below:

Using this information, can you narrow down any further the possible cations or anions that compose your unknown salt solution? If so, which ones can you eliminate? If you have already arrived at only one possible salt in your previous answers, does this new evidence support or contradict that answer? Make sure to justify your answer. ***(2 points)***

f) As a last test, you pour your unknown salt solution into a concentrated solution of hydroiodic acid (HI). Do you observe any change in pH after pouring in your unknown solution? Why or why not? ***(2 points)***

g) Taking into account all of this evidence, what is your unknown? If there are multiple answers, list all possible combinations of cations and anions. ***(2 points)***

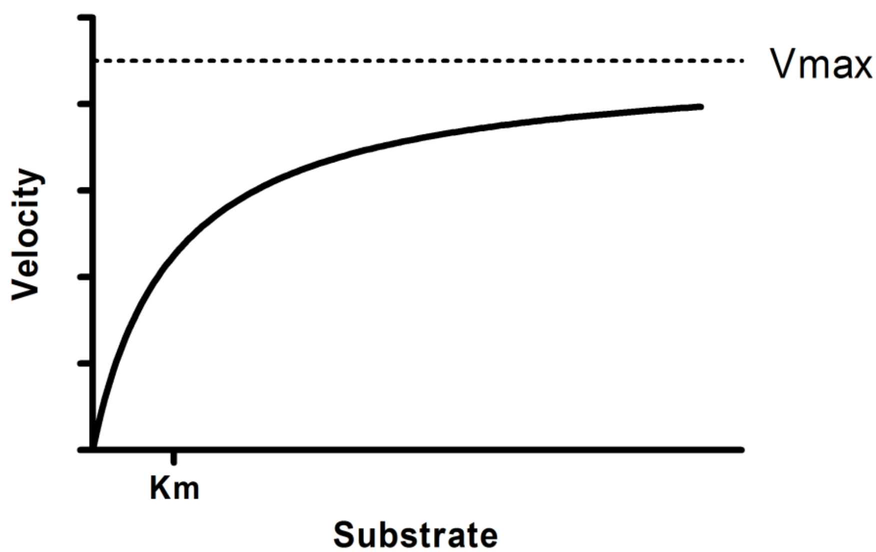
<u>Problem #5</u>: ***(8 points)***

Enzyme kinetics is the study of rates of chemical reactions that are catalyzed by enzymes. The reaction rates are measured and the effects of varying the conditions of the reaction are investigated. Studying an enzyme's kinetics is valuable because it can reveal an enzyme's role in metabolism, its catalytic mechanism, and how its activity is controlled.

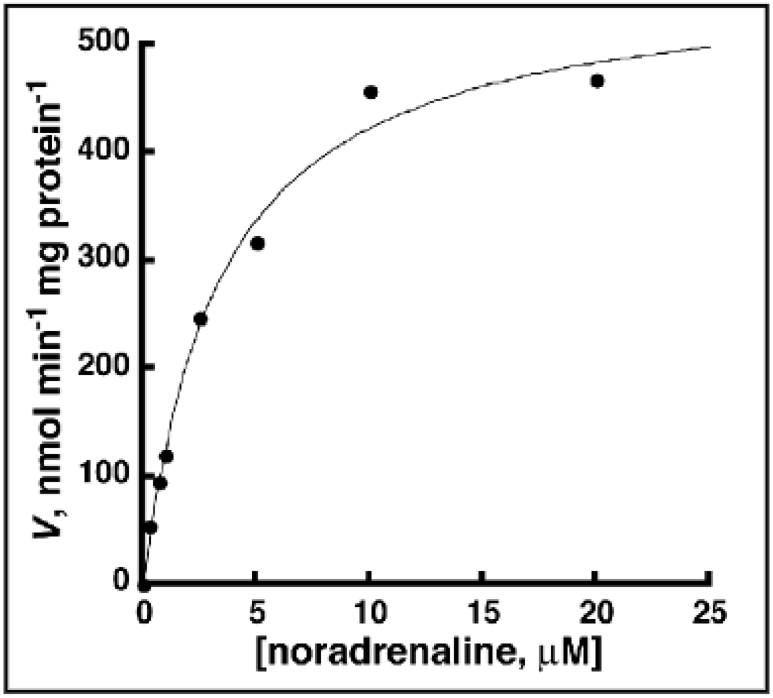
Enzymes (E) are typically protein molecules that act as biological catalysts and promote a reaction of another molecule: the substrate (S). The binding of the enzyme to the substrate produces an enzyme-substrate complex (ES) and the ES complex will result in the formation of the product (P), via a transition state. This process can be described by the equation below:

$$E + S \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} ES \overset{k_p}{\Rightarrow} E + P$$

The Michaelis–Menten kinetic model of a single-substrate reaction, shown below, is one of the best-known models of enzyme kinetics and describes the rates of enzymatic reactions by relating reaction velocity to the concentration of a substrate.



In the Michaelis-Menten kinetic model, Vmax represents the maximum rate of an enzyme-catalyzed reaction. Km is a measure of how easily the enzyme can be saturated by the substrate. Km can also be defined as the concentration of the substrate which permits the enzyme to achieve half Vmax.



a) You are studying an enzyme that methylates noradrenaline. From the Michaelis–Menten graph above, which of the following Vmax and Km values most reasonably estimates the value of Vmax and Km? Circle the correct option. ***(1 point)***

i) Vmax = 200 nmol min-1 mg protein-1, Km = 1 μM
ii) Vmax = 1000 nmol min-1 mg protein-1, Km = 3 μM
iii) Vmax = 1000 nmol min-1 mg protein-1, Km = 1 μM
iv) Vmax = 550 nmol min-1 mg protein-1, Km = 4 μM
v) Vmax = 550 nmol min-1 mg protein-1, Km = 25 μM

b) Explain your answer in part a in 2 - 3 sentences. ***(2 points)***

c) Imagine that you want your rate of enzymatic reaction to be at roughly 400 nmol min^{-1} mg $protein^{-1}$. How much noradrenaline do you need? ***(2 points)***

d) The Michaelis-Menten equation, shown below, can be used to accurately calculate the enzymatic rate of reaction at different substrate level concentrations. What would be the enzymatic rate of reaction when 20 µM of noradrenaline is used? ***(3 points)***

$$v_0 = \frac{(v_{max}[S])}{(k_M + [S])}$$

Problem #6: ***(12 points)***

According to Slater's rules, effective nuclear charge, ***Z****, is defined as a measure of the attraction of the nucleus for a particular electron. Effective nuclear charge can be calculated by the equation below,

$Z^* = Z - S$, where Z = nuclear charge and S = shielding constant.

Slater's rules defines a specific set of rules for calculating the shielding constant, ***S***, for a specific electron:

Rule #1. The atom's electronic structure is written in order of increasing quantum numbers, *n* and *l*, grouped as follows: (1*s*) (2*s*, 2*p*) (3*s*, 3*p*) (3*d*) (4*s*, 4*p*) (4*d*) (4*f*) (5*s*, 5*p*) (5*d*) (and so on)

Rule #2. Electrons in groups to the right in this list do not shield electrons to their left.

Rule #3. For *ns* and *np* valence electrons:

a. Each electron in the same group contributes 0.35 to the value of ***S*** for each other electron in the group. An exception to this rule is that a 1*s* electron contributes 0.30 to ***S*** for another 1*s* electron.

   For example, for an electronic configuration of $2s^2\ 2p^5$, a particular 2*p* electron has six other electrons in the (2*s*, 2*p*) group. Each of these contributes 0.35 to the value of ***S***, for a total contribution to ***S*** of 6 * 0.35 = 2.10.

b. Each electron in $n - 1$ groups contributes 0.85 to ***S***

   For example, for the 3*s* electron of sodium, there are eight electrons in the (2*s*, 2*p*) group. Each of these electrons contributes 0.85 to the value of ***S***, a total contribution of 8 * 0.85 = 6.80.

c. Each electron in $n - 2$ or lower groups contributes 1.00 to ***S***.

Rule #4. For *nd* and *nf* valence electrons:

a. Each electron in the same group contributes 0.35 to the value of ***S*** for each other electron in the group. (Same rule as 3a.)
b. Each electron in groups to the left contributes 1.00 to ***S***.

a) Use Slater's rules to calculate the effective nuclear charge on a 5*s* and 4*d* electron in the tin (Sn) atom. ***(4 points)***

b) Using Slater's rules, you calculate that the $\boldsymbol{Z^*}$ for the outermost electron of a ground-state phosphorus atom is 4.80. Would the $\boldsymbol{Z^*}$ for the outermost electron of sulfur that has lost one electron (S^+) be higher or lower than 4.80? Explain your reasoning in 1 - 2 sentences. ***(3 points)***

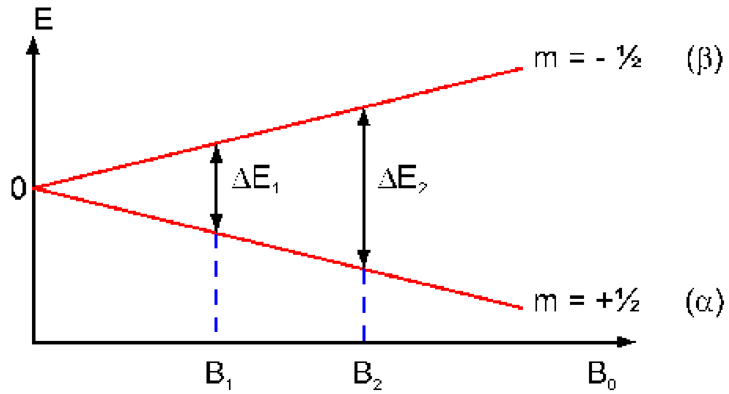
c) You were told that the ***Z**** for an outermost electron of a ground-state unidentified element is 6.10. Which element is it? ***(3 points)***

d) Explain the relationship between ***Z**** and ionization energy in 1 - 2 sentences. ***(2 points)***

<u>Problem #7</u>: *(16 points)*

Organic chemists use different spectra to derive the structures of molecules. One such spectrum is a Nuclear Magnetic Resonance (NMR) Spectrum. Just as electrons have a spin of +½ or -½, nuclei with an odd atomic number or an odd mass number, such as hydrogen-1 and carbon-13, can be described as having an alpha spin state and a beta spin state. The spinning of a positive charge, like that of a nucleus, produces its own magnetic field. When there is no external magnetic field, the nuclei have random spin states. However, when an external magnetic field is applied, the nuclei's spins will produce a magnetic field that is either aligned with or against this external field. The alpha spin state has a magnetic field in the same direction as the external magnetic field, and since these fields are aligned, this state exists at a lower energy. By contrast, the beta spin state creates a magnetic field that opposes the external magnetic field, which gives that nucleus a higher, more unstable energy.

The greater the external magnetic field, the greater the difference in energy is between the lower-energy alpha spin state and the higher-energy beta spin state. This difference in energy can often be overcome by electromagnetic waves of the same energy, which generally lie in the radio frequency region. When these photons are applied, the nucleus switches from the alpha spin to beta spin state. When the combination of external magnetic field and radio waves is exactly correct for the change of spin states, the nucleus is said to be in resonance.



a) The equation that represents how energy difference is related to the size of the applied external magnetic field is:

$$\Delta E = h\gamma B_0$$

ΔE = energy difference between alpha and beta spin states (in MJ)
h = Planck's constant (in J s)
γ = a constant known as the gyromagnetic ratio (in MHz/T)
B_0 = size of the external magnetic field (in T)

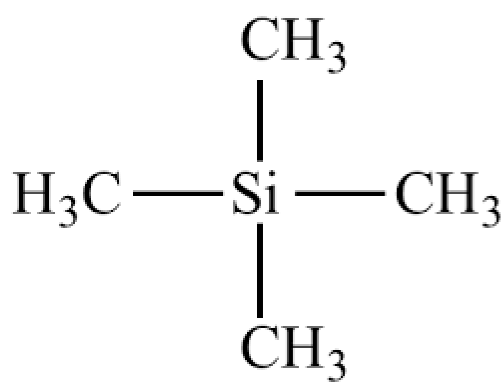
i) If a proton (or a hydrogen-1 nucleus) is placed in a magnetic field of 21 T magnetic field, it resonates at 900 MHz. Using this information, what is the gyromagnetic ratio of this nucleus? ***(2 points)***

ii) A carbon-13 nucleus is placed into a NMR spectrometer with an unknown external magnetic field. Waves with a wavelength of 3.1558 m from a BBC radio broadcast pass through the spectrometer, causing the nucleus to go from its alpha spin state to its beta spin state. If the gyromagnetic ratio for a carbon-13 nucleus is 10.705 MHz/T, how strong is the magnetic field in Tesla? If needed, use 343 m/s as the speed of sound in air. ***(2 points)***

b) So far, we have only dealt with isolated nuclei. However, NMR spectrometry is often used for molecules with multiple nuclei and many electrons forming a cloud around these nuclei. As spinning negative charges, electron clouds produce their own magnetic field that opposes the external magnetic field. As a result, the nucleus can feel a smaller effective magnetic field. Since the frequency required for resonance of an individual nucleus depends on the magnetic field actually "felt" by the nucleus, the closeness of an electron cloud to the nucleus affects the resonance frequency, which provides information about what nuclei may surround the nucleus of interest.

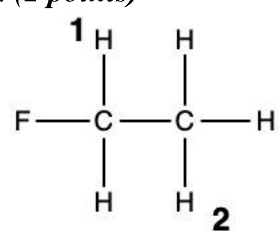
Let's focus on the hydrogen-1 nucleus. When the atoms near a hydrogen atom are more electronegative than the hydrogen itself, the hydrogen atom has less electron density surrounding it. There is less opposition to the external magnetic field, so the hydrogen atom feels a stronger magnetic field and needs a correspondingly larger frequency to move to the higher energy spin state. If the electron cloud is not pulled away as much from the hydrogen atom, the nucleus is more shielded from the external magnetic field and requires a smaller resonance frequency. In summary, when the nucleus of interest is closer to electron-withdrawing groups, it is more deshielded, feels a larger effective magnetic field, and requires a higher frequency to resonate. When the nucleus is farther from electron-withdrawing groups, it is more shielded, feels a smaller effective magnetic field, and requires a lower frequency to resonate.

i) The molecule tetramethylsilane (TMS) is often used to compare different resonance frequencies for hydrogen nuclei because they require a lower frequency to switch spin states than almost every other molecule. Why do the hydrogen nuclei in TMS require such low frequencies to resonate? ***(2 points)***

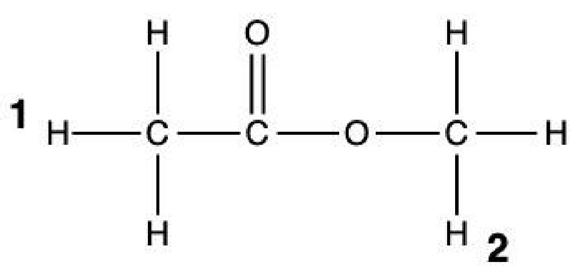


ii) The molecules shown below are placed into a fixed external magnetic field. Write the number of the hydrogen nucleus that has the highest resonance frequency, and is thus the farthest from the resonance frequency of TMS. Explain your reasoning in 1-2 sentences. ***(2 points)***

1)



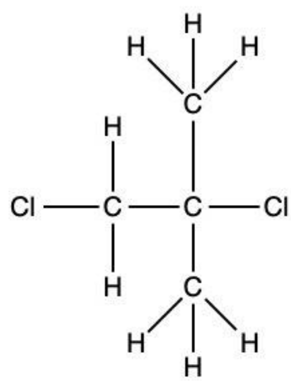
2)

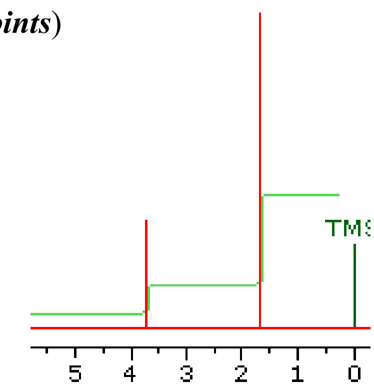


c) An NMR spectrum uses the fact that a hydrogen-1 nucleus will require different frequencies when surrounded by different atoms. To show these frequencies in a clearer way, each frequency is scaled relative to the frequency required by a hydrogen-1 nucleus in TMS. These new values are known as chemical shift values and are given the unit of parts per million, or ppm. When nuclei have identical surroundings, they require the same exact frequency and thus have the same chemical shift value. As a result, all nuclei with the same surroundings show up as a single signal, or peak, on a spectrum. All of the hydrogen atoms in TMS appear on a spectrum as one peak located at 0 ppm. The hydrogen nuclei in the molecule of interest have chemical shift values that show up at different locations depending on their position in a molecule and the atoms that surround them. The farther right the signal is, the more shielded the nucleus is, and the lower the frequency needed for the nucleus to switch spin states.

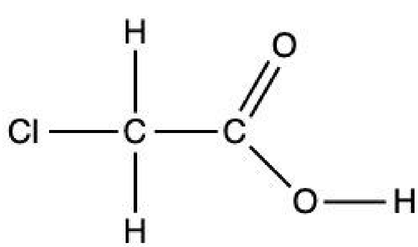
i) For each of the following molecules, with their corresponding spectrum, assign each proton to its peak. Redraw the molecule and spectrum on your answer sheet. Write a different number above each peak on the spectrum. Then, write the number that goes with each hydrogen next to its corresponding hydrogen in the provided Lewis structure. Ignore the green horizontal lines in the spectra, the integration number, and the peak for TMS. ***(4 points)***

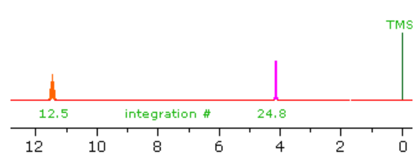
1)





2)





d) Pulling together all of the information learned above, as well as your own knowledge of electronegativity, sketch a simplified NMR spectrum for the following molecule. This molecule comes from an alternate universe, where X is an element identical to carbon in every way except that its electronegativity is greater than that of oxygen. Use the following steps as a guide. ***(4 points)***

1. Draw a horizontal line as your axis. This will have increasing chemical shift values going from right to left, starting at 0.
2. Draw a peak for TMS at the appropriate chemical shift value.
3. Identify hydrogen atoms that have identical environments. Decide which hydrogen atoms will require higher frequencies for a given external magnetic field and which will require lower frequencies, comparatively.
4. Draw one peak for each distinct chemical shift value. We are only looking for the relative locations of the peaks, NOT actual values.

Molecule: