

Individual Exam

(Sample Questions)

WUCT 2018

The three questions below are meant to give a sense of the kinds of questions that might be asked on the exam in April 2018. The actual exam is 65 minutes long, and it may differ in topic areas covered and difficulty. During the actual exam, necessary constants, equations, and conversions may be found on the last page of this document. Unless otherwise stated, explanations must be written in complete sentences, diagrams must be labeled, and units must be shown in calculations to receive full credit. Please answer the questions in the space provided. No work on the back of the sheets or attached sheets will be graded. The amount of points each question is worth will be indicated on the actual exam. Note that not all lone pairs are necessarily shown on every chemical structure.

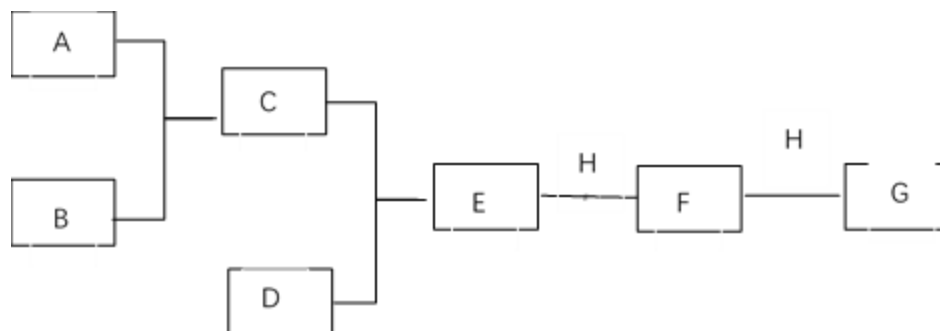
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High School: _____

Individual

Team ID: _____

1. The following flowchart below outlines the mixture of several chemicals. Each box contains a single chemical, which is combined with another chemical to generate a third chemical. Minor products for each reaction may not be included in the following cell.



A-H are all common chemicals. A is a reddish-orange metal and C is blue solution. You notice that combining A with B forms a smelly gas. Next, you notice that adding BaCl_2 solution into C solution forms a white precipitate.

- a. According to information above, what might be the possible concentration and chemical formula of B? Please choose the single, most correct answer.

- (1) 8M HCl
- (2) 1M H_2SO_4
- (3) 18M H_2SO_4
- (4) 1M HNO_3
- (5) 14M HNO_3

We can eliminate options 1, 4, and 5 immediately because the problem states that C is a blue solution which is likely to be CuSO_4 . A likely method to synthesize CuSO_4 is if chemical A (the reddish-orange metal) is copper and chemical B is some agent to oxidize the metal into Cu^{2+} then provide a SO_4^{2-} source to create CuSO_4 . In order to oxidize the copper metal to Cu^{2+} , we need a concentrated acid, so 3 is the correct solution.

- b. Please write down the molecular equation for $\text{A} + \text{B} \rightarrow \text{C}$ (Minor reactants or products may NOT be shown). Which element is oxidized and which element is reduced?



Cu is oxidized and H_2SO_4 is reduced.

Individual

Team ID: _____

- c. A WUCT Member tried to measure the pH of B with unknown concentration. The member put a drop of B onto a pH paper. Instead of becoming red, the litmus paper was destroyed and turned black.

- i. Could you explain this observation?

Chemical B is so corrosive that it destroyed the chemical structure of paper.

- ii. Could you propose a method to determine the concentration of B using pH paper?

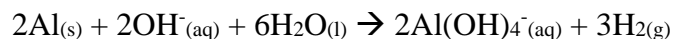
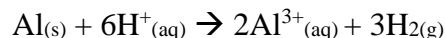
Continually dilute the sample until it can be measured with pH paper. Then, calculate the initial pH of the undiluted sample using the pH value and dilution level just concentrated.

- d. Given D is $\text{Al}_{(s)}$, please write down the net ionic equation of $\text{C} + \text{D} \rightarrow \text{E}$. Hint, look at reduction potential charts.



This occurs because the reduction potential for copper is greater than the reduction potential for aluminum.

- e. Al is a solid that can react with both acid and base to form $\text{H}_2(\text{g})$. The net ionic equations are:



$$K_{sp}(\text{Al}(\text{OH})_3) = 1.9 \times 10^{-33}$$

You add chemical H dropwise into solution E, and a white precipitate F is formed. However, as you add more chemical H the precipitate eventually disappears.

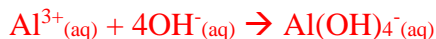
- i. Chemical H must contain OH⁻ ions and Chemical F is the Al(OH)₃ precipitate.

In aqueous solutions, aluminum metal will be converted to the insoluble $\text{Al}(\text{OH})_3$ solid. However, as the base concentration increases, the equilibrium shifts to the $\text{Al}(\text{OH})_4^{-}$ ion, which is soluble in water.

- ii. What is the net ionic equation for $\text{E} + \text{H}(\text{excess}) \rightarrow \text{G}$?

Individual

Team ID: _____



- iii. Pretend we wanted to change the direction of the flowchart, and add excess chemical E directly into the solution of chemical H. As chemical E is added drop by drop, describe the change in the appearance of the solution.

Initially, there should be no observable change in appearance (or white precipitate disappears immediately). After adding a large quantity of chemical E into solution H, the white precipitate starts to form.

2. We've figured out how to produce light through the iPhone, the car, and the TV within the last century. But the human race has not yet found a way to make light out of the body itself- like fireflies can. Fireflies use bioluminescence, a process in which their own chemical energy is converted into light.
- a. Based on a certain mechanism that explains this bioluminescence, red light emission ($\lambda_{\text{max}} = 615 \text{ nm}$), which is observed at pH 6.0, results from the keto form of the oxyluciferin emitter of the firefly. At pH 8.0, yellow-green light emission ($\lambda_{\text{max}} = 560 \text{ nm}$) is produced from the enolate form of this emitter.

If the firefly happens to be perfectly functional in a solution of $1.0 \times 10^{-6} \text{ M}$ phosphoric acid ($\text{pK}_{\text{a}1} = 2.15$, $\text{pK}_{\text{a}2} = 7.20$, and $\text{pK}_{\text{a}3} = 12.35$),

- i. What form of the emitter is most likely to be present- enolate or keto? Explain your reasoning and show all work to get full credit.

Using the first phosphoric acid dissociation constant is sufficient, and it yields a pH of just above 6 (around 6.002). Therefore, the keto form of the emitter is more likely to be present.

- ii. What is the energy of the photons emitted from the firefly emitter?

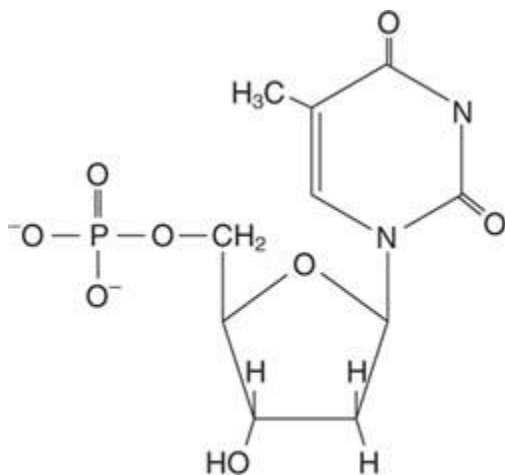
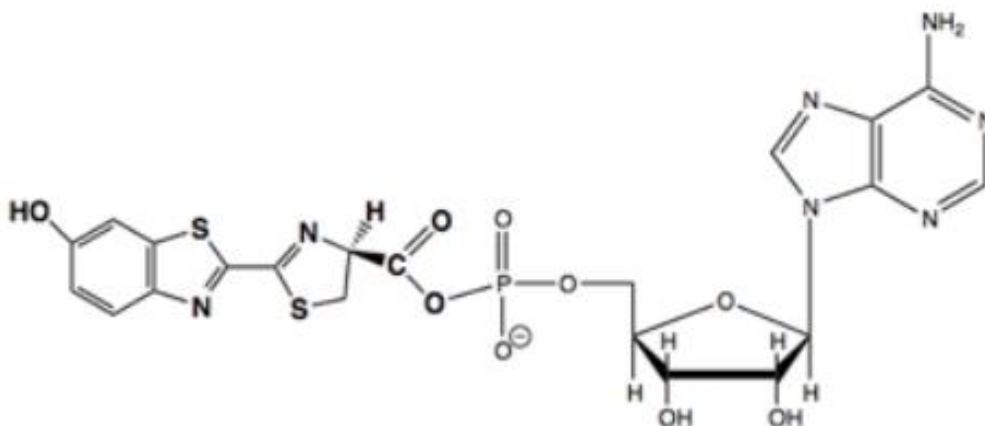
Since red light emission is most prevalent, the wavelength of light used to calculate the energy of the photons is 615nm. Using the formula $E = hc/\lambda$ yields the correct energy of $3.21 \times 10^{-19} \text{ J}$.

- b. D-Luciferin (molar mass = 280.316 g/mol) is the natural substrate for firefly luciferase, one of the key enzymes required for the firefly to produce light. In the

Individual

Team ID: _____

following compound, D-Luciferin has combined with a monophosphate nucleotide molecule in a hydrolysis reaction.



Thymidine Monophosphate,
a Deoxyribonucleotide

- i. What is the chemical formula for D-Luciferin? An image of a monophosphate nucleotide is shown. (Hint: this compound contains a carboxylic acid functional group in its protonated form).

Everything to the left of the phosphorous atom in the monophosphate molecule should be considered D-Luciferin in addition to a hydrogen atom that was displaced as part of the reaction. A carboxylic acid group in D-Luciferin reacted with the phosphate group to remove a molecule of water. Therefore the chemical formula of D-Luciferin is $C_{11}H_8O_3N_2S_2$

Individual

Team ID: _____

- ii. Based on the structure above, is this molecule more likely to dissolve in substances such as hydrocarbon oils and chloroform vs. polar solvents like water? Explain in terms of intermolecular forces.

Hydrocarbon oils and chloroform are nonpolar, and since D-Luciferin has many polar functional groups, it would likely not dissolve in such substances. In order for a substance to dissolve, it must be “solvated” by the surrounding solvent molecules. D-Luciferin has many polar groups that can form hydrogen bonds/dipole-dipole interactions with polar solvents. These are much stronger interactions than the Dipole-induced dipole interactions that D-Luciferin and the hydrocarbon oils will engage in, so D-Luciferin will energetically prefer to be solvated in polar solvents like water.

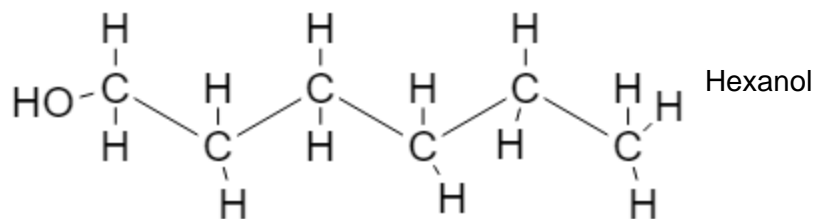
- c. The Mosquito Bioluminescent Bay on the island of Vieques, Puerto Rico is the most bioluminescent in the world. However, instead of fireflies, microscopic dinoflagellates in the bay react to produce a blue-green light emission ($\lambda_{\text{max}} = 495\text{nm}$) for a duration of 0.1s when agitated. What is the power of this light emission?

The energy of the emission can be calculated as $E = hc/\lambda$ to get $3.97 \times 10^{-19} \text{ J}$. Power is calculated as E/t and so the power is $3.97 \times 10^{-18} \text{ W}$ or J/s .

3. WUCT has been looking to begin production on a side product to help fund its extravagant tournaments. In particular, Stinky Joe has decided that WUCT should begin production of a brand of deodorant called WU-Spice. This will be liquid deodorant in an aerosol bottle.
- a. For a base scent, Stinky Joe wants to add a sweet, woody scent to his perfume. Hexanol ($\text{C}_6\text{H}_{14}\text{O}$, MW 102.2grams/mol) has the green, herbaceous fragrance Joe is looking for. The best scent is created when hexanol is 10% of the solution by mass. How many moles of hexanol are needed to make a 100ml bottle of perfume to reach the 10% of hexanol by mass? (assume the density of the solution is 1 g/ml)

Individual

Team ID: _____



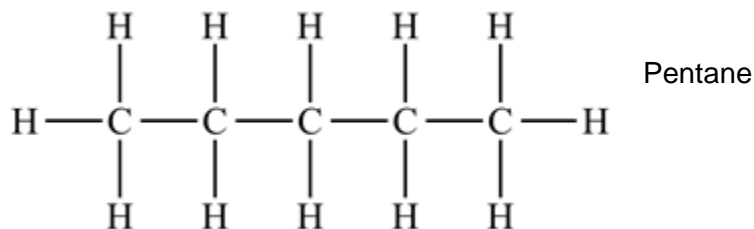
MW of hexanol = 102.2 grams/mole

Grams of hexanol = 0.10 * 100ml * 1 gram/milliliter = 10 grams

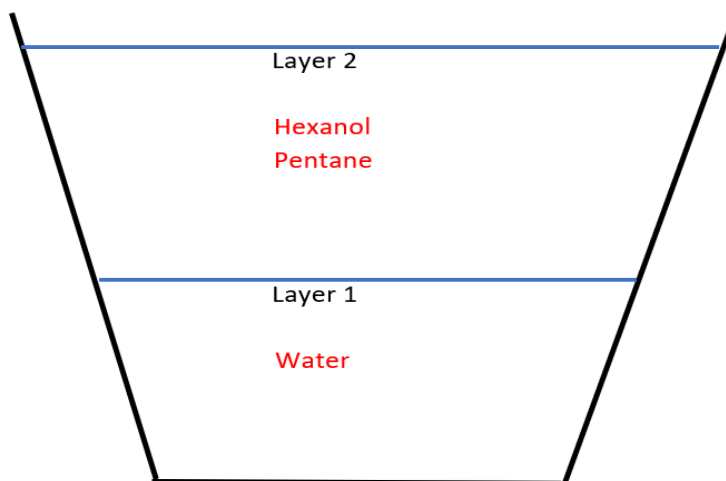
Moles of hexanol = 10 grams * 1 mol/102.2grams = 0.098 moles

Ans: 0.098 moles

- b. After adding the hexanol, Stinky Joe now wants to add a scent of cauliflower to form the high notes of deodorants, which is remarkably similar to pentane (C_5H_{12}). After mixing hexanol, pentane, and water, he notices there are two separate layers of fluid. Write the names of the molecules expected in each layer in the figure below.



Ans:



Individual

Team ID: _____

- c. Stinky Joe really likes the smell of rotten eggs underneath his armpits, but is unsettled by the thought of colonies of bacteria living on his body. Therefore, Stinky Joe is considering either adding acetic acid or dodecanethiol to the deodorant to kill bacteria and provide this odor. Assume all bacteria die if the pH is lower than 2.5 or greater than 8.
- i. What concentration of acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) ($K_a = 1.8 \times 10^{-5}$) is needed for the deodorant to have a pH of 2.5? Assume the perfume bottle is filled with only water.

Ans: $[\text{CH}_3\text{CO}_2\text{H}] = 0.559\text{M}$

- ii. If Stinky Joe uses dodecanethiol instead of acetic acid to kill the bacteria and make the perfume smell stinky. Because dodecanethiol is basic, Stinky Joe is careful about not adding too much and reduce the acidity of the solution. What concentration of dodecanethiol acid ($\text{C}_{12}\text{H}_{26}\text{S}$) ($pK_a = 13.4$) is needed for the deodorant to have a pH of 8.0?

Ans: Initial $[\text{OH}^-] = 1 \times 10^{-7}$ Final $[\text{OH}^-] = 1 \times 10^{-6}$ Difference = $+9 \times 10^{-7}$

	$[\text{AOH}]$	\leftrightarrow	$[\text{A}^+]$	+	$[\text{OH}^-]$
I	x		0		1×10^{-7}
C	-9×10^{-7}		$+9 \times 10^{-7}$		$+9 \times 10^{-7}$
E	$x - 9 \times 10^{-7}$		9×10^{-7}		1×10^{-6}

$$KOH = 10^{14-13.4} = \frac{10^{-6} \cdot 9 \times 10^{-7}}{x - 9 \times 10^{-7}} \text{ Solving this expression gives } x = 9 \times 10^{-7}$$

So, the final answer is: Ans: $[\text{dodecanethiol}] = 0.9\mu\text{M}$

Individual

Team ID: _____

END OF EXAM