2025 WUCT: Illumination Exam

This exam consists of 6 questions and is worth 100 points. You will complete this exam as a pair. 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.

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

Ammonium perchlorate (NH_4ClO_4) is a powerful oxidizer widely used in fireworks as it can rapidly decompose and release a significant amount of energy, causing the bright white flash observed when fireworks are set off. The molar mass of NH_4ClO_4 is given as 117.49 g/mol.

a. The following unbalanced chemical equation produces the bright flash seen in fireworks:

$$NH_4ClO_4(s) \rightarrow N_2(g) + H_2O(g) + HCl(g) + O_2(g)$$

i. Balance the chemical equation. ***(2 points)***

$$\_\_4\_\_NH_4ClO_4(s) \rightarrow \_\_2\_\_N_2(g) + \_\_6\_\_H_2O(g) + \_\_4\_\_HCl(g) + \_\_5\_\_O_2(g)$$

+1 point if at least two blanks are filled in correctly

+1 point if all five blanks are filled in correctly

ii. 2.0 mol of the N_2 gas that was produced then underwent an isothermal expansion. Initially, the gas was at a fixed pressure of 1.0 atm and a volume of 3.0 L, and after the expansion, it was at a final volume of 20.0 L. Assuming the N_2 gas behaves ideally, calculate the ΔS in J/K. ***(2 points)***

At constant temperature, $\Delta S = nRln(\frac{V_2}{V_1})$

$\Delta S = (2.0\ mol)(8.314\ \frac{J}{mol\cdot K})(ln(\frac{20.0L}{3.0L}))$ **(+1 point)**

$\Delta S = 31.55\ J/K$ **(+1 point)**

+1 point for correctly using/substituting the ΔS equation

+1 point for correct answer

b. The reaction with the ammonium perchlorate is performed in a bomb calorimeter. If the temperature of the calorimeter rises from 35.4 $°C$ to 558.89 $°C$, and the heat capacity of the calorimeter is 6780 $\frac{J}{°C}$, determine the heat of decomposition of 704.94 g NH_4ClO_4 in kJ/mol. ***(3 points)***

$q_{calorimeter} = C_{cal}\Delta T = (6780\ \frac{J}{°C})(\frac{1\ kJ}{1000\ J})(558.89\ °C - 35.4\ °C) = 3549.26\ kJ$

$q_{rxn} = -q_{calorimeter} = -3549.26\ kJ$ **(+1 point)**

$704.94\ g\ NH_4ClO_4 \times \frac{1\ mol\ NH_4ClO_4}{117.49\ g\ NH_4ClO_4} = 6\ mol\ NH_4ClO_4$ **(+1 point)**

$-\frac{3549.26\ kJ}{6mol\ NH_4ClO_4} = -591.54\ kJ/mol$ **(+1 point)**

+1 point for correctly solving for q_{rxn} (negative value)

+1 point for correctly solving for mol NH_4ClO_4 reacted

+1 point for correct answer

c. Now consider the chemical reaction under standard temperature and pressure conditions. Using -590 kJ/mol as the heat of decomposition, calculate ΔH°_f for NH_4ClO_4 in kJ/mol using the heats of formation provided. ***(3 points)***

Compound	ΔH°_f (kJ/mol)
$HCl_{(g)}$	-92.3
$H_2O_{(g)}$	-241.8

ΔH°_f is calculated for 1 mol of NH_4ClO_4, therefore the decomposition reaction for NH_4ClO_4 is:

$$NH_4ClO_4(s) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(g) + HCl(g) + \frac{5}{4}O_2(g)$$

$$\Delta H^\circ_{rxn} = \sum n_{product}\Delta H^\circ_f(products) - \sum n_{reactant}\Delta H^\circ_f(reactants)$$

$$\sum n_{product}\Delta H^\circ_f(products) = \frac{3}{2}(-241.8\ kJ/mol) + (-92.3\ kJ/mol)$$

$= -455\ kJ/mol$ **(+1 point)**

$$\Delta H^\circ_{rxn} = -455\ kJ/mol - \Delta H^\circ_f(NH_4ClO_4)$$

$-590\ kJ/mol = -455\ kJ/mol - \Delta H^\circ_f(NH_4ClO_4)$ **(+1 point)**

$\Delta H^\circ_f(NH_4ClO_4) = 135\ kJ/mol$ **(+1 point)**

Alternate: (using originally balanced equation)

$$\sum n_{product}\Delta H^\circ_f(products) = 6(-241.8\ kJ/mol) + 4(-92.3\ kJ/mol)$$

$= -1820\ kJ/mol$ **(+1 point)**

$$4(\Delta H^\circ_{rxn}) = -1820\ kJ - 4(\Delta H^\circ_f(NH_4ClO_4))$$

$-2360\ kJ/mol = -1820\ kJ/mol - 4(\Delta H^\circ_f(NH_4ClO_4))$ **(+1 point)**

$\Delta H^\circ_f(NH_4ClO_4) = 135\ kJ/mol$ **(+1 point)**

+1 point for correctly solving for $\Delta H°_f\ (products)$

+1 point for correctly using/substituting into $\Delta H°_{rxn}$ equation

+1 point for correct answer

d. Using the following bond enthalpies, estimate the value of energy released when the bonds of the product molecules are formed in kJ/mol. ***(2 points)***

Bond	Enthalpy (kJ/mol)
N—N	163
N=N	418
N≡N	945
O—H	463
O—O	146
O=O	498
H—Cl	432

Products Formed: $2N_2 + 6H_2O + 4HCl + 5O_2$

Energy Released to Form:

$2(945\ kJ/mol) + 12(463\ kJ/mol) + 4(432\ kJ/mol) + 5(498\ kJ/mol)$ **(+1 point)**

$= 11664\ kJ/mol$ **(+1 point)**

+1 point for correctly using/substituting into energy released equation
+1 point for correct answer

e. There are two methods to calculate $\Delta H°_f\ NH_4ClO_4(s)$: **(1)** using the heats of formation for the constituent elements or **(2)** using the bond enthalpies to calculate $\Delta H°_f\ NH_4ClO_4(g)$ and then using ΔH for the phase change to the solid state. Focusing on the heats of formation and bond enthalpies (and not the ΔH phase change), explain what each is and provide an explanation as to why calculations using the two methods would provide slightly different values. ***(3 points)***

Heat of formation is the **energy absorbed or released in order to form a molecule at constant pressure (+1 point)**, while bond enthalpy represents the **energy required to break a chemical bond in the gaseous phase (+1 point)**. Bond enthalpy values are calculated as an **average across all molecules containing the particular bond (+1 point)** leading to the different values for computations using each method.

+1 point for correctly defining heat of formation
+1 point for correctly defining bond enthalpy
+1 point for stating that bond enthalpies are average values (less accurate)

Problem #2: ***(16 points)***

When plant material is placed in an ozone chamber, a chemiluminescence reaction occurs where nitric oxide, $NO(g)$, from the plant reacts with ozone, $O_3(g)$. This generates excited-state nitrogen dioxide gas, $NO_2(g)$, that emits light to return to its ground state, causing the plant material to become a "green lamp." The reaction steps that occur are as follows:

Step 1:

$$\mathrm{NO\,(g) + O_3\,(g)} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \mathrm{NO_2^*\,(g) + O_2\,(g)}$$

Step 2:

$$\mathrm{NO_2^*\,(g)} \underset{h\upsilon}{\overset{k_2}{\longrightarrow}} \mathrm{NO_2\,(g)}$$

Note: * means the molecule is excited

a. Briefly explain what would happen to the formation of $NO_2(g)$ if you increase the pressure of your experiment. ***(3 points)***

There is an **equal number of moles of product and reactant gas in Step 1 (+1 point).** Therefore, increasing the pressure **would not shift the reaction in Step 1, so the formation of NO_2^* would remain unaffected (+1 point)**. From the reaction in Step 2, we see that if the formation of NO_2^* is unaffected, then **the formation of NO_2 is also unaffected (+1 point)**.

+1 point for stating the there are equal number of moles of product/reactant gas in Step 1
+1 point for stating that reaction in Step 1 would not shift/formation of NO_2^* is unaffected
+1 point for stating that formation of NO_2 is unaffected

b. The second step is the rate-determining step. Given the rate constant $k = 0.15\frac{1}{s}$, calculate the time it takes for the reaction to go halfway to completion. ***(3 points)***

For a first-order reaction, $ln[A] = -kt + ln[A]_0$, let $[A] = \frac{[A]_0}{2}$ **(+1 point)**

$ln(\frac{[A]_0}{[A]}) = kt$

$ln(2) = 0.15\frac{1}{s}t$ **(+1 point)**

$t = \frac{ln(2)}{0.15\frac{1}{s}}$

$t = 4.62\ s$ **(+1 point)**

+ 1 point for correctly using $[A] = \frac{[A]_0}{2}$

+1 point for correctly using/substituting into the first-order equation

+1 point for correct answer

c. Using a steady-state approximation, find the rate of formation of $NO_2(g)$. Use partial pressures when writing the rate laws. ***(3 points)***

$Rate = k_2P_{NO_2^*}$ **(+1 point)**

For a steady-state approximation, the production and consumption rates of the intermediate NO_2^* are equal

$k_1P_{NO}P_{O_3} = k_{-1}P_{NO_2^*}P_{O_2} + k_2P_{NO_2^*}$ **(+1 point)**

$P_{NO_2^*} = \frac{k_1P_{NO}P_{O_3}}{k_{-1}P_{O_2}+k_2}$

$Rate = \frac{k_1k_2P_{NO}P_{O_3}}{k_{-1}P_{O_2}+k_2}$ **(+1 point)**

+1 point for using the correct rate law expression

+1 point for correctly equating the production and consumption rates of NO_2^*

+1 point for correct answer

d. When running the overall chemiluminescence reaction, at 298 K, you record a rate constant of $0.12\frac{1}{s}$, and at 318 K, you record a rate constant of $0.45\frac{1}{s}$. Calculate your experimental activation energy E_a in $\frac{kJ}{mol}$ for the reaction. ***(2 points)***

$$ln(\frac{k_2}{k_1}) = \frac{-E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

$ln(\frac{0.45\frac{1}{s}}{0.12\frac{1}{s}}) = \frac{-E_a}{0.008314\frac{kJ}{mol\cdot K}}(\frac{1}{318\,K} - \frac{1}{298\,K})$ **(+1 point)**

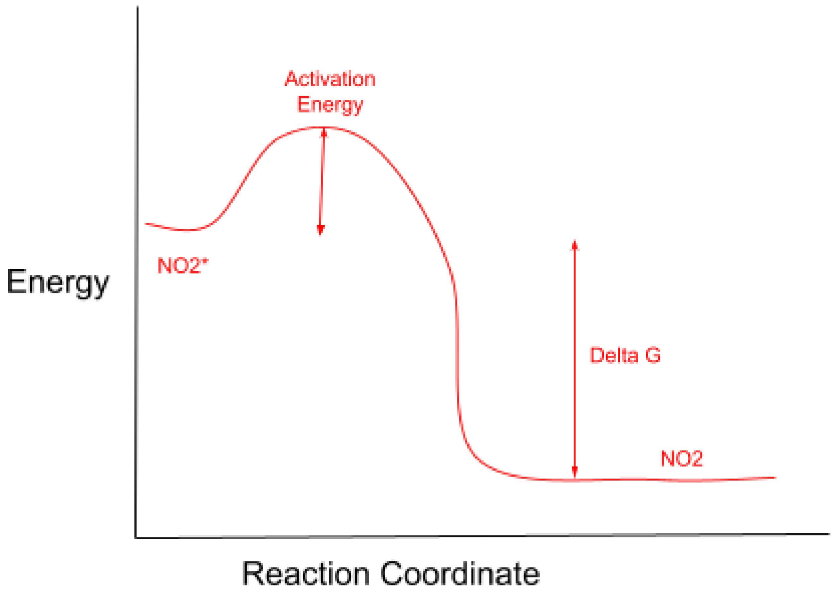
$$1.322 = (-0.0254\,\frac{mol}{kJ})(-E_a)$$

$E_a = 52.1\,kJ/mol$ **(+1 point)**

+1 point for correctly using/substituting into the equation to find E_a

+1 point for correct answer

e. Draw the reaction coordinate diagram for the reaction in Step 2 on the axes provided below. Label the reactants, products, activation energy, and ΔG. ***(5 points)***



+1 point for correct shape of graph (exothermic since emits light)

+1 points for correctly labeling reactants (NO_2^*)

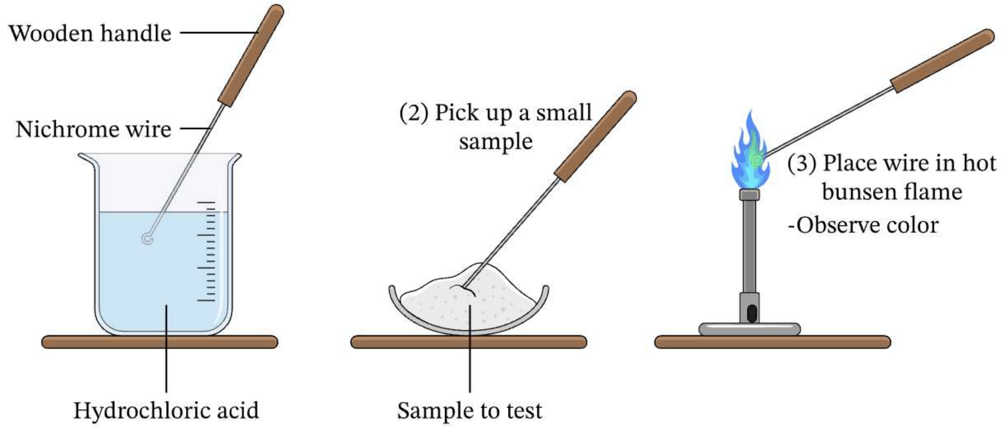
+1 points for correctly labeling products (NO_2)

+1 points for correctly labeling activation energy

+1 points for correctly labeling ΔG

<u>Problem #3</u>: ***(19 points)***

One way to identify what metal ions are present in a mixture is through a flame test, where a metal sample is lit on fire, causing it to give off a characteristic color. This occurs as the heat excites the atoms, promoting their electrons to higher energy orbitals, and when they return to their ground state, the atoms emit light within the visible region. Since the gaps between energy levels are unique to each element, we can use the specific color given off to determine the metal ion species present. Investigate this phenomenon and use the following table throughout.



Color	Wavelength Range (nm)
Red	625 - 740
Orange	590 - 625
Yellow	565 - 590
Green	520 - 565
Blue	465 - 520
Violet	380 - 465

a. Write out the **<u>ground state electron configuration</u>** for each of the following elements. Do not use a noble gas abbreviation.

i. Barium (Ba) ***(1 point)***

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$

ii. Sodium (Na) ***(1 point)***

$1s^2 2s^2 2p^6 3s^1$

iii. Cesium (Cs) ***(1 point)***

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$

b. The color that appears in the flame test is related to the most probable electronic transition for the metal atom. This is typically the transition from the highest energy **occupied** atomic orbital to the next **unoccupied** atomic orbital that an additional electron would occupy. State these atomic orbitals for each of the following elements.

i. Barium (Ba)

Highest Occupied: ___6s_________________ ***(1 point)***

Next Unoccupied: ___4f_________________ ***(1 point)***

ii. Sodium (Na)

Highest Occupied: ___3s_________________ ***(1 point)***

Next Unoccupied: ___3p_________________ ***(1 point)***

iii. Cesium (Cs)

Highest Occupied: ___6s_________________ ***(1 point)***

Next Unoccupied: ___4f___________________ ***(1 point)***

c. When sodium undergoes a flame test, it emits yellow light. Assume that the magnitude of the energy of the outermost electron in its **final** state is $5.2480 \times 10^{-19} J$. Use the table given at the start of this question to determine the range of allowable energy magnitudes for the electron's initial state. Write your answer on the line below. ***(4 points)***

Energy Range for the Initial State: __$1.7321 \times 10^{-19} J$ to $1.8811 \times 10^{-19} J$______

From the table: yellow light has a wavelength ranging from 590 nm to 565 nm

Upper Bound: 565 nm

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} Js)(2.998 \times 10^{8} m/s)}{565 \times 10^{-9} m} = 3.5159 \times 10^{-19} J \textbf{ (+1 point)}$$

$$\Delta E = E_f - E_i$$

$$E_i = 5.2480 \times 10^{-19} J - 3.5159 \times 10^{-19} = 1.7321 \times 10^{-19} J \textbf{ (+1 point)}$$

Lower Bound: 590 nm

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} Js)(2.998 \times 10^{8} m/s)}{590 \times 10^{-9} m} = 3.3669 \times 10^{-19} J \textbf{ (+1 point)}$$

$$\Delta E = E_f - E_i$$

$$E_i = 5.2480 \times 10^{-19} J - 3.3669 \times 10^{-19} = 1.8811 \times 10^{-19} J \textbf{ (+1 point)}$$

+1 point for correctly solving for ΔE for upper bound (565 nm)
+1 point for correctly solving for E_i for upper bound (565 nm)

+1 point for correctly solving for ΔE for lower bound (590 nm)
+1 point for correctly solving for E_i for lower bound (590 nm)

d. When cesium undergoes a flame test, the outermost electron experiences an energy change of 2.684 eV. What wavelength of light does this correspond to (in nm)? According to the table, what color is this? ***(2 points)***

Wavelength: ___462 nm_________________

Color: ___Violet_________________

$$2.684\ eV \times \frac{1.602\times10^{-19}\ J}{1\ eV} = 4.2998\times10^{-19}\ J$$

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\ Js)(2.998\times10^{8}\ m/s)}{4.2998\times10^{-19}\ J} = 4.6200\times10^{-7}\ m = 462\ nm$$ **(+1 point)**

Using the table given, 462 nm corresponds to a violet color. **(+1 point)**

+1 point for correctly solving for λ
+1 point for correctly stating violet as the color

e. When barium undergoes a flame test, it emits a green light. Based on your answer in part d, do you expect the magnitude of the energy change of the barium atom to be greater or less than that of a cesium atom? ***(2 points)***

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____

____

From part d, we can see that cesium emits a violet light, **corresponding to a lower wavelength and therefore a greater magnitude of energy change (+1 point)** compared to the green light emitted by barium. Therefore, the **magnitude of energy change of the barium atom should be less than that of a cesium atom (+1 point)**.

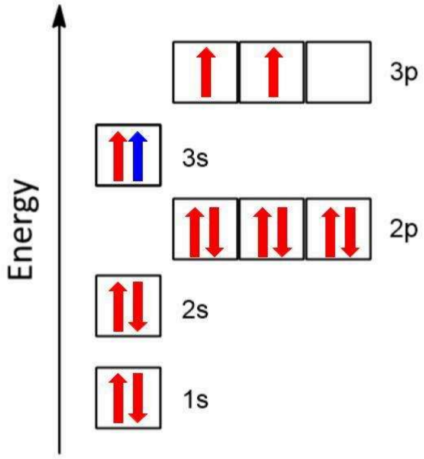
+1 point for correctly comparing wavelength and magnitude of energy change between the two metal atoms

+1 point for stating that the barium atom should have a lower magnitude of energy change

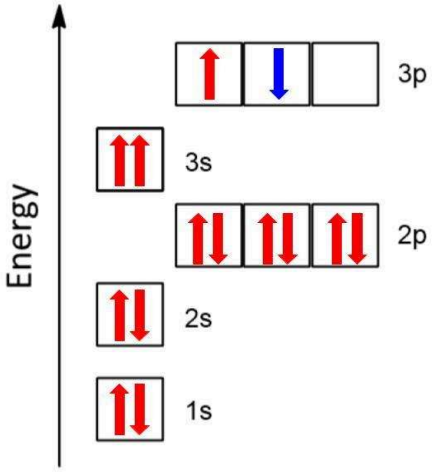
*answers may vary depending on how student answered part d

f. Using the two energy level diagrams below, depict two different electron configurations for neutral Si, one which **(i)** violates the Pauli Exclusion Principle, and the other which **(ii)** violates Hund's Rule. Note: you should still follow the ground configuration rule for both parts.

i. Pauli Exclusion Principle Violation ***(1 point)***:



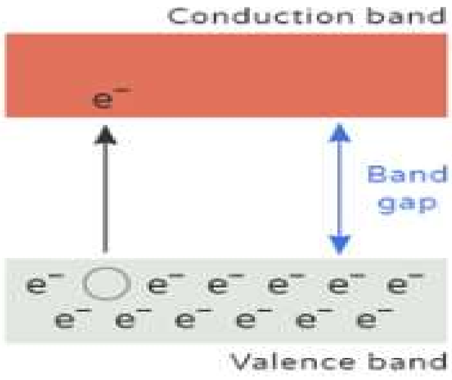
ii. Hund's Rule Violation ***(1 point)***:



Other variations are possible, but they should be similar to what is shown in the key.

<u>Problem #4</u>: *(18 points)*

Semiconductors are a class of metalloid elements defined by having a conductivity between a metal and an insulator. Like metals, semiconductors can absorb light when electrons are excited to higher energy states and release light when the electrons relax to lower energy states. We can think of the continuous range of energy levels that an electron can occupy within metal and metalloid solids as energy "bands". In a semiconductor crystalline structure, electrons must be excited from the valence band (the highest energy band the electrons normally occupy) to the conduction band (which normally contains no electrons) to allow the electrons to move freely between atoms and therefore conduct electricity. The energy difference between these two bands is called the "band gap." When these electrons are excited, they leave behind a positive "hole" in the valence band. As electrons move through metal and metalloid atoms, they can fall from the conduction band to fill a hole in the valence band, thus emitting light.



a. One use of semiconductors is in photodiodes - an electronic component that converts light into a current proportional to the light's intensity. Consider an automatic street light that uses a photodiode to sense when the sunlight's power is below 25 W. The radiation emitted by the sun when the power falls below the threshold is 500 nm. What is the photon rate ($\frac{photons}{second}$) of the sunlight when the street light first turns on? Note: Power is equal to the energy of a photon times the photon rate and 1 W = 1 J/s. ***(3 points)***

$E_{ph} = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34} Js)(2.998\times10^{8}\ m/s)}{(500\times10^{-9}\ m)} = 3.973 \times 10^{-19}\ J$ **(+1 point)**

$Power = E_{ph} \times Photon\ Rate = (3.973 \times 10^{-19}\ J)(Photon\ Rate) = 25\ W$ **(+1 point)**

$Photon\ Rate = 6.293 \times 10^{19}\ \frac{photons}{second}$ **(+ 1 point)**

+1 point for correctly using/substituting into equation for E_{ph}

+1 point for correctly using/substituting into equation for power

+1 point for correct answer

b. Given that germanium has a band gap of 0.77 eV, explain whether or not light from the visible spectrum (380 to 700 nm) can activate the street light. Show your calculations and then write your explanation below. ***(3 points)***

$0.77\ eV \times \frac{1.602\times10^{-19} J}{1\ eV} = 1.2235 \times 10^{-19} J$

$E_{ph} = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34} Js)(2.998\times10^{8} m/s)}{\lambda} = 1.2235 \times 10^{-19} J$ **(+1 point)**

$\lambda = 1610\ nm$ **(+1 point)**

Alternate:

We only need to check if the energy from the longest wavelength of light (which corresponds to the lowest energy) will activate the light.

Band Gap is $0.77\ eV \times \frac{1.602\times10^{-19} J}{1\ eV} = 1.2235 \times 10^{-19} J$

$E_{ph} = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34} Js)(2.998\times10^{8} m/s)}{700\times10^{-9} m}$ **(+1 point)**

$E_{ph} = 2.838 \times 10^{-19} J$ **(+1 point)**

Therefore a wavelength of 1610 nm is needed to provide enough energy to activate the street light. Since all light from the visible range has a shorter wavelength than this, all of the visible light spectrum will provide enough energy to activate the street light. **(+ 1 point)**

Alternate:

The lowest energy that light can provide is greater than the band gap, therefore all of the visible light spectrum will provide enough energy to activate the street light. **(+1 point)**

+1 point for correct substitution into equation for energy of a photon depending on method

+1 point for correctly solving for λ or E_{ph} depending on method

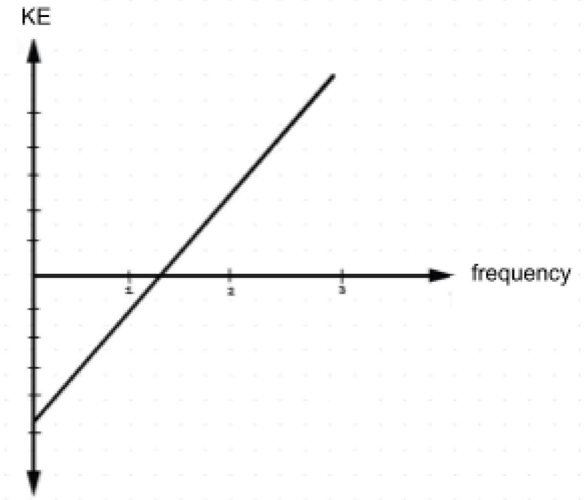
+1 point for correctly stating that all light from the visible spectrum will activate the light

c. The work function of a metal is the minimum amount of energy required to remove an electron from its surface. Explain why Silicon's work function (4.85 eV) is slightly greater than Germanium's (4.80 eV) using effective nuclear charge and electron shielding to explain your answer. ***(2 points)***

The highest energy electron is in a 3p orbital for Silicon and a 4p orbital for Germanium. Therefore, Germanium's valence electrons are **more shielded due to the greater number of core electrons (+1 point)**. As a result, **Germanium's effective nuclear charge is lower and it is easier to remove its outermost electron (+1 point)** giving it a lower work function.

+1 point for relating highest energy orbital to shielding effect
+1 point for relating effective nuclear charge to work function

d. Semiconductors such as diodes are also used in solar panels to convert light energy into a current. Consider a silicon solar panel with a work function of 4.85 eV. Below is a graph plotting the relationship $KE = h\nu - \phi$, with kinetic energy of an excited electron **(eV)** on the y-axis and the frequency of the incident radiation **(10^{15} Hz)** on the x-axis. Calculate and interpret the values of the slope, x-intercept, and y-intercept of the graph. **(Write your answers in the space provided on the next page.)**



Interpretation of slope ***(1 point)***:

Using the equation $KE = hv - \phi$, we see that the value of the slope is Planck's constant.

Value of slope ***(1 point)***:

$6.626 \times 10^{-34} Js \times \frac{1\ eV}{1.602\times10^{-19} J} = 4.136 \times 10^{-15} eVs$ (unit of y axis is eV)

Interpretation of y-intercept ***(1 point)***:

Using the equation $KE = hv - \phi$, we see that the value of the y-intercept is the work function.

Value of y-intercept ***(1 point)***:

$4.85\ eV$

Interpretation of x-intercept ***(1 point)***:

The x-intercept represents the threshold frequency required for an electron to be ejected.

Value of x-intercept ***(1 point)***:

$v = \frac{(4.85\ eV)(1.602\times10^{-19} J/eV)}{6.626\times10^{-34} Js} = 1.1726 \times 10^{15}\ Hz$ (occurs when $hv = \phi$)

Alternate:

$v = \frac{4.85\ eV}{4.136\times10^{-15}\ eV\ s} = 1.1726 \times 10^{15}\ Hz$ (uses value of slope)

*will also accept 1.1726 if calculations shown are correct since graph is in units of 10^{15} Hz

e. LEDs (Light Emitting Diodes) function similarly to photodiodes, but convert electrical energy to light instead. These semiconductors can be "doped", meaning that different chemical materials can be added to change their electrical conductivity. Typically, the valence band is doped with a p-type material that provides excess holes, and the conduction band is doped with an n-type material that provides excess electrons to fill the valence band holes. When an electrical current is passed through the LED, electrons fall down from the conduction band to fill the excess holes and emit light.

   i. Propose an explanation for why Group 3 elements such as boron, aluminum, and gallium make good p-type materials by providing excess holes in the valence band. *Hint: focus on the number of valence electrons and covalent bonds formed for these elements.* ***(2 points)***

Group 3 elements have **3 valence electrons, thus, they will only form 3 bonds (+1 point)** with nearby atoms. Therefore **there aren't enough valence electrons to fill their octet, thus creating a hole. (+ 1 point)**

+1 point for relating number of valence electrons to number of bonds formed
+1 point for relating lack of valence electrons/bonds to formation of hole

   ii. Propose an explanation for why group 5 elements such as phosphorus make good n-type materials by providing excess electrons to fill in valence band holes. *Hint: focus on the number of valence electrons and covalent bonds formed for these elements.* ***(2 points)***

Group 5 elements have **5 valence electrons, thus, they will form 4 bonds with nearby atoms (+1 point)** to fill their octet and then have **a single remaining electron that can fill in excess holes in the valence band**. **(+ 1 point)**

+1 point for relating number of valence electrons to number of bonds formed
+1 point for relating extra available electron to filling of hole in valence band

Problem #5: ***(16 points)***

Many organisms in our world exhibit the fascinating phenomenon of bioluminescence. Fireflies, jellyfish, squids, fungi, worms, and various insects all have the ability to naturally produce light. But how do they do it? To answer this question, let's look at perhaps the most famous bioluminescent creature, the firefly, which uses a molecule known as luciferin in order to glow. The overall bioluminescence reaction is given as follows:

$$Luciferin + ATP + O_2 \rightarrow PP_i + AMP + CO_2 + OxyL + Light$$

a. The table below displays a list of experiments that were carried out involving this bioluminescence process. Use the given data to answer the following questions.

Experiment #	[Luciferin] (M)	[ATP] (M)	$[O_2]$ (M)	$[PP_i]$ (M)	Initial Reaction Rate (M/s)
1	0.010	0.020	0.030	0.010	4.79×10^{-6}
2	0.020	0.020	0.030	0.010	9.58×10^{-6}
3	0.010	0.040	0.030	0.010	9.58×10^{-6}
4	0.010	0.020	0.060	0.010	9.58×10^{-6}
5	0.010	0.020	0.030	0.020	2.40×10^{-6}

i. List the reaction order with respect to each molecule tested and with respect to the overall reaction. ***(2 points)***

Luciferin, ATP, and O_2 have an reaction order of 1, and PP_i has a reaction order of -1. **(+1 point)**

The overall reaction order is 2 $(1 + 1 + 1 - 1 = 2)$. **(+1 point)**

ii. Using the reactant orders determined in part (i), write the rate law for the reaction. ***(1 point)***

$Rate = k[luciferin][ATP][O_2][PP_i]^{-1}$ or $Rate = k\frac{[luciferin][ATP][O_2]}{[PP_i]}$

*answer may vary depending on how student answered part (i)

b. Calculate the rate constant k for the following hypothetical scenarios with proper units. Assume that all four molecules in the given table are present in the rate law for the overall reaction and have whole number reaction orders. If not enough information is provided to make the calculation, write "N/A" and provide a brief justification for why it is not possible.

   i. Experiment 4, where the overall reaction order is 8, luciferin and PP_i each have a reaction order of 1, and the reaction order of ATP is twice that of O_2. ***(2 points)***

The values for the reaction orders that make the conditions true are that luciferin and PP_i have a reaction order of 1, ATP has a reaction order of 4, and O_2 has a reaction order of 2. Therefore, the rate law expression is:

$Rate = k[luciferin][ATP]^4[O_2]^2[PP_i]$ **(+1 point)**

Plugging in the values from Experiment 4:

$9.58 \times 10^{-6} M/s = k(0.01\ M)][0.02\ M]^4[0.06\ M]^2[0.01\ M]$

$k = 1.663 \times 10^8\ M^{-7}s^{-1}$ **(+1 point)**

+1 point for correct reaction orders/rate law

+1 point for correct answer for k

   ii. Experiment 5, where the overall reaction order is 3, ATP has the highest reaction order of the reactants with a reaction order of 2, and O_2 and PP_i have the same reaction order. ***(2 points)***

N/A, there are multiple possible negatives values for O_2 and PP_i that would make the given conditions true.

+1 point for correct answer of N/A

+1 point for valid explanation (see above)

c. The reaction steps for the bioluminescence reaction are given below:

Step 1 (*Fast*):

$$\mathrm{Luciferin + ATP + Luciferase} \overset{k_1}{\underset{k_{-1}}{\leftrightarrow}} \mathrm{L - AMP + PP}_i$$

Step 2 (*Slow*):

$$\mathrm{L - AMP + O_2} \overset{k_2}{\longrightarrow} \mathrm{OxyL^{*} + AMP + CO_2 + Luciferase}$$

Step 3 (*Fast*):

$$\mathrm{OxyL^{*}} \overset{k_3}{\leftrightarrow} \mathrm{OxyL + Light}$$

i. Identify the intermediate(s) in the overall reaction. If there are none present, state "none." ***(1 point)***

The intermediates are $L - AMP$ and $OxyL^{*}$.

ii. Identify the catalyst(s) in the overall reaction. If there are none present, state "none." ***(1 point)***

The catalyst is luciferase.

d. Using the reaction steps provided, write the overall rate law for the reaction. Show ALL work. If the rate law is provided without adequate work shown, NO credit will be given. ***(4 points)***

The overall rate law is based on the rate law for the rate-determining step:

$Rate = k_2[L - AMP][O_2]$ **(+1 point)**

Since $L - AMP$ is an intermediate, it cannot be in the overall rate law, and therefore must be replaced using the fast equilibrium step, where the forward and reverse reaction rates are equal.

$k_1[luciferin][ATP] = k_{-1}[L - AMP][PP_i]$ **(+1 point)**

$[L - AMP] = \frac{k_1[luciferin][ATP]}{k_{-1}[PP_i]}$ **(+1 point)**

$Overall\ Rate = \frac{k_1 k_2[luciferin][ATP][O_2]}{k_{-1}[PP_i]}$ **(+1 point)**

+1 point for correctly using rate-determining/slowest step for rate law

+1 point for correctly equating forward/reverse reaction rates to solve for concentration of intermediate ($L - AMP$)

+1 point for stating correct expression for $[L - AMP]$

+1 point for correct answer if adequate work is shown

e. A firefly's ability to produce light is dependent on the environment. At higher elevations, less oxygen is available due to the lower atmospheric pressure. This means that if a firefly traveled from a low altitude to a sufficiently higher altitude, it would no longer have enough O_2 to carry out Step 2 in the bioluminescence process, and thus would no longer be able to produce light. Predict how a lack of oxygen availability would affect the reactions in Steps 1, 2, and 3. ***(3 points)***

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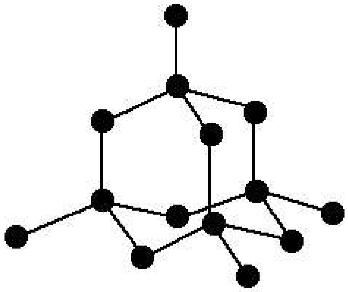
If there was a lack of O_2, then the **intermediate L-AMP would not be consumed as a reactant (+1 point)**, and the **reaction in Step 1 would reach a new equilibrium between its reactants and products (+1 point)**. The **reactions in Steps 2 and 3 would not proceed (+1 point)**.

+1 point for relating lack of O_2 to lack of consumption of L-AMP
+1 point for stating that the reaction in Step 1 would reach a new equilibrium
+1 point for stating that the reactions in Steps 2 and 3 would not proceed

Problem #6: ***(16 points)***

Gemstones are known for their luster or high shine. In the following questions, you will investigate some of the phenomena behind this characteristic.

a. We will start by examining diamonds. Diamonds are carbon allotropes and are considered to be covalent network solids, categorized by extensive covalent bonding and high melting points. A portion of the structure of diamond is provided below.

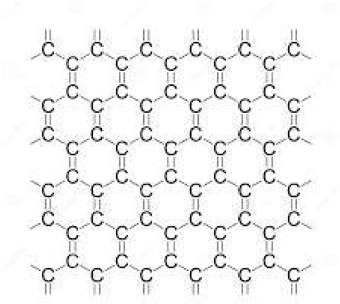


   i. Diamonds are known to be extremely hard as well as quite brittle. Using your knowledge of covalent network solids and the bonding in diamonds, provide a brief explanation for this duality. ***(2 points)***

Diamonds are **strong due to the continuous network of strong covalent bonds (+1 point)** that form the molecule. However, because this network is so rigid, when force is applied, the **bonds cannot shift to absorb all the energy and crack, thus making diamond brittle (+1 point)**.

+1 point for relating hardness of diamond to strong continuous network of covalent bonds
+1 point for relating rigidity of diamond to its brittleness (inability for bonds to shift to absorb all the energy)

ii. Provided below is the structure of graphene, another carbon allotrope.



Graphene is known to be a good electrical conductor, while diamonds are known to be poor electrical conductors. Based on the structural differences between these two carbon allotropes, provide a brief explanation for the difference seen in electrical conductivity. ***(4 points)***

The carbons in diamond are all *sp*^{3} **hybridized (+1 point) with no pi bond present, therefore there are no delocalized electrons that can carry charge (+1 point)** throughout the structure. On the other hand, the carbons in graphene are all *sp*^{2} **hybridized (+1 point), meaning that there is a large conjugated pi system that allows for the delocalization of electrons to carry charge (+1 point)** throughout the structure.

+1 point for stating correct hybridization of diamond (*sp*^{3})

+1 point for stating correct hybridization of graphene (*sp*^{2})

+1 point for correctly relating the hybridization of diamond to its electrical conductivity/carrying of charge
+1 point for correctly relating the hybridization of graphene to its electrical conductivity/carrying of charge

b. Next, we will explore the color of emeralds and rubies. To do this, we will examine phenomena that occur within the d orbitals of elements in the third row of the periodic table and beyond. Empty d orbitals can be used to form hybrid atomic orbitals allowing for the bonding seen in expanded octets. Predict the hybridization of the following compounds. Note: Not all compounds hybridize their d orbitals!

i. ClF_3 _____sp^3d_______ ***(1 point)***

ii. PCl_4^+ _____sp^3_______ ***(1 point)***

iii. IF_4^- _____sp^3d^2______ ***(1 point)***

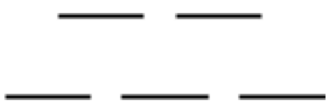
iv. SF_4 _____sp^3d_______ ***(1 point)***

c. As transition metal complexes absorb light, the electrons in the lower energy d orbitals can then be excited to the higher energy d orbitals, allowing the complexes to display a variety of brilliant colors. The red color in rubies and the green color in emeralds are both caused by chromium ions. Using your knowledge of the electromagnetic spectrum, which gemstone must be absorbing light of a longer wavelength? Provide a brief explanation for your reasoning. ***(2 points)***

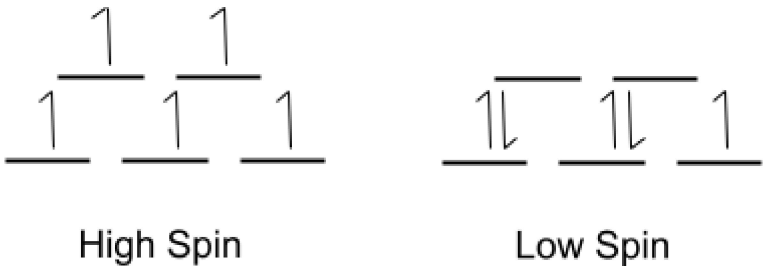
Rubies reflect red light, meaning they absorb green light, while emeralds reflect green light, meaning they absorb red light (+1 point). Red light has a longer wavelength than green light, therefore, **emeralds absorb light of a longer wavelength (+1 point)**.

+1 point for reasonable justification of the light rubies and emeralds each absorb
+1 point for correct answer that emeralds absorb light of a longer wavelength

d. In coordinated complexes involving transition metals, the electrons in the ligands repel electrons in the metals’ d orbitals, leading to a phenomenon called “d-orbital splitting”, where two of the d orbitals experience more repulsion and therefore have a higher energy state. We can generalize what these d orbitals would look like below.



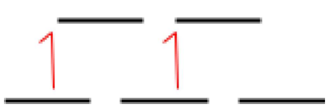
We can place valence electrons of transition metals in these orbitals following Hund’s Rule. For certain elements, there are multiple configurations - the one with more unpaired electrons is the “high spin” configuration, and the one with more paired electrons is the “low spin” configuration. The d orbital electron configurations for Mn^{2+} are provided below.



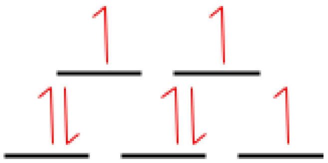
Note that “low spin” configurations prioritize filling the three degenerate (same energy level) lower energy d orbitals, while “high spin” configurations fill the five d orbitals as if they were all degenerate.

For the following transition metal ions, fill in the provided d orbitals with their valence electrons. If multiple configurations are possible, the "high spin" or "low spin" configuration is specified.

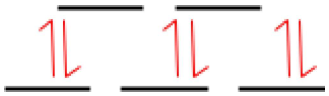
i. V^{3+} ***(1 point)***



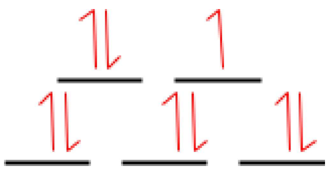
ii. Co^{2+}(high spin) ***(1 point)***



iii. Co^{3+}(low spin) ***(1 point)***



iv. Cu^{2+} ***(1 point)***



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