2025 WUCT: Team Exam

This exam consists of 6 questions and is worth 100 points. You will complete this exam as a team. 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: (*19* points)

Water is known as the "universal solvent" in biochemistry because a wide spectrum of solutes can be readily dissolved in water. However, for species that are hard to dissolve in water, we need to use equilibrium to determine the accurate amount a chemical will dissolve. This question will start from solubility calculation in aqueous solution. Then we will explore how water changes when organic compounds dissolve, and discuss the limited solubility of organic compounds in water using thermodynamic data.

a. List one characteristic of the species that are soluble in water. ***(1 point)***

Polar **(+1 point)** (ionic, charged, able to form hydrogen bonds, etc. are also acceptable)

b. Write the expression for the solubility equilibrium constant K_{sp} of $Zn(OH)_2$. ***(1 point)***

$K_{sp}=[Zn^{2+}][OH^{-}]^2$

+1 point for correct expression of K_{sp}

c. If the K_{sp} for $Zn(OH)_2$ is 3.00×10^{-16}, calculate the concentration of OH^- ions in water, assuming nothing is dissolved in the water initially. ***(3 points)***

ICE Table **(+1 point)**

$$Zn(OH)_2 + H_2O(l) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

Initial	0	0
Change	+x	+2x
Equilibrium	x	2x

Using the K_{sp} formula:

$(x)(2x)^2 = 4x^3 = 3.00 \times 10^{-16}$ **(+1 point)**

$x^3 = 7.50 \times 10^{-17}$

$x = 4.22 \times 10^{-6}$

$[OH^-] = 2x = 8.43 \times 10^{-6}$ M **(+1 point)**

+1 point for correct ICE table setup

+1 point for setting up the correct equation using the K_{sp} formula

+1 point for the correct final answer

d. Assume 1.0 M of NaOH is added to water before the experiment begins. How would this affect the solubility of $Zn(OH)_2$? Explain by showing calculations. ***(5 points)***

Assumption: NaOH fully dissociates in water, so the initial concentration of OH^- is 1.0 M. **(+1 point)**

ICE Table **(+1 point)**

$$Zn(OH)_2 + H_2O\ (l) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

Initial	0	1
Change	$+ x$	$+ 2x$
Equilibrium	x	$1 + 2x$

Using the K_{sp} formula:

$(x)(1 + 2x)^2 = 3.00 \times 10^{-16}$ **(+1 point)**

Since x is small compared to 1.0, $2x$ is negligible compared to 1:

$(x)(1)^2 = 3.00 \times 10^{-16}$

$x = 3.00 \times 10^{-16}$ **(+1 point)**

Thus, only 3.00×10^{-16} M of Zn^{2+} dissolves, which is significantly smaller than the 4.22×10^{-6} M calculated in the previous question. **(+1 point)**

+1 point for identifying that 1.0 M of NaOH corresponds to 1.0 M of initial [OH^-]
+1 point for correct ICE table setup.
+1 point for setting up the correct equation using the K_{sp} formula
+1 point for the correct concentration of Zn^{2+}
+1 point for correct comparison of the concentration of Zn^{2+} in this question with the previous scenario.

When working with organic materials, water can be tricky to deal with because most organic molecules do not dissolve in water and will form immiscible layers instead. The following table provides thermodynamics data for dissolving some organic compounds in water at 303 K, based on Mirgorod's work (2014).

Hydro-carbon	ΔG°_s, kJ/mol	$-\Delta H^\circ_h$, kJ/mol	$-\Delta S^\circ_h$, J/(mol K)	$-\Delta H^\circ_{ph.tr}$, kJ/mol
Butane	–	26.0	176.3	5.0
Pentane	28.6	28.4	188.7	4.9
Hexane	32.5	31.5	197.7	4.8

e. Calculate the equilibrium constant K of dissolving pentane in water at 303 K, using the provided ΔG_s° (change in standard Gibbs free energy of dissolution) values in the table. ***(2 points)***

$\Delta G_s^\circ = -RT\ln K$ **(+1 point),** $R = 8.314\ \frac{J}{mol \cdot K}$, $T = 303$ K

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{28.6\ kJ/mol}{-8.314\times10^{-3} kJ/mol\cdot K \times 303\ K} = -11.35$$

$$K = e^{\ln K} = e^{-11.35} = 1.17 \times 10^{-5}$$ **(+1 point)**

+1 point for using the correct equation relating ΔG° and K.
+1 point for the correct final answer.

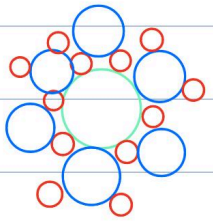
f. Sketch how water molecules and a pentane molecule interact when pentane is added to water. Represent pentane as a sphere (draw only one pentane molecule) and include approximately five water molecules around it to illustrate their interaction. Draw each water molecule with its bent molecular structure, clearly showing the hydrogen (H) atoms and oxygen (O) atoms. Label the pentane molecule to distinguish it from the water molecules. ***(2 points)***

Color Code:

Red sphere: H atoms

Blue sphere: O atoms

Green sphere: Pentane molecule



+1 point for showing water molecules forming a hydrogen bonded cage around the pentane (the bent structure of water molecules must be shown)
+1 point for demonstrating the correct non-uniform alignment of water molecules (i.e. hydrogen atoms shouldn't all be facing away from or toward the pentane molecule)

g. Refer solely to the ΔS_h° (change in standard entropy of hydrophobic hydration) value provided in the table (Note that the table lists $-\Delta S_h^\circ$, not ΔS_h°): Is dissolving pentane in water entropically favorable? Then, explain why the ΔS_h° value makes sense, focusing on how the presence of pentane affects the arrangement and mobility of water molecules. ***(4 points)***

Dissolving pentane in water is **not entropically favorable (+1 point),** because the table shows that ΔS°_{h} of dissolving pentane in water is -188.7 J/mol·K, which is a negative value **(+1 point)**.
When pentane is introduced, water molecules are forced to be in this **"cage" conformation** as indicated by the drawing in part f **(+1 point), reducing their mobility** and making the system **more ordered (+1 point).** This leads to a decrease in entropy.

+1 point for answering that dissolving pentane in water is entropically unfavorable
+1 point for associating negative ΔS°_{h} with the reduced entropy and unfavorable dissolving
+1 point for stating that water molecules form a cage surrounding the pentane molecule.
+1 point for associating the cage formation with reduced mobility and a more ordered system, hence reducing entropy (mentioning either reduced mobility or more ordered system will receive full point)

h. Based on the table, how can you make dissolving pentane in water more energetically favorable? Assume ΔS°_{h} & ΔH° are constant across all temperatures. (No calculations needed) ***(1 point)***

To make this reaction more energetically favorable (i.e., make the ΔG°_{S} more negative), **lower the temperature of the reaction (+1 point)**

+1 point for mentioning lower the temperature of the reaction

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

In the nuclear model of the atom, electrons are assumed to revolve around a fixed nucleus. Classically, since the electrons are constantly accelerating, they should eventually lose all the energy and spiral into the nucleus. Bohr, however, makes the assumption that the angular momentum of the electrons must be quantized, allowing the nuclear model to work and enabling us to calculate the orbital energies and radii for one-electron systems.

a. The energy of the second excited state for a one-electron ion is -37.78 eV. Identify the ion (include both the element symbol and the ionic charge). ***(4 points)***

$E_n = -13.6\,eV \times (\frac{Z^2}{n^2}) = -37.78\,eV$

$-13.6\,eV \times (\frac{Z^2}{3^2}) = -37.78\,eV$

$\frac{Z^2}{3^2} = 2.777841176 \Rightarrow Z^2 = 25 \Rightarrow Z = 5$ **(+1 point)**

Therefore, this one-electron ion is B^{4+}

+1 point for identifying that the second excited state corresponds to n=3
+0.5 points for using the correct E_n equation to solve for Z
+0.5 points for getting the correct Z
+1 point for getting the correct element symbol (B or boron)
+1 point for getting the correct ionic charge

b. Considering a one-electron beryllium ion (Be^{3+}), calculate the energy emitted (in eV) when the electron transitions from the $n = 4$ to the $n = 3$ state. Round your answer to three decimal places. ***(2 points)***

$\Delta E = E_3 - E_4 = [-13.6\,eV\,(\frac{4^2}{3^2})] - [-13.6\,eV\,(\frac{4^2}{4^2})] \approx -10.578\,eV$

$E_{emitted} = -\Delta E = 10.578\,eV$

+1 point for setting up the correct equation
+1 point for obtaining the correct energy value (Both 10.578 eV and -10.578 eV are accepted as correct)

c. Calculate the wavelength (in nm) of a photon emitted during an electronic transition that releases 16.528 eV of energy. Round your answer to the nearest integer. ***(1 point)***

$16.528\,eV = 16.528 \times 1.6021773 \times 10^{-19} J = 2.64807864 \times 10^{-18} J$

$\lambda = \frac{hc}{\Delta E} = \frac{6.626076 \times 10^{-34} J{\cdot}s \times 2.99792458 \times 10^{8} m{\cdot}s^{-1}}{2.64807864 \times 10^{-18} J} = \frac{1.98644761 \times 10^{-25} J{\cdot}m}{2.64807864 \times 10^{-18} J} = 7.5 \times 10^{-8} m = 75\,nm$

+1 point for getting the correct wavelength value

d. A metal is irradiated with light that has a wavelength of 100 nm. Knowing that the ejected electron has a kinetic energy of 10 eV, calculate the work function of the metal (in eV, and round to the second decimal place). ***(3 points)***

$\lambda = 100\,nm$**:**

Energy of the photon:

$E = h\frac{c}{\lambda} = 6.626076 \times 10^{-34} J \cdot s \times \frac{2.99792458 \times 10^{8} m/s}{100 \times 10^{-9} m} \approx 1.986 \times 10^{-18} J = 12.40\,eV$

Work function:

$KE = h\nu - \phi = E_{photon} - \phi$

$\phi = E_{photon} - KE = 12.40\,eV - 10\,eV = 2.40\,eV$

+1 point for getting the correct photon energy
+1 point for using the correct equation to calculate the work function
+1 point for getting the correct work function

e. Using the kinetic energy of the electrons given in part d (10 eV), calculate the momentum p (in $kg \cdot \frac{m}{s}$) and the de Broglie wavelength λ (in pm) of the ejected electron. Hint: $p = mv = \sqrt{2m \times (\frac{1}{2}mv^2)}$ ***(3 points)***

$10\,eV = 10 \times 1.6021773 \times 10^{-19} J = 1.6021773 \times 10^{-18} J$

momentum:

$p = \sqrt{2m_e \times KE} = \sqrt{2 \times 9.109390 \times 10^{-31} kg \times 1.6021773 \times 10^{-18} J} \approx 1.708 \times 10^{-24} kg \cdot \frac{m}{s}$

wavelength: $\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{6.626076 \times 10^{-34} J{\cdot}s}{1.708 \times 10^{-24} kg \cdot \frac{m}{s}} \approx 3.878 \times 10^{-10} m = 387.8\,pm$

+1 point for identifying the relationship between p and KE
+1 point for getting the correct momentum
+1 point for getting the correct wavelength

f. Since electrons behave as circular standing waves around the nucleus, an integer number of complete wavelengths must fit around the circumference of the orbit, which gives us the equation $2\pi r = n\lambda$, where n=1,2,3,4… If this electron is in the first Bohr orbit (n=1) of the Be^{3+}, calculate the velocity of the electron. ***(3 points)***

$r_1 = \frac{n^2 \cdot a_0}{Z} = \frac{1^2 \times 52.9pm}{4} = 13.225\ pm$ **(+1 point)**

$2\pi r = n\lambda$

$2\pi r = n\frac{h}{mv}$ **(+1 point)**

$\Rightarrow v = \frac{nh}{2\pi rm} = \frac{1 \times 6.626076 \times 10^{-34}\ J \cdot s}{2\pi \times 13.225 \times 10^{-12} m \times 9.109390 \times 10^{-31} kg} \approx 8.75 \times 10^6\ m/s$ **(+1 point)**

+1 point for getting the correct Bohr radius
+1 point for substituting λ with de Broglie wavelength equation
+1 point for getting the correct velocity

Problem #3: ***(16 points)***

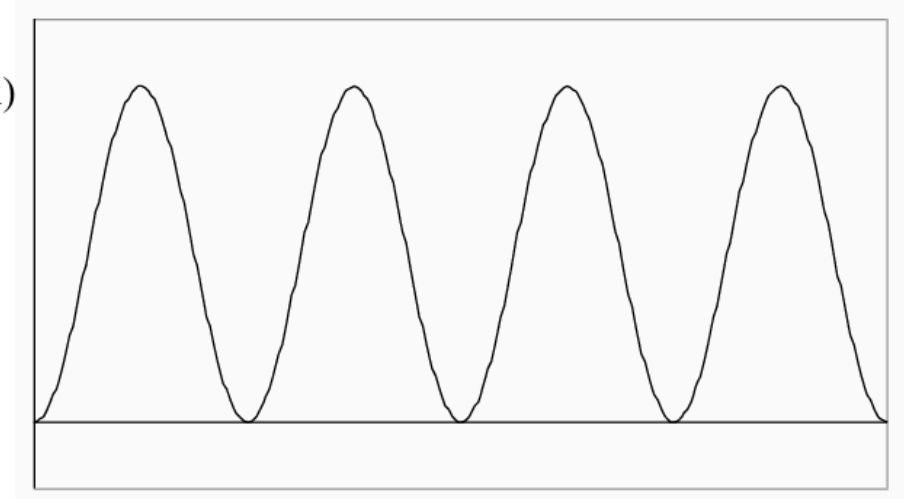
The Particle-in-a-box (PIB) model is a foundational quantum mechanics model describing a particle confined within an infinitely high potential, and the potential energy within the box is assumed to be zero. The wave function of a particle in a one-dimensional box is given by: $\psi_n(x) = \sqrt{\frac{2}{L}}\, sin(\frac{n\pi x}{L})$, where L is the length of the box, and n is the quantum number.

a. A particle in a one-dimensional box has a wave function of $\psi(x) = \psi_n(x)$. Given that this wave function has four nodes (a node is where the wavefunction is zero and changes signs), and the distance between two nearby nodes is 20 pm, determine the length of the box L and the quantum number n. ***(2 points)***

4 nodes → n = 5 **(+1 point)**
length of the box: $20\ pm\ \times\ 5\ =\ 100\ pm$ **(+1 point)**

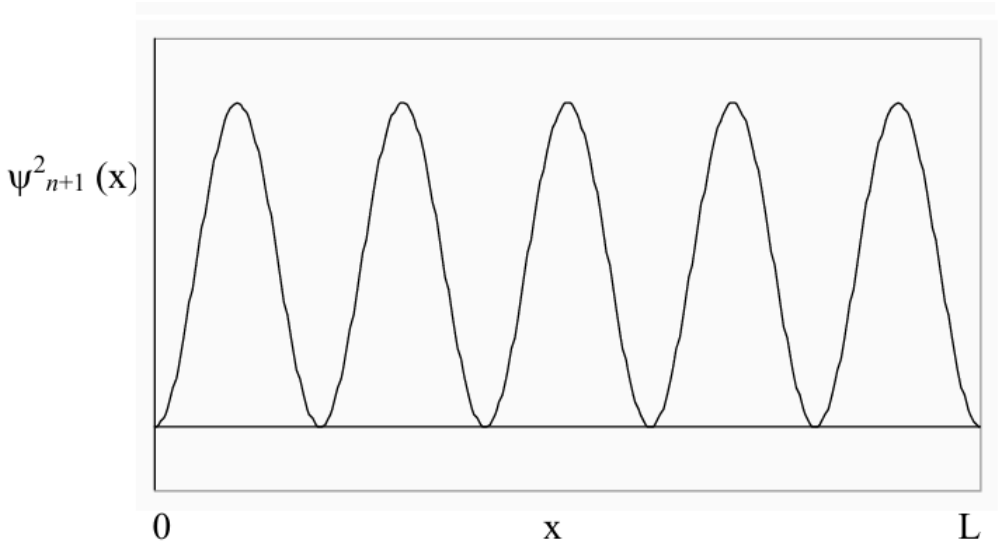
b. Sketch the probability density distribution function $|\psi_n(x)|^2$ for a particle confined to a one-dimensional box of length 80 pm in the n=4 state. Additionally, sketch the probability density distribution function for the next energy state $|\psi_{n+1}(x)|^2$. Clearly indicate the position of the nodes in your drawing. Assume that the box starts at x = 0 pm and ends at x=80 pm. ***(4 points)***

$|\psi_n(x)|^2$:



For n=4, there are 3 nodes at x=20, 40, and 60 pm, with boundaries at x=0 and 80 pm

$\left|\psi_{n+1}(x)\right|^2$:



For n+1=5, there are 4 nodes at x=16, 32, 48, and 64 pm, with boundaries at x=0 and 80 pm.

+1 point for the correct drawing for each graph (points are awarded for the correct general shape)
+1 point for correctly denoting the positions of the nodes and boundaries (for each graph)

c. What is the probability of finding the particle in part b (in the n=4 state) in the region 20 pm $\leq x \leq$ 70 pm? ***(1 point)***

$p\,(20\ pm \leq x \leq 70\ pm) = \frac{(70-20)\ pm}{80\ pm} = \frac{2.5}{4} \times 100\% = 62.5\% = 0.625$ **(+1 point)**

d. Calculate the total energy of the particle (in J) in part b (in the n=4 state). Assume that the particle is an electron. ***(2 points)***

$E_{tot} = KE + 0 = \frac{n^2h^2}{8mL^2} = \frac{4^2h^2}{8\times9.109390\times10^{-31}\ kg\times(80\times10^{-12}\ m)^2} \approx 1.5062 \times 10^{-16} J$

+1 point for identifying that the total energy is equal to kinetic energy
+1 point for calculating the correct total energy

e. Knowing that an electron can be described as a standing de Broglie wave in a one-dimensional particle-in-a-box model, calculate its lowest allowed velocity in a one-dimensional box of length 2×10^{-13} m. ***(4 points)***

Lowest allowed velocity is found when the particle is in n=1 state **(+1 point)**

$\lambda = 2L = 4 \times 10^{-13} m$ **(+1 point)**

$p = \frac{h}{\lambda} = \frac{6.626076 \times 10^{-34} J \cdot s}{4 \times 10^{-13} m} = 1.656519 \times 10^{-21} kg \cdot m \cdot s^{-1}$ **(+1 point)**

$v = \frac{p}{m} = \frac{1.656519 \times 10^{-21} kg \cdot m \cdot s^{-1}}{9.109390 \times 10^{-31} kg} \approx 1.81847 \times 10^{9} m/s$ **(+1 point)**

Alternative answer:

$KE = \frac{n^2 h^2}{8mL^2} = \frac{1^2 h^2}{8 \times 9.109390 \times 10^{-31} kg \times (2 \times 10^{-13} m)^2} \approx 1.506168 \times 10^{-12} J$ **(+2 points)**

$\frac{1}{2} m v^2 = 1.506168 \times 10^{-12} J \Rightarrow v = \sqrt{\frac{2 \times 1.506168 \times 10^{-12} J}{9.109390 \times 10^{-31} kg}} \approx 1.81847 \times 10^{9} m/s$ **(+1 point)**

+1 point for identifying that n=1
+1 point for the correct wavelength and +1 point for the correct momentum
or
+1 point for using the correct equation to calculate KE and +1 point for getting the correct KE (for the alternative answer)
+1 point for the correct velocity

f. Consider a modified model where the potential energy at the walls and outside the box is not infinitely large but instead has a finite value V_0. This adjustment allows the particle to have non-zero probability of being found outside the box. Describe qualitatively how this change would affect the probability distribution graphs you sketched in part b. Focus on how the probability varies across the available positions, without requiring precise mathematical details or exact function shapes. ***(1 point)***

Since the wavefunction would now have a non-zero value outside the box, the graph will need to **extend into the region outside of the box**.

+1 point for saying that the graph will extend into the region outside of the box

g. If $V_0 = 5 \times 10^{-15} J$ and the particle's total energy is $4 \times 10^{-26} J$, discuss why this scenario is problematic from a classical perspective. ***(2 points)***

Since the particle can be found outside of the box, the kinetic energy of the particle can be calculated by subtracting V_0 from E_{tot}. Since V_0 is way bigger than E_{tot}, the kinetic energy of the particle will be negative, which is classically impossible.

+1 point for mentioning that the particle can be found outside the box
+1 point for identifying that the particle's kinetic energy will be negative

Problem #4: ***(19 points)***

Molecular orbital theory (MOT) is a theory used to describe the distribution of electrons over a molecule by looking at the interactions between atomic orbitals. In this theory, *n* atomic orbitals interact to form *n* molecular orbitals.

a. Briefly describe how the energy levels for bonding and antibonding molecular orbitals compare to one another. ***(1 point)***

Bonding orbitals, which experience a decrease in energy due to constructive interference, are lower in energy than antibonding orbitals,

+1 point for mentioning that antibonding orbitals are higher in energy than bonding orbitals.

b. To understand MOT, one must first look at the different characteristics of each atom and then molecule. The four quantum numbers used to describe these characteristics are n, l, m_l, and m_s.

i. What does each quantum number determine? What are their possible values? ***(4 points)***

n:

l:

m_l:

m_s:

n: determines **size** / **energy level** of the orbital → n = 1, 2, 3, …
l: determines **shape** / **subshell** of the orbital → l = 0, 1, 2, …, n-1
m_l: determines **orientation** of orbitals, **number of orbitals** in a subshell → m_l = (-l, l)
m_s: determines electron behavior in the presence of a **magnetic** field; **spin** of electrons → $m_s = \pm \frac{1}{2}$

+0.5 points for correctly answering what each quantum number determines (points are awarded for mentioning the keywords)
+0.5 points for correctly answering the possible values for each quantum number

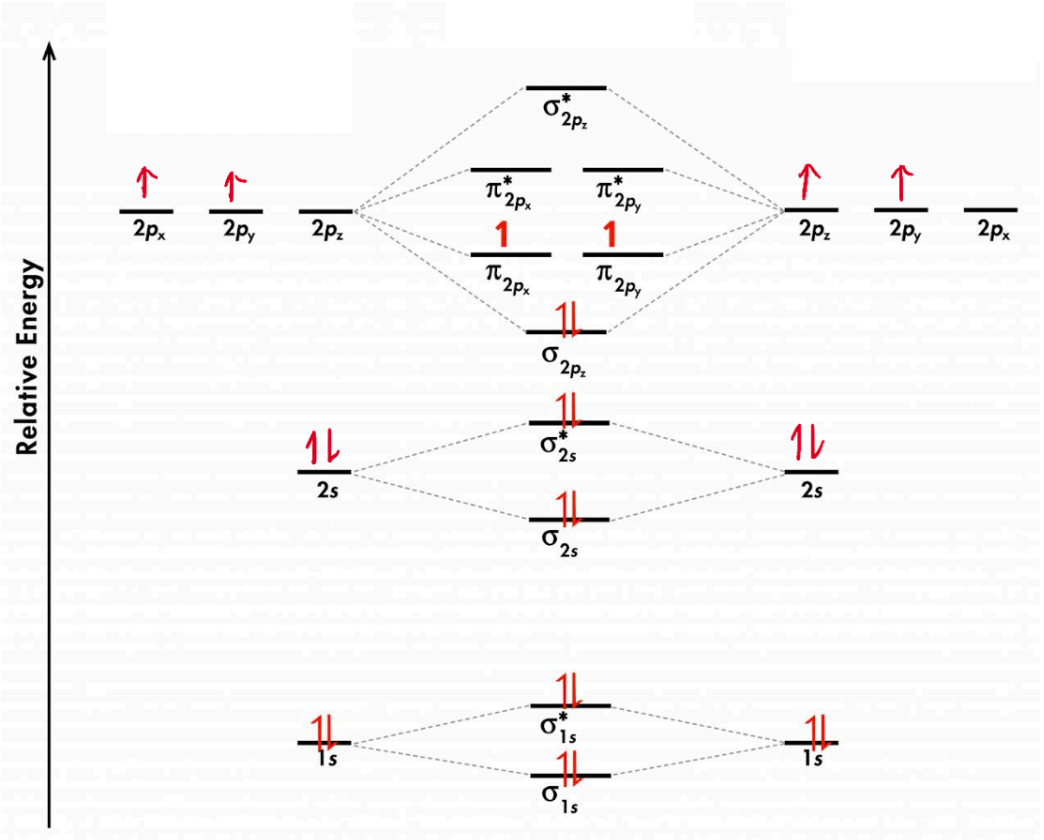
ii. Fill in the chart below. ***(5 points)***

Set of Quantum Numbers	Allowed? (yes or no)	If not allowed, list a valid set of quantum numbers by changing **one** of the quantum numbers in the original set.
$(0, 0, 0, +\frac{1}{2})$	No	$(1, 0, 0, +\frac{1}{2})$ (Change the 1st quantum number to a positive integer)
$(3, 3, -2, +\frac{1}{2})$	No	$(3, 2, -2, +\frac{1}{2})$ (Change the 2nd quantum number to 0,1, or 2) or $(4, 3, -2, +\frac{1}{2})$ (Change the 1st quantum number to be greater than 3)
$(6, 4, -1, -\frac{1}{2})$	Yes	/ or blank
$(2, 0, -1, -\frac{1}{2})$	No	$(2, 0, 0, -\frac{1}{2})$ (Change the third quantum number to 0) or $(2, 1, -1, -\frac{1}{2})$ (Change the second quantum number to 1)
$(4, 1, 0, +\frac{1}{2})$	Yes	/ or blank

+0.5 points each (Note: there are more than one answers for the corrected sets of quantum numbers)

c. To develop a better understanding of MOT, you are assigned to study the molecule O_2. ***(6 points)***

i. Fill in the molecular orbital diagram below for O_2. Make sure that you fill in the electrons for both the atomic orbitals and the molecular orbitals. ***(2 points)***



+1 point for correctly filling in the atomic orbitals
+1 point for correctly filling in the molecular orbitals

ii. Is O_2 a paramagnetic or a diamagnetic molecule? Explain. ***(1 point)***

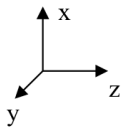
O_2 is a paramagnetic molecule. **(+0.5 points)** This is because it has **2 unpaired electrons** in the π molecular orbitals. **(+0.5 points for mentioning unpaired electrons)**

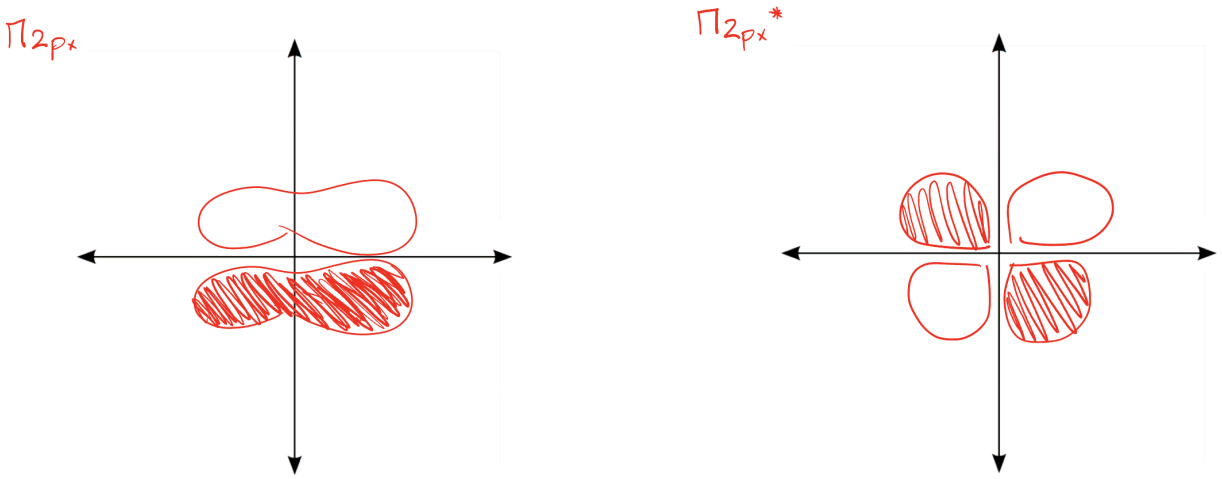
iii. Using your answer from ii, determine if the following statement is true or false by circling your answer below: O_2 would be attracted to an external magnetic field. ***(1 point)***

TRUE / FALSE

TRUE **(+1 point)**

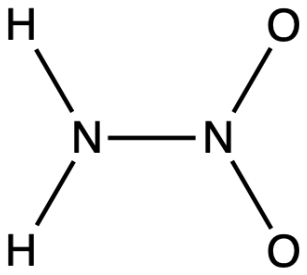
iv. For O_2, sketch the molecular orbitals of π_{2p_x} and $\pi^*_{2p_x}$ using the coordinate systems shown below. Note: make sure to use shading to indicate the correct phase of each lobe. ***(3 points)***



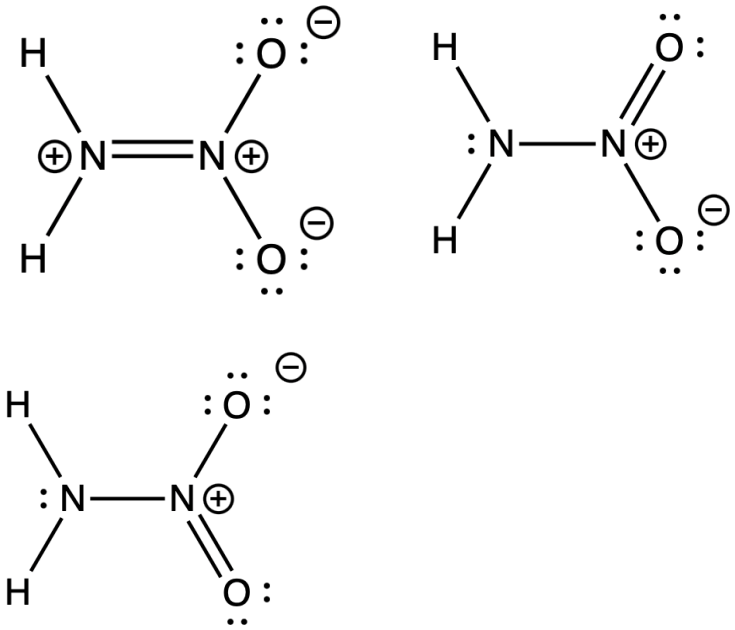


+0.5 points for each correct drawing of the shape of the orbitals
+0.5 points for each correct indication of phase using shading
+0.5 points each for correctly showing the position of the nodes in each diagram
(students do not need to draw dash lines to indicate the nodes; they just have to make sure that nodes can be clearly seen)

d. The Lewis structure for the molecule $H_2N_2O_2$ (shown below) is incomplete. Sketch the proper Lewis structure and any equivalent resonance forms with all the atoms (except for H) have complete octets. Please be sure to include any lone pairs and formal charges. ***(2 points)***



Answers:



+1 point for one correct Lewis structure
+0.5 points for each additional resonance form (maximum: +1 points; 2 additional structures)

Problem #5: ***(15 points)***

S-AdenosylMethionine (SAM)'s family is preparing for a trip to the Andes. As a chemistry enthusiast, SAM would like to determine how much time it would take to boil an egg in his hotel. For all following questions, ignore the temperature difference due to heat conductance (assume homogeneous temperature for all parts of the system in question).

a. At sea level (1 atm), water boils at 100 degrees celsius. The process of water boiling can be represented as: $H_2O\ (l) \rightleftharpoons H_2O\ (g)$. Using $\Delta G^{o} = -RTlnK$, show why ΔG_{vap}^{o} for water at 100 ℃ is equal to 0 and explain your reasoning. (ΔG_{vap}^{o} is the change in standard Gibbs free energy for vaporization under standard conditions) ***(4 points)***

For the vaporization of water, $K = \frac{P(H_2O)}{[H_2O]} = P(H_2O)$ **(+1 point).** At boiling point, **vapor pressure of water is equal to the atmospheric pressure (+1 point)**, which is 1 atm. So $K = 1$ **(+1 point)** and $\Delta G_{vap}^{o} = -RTlnK = 0$. **(+1 point)**

+1 point for correctly identifying the expression for K
+1 point for correctly relating K with vapor pressure of water and the atmospheric pressure
+1 point for correctly identifying that K=1
+1 point for correctly identifying $\Delta G_{vap}^{o} = 0$ by substitution K=1 into $\Delta G_{vap}^{o} = -RTlnK$

b. Atmospheric pressure decreases with elevation according to the relation: $P\,(h) = 1\,atm \times (1 - 2.25577 \times 10^{-5} m^{-1} \cdot h)^{5.25588}$, where h is the elevation (in meters) with respect to sea level. Calculate the boiling point of water at the top of the Andes, at an elevation of 6962 m. ***(3 points)***

Given: $\Delta G_{vap}{}^{o} = 0$ and $\Delta S_{vap}{}^{o}\,(H_2O) = 109.1 \frac{J}{mol \cdot K}$ at 373 K. You may assume that $\Delta H_{vap}{}^{o}\,(H_2O)$ and $\Delta S_{vap}{}^{o}\,(H_2O)$ are temperature and elevation independent.

$P\,(6962\,m) = 0.4074\,atm$ **(+1 point)**

When boiling at an elevation of 6962 m, $P_{vap}\,(or\ P^{\bullet}) = P\,(6962\,m) = 0.4074\,atm$

Calculate ΔH^{o}_{vap}:

$\Delta G^{o}_{vap}(373\,K) = \Delta H^{o}_{vap} - T\Delta S^{o}_{vap} = 0,$

$\Delta H^{o}_{vap}(373\,K) = T\Delta S^{o}_{vap}(373\,K) = 373\,K \times 109.1\,J/(mol \bullet K) = 40.6943\,kJ/mol$

(+1 point)

Method a:

Clausius-Clapeyron: $ln\frac{P_2}{P_1} = -\frac{\Delta H_{vap}{}^{o}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$ln\frac{0.4074}{1} = -\frac{40694.3\,J/mol}{8.314\,J/(mol\,K)}\left(\frac{1}{T_2} - \frac{1}{373\,K}\right)$

$T_2 = 349.11\,K$ **(+1 point)**

Method b:

$lnP = -\frac{\Delta H_{vap}{}^{o}}{RT} + \frac{\Delta S_{vap}{}^{o}}{R}$

Plug in $\Delta H_{vap}{}^{o}$ and $\Delta S_{vap}{}^{o}$ and solve for T

$T = 349.11\,K$ **(+1 point)**

+1 point for the correct atmospheric pressure at an elevation of 6962 m

+1 point for the correct ΔH^{o}_{vap}

+1 point for the correct boiling point

c. Thinking about the process of an egg boiling as following first-order kinetics, we can equate the amount of time it takes for the egg to be half-boiled as its half life. At sea level, it takes 5 mins in boiling water for the egg to be half boiled, but 30 mins in 80 ℃ water. Using the Arrhenius equation and assuming the Arrhenius (pre-exponential) factor A and activation energy E_a are independent of temperature and elevation, calculate the time it takes for the egg to become half-boiled at 90 ℃. ***(3 points)***

Calculate E_a:

Half-life (First-order kinetics): $t_{1/2} = \frac{ln\,2}{k}$, where k is the rate constant

So, $k\,(T) = \frac{ln2}{t_{1/2}(T)}$, where T is temperature **(+1 point)**

$$\frac{k\,(100℃)}{k\,(80℃)} = \frac{ln\,2}{t_{1/2}(100℃)} \cdot \frac{t_{1/2}(80℃)}{ln\,2} = \frac{t_{1/2}(80℃)}{t_{1/2}(100℃)}$$

$$ln(\frac{k\,(100℃)}{k\,(80℃)}) = \frac{-E_A}{R}(\frac{1}{100℃} - \frac{1}{80℃})$$

$$ln(\frac{t_{1/2}(80℃)}{t_{1/2}(100℃)}) = \frac{-E_A}{R}(\frac{1}{100℃} - \frac{1}{80℃})$$ **(+0.5 points)**

$$ln(\frac{30\,mins}{5\,mins}) = \frac{-E_A}{8.314\,J/(mol\,K)}(\frac{1}{373\,K} - \frac{1}{80+273K})$$

$E_A = 98.07\,kJ/mol$ **(+0.5 points)**

Calculate $t_{1/2}(90℃)$:

$$ln(\frac{t_{1/2}(90℃)}{t_{1/2}(100℃)}) = \frac{-E_A}{R}(\frac{1}{100℃} - \frac{1}{90℃})$$

$$ln(\frac{t_{1/2}(90℃)}{t_{1/2}(100℃)}) = \frac{-98.07\,kJ/mol}{8.314\,J/(mol\,K)}(\frac{1}{373\,K} - \frac{1}{90+273K})$$

$$\frac{t_{1/2}(90℃)}{t_{1/2}(100℃)} \approx 2.39$$

$t_{1/2}(90℃) = 2.39 \times t_{1/2}(100℃) \approx 11.95\,mins$ **(+0.5 points)**

+1 point for identifying the correct relationship between k and $t_{1/2}$

+0.5 points for setting up the correct Arrhenius equation to solve for activation energy

+0.5 points for the correct activation energy

+0.5 points for setting up the correct Arrhenius equation to solve for $t_{1/2}(90℃)$

+0.5 points for the correct answer

d. As a seasoned chemist, SAM is aware that the above calculations are over-simplifying the problem. In fact, we've been assuming that the pressure experienced by the liquid water is solely its vapor pressure, which is the partial pressure of water vapor. However, in reality, when boiling an egg, the water is also subject to atmospheric pressure in addition to the vapor pressure of water. To accurately determine the time required to boil an egg, we need to first explore the idea of chemical potential.

The chemical potential of a substance i in a system with multiple phases is defined as:

$$\mu_i = \overline{G}_i$$

In essence, the chemical potential of substance i (μ_i) in a particular phase is equal to its molar Gibbs free energy ($\overline{G}_i$). Based on what you know, prove that for water at its boiling point (an equilibrium state), the chemical potential of the liquid phase must be equal to the chemical potential of the gaseous phase. Note: μ_i must be the same in all phases of a system for equilibrium to exist. ***(2 points)***

For any phase change $i_{phase\ 1} \leftrightarrow i_{phase\ 2}$, $\Delta G = G_{i,\,phase\ 2} - G_{i,\,phase\ 1} = \mu_{i,\,phase\ 2} - \mu_{i,\,phase\ 1}$ **(+1 point)**

At equilibrium, $\Delta G = 0$. Therefore, $\mu_{i,\,phase\ 2} = \mu_{i,\,phase\ 1}$ **(+1 point)**

+1 point for correctly relating chemical potential with Gibbs free energy
+1 point for mentioning that $\Delta G = 0$ for an equilibrium which gives rise to the constant chemical potential

e. The chemical potential of a liquid is related to pressure by the following equation:

$$\mu_{liquid,\,i}(T,\,P_2) = \mu_{liquid,\,i}(T,\,P_1) + \overline{V} \cdot (P_2 - P_1)$$

Using this information, calculate the corrected boiling point of water at sea level, where the atmospheric pressure is 1 atm. ***(3 points)***

Given: $P_1 = 1$ atm, $P_2 = P_1 + P_{atmospheric} = 2$ atm, $T = T_b$ (boiling point), $\overline{V}$ is the molar volume of liquid i (in this case, H_2O), $\Delta S_{vap}^{o}(H_2O) = 109.1\,J/(mol \bullet K)$, and $\Delta H_{vap}^{o}(H_2O) = 39\,kJ/mol$.

Hint: when boiling, $\mu_{liquid,\,H_2O}(T_b,\,P_2) = \mu_{gas,\,H_2O}(T_b,\,P_1)$

$\mu_{liquid,\,H_2O}(T_b,\,P_2) = \mu_{gas,\,H_2O}(T_b,\,P_1)$

Since $\mu_{liquid,\,i}(T_b,\,P_2) = \mu_{liquid,\,i}(T_b,\,P_1) + \overline{V} \cdot (P_2 - P_1)$,

$\mu_{liquid,\,H_2O}(T_b,\,P_1) + \overline{V} \cdot (P_2 - P_1) = \mu_{gas,\,H_2O}(T_b,\,P_1)$

$\mu_{gas,\,H_2O}(T_b,\,P_1) - \mu_{liquid,\,H_2O}(T_b,\,P_1) = \overline{V} \cdot (P_2 - P_1)$

$\Delta G_{vap}^{o}(H_2O) = \overline{V} \cdot (P_2 - P_1)$ **(+1 point)**

$\Delta G_{vap}^{o}(H_2O) = \Delta H_{vap}^{o}(H_2O) - T_b \cdot \Delta S_{vap}^{o}(H_2O) = \overline{V} \cdot (P_2 - P_1)$

$\overline{V} = \frac{M}{\rho} = \frac{18.015\ g/mol}{1.00\ g/cm^3} = \frac{18.015\ g/mol}{1\times10^6\ g/m^3} = 1.80 \times 10^{-5} m^3/mol$ **(+0.5 points)**

$T_b = \frac{\Delta H_{vap}^{o}(H_2O) - \overline{V} \cdot (2\ atm - 1\ atm)}{\Delta S_{vap}^{o}(H_2O)}$ **(+1 point)**

$= \frac{39000\ J/mol - 1.80\times10^{-5} m^3/mol \times (2\ atm - 1\ atm) \times 1.01325\times10^5 Pa/atm}{109.1\ J/(mol \bullet K)} \approx 357.45349\ K$ **(+0.5 points)**

+1 point for the correct substitution of ΔG_{vap}^{o}

+0.5 points for the correct molar volume

+1 point for setting up the correct equation to solve for T_b.

+0.5 points for the correct corrected boiling point

Problem #6: ***(15 points)***
In this question, we will explore the electron configuration of atoms, the rules behind electron filling, and the ionization of atoms.

a. Write out the full electron configuration of Cu without using noble gas abbreviation. ***(1 point)***

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

+1 point for the correct configuration

b. Fill in the missing information in the table below. (For the violated electron filling rules: select from Aufbau Principle, Hund's Rule, and Pauli Exclusion Principle). ***(4 points)***

Atomic Number	Electron Configuration	Ground or Excited State or Forbidden	# of unpaired electrons	Which Electron filling rules violated.
24	$[Ar]4s^2 3d^4$	Excited	0	Hund's Rule Aufbau Principle
27	$[Ar]4s^2 3d^7$	Ground	3	None
39	$[Kr]5s^3$	Forbidden	1	Pauli Exclusion Principle
53	$[Kr]5s^1 4d^{10} 5p^6$	Excited	1	Aufbau Principle

+0.5 points for each correct answer in the blank.

c. When forming a zinc ion (Zn^{2+}) from a zinc atom, why is the electron removed from the 4s orbital instead of the 3d orbital? Justify your answer in a few sentences. ***(2 points)***

Removing an electron from $4s$ orbital results in an electron configuration of $[Ar]4s^{1}3d^{10}$, which is favorable because it has a **half-filled** $4s$ **orbital and a fully-filled** $3d$ **orbital**. **(+1 point)** However, removing a $3d$ electron would result in $[Ar]4s^{2}3d^{9}$. This **disrupts the stability of the fully filled 3d orbital**. **(+1 point)** Hence, the former configuration is favored and $4s$ electrons will be removed first.

+1 point for explaining the stability of the resulted ion when 4s electrons are removed
+1 point for correct comparison of the two configurations

Alternative Answer: Shielding
The $4s$ electrons experience **more shielding (+1 point)** and are farther from the nucleus compared to $3d$ electrons. Therefore, $4s$ electrons are **less attracted to the nucleus and easier to remove (+1 point)**

+1 point for mentioning the more shielding experienced by 4s electrons (1 point is also awarded for mentioning that 4s electrons have lower effective nuclear charge)
+1 point for explaining that 4s electrons are therefore easier to be removed

d. Radial wavefunctions describe the probability of finding an electron in a region of space as a function of distance from the nucleus. It is determined from the Schrödinger equation of H atom. In this question, a radial wavefunction is provided for an electron in $3s$ orbital.

$R(r) = 2 \cdot (\frac{Z}{3a_0})^{\frac{3}{2}} \cdot (1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2}) \cdot e^{-\frac{Zr}{3a_0}}$, where Z is the atomic number, and a_0 is the Bohr Radius.

i. Using the equation above and basic algebra, describe in a few sentences how the probability of finding an electron changes as the radius r increases.***(2 points)***

Initially, as the electron moves away from the nucleus, the possibility of finding it will increase, because the polynomial term will increase faster than the decrease of the exponential term (e term). **(+1 point)** However, as r gets larger, eventually the rate of decay for the exponential term will make the polynomial term negligible. So, the probability of finding electrons after electrons moved farther than a certain distance will keep decreasing. **(+1 point)** This observation makes sense because electrons are more likely to be found closer to the nucleus but can barely be found when the distance to the nucleus is very far.

+1 point for stating that the probability will increase initially

+1 point for stating that the probability will decrease eventually

ii. In Physical Chemistry, a node is defined as a position in space where the probability of finding the electron (or particle) is zero. The probability density of finding an electron is described as $R^2(r)$ (or $|R(r)|^2$). It is known that the $3s$ orbital has 2 radial nodes. Using this information, find the positions of radial nodes for the $3s$ orbital. ***(3 points)***

When there is a node, the probability of finding an electron is 0 ($R^2(r) = 0$). In this case, $R(r)$ must be equal to 0 as well. For $R(r)$ to be zero, the polynomial part needs to be 0, because $(\frac{Z}{3a_0})^{\frac{3}{2}}$ and $e^{-\frac{Zr}{3a_0}}$ cannot be 0.

Therefore, $1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2} = 0$ **(+1 point)**

This is a quadratic equation. We can treat $\frac{Zr}{3a_0}$ as a single variable x, then we can use the formula $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ to solve it. The two roots are $x = 2.366 = (\frac{3+\sqrt{3}}{2})$ or $0.634 = (\frac{3-\sqrt{3}}{2})$. Note that $x = \frac{Zr}{3a_0}$, where $Z = 1$ (Hydrogen) $a_0 = 52.9$ pm. So, $r = \frac{3a_0 * 2.366}{Z} = 187.744$ pm and $r = \frac{3a_0 * 0.634}{Z} = 50.306$ pm **(+1 point)**

+1 point for identifying that the polynomial part will be 0, not the constant or the exponential decay part.
+1 point for setting up the correct quadratic equation
+1 point for the correct positions of radial nodes

e. Finally, we will come back to electron configuration. Considering that the electron configuration of Ru is $[Kr]5s^1 4d^7$, explain why the statement below is true. Make sure you include the electron configuration of Ru^+ in your explanation. ***(3 points)***

"The most probable distance of finding the highest energy valence electron in Ru is much larger than the most probable distance of finding the highest energy valence electron in Ru^+."

The electron configuration of Ru is $[Kr]5s^1 4d^7$, while Ru^+ is $[Kr]4d^7$ **(+1 point).** In Ru, the highest energy valence electron is in the 5s orbital, which has a principal quantum number of 5, while the highest energy valence electron in Ru^+ has a principal quantum number of 4. Because the quantum number is **1 less in the Ru^+ electron**, **(+1 point)** the highest energy valence electron in Ru^+will **extend a shorter distance in the radial probability diagram. (+1 point)** As a result, the most probable distance will be smaller as well.

+1 point for giving the correct electron configuration of Ru^+

+1 point for stating that Ru^+ has a smaller principal quantum number

+1 point for saying that due to the smaller n, the highest energy valence electron in Ru^+ will extend a shorter distance in the radial probability diagram (or simply say smaller most probable distance).

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