2023 WUCT: Individual Exam ANSWER KEY

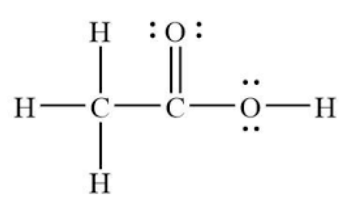
This exam consists of 6 questions and is worth 100 points. You will complete this exam individually. You will have 1 hour to take the exam. The only allowed resources for this exam are a calculator and the provided equation sheet. You may NOT use any other notes or books. You must show your work and 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.

<u>Problem #1</u>: *(13 points)*

When acetic acid is added to water, it reacts with water in a reversible manner to form acetate ions and hydronium. The equation can be modeled below:

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+ \qquad K_a = 1.8 \text{ x } 10^{-5}$$

a. Draw the most preferred Lewis structure for CH_3COOH. Include all lone pairs and any non-zero formal charges on appropriate atoms if applicable. ***(3 points)***



No non-zero formal charges. Connectivity and lone pairs shown in structure above.
2 points for correct atomic connectivity and bonds
1 point for lone pairs on oxygen and no non-zero formal charges

b. Write the general expression for the equilibrium constant, K_a, for the reaction above. ***(1 point)***
$K_a = [CH_3CO_2^-] [H_3O^+] / [CH_3COOH]$
1 point for correct equilibrium expression

c. The reaction above is a Brønsted–Lowry acid/base reaction. Define a Brønsted–Lowry acid and base. ***(2 points)***

Brønsted–Lowry acid: H+ donor

Brønsted–Lowry base: H+ acceptor

1 point for correctly defining Brønsted–Lowry acid

1 point for correctly defining Brønsted–Lowry base

d. Calculate the pH of a 0.43 M solution of acetic acid (CH_3COOH). Round to two decimal places. ***(4 points)***

R	CH_3COOH +	H_2O ⇄	$CH_3CO_2^-$ +	H_3O^+
I	0.43	excess	0	0
C	-x		+x	+x
E	0.43 - x	excess	x	x

$K_a = [CH_3CO_2^-]\,[H_3O^+] / [CH_3COOH]$

$K_a = (x)(x) / (0.43 - x)$

$1.8 \times 10^{-5} = (x)(x) / (0.43 - x)$

Assume x << 0.43

$1.8 \times 10^{-5} = x^2 / (0.43)$

x = 0.00278 M

$[H_3O^+] = x = 0.00278$ M

$pH = -\log([H_3O^+])$

pH = -log(0.00278) = 2.56

1 points for correctly setting up ICE table

1 point for calculating correct "x" term (or concentration of $[H_3O^+]$)

2 points for final correct answer

e. If a 100 mL sample of 0.50 M CH_3COOH was mixed with a 100 mL sample of 0.50 M NaOH, would the pH be less than 7, equal to 7, or greater than 7? Explain. ***(2 points)***

Moles are equal and NaOH is a strong base whereas acetic acid is a weak acid so the pH will be greater than 7.

1 point for correct answer

1 point for correct explanation

f. List two common laboratory techniques/procedures a student can use to determine the $[H_3O^+]$ of a solution. ***(1 point)***

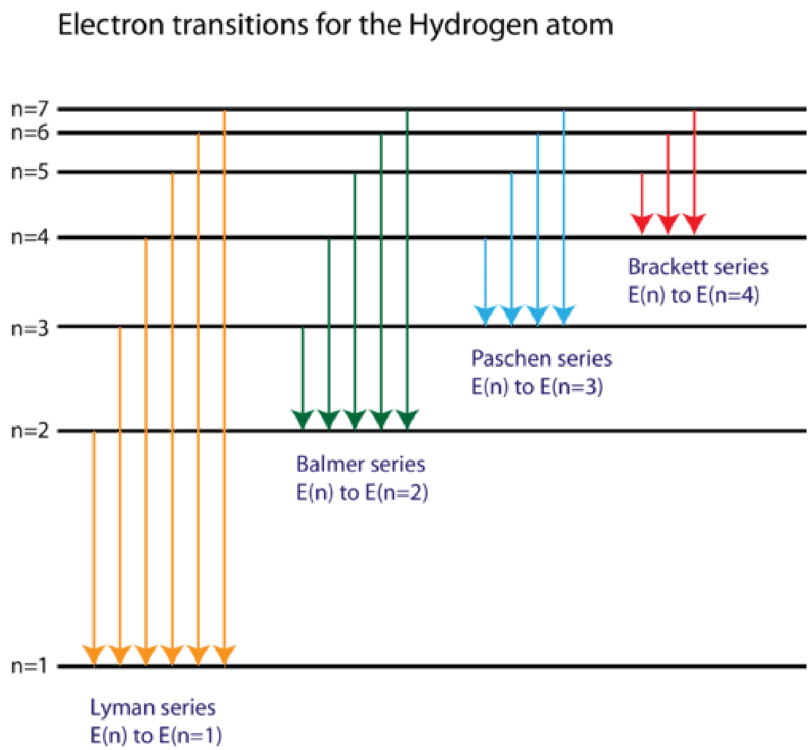
Titration or pH meter

1 point for stating titration or pH meter

****any reasonable answers will also be accepted*

<u>Problem #2</u>: *(10 points)*

Lyman, Balmer, Paschen, and Bracket series describe different transition states that arise from the hydrogen atom. The relative length of the arrow represents the amount of energy released when the electron undergoes the transition, with longer arrows representing more energy being released. The energy diagram for a hydrogen atom is shown below:



a. The n = 2 to n = 1 transition emits a wave with a wavelength of 122 nm. Calculate the energy of the wave. (Planck's constant h = 6.626 * 10^{-34} m^2 kg/s) ***(3 points)***

   $E = hc / \lambda = 6.626 * 10^{-34}$ m^2 kg/s * 3 * 10^8 m/s / [122 * 10^9 m] = 1.629 * 10^{-18} J
   1 point for correct equation set up
   2 points for correct answer

b. Calculate the frequency of the wave that is released from the n = 2 to n = 1 transition. ***(3 points)***

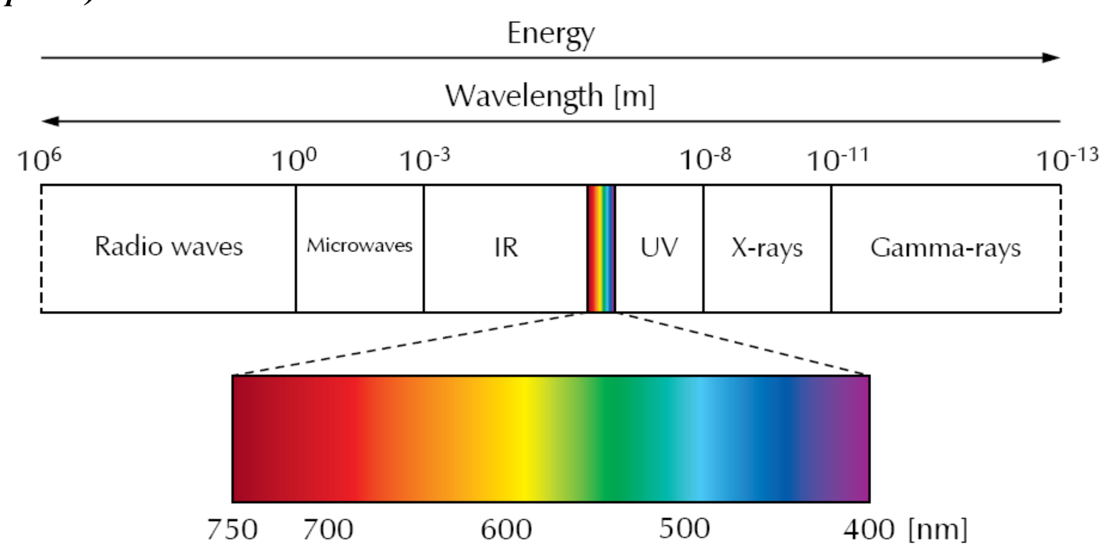
   $E = h\nu$ = 1.629 * 10^{-18} J = 6.626 * 10^{-34} m^2 kg/s * ν
   ν = 2.45 * 10^{15} Hz
   1 point for correct equation set up
   2 points for correct answer

c. Which of the following transitions will result in the emission of waves with the smallest energy? Circle one answer and explain your reasoning. ***(2 points)***

   i. n = 4 to n = 2
   ii. n = 5 to n = 2
   iii. n = 3 to n = 1
   iv. n = 6 to n = 5
   v. Unable to determine due to not enough information.

The question tells us that longer arrows represent more energy being released. Therefore, a shorter length gap between n states will represent the transition with the smallest energy. The gap between n = 6 to n = 5 is the smallest of the given options.
1 point for correct answer
1 point for correct explanation

d. The electromagnetic spectrum is shown below. The Lyman series produces waves with wavelengths of around 90 - 120 nm. The Balmer series produces waves with wavelengths of around 400 - 650 nm. Paschen series produces waves with wavelengths of around 1000 - 1900 nm. Which of the 3 transition series falls in the infrared (IR) region? ***(2 points)***



Paschen series
+2 points for correct answer

<u>Problem #3</u>: *(15 points)*

Use the following redox reaction to answer the questions below. Round all numerical answers to three decimal places. Work must be shown to support your answers for all parts of this question.

$$MnO_4^{-} + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$$

a. Assign oxidation states to each of the elements ***(4 points)***

MnO_4^{-}		+	$C_2O_4^{2-}$		→	Mn^{2+}	+	CO_2	
+7	-2		+3	-2		+2		+4	-2

1 point for correct states on MnO_4^{-}
1 point for correct states on $C_2O_4^{2-}$
1 point for correct states on Mn^{2+}
1 point for correct states on CO_2

b. Balance the REDUCTION half reaction in acidic medium ***(2 points)***

$MnO_4^{-} \rightarrow Mn^{2+}$

$MnO_4^{-} \rightarrow Mn^{2+} + 4H_2O$

$MnO_4^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_2O$

$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O$

2 points for correct equation

c. Balance the OXIDATION half reaction in acidic medium ***(2 points)***

$C_2O_4^{2-} \rightarrow CO_2$

$C_2O_4^{2-} \rightarrow 2CO_2$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^{-}$

2 points for correct equation

d. Write out the fully balanced redox reaction ***(1 point)***

$[\, MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O] * 2$

$[\, C_2O_4^{2-} \rightarrow 2CO_2 + 2e^{-}] * 5$

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$
$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

1 point for correct equation

e. If 500 mL of a 2.5 M MnO_4^- solution and 250 mL of a 1.0 M $C_2O_4^{2-}$ solution are combined, what are the new concentrations of each species before any reaction occurs? ***(2 points)***

Molarity of mixed MnO_4^-:

$$M_1V_1 = M_2V_2$$
$$M_2 = \frac{M_1V_1}{V_2}$$
$$M_2 = \frac{(2.5\,M)\,(0.5\,L)}{(0.75\,L)} = 1.667\,M$$

Molarity of mixed $C_2O_4^{2-}$:

$$M_1V_1 = M_2V_2$$
$$M_2 = \frac{M_1V_1}{V_2}$$
$$M_2 = \frac{(1.0\,M)\,(0.25\,L)}{(0.75\,L)} = 0.333\,M$$

1 point for correct MnO_4^- molarity
1 point for correct $C_2O_4^{2-}$ molarity

f. What is the limiting reactant of the reaction described in (e)? ***(2 points)***

Moles of MnO_4^-:

$$mol = ML = (1.67\,M)(0.75\,L) = 1.25\,mol$$
OR
$$mol = ML = (2.5\,M)(0.5\,L) = 1.25\,mol$$

Moles of $C_2O_4^{2-}$:

$mol = ML = (0.333\ M)(0.75\ L) = 0.25\ mol$
OR
$mol = ML = (1.0\ M)(0.25\ L) = 0.25\ mol$

Determining the limiting reactant:

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

$$1.25\ mol\ MnO_4^- \times \frac{10\ mol\ CO_2}{2\ mol\ MnO_4^-} = 6.250\ mol\ CO_2$$

$$0.25\ mol\ C_2O_4^{2-} \times \frac{10\ mol\ CO_2}{5\ mol\ C_2O_4^{2-}} = 0.500\ mol\ CO_2$$

Limiting Reactant: $C_2O_4^{2-}$

1 point for showing work to calculate mol of each species
1 point for correctly determining limiting reactant as $C_2O_4^{2-}$

g. How much CO_2 gas is produced (in grams) from the reaction, using the quantities described in (e,f)? ***(1 points)***

$$0.5\ mol\ CO_2 \times \frac{44.009\ g\ CO_2}{1\ mol\ CO_2} = 22.0045\ g\ CO_2$$

1 point for correct calculations

h. If the CO_2 gas was collected using water displacement, what would be the problem with the gas collected? ***(1 point)***

The collected gas would be a mixture of the pure CO_2 created in the reaction and the water vapor present in the collection vessel.

1 point for correct reasoning

Problem #4: ***(22 points)***

Plants use photosynthesis to produce their own foods. This process can be modeled by the equation below:

$$CO_2 + H_2O \rightarrow C_6H_{12}O_6 + O_2$$

a. Write out the balanced equation by adding the correct coefficients below. ***(2 points)***

$$6\ CO_2 + 6\ H_2O \rightarrow 1\ C_6H_{12}O_6 + 6\ O_2$$

2 points for correct balanced equation

Raw data was collected for photosynthesis at a particular temperature as shown below:

Experiment	**CO_2 (mol/L)**	**H_2O (mol/L)**	**Change in $[O_2]$ Rate (M/s)**
1	2.14×10^{-6}	3.01×10^{-6}	3.41×10^{-12}
2	6.42×10^{-6}	3.01×10^{-6}	1.02×10^{-11}
3	2.14×10^{-6}	6.02×10^{-6}	6.82×10^{-12}
4	4.28×10^{-6}	3.01×10^{-6}	6.82×10^{-12}

b. Write the rate-law expression for photosynthesis. Show all of your work. ***(3 points)***

From experiment 1 and 4: As CO_2 double with H_2O at constant concentration, the rate of O_2 change doubles → tells us that the order with respect to CO_2 is 1

From experiment 1 and 3: As H_2O double with CO_2 at constant concentration, the rate of O_2 change doubles → tells us that the order with respect to H_2O is 1

Rate-law expression: rate = $k[H_2O][CO_2]$

1 point for showing work
2 points for correct rate-law expression

c. Calculate the value of the rate constant, *k*, with the correct units. **(2 points)**

From equation 1: rate = 3.41×10^{-12} M/s = k * 2.14×10^{-6} mol/L * 3.01×10^{-6} mol/L
k = 0.529 $M^{-1}\ s^{-1}$

1 point for correct calculation of rate constant
1 point for correct units

d. When temperature is increased, the rate of photosynthesis increases. Circle ALL of the correct reasons for why increased temperature results in a faster rate of photosynthesis. ***(3 points)***

i) Lowering of activation energy
ii) Raising of activation energy
iii) Increased surface area of CO_2 and H_2O
iv) Increased number of collisions
v) Promotes proper orientation of collision between reactants
vi) Decrease in volume of the system
vii) A change from inelastic collision to elastic collision among reactants

3 points for correctly circling iv.
-1 point for any circled wrong answers. (Minimum points possible: 0)

e. Using the given values, calculate the ΔH, ΔS, and ΔG of photosynthesis at 25°C. Does the data indicate that photosynthesis is a spontaneous process? ***(7 points)***

	ΔH_f	**ΔS**
$C_6H_{12}O_6$	-1273.3 kJ/mol	212 J/K•mol
O_2	0 kJ/mol	205 J/K•mol
H_2O	-285.8 kJ/mol	69.9 J/K•mol
CO_2	-393.5 kJ/mol	213.5 J/K•mol

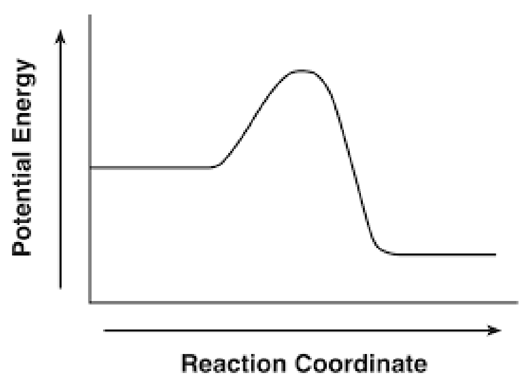
ΔH = [-1273.3 + 6 * 0] - [(-285.8) * 6 + (-393.5) * 6] = **2802.5 kJ/mol**
ΔS = [212 + 205 *6] - [69.9 * 6 + 213.5 *6] = **-258.4 J/K-mol** = **-0.2584kJ/K-mol**
T = 25 + 273.15 = 298.15 K

ΔG = ΔH - TΔS = 2802.5 kJ/mol - [(25 + 273.15) * -0.2584kJ/K-mol] = **2879.5 kJ/mol**
It is **non-spontaneous** because ΔG is positive

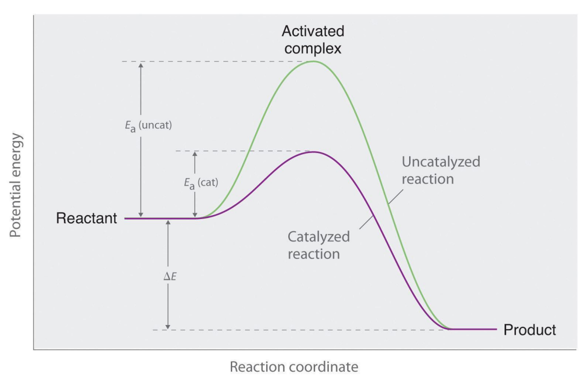
2 points for correct calculations of ΔH
2 points for correct calculations of ΔS
2 points of correct calculator of ΔG
1 point for stating that is is non-spontaneous

f. Rubisco is an enzyme present in plants that serve as an initial catalyst for photosynthesis. What happens to the speed of the reaction when rubisco is present? What happens to the equilibrium constant of the reaction? ***(2 points)***
Rubisco will speed up the rate of reaction
Rubisco does not alter the equilibrium constant
1 point for stating rubisco speeds up rate
1 point for stating rubisco does not change equilibrium constant

g. The potential energy graph below shows the reaction without rubisco. On top of the diagram below, draw out what the graph would look like in the presence of rubisco. ***(3 points)***



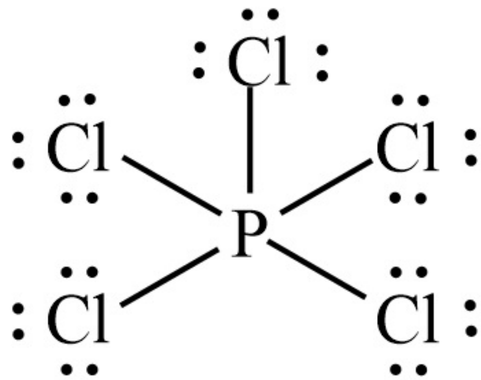
A drawing that has the same reactant and product potential energy but has a lower activation energy. Example answer is shown below



3 points for correct graph

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

a. Draw the Lewis structure for phosphorus pentachloride (PCl_5) and classify its VSEPR geometry. ***(3 points)***



trigonal bipyramid
2 points for correct Lewis structure
1 point for correct geometry

b. In addition to VSEPR geometry, inorganic chemists can classify molecules based on their symmetry elements. To contain a certain symmetry element, the molecule must look exactly the same after performing an operation, such as rotation, inversion, or reflection.

A C_n rotation axis describes rotation through 360°/n. What is the highest value of n present in PCl_5? Write your answer in the format C_n. ***(3 points)***

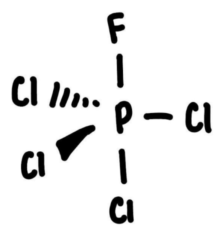
C_3
3 points for correct answer

c. Given that there are 2 axial Cls and 3 equatorial Cls in PCl_5, which bond length is longer: Cl_{eq}-P-Cl_{eq} or Cl_{ax}-P-Cl_{ax}? Explain your answer using bonding pair repulsion properties. ***(3 points)***

The axial bond length is longer. The axial position has 3 90 degrees bonding pair interactions, while the equatorial position has 2 90 degrees bonding pair interactions. There is more repulsion in the axial position leading to a longer bond.
1 point for correct answer
2 points for correct explanation

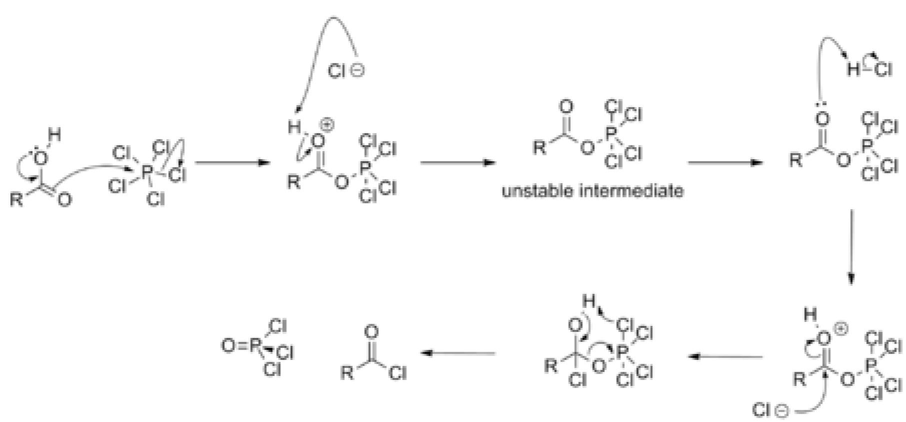
d. If a chlorine atom was replaced by fluorine, predict which position this substitution would be most stable (axial or equatorial)? Explain your answer using electronegativity and bonding pair repulsion properties and include a Lewis structure of this new molecule. ***(4 points)***

The substitution is likely going to occur in the axial position. This is because fluorine is more electronegative than chlorine. It pulls relatively more electron density away from the central atom S, leading to less repulsion between bonding pairs. The axial position has 3 90 degrees bonding pair interactions, while the equatorial position has 2 90 degrees bonding pair interactions. This is why it is more favorable to put the fluorine axial and leave chlorines equatorial.



1 point for correct answer
2 points for correct explanation
1 point for correct Lewis structure

e. PCl_5 is commonly used as a chlorinating agent for carboxylic acids to make acid chlorides. Below is the mechanism for this reaction:

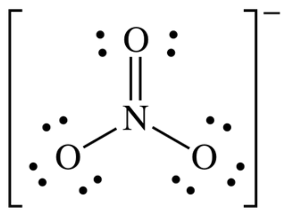


Does the carbon on the carboxylic acid become more reactive, less reactive, or neither? ***(3 points)***

It becomes more reactive because Cl is more electronegative than OH, making the carbonyl C more electrophilic and susceptible to nucleophilic attack.
1 point for correct answer
2 points for correct explanation

<u>Problem #6</u>: *(24 points)*

Sodium nitrate ($NaNO_3$), a white salt that is soluble in water, serves as a source of the nitrate ion (NO_3^-). This anion is commonly used in industrial reactions for explosives, fertilizer, food preservatives, and rocket propellant. The lewis structure of nitrate is shown below:



a. What is the bond order of the nitrogen-oxygen bonds in the nitrate ion? ***(1 point)***
   B.O. = **4/3**
   1 point for correct answer

b. What is the basic and molecular geometry of the nitrate ion? ***(2 points)***
   basic geometry: **trigonal planar**
   Molecular geometry: **trigonal planar**
   1 point for correct basic geometry
   1 point for correct molecular geometry

c. One common synthesis to produce sodium nitrate is shown below:

   $$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

   This reaction utilizes a Bronsted-Lowry base and a Bronsted-Lowry acid. Identify the acid, base, conjugate acid, and conjugate base of the reaction. ***(4 points)***

   Reactant side: Acid - HNO_3 (or H^+)
   Base - NaOH (or OH^-)
   Product side: Conjugate acid - H_2O
   Conjugate base - $NaNO_3$ (or NO_3^-)
   1 point for correct acid
   1 point for correct base
   1 point for correct conjugate acid
   1 point for correct conjugate base

d. Another type of acid-base definition is given by the Lewis acids and bases. Identify the Lewis acid and the Lewis base on the reactant side of the chemical equation. ***(2 points)***
   Lewis acid: HNO_3 (or NO_3^-)
   Lewis base: NaOH (or OH^-)
   1 point for correct lewis acid

1 point for correct lewis base

e. Assume the reaction goes to completion at 25°C. What is the pOH of the reaction solution at that point? ***(1 point)***
Neutral solution after reaction goes to completion → pH = 7.00
pH + pOH = 14
pOH = 14 - 7.00 = **7.00**
1 point for correct answer

f. Your lab instructor gives you some nitric acid (HNO_3) of unknown concentration to use for this reaction. However, in order to know how much of 10% NaOH solution to add (grams per Liter of solution), you need to do a titration to find the concentration of the nitric acid stock solution. You place 35 mL of HNO_3 into an Erlenmeyer flask. The solution of HNO_3 changes color after you add 40 mL of the NaOH solution. What is the percent of the HNO_3 solution (mass per Liter of solution)? ***(4 points)***
NaOH MW = 22.990 + 15.999 + 1.0079 = 39.9969 g/mol
HNO_3 MW = 1.0079 + 14.007 + (3)(15.999) = 63.0119 g/mol
40 mL 10% NaOH solution = x g NaOH/0.040 L solution = 0.10 → 0.004 g NaOH

$$0.004\ g\ NaOH \times \frac{1\ mol\ NaOH}{39.9969\ g\ NaOH} = 1.000077506 \times 10^{-4}\ mol\ NaOH$$

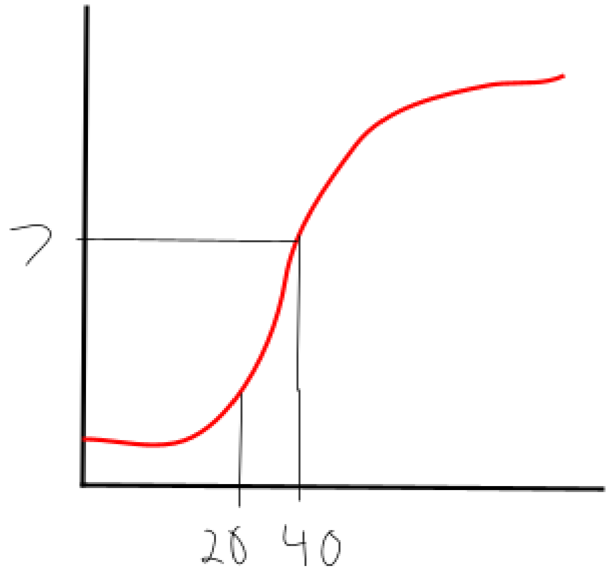
$$1.000077506 \times 10^{-4}\ mol\ NaOH = 1.000077506 \times 10^{-4}\ mol\ HNO_3$$

$$1.000077506 \times 10^{-4}\ mol\ HNO_3 \times \frac{63.0119\ g\ HNO_3}{1\ mol\ HNO_3} = 0.0063016784\ g\ HNO_3$$

$$\frac{0.0063016784\ g\ HNO_3}{0.035\ L\ solution} \times 100\% = 18\%$$

18% HNO_3 solution
1 point for correct calculation of moles of NaOH
1 point for correct calculation of grams of HNO_3
2 points for correct final answer

g. Sketch a titration curve below for this titration (described above in part (f)), with the NaOH solution as the titrant. Be sure to label the axes. The only numerical values you need to include are the pH at the equivalence point, the volume of titrant added at the equivalence point, and the volume of titrant added at the half-equivalence point. ***(3 points)***



2 points for correct titration curve with correct numerical values
1 point for correct axis with x-axis being volume added and y axis being pH

h. Given the table below of indicators and their pK_{in} values, what indicator is your instructor most likely to have included in the HNO_3 solution they gave you? Be sure to justify your answer in 1-2 sentences. ***(2 points)***

Acid-Base Indicator	pK_{in}
Thymol Blue	1.7
Methyl Orange	3.7
Methyl Red	5.0
Bromothymol Blue	7.1
Phenolphthalein	9.6

Bromothymol blue because the pH at the equivalence point is 7, and bromothymol blue has a pK_{in} value most similar to this. The pK_{in} value represents the pH at which the indicator will change color, and we want the color to change at the equivalence point of a titration, which in this case is at pH 7.
1 point for choosing Bromothymol blue
1 point for correct explanation

i. After the reaction goes to completion so that there are no more reactants left, you place two graphite electrodes into the solution. You hook these electrodes up to a battery, and current starts running through the wires.

i) What current do you need to observe sodium metal form in this hydrolytic cell? Assume you are working under conditions of standard temperature and pressure and at a temperature of 25 ℃. In addition, keep in mind that the amounts of hydronium and hydroxide ions present are considered negligible relative to the quantities of the other species in solution. (***3 points)***

Chemicals in solution at this point: Na^+, NO_3^-, H_2O

Reduction occurs at the cathode.

$Na^+ + e^- \rightarrow Na\ (s)$

E = -2.71 V

Oxidation occurs at the anode.

Only oxidation that can happen is : $6\ H_2O\ (l) \rightarrow O_2\ (g) + 4\ H_3O^+\ (aq) + 4\ e^-$

E = -0.82 at pH 7

Balancing/Combining half-reactions:

$4\ Na^+\ (aq) + 4\ e^- \rightarrow 4\ Na\ (s)$ E = -2.71 V

$6\ H_2O\ (l) \rightarrow O_2\ (g) + 4\ H_3O^+\ (aq) + 4\ e^-$ E = -0.82 V

Full reaction: $4\ Na^+\ (aq) + 6\ H_2O\ (l) \rightarrow 4\ Na\ (s) + O_2\ (g) + 4\ H_3O^+\ (aq)$

E = -2.71 + -0.82 = -3.53 V

Q (charge) = nF = (4 mol e^-/1 mol-rxn)(96,485.31 C/1 mol e^-) = 385941.24 C/1 mol-rxn

I = Q/t = 385941.24 C/60 s = **6432.354 A**

1 point for correct identification of species at cathode and anode

1 point for correct calculations of E = - 3.53V

1 point for correct final answer

ii) Alkali metals are known to explode in water. If you did not run a current in this solution, would it be dangerous to leave the solution alone for a couple of hours? Why or why not? ***(2 points)***

No, because it needs a very large current put into the cell to start the reaction. This is not a spontaneous reaction, so the sodium ions will remains as sodium ions unless a current is run through the solution.

1 point for correct answer

1 point for correct reasoning