

Name _____

Topics ID # _____

Team Name _____

2024 WUCT: History of Chemistry

April 6th, 2024
11:00 a.m. – 12:00 p.m.

1 HOUR will be allowed for the exam. The examination contains 7 questions on **27** numbered pages, including the last **SCRATCH PAGE**.

**TURN IN THE ENTIRE EXAM (INCLUDING THE SCRATCH PAGE)
WHEN YOU ARE FINISHED!**

Exam Points Breakdown:

1. (12 pts)
2. (14 pts)
3. (19 pts)
4. (15 pts)
5. (19 pts)
6. (12 pts)
7. (9 pts)
Total Points: (100 pts)

Please fill in the numbers of your 6-digit topics ID:

Topics ID

9	9	9	9	9	9
8	8	8	8	8	8
7	7	7	7	7	7
6	6	6	6	6	6
5	5	5	5	5	5
4	4	4	4	4	4
3	3	3	3	3	3
2	2	2	2	2	2
1	1	1	1	1	1
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2024 WUCT: History of Chemistry

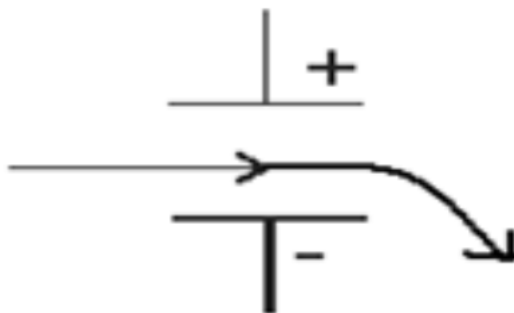
This exam consists of 7 questions and is worth 100 points. You will complete this exam as a team of two. You will have 1 hour to take the exam. The only allowed resources for this exam are a calculator and the provided equation sheet. You may NOT use any other notes or books. You must show your work 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: (12 points)

The idea of the atom, an “indivisible” particle that is the building block of all matter was first proposed by the Greek philosopher Democritus in 430 B.C.E. Since then, scientists have been further examining the atom and its properties, and performing experiments to better understand what really constitutes matter.

- a. In the late 19th century, physicist J.J. Thomson performed experiments with cathode ray tubes where a beam of particles streamed from a negatively-charged cathode to a positively-charged anode. These rays were passed through electric plates and magnets, where it was discovered that this beam of particles consisted of negatively-charged electrons.

Given below is a diagram for how a positive charge would move through an electric field created by two electric plates.



What must Thomson and his colleagues have observed for how an **electron** would move through these plates? *(1 point)*

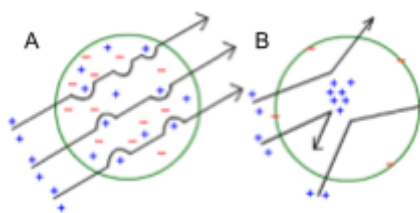
- b. From the discovery of the electron, Thomson was also able to establish that atoms contain a positive charge as well. How was Thomson able to figure this out? *(1 point)*
- c. Consider the following:
- i. An electron and a proton with charges of -1 and +1 respectively are passed through the same electric field at different times as shown above. Which of the following would be true? Circle your answer. *(1 point)*
 - a. The electron and proton would be deflected with the same acceleration.
 - b. The electron would be deflected with a greater acceleration than the proton.
 - c. The proton would be deflected with a greater acceleration than the electron.
 - ii. Provide an explanation for your choice. *(2 points)*

- d. In the early 20th century, Robert Millikan performed an experiment where he sprayed charged oil drops through electrical plates and adjusted the electric field until the force from the plates and the force from gravity balanced to suspend the oil drops in air. This allowed him to determine the charge of an electron to be $-1.602 \times 10^{-19} \text{ C}$, which is the fundamental unit of charge (i.e. the smallest unit of charge possible).

If a similar experiment was performed using an electric field of $2.74 \times 10^3 \text{ N/C}$ for an oil drop containing 4 fundamental units of charge, solve for the mass **in kg** of the oil drop used in the experiment. *(2 points)*

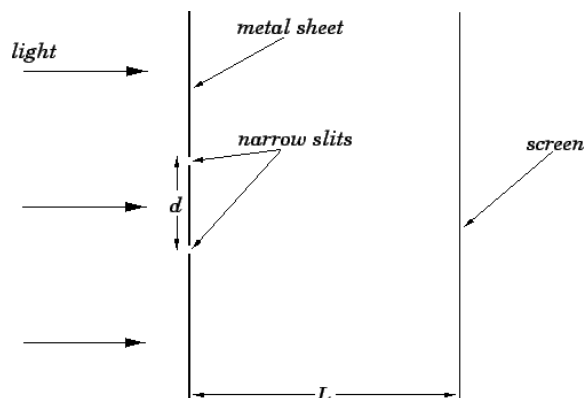
- e. In the original experiment, the electric field was created with a positive electric plate on top and a negative electric plate underneath. If the two plates were switched, which, if any, of the oil droplets would be suspended? Why or why not? *(1 point)*
- f. Circle the following response that makes each statement true based on Part D:
- An oil droplet with twice the charge and half the mass as the one used in Part D would need a(n) _____ electric field to be suspended compared to the electric field in Part D. *(0.5 points)*
 - Stronger
 - Weaker
 - Equal
 - More information is needed

- ii. If the charge-to-mass ratio of the oil drop in Part D is tripled, the electric field must be made _____ to balance the oil drop between the plates. **(0.5 points)**
- Stronger
 - Weaker
 - Equal
 - More information is needed
- g. Following Thomson's and Millikan's experiments, it was deduced that the atom was made up of diffuse, positive material with negatively charged electrons embedded, a depiction known as the Plum Pudding Model. In order to test this theory, a man of the name Ernest Rutherford devised an experiment where he would shoot positively charged alpha particles at a high velocity at a sheet of gold foil and observe how the particles were deflected. Given below are two images of the results Rutherford expected from the experiment and what actually occurred. **(3 points)**



- Which image represents Rutherford's expected deflection results? _____
- Which image represents the actual results Rutherford observed? _____
- Provide an explanation for what was wrong with the Plum Pudding Model that accounted for Rutherford's actual observations.

- b. In 1802, Thomas Young conducted the double-slit experiment by passing light through a double slit. On the other side of the slits was a detector where he observed his results. A schematic of his set-up is provided below. He expected to see two bright spots directly across from the center of each slit, however he ended up with a pattern of constructive and destructive interference.



- i. If the distance between the slits (d) must be between $\frac{1}{10}\lambda$ and 10λ in order to see the desired pattern, what is the minimum and maximum slit distance necessary when using light with a frequency of 6.60×10^{15} Hz? Label each of your answers as the minimum or maximum and report them in nanometers. **(2 points)**
- ii. Does this experiment support the wave nature of the electron, the particle nature, or both? Circle your answer. **(0.5 points)**

Wave

Particle

Both

- c. In 1923, Arthur Compton conducted the Compton scattering experiments right here at WashU! Compton Hall is named in honor of him. He shot x-rays at electrons and observed how the electron scattered and a photon of lesser energy also scattered.
- i. An x-ray with a wavelength of 8 nm is shot at an electron. The electron is scattered with a speed of 4.6×10^6 m/s. What is the frequency of the photon that is also scattered (in Hz)? **(4 points)**
- ii. Does this experiment support the wave nature of the electron, the particle nature, or both? Circle your answer. **(0.5 points)**

Wave

Particle

Both

- d. In 1924, Louis de Broglie proposed the following relationship between the wavelength of a particle and the momentum of that particle:

$$\lambda = \frac{h}{p}$$

- i. Calculate the wavelength of a proton (in femtometers, *fm*) moving at 75% the speed of light. **(2 points)**
- ii. Does this relationship support the wave nature of the electron, the particle nature, or both? Circle your answer. **(0.5 points)**
- Wave Particle Both
- iii. Why don't we observe cars behaving as waves when they speed down the highway at 100 miles an hour? Justify your answer in 1-2 sentences. **(1 point)**

Problem #3: (19 points)

The periodic table is an iconic staple of any chemistry classroom. According to chemistry lore, its structure came to Dmitri Mendeleev in a dream, which he quickly wrote down when he woke up. He observed the properties of the elements known at the time and changed the order of them accordingly, becoming the first to organize them not just in atomic mass order. Mendeleev was unaware of it then, but he actually put everything in order of atomic number! He left blank spaces in his table and predicted the properties of elements yet to be discovered. Gallium, germanium, and scandium were later discovered and had the exact same properties that Mendeleev predicted they would. Thanks Dmitri!

- a. Use the periodic table to write out the electronic configuration for the following species. Do not use any noble gas abbreviations.

i. Ge (1 point)

ii. Cu^{2+} (1 point)

iii. Sm (1 point)

iv. Rb^+ (1 point)

- b. Using your electron configurations from part (a), determine whether each species is paramagnetic (at least one electron unpaired) or diamagnetic (all electrons paired up). Circle your answer.

i. Ge: paramagnetic diamagnetic (0.5 points)

- ii. Cu^{2+} : paramagnetic diamagnetic **(0.5 points)**
- iii. Sm: paramagnetic diamagnetic **(0.5 points)**
- iv. Rb^+ : paramagnetic diamagnetic **(0.5 points)**

c. Rank the following species using the periodic table trends listed below:

- i. Atomic Radius: In, K, Cr, Sn **(1 point)**

_____ > _____ > _____ > _____

- ii. Electronegativity: S, As, Cd, Si **(1 point)**

_____ > _____ > _____ > _____

- iii. First Ionization Energy: Sr, Rb, Ca, Zr **(1 point)**

_____ > _____ > _____ > _____

d. Circle the correct class of elements that best matches with the properties described below:

- i. I easily lose my electrons and a subclass of me typically form vibrantly colored complexes. I am a: **(1 point)**

Metal Metalloid Nonmetal

- ii. The majority of me are gaseous at room temperature and a subclass of me link up with hydrogen to form very dangerous acids. I am a: **(0.5 points)**

Metal Metalloid Nonmetal

- iii. I am easily shattered and one of me is used in almost all of your electronic devices. I am a: **(0.5 points)**

Metal

Metalloid

Nonmetal

- e. Use the following hints and the periodic table trends you are familiar with to identify the species being described by parts (i) through (v). No work is required for this question, but you can use the space to write notes for yourself. **(4 points)**
- i. There is no simple way for me to tell you how many valence electrons I have.
- ii. My atomic radius is larger than Xenon, but smaller than Rubidium.
- iii. Palladium has a larger first ionization energy than me.
- iv. I have the same number of protons as I do electrons.
- v. When I form a cation with a 2+ charge, I have 5 electrons in my outermost d-orbital.

What species am I? Write my chemical symbol and indicate any charges.

- f. Use the following hints and the periodic table trends you are familiar with to identify the species being described by parts (i) through (v). No work is required for this question, but you can use the space to write notes for yourself. **(4 points)**
- i. I am a brittle semiconductor.

 - ii. I have the same number of valence electrons as oxygen.

 - iii. Sulfur has a higher electron affinity than me.

 - iv. I am a charged species.

 - v. In my abbreviated electron configuration, the noble gas used is [Kr].

What species am I? Write my chemical symbol and indicate any charges.

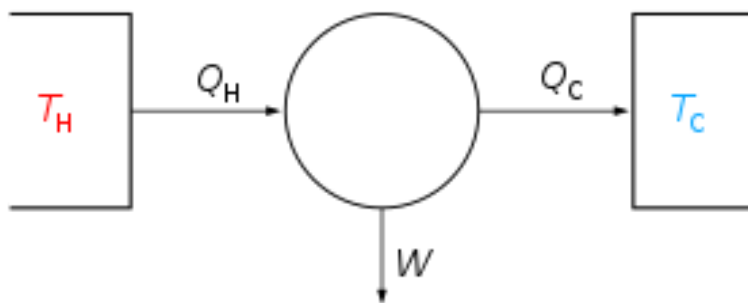
Problem #4: (15 points)

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and it has a wide application in various fields of science and engineering. The first book on thermodynamics was written during the time of the industrial revolution. One of the most important technologies developed during the industrial revolution is the steam engine. The word “thermodynamics” is originally a word that was used to describe “thermo-dynamic engines,” which are the devices that convert heat into motion (i.e. work).

- a. Suppose that there is a steam engine that converts 1 kg of water at 100 °C into steam at 100 °C. Calculate the enthalpy change during this process. Note:

$$\Delta H_{\text{vap, water}} = 40.79 \text{ J/g. (1 point)}$$

- b. In 1824, a French Physicist Sadi Carnot proposed an ideal thermodynamic cycle that provides an upper limit for the efficiency of any thermodynamics engine that converts heat into work. Consider a heat engine like following: Heat Q_H is transferred from a hot reservoir with a temperature of T_H to the engine in the middle. Then, the engine converts some of the heat into work W . The rest of the heat, Q_C , is transferred to the cold reservoir whose temperature is T_C . Calculate the heat and work done in each step. Note: Q_H , Q_C , W are all greater than zero.



- i. Step 1: a reversible isothermal expansion. In the engine, there is 1 mole of monatomic ideal gas that has an initial temperature of T_H , initial volume of V_1 , the end volume is V_2 . Calculate the work and heat exchange in this process in terms of the variables given and R. (**2 points**)

- ii. Step 2: a reversible adiabatic expansion. The initial temperature is T_H , the final temperature is T_C , and the final volume is V_3 . Calculate the work and heat exchange in this process in terms of the variables given and R. (**2 points**)

- iii. Step 3: a reversible isothermal compression. The initial volume is V_3 and the final volume is V_4 . Calculate the work and heat exchange in this process in terms of the variables given and R. (**2 points**)

- iv. Step 4: a reversible adiabatic compression. The initial volume is V_4 , the final volume is V_1 , and the final temperature is T_H . Calculate the work and heat exchange in this process in terms of the variables given and R . **(2 points)**
- c. Calculate the net work W in this cycle. Using that W , calculate the efficiency η of the conversion of heat into work ($\frac{W}{Q_H}$). Then express the net efficiency using an expression that contains only two variables, T_H and T_C . Note that $\frac{V_4}{V_3} = \frac{V_1}{V_2}$. **(3 points)**

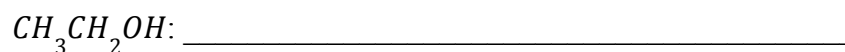
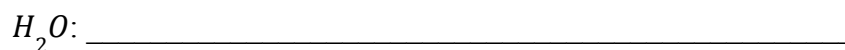
- d. Derive the expression of net efficiency η that contains only two variables T_H and T_C again using the fact that the net entropy change is 0. Hint: What does the net entropy change tell you about the relationship among Q_H , Q_C , T_H and T_C ? (**3 points**)

Problem #5: (19 points)

Scientists have come up with many methods to classify acidic and basic compounds, such as the ancient Greeks categorizing sour-tasting compounds as acids and bitter-tasting compounds as bases. While this was helpful at the time to begin distinguishing the chemical properties of these substances, modern acid-base theory has evolved to now include several definitions for acids and bases that can be used without posing such a health risk.

- a. The first modern theory for describing acids and bases was proposed by Svante Arrhenius in 1884 based on the ionization of hydrogen-containing and hydroxide-containing compounds.
 - i. Under the Arrhenius definition, chlorous acid (HClO_2), chloric acid (HClO_3), and perchloric acid (HClO_4) are categorized as acids. An aqueous solution of each acid is made. Each solution has the same concentration of acid, but the solutions of chloric acid and perchloric acid have much lower pH values compared to chlorous acid. Propose a reason as to why this is. A molecular-level explanation is not necessary. **(2 points)**

- b. In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry separately came up with a new classification for acids and bases depending on a compound's ability to donate or accept protons. In the Brønsted-Lowry theory, the process of donating and accepting protons leads to the formation of conjugate acids and bases.
 - i. For the following acidic species, identify their conjugate base: **(1.5 points)**



- ii. For the following basic species, identify their conjugate acid: **(1.5 points)**

O^{2-} : _____

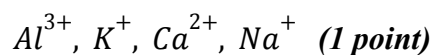
HCO_3^- : _____

$[Co(CO)_4]^-$: _____

- iii. Write an acid-base reaction for water demonstrating its amphoteric properties (its ability to act as both an acid and a base): **(1 point)**
- iv. What is the relationship between the strength of acids and the strengths of their conjugate bases? **(1 point)**
- c. In 1923, Gilbert N. Lewis proposed Lewis acid-base theory which expands the concept of acids and bases beyond the Arrhenius and Bronsted-Lowry theories. In this theory, acids are defined as a substance that can accept a pair of electrons, and bases are defined as a substance that can donate a pair of electrons.
- i. Rank the following Lewis bases in terms of their basicity (from highest to lowest) and justify the reason: CH_3O^- , CH_3N^{2-} , CH_3F **(1 point)**

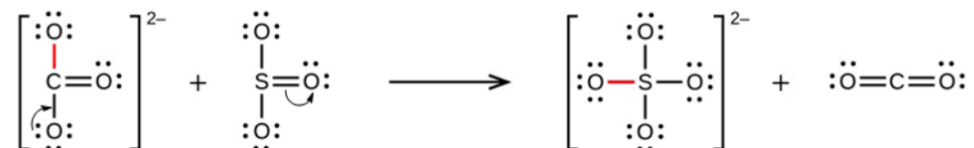
_____ > _____ > _____

ii. Rank the following Lewis acids in terms of their acidity (from highest to lowest):



_____ > _____ > _____ > _____

iii. Label the Lewis acid and base from the reactants of this reaction. (1 point)



d. For the molecules given below, classify them as the most specific acid-base definition (if any) they fall under. Note that the Lewis theory is the most broad definition and the Arrhenius theory is the most specific. (3 points)

CH_3COOH : _____

CH_4 : _____

BF_3 : _____

$Mg(OH)_2$: _____

NH_3 (Reaction: $NH_3 + H_2O \rightleftharpoons NH_4 + OH^-$): _____

CO_2 : _____

- e. Formic acid ($HCOOH$) is a naturally-occurring monoprotic acid. At $25^\circ C$, it has $K_a = 1.77 \times 10^{-4}$. Calculate the pH value of a solution made by adding 300 mg of pure formic acid into 100 mL of pure water at $25^\circ C$. (3 points)

- f. You have the option to choose one of the following chemicals to make an aqueous buffer at $25^\circ C$ with a pH of 9. Sodium hydroxide ($NaOH$) is also available.

Acid Name	Acid Formula	K_a
Formic Acid	$HCOOH$	1.77×10^{-4}
Hydrofluoric Acid	HF	6.6×10^{-4}
Carbonic Acid	H_2CO_3	4.3×10^{-7}
Hydrocyanic Acid	HCN	6.17×10^{-10}
Acetic Acid	CH_3COOH	1.76×10^{-5}

- i. Which acid would you use to prepare this buffer solution? **(1 point)**
- ii. What is the ratio of the moles of conjugate acid to conjugate base needed to produce the desired buffer? Use the acid you chose in part (i) and its conjugate base. If you did not get an answer for part (i), use hydrocyanic acid for this part. **(2 points)**

Problem #6: (12 points)

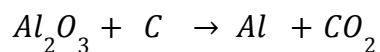
Until about 150 years ago, aluminum was more valuable than gold because it was so difficult to extract from minerals. In 1886, two chemists, Hall and Heroult, independently found a way to extract aluminum metal from naturally occurring alumina, an ionic salt containing aluminum and oxygen.

- a. Alumina has the empirical formula, Al_2O_3 . What is the oxidation state(s) of aluminum and of oxygen in alumina? (2 points)

Aluminum: _____

Oxygen: _____

- b. The overall **unbalanced** reaction of the Hall-Heroult extraction of aluminum is given as:



- i. Write down the half reaction that occurs at the anode. DO NOT include oxygen atoms in either reactants or products. You do not have to specify physical states (i.e. solid, liquid, etc). (1 point)
- ii. The process that occurs at the anode is called (circle one): (1 point)
- | | |
|-----------|-----------|
| Oxidation | Reduction |
|-----------|-----------|
- iii. Write down the half reaction that occurs at the cathode. DO NOT include oxygen atoms in either reactants or products. You do not have to specify physical states. (1 point)

iv. The process that occurs at the cathode is called (circle one): **(1 point)**

Oxidation

Reduction

v. Write down the balanced chemical equation of the Hall-Heroult extraction of aluminum. INCLUDE oxygen atoms and the physical states of all reactants and products under standard temperature and pressure. **(2 points)**

c. The reduction potentials are as given:

Aluminum 3+ (Al^{3+}) to aluminum metal (Al): -1.677 V

Carbon dioxide (CO_2) to carbon (C): + 0.207 V

i. Calculate the overall voltage of this reaction. **(1 point)**

d. Does this reaction require an electrolytic cell or a galvanic cell? No justification is required. **(1 point)**

- e. Crude samples of alumina often contain impurities. Of the following impurities, circle all that you would expect to be reduced before aluminum. Their reduction potentials are given below for reference. No justification is required. **(1 point)**



SiO_2 : -0.990V

Fe_2O_3 : -0.037V

H_2O : -0.828 V

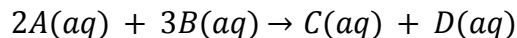
- f. In general, which element type usually has the most **unfavorable** reduction potential (i.e. the one that is least likely to be reduced)? Circle your answer: **(1 point)**

Metals

Nonmetals

Problem #7: (9 points)

Chemical kinetics is the study of the rate and the mechanism of chemical reactions. It is an important subfield of chemistry that not only enriches our understanding of chemical reactions but also embarks on the development of many practical applications of chemical processes in various fields. Tracing through the historical development of chemical kinetics, there are several important theories and advancements that shape our modern understanding of chemical kinetics and its implications. Use the following reaction:



- a. The law of mass action was first formulated by Cato Maximilian Guldberg and Peter Waage in 1864, and it states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reacting substances.

When you increase the concentration of A by two-fold, the reaction rate doubles, and when you increase the concentration of B by three-fold, the reaction rate increases to 9 times of the original. Express the rate law for this reaction. Denote your rate constant as *k*. (2 points)

- b. Experimental data shows that, at 298 K, when the concentration of A is 0.2 M and the concentration of B is 0.1 M, the initial rate of the reaction is $2.0 \times 10^{-3} M/s$. Determine the value of the rate constant *k*, including its units. (2 points)

- c. The understanding of temperature dependency in chemical kinetics has its roots in the Arrhenius equation which was formulated by Svante Arrhenius in 1889. Knowing that at 328 K, the rate constant of the reaction is 2.5 times as large as that at 298 K, calculate the activation energy for this reaction in kJ/mol. **(1 point)**
- d. The history of catalysis encompasses many critical observations and discoveries which leads to the advancement of many industrial processes. Suppose that a catalyst is able to increase the rate constant of the reaction above at 298 K by two-folds, and calculate the activation energy of the reaction after the catalyst is applied. **(2 points)**
- e. A student claims that since a catalyst is not consumed in a reaction, it does not participate in the reaction. Explain why his statement is incorrect, and explain how a catalyst can speed up a reaction in relation to reaction mechanism. **(2 points)**

Scratch Paper