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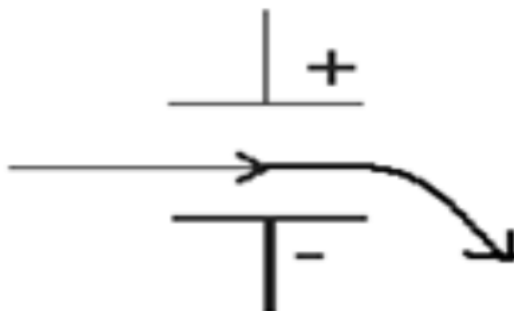
What must Thomson and his colleagues have observed for how an **electron** would move through these plates? *(1 point)*

The electron would be accelerated towards the positive plate.
The electron would move up.
The trajectory would curve upward.

+1 point for any of these explanations

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)*

The atom is known to have an overall neutral charge. Therefore, if there are negative charges present, there must also be positive charges present to bring the overall charge back to neutral.

+1 point for connecting the presence of negative charges to the need for there to be positive charges to maintain neutrality

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)*

The **same amount of force** acts on the electron and proton as they are passing through the same electric field. Force is equal to mass times acceleration. Since the electron has a **smaller mass** than the electron, for the same force, the electron will have a **greater acceleration** compared to the proton.

+1 point for stating that the proton and electron experience the same amount of force
+1 point for using F = ma to say that smaller mass implies greater acceleration

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 -1.602×10^{-19} 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 2.74×10^3 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)*

Force of gravity = Force of electric field
$ma = qE$ **(+1 point)**
$m \times 9.81 \, m/s^2 = 4(1.602 \times 10^{-19}C) \times (2.74 \times 10^3 \, N/C)$
$m \times 9.81 \, m/s^2 = 1.76 \times 10^{-15} \, N$
$m = 1.79 \times 10^{-16} \, kg$ **(+1 point)**

+1 point for equating the force of gravity to the force of the electric field
**+1 point for correct final answer**

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)*

Yes, the **positively charged oil droplets** would be suspended rather than the negatively charged ones as the **force from the electric field would act in an upwards direction** while the force from gravity would act in a downwards direction.

+1 point for stating that the positive charges will be suspended because the direction of the electric field switches

f. Circle the following response that makes each statement true based on Part D:
    i. 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)*
        A) Stronger
        B) Weaker
        C) Equal
        D) 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)*
   A) Stronger
   B) Weaker
   C) Equal
   D) 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)*
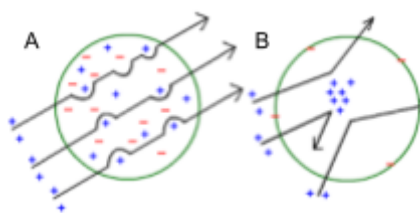
   i. Which image represents Rutherford's expected deflection results? __A____
   (+1 point)

   ii. Which image represents the actual results Rutherford observed? ___B____
   (+1 point)

   iii. Provide an explanation for what was wrong with the Plum Pudding Model that accounted for Rutherford's actual observations.

The Plum Pudding Model didn't account that the atom is **mostly** made up of **empty space**, where **all the positive charge is located in the nucleus** in the center of the atom.

+1 point for something along the lines of "mostly empty space" and "concentrated positive charge"

Problem #2: *(14 points)*

When it comes to the electron, there was one question that plagued scientists of the 19th and 20th centuries: is it a particle or is it a wave? Spoiler alert: it's both! Electrons have wave-particle duality, so it exhibits properties of both. Investigate the findings of the following experiments and explore the story of the electron!

a. In 1905, Albert Einstein proposed that light exists in tiny packets known as photons. When a photon strikes the surface of a metal, it can knock electrons off only if it has the minimum amount of energy required to do so.

   i. A photon with a wavelength of 150 nm strikes a titanium surface. It takes 4.33 eV of energy to eject an electron from titanium. What is the speed of the electron that is ejected? *(3 points)*

$$KE = \frac{hc}{\lambda} - \phi = \frac{(6.626 \times 10^{-34} \, Js)(2.998 \times 10^{8} \, m/s)}{150 \, nm \times \frac{1 \, m}{1 \times 10^{9} \, nm}} - (4.33 \, eV \times \frac{1.602 \times 10^{-19} \, J}{1 \, eV})$$

$$= 6.31 \times 10^{-19} \, J \text{ (+1 point)}$$

$$KE = \frac{1}{2} m_e v^2 \text{ (+1 point)}$$

$$6.31 \times 10^{-19} \, J = \frac{1}{2} (9.11 \times 10^{-31} \, kg) v^2$$

$$v = 1.18 \times 10^{6} \, m/s \text{ (+1 point)}$$

+1 point for solving for KE using the difference between the photon energy and the work function
+1 point for relating KE and speed with the right equation
+1 point for the correct speed in m/s

   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

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.
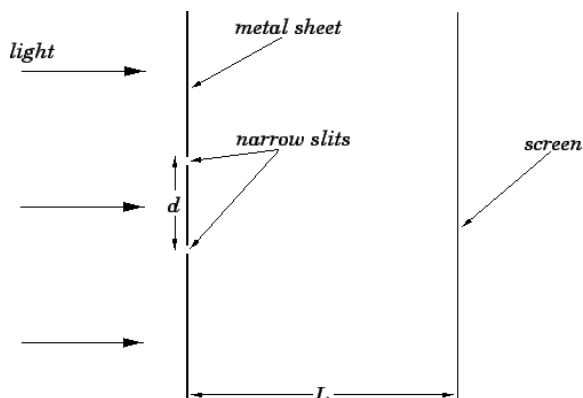
i.   If the distance between the slits (d) must be between $\frac{1}{10}\lambda$ and 10λ in order to see the desired pattern, what is the minimum and maximum slit distance necessary when using light with a frequency of 6.60×10^{15} Hz? Label each of your answers as the minimum or maximum and report them in nanometers. *(3 points)*

$6.60 \times 10^{15} \, Hz = \frac{c}{\lambda}$

$\lambda = \frac{2.998 \times 10^{8} \, m/s}{6.60 \times 10^{15} \, Hz} = 4.54 \times 10^{-8} \, m = 45.4 \, nm$ **(+1 point)**

$d_{min} = \frac{1}{10}\lambda = 4.54 \, nm$ **(+0.5 points)**

$d_{max} = 10\lambda = 454 \, nm$ **(+0.5 points)**

+1 point for correctly solving for λ

+1 point for correctly reporting $\frac{1}{10}\lambda$

+1 point for correctly reporting 10λ

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)*

$$E_{x-ray} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} Js)(2.998 \times 10^8 m/s)}{8\,nm \times \frac{1\,m}{1 \times 10^9\,nm}} = 2.483 \times 10^{-17} J \text{ (+1 point)}$$

$$KE_{electron} = \frac{1}{2}m_e v^2 = \frac{1}{2}(9.11 \times 10^{-31} kg)(4.6 \times 10^6 \frac{m}{s})^2$$
$$= 9.638 \times 10^{-18} J \text{ (+1 point)}$$

$$E_{photon} = E_{x-ray} - KE_{electron} = (2.483 \times 10^{-17} J) - (9.638 \times 10^{-18} J)$$
$$= 1.519 \times 10^{-17} J \text{ (+1 point)}$$

$$\nu_{photon} = \frac{E_{photon}}{h} = \frac{1.519 \times 10^{-17} J}{6.626 \times 10^{-34} Js} = 2.293 \times 10^{16} Hz \text{ (+1 point)}$$

+1 point for correct substitution to solve for E_{x-ray}
+1 point for correct substitution to solve for $KE_{electron}$
+1 point for correct substitution to solve for E_{photon} by taking the difference of the previous two energies
+1 point for correct final answer of the frequency of the photon

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)*

$$v_{proton} = (0.75) \times (2.998 \times 10^8 \tfrac{m}{s}) = 2.2485 \times 10^8 \tfrac{m}{s} \textbf{ (+1 point)}$$

$$m_{proton} = 1.67 \times 10^{-27} kg$$

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} Js}{(1.67 \times 10^{-27} kg)(2.2485 \times 10^8 \tfrac{m}{s})} = 1.765 \times 10^{-15} m$$

$$1.765 \times 10^{-15} m \times \frac{1 \times 10^{15} fm}{1 m} = 1.765 fm \textbf{ (+1 point)}$$

+1 point for correct substitution to find the speed of the proton
+1 point for correct final answer in either meters or femtometers

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)*

According to de Broglie's equation, anything with mass also has wavelength. However, the **mass of a car is so large** that the wavelength is very small, making it **unobservable**.

+1 point for relating the large mass to an unobservable wavelength

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.
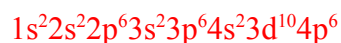
    i. Ge *(1 point)*

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

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

       $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

    iii. Sm *(1 point)*

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

    iv. Rb^+ *(1 point)*

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

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)*

   ___In___ > ___Sn___ > ___K___ > ___Cr___

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

   ___S___ > ___As___ > ___Si___ > ___Cd___

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

   ___Zr___ > ___Ca___ > ___Sr___ > ___Rb___

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.
Must be a transition metal, lanthanoid, or actinoid

ii. My atomic radius is larger than Xenon, but smaller than Rubidium.
Somewhere in row 5

iii. Palladium has a larger first ionization energy than me.
Somewhere from strontium to rhodium

iv. I have the same number of protons as I do electrons.
Neutral atom, not an ion

v. When I form a cation with a 2+ charge, I have 5 electrons in my outermost d-orbital.
Technetium (transition metals lose their s-electrons first)

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

_____Tc (Technetium)_____

+4 points for the correct final answer - no partial credit

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.
    Metalloid

    ii. I have the same number of valence electrons as oxygen.
    Group 6, will form a 2- anion

    iii. Sulfur has a higher electron affinity than me.
    Selenium, tellurium, or polonium

    iv. I am a charged species.
    Will be a 2- anion

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

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

    _____Te^{2-} (Tellurium 2- Anion)_____

+4 points for the correct final answer - no partial credit

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

$$\Delta H = \Delta H_{vap}(water) \times 1000 \, g = 40.79 \, J/g \times 1000 \, g = 40790 \, J = 40.79 \, kJ$$

+1 point for the correct final answer in either J or kJ

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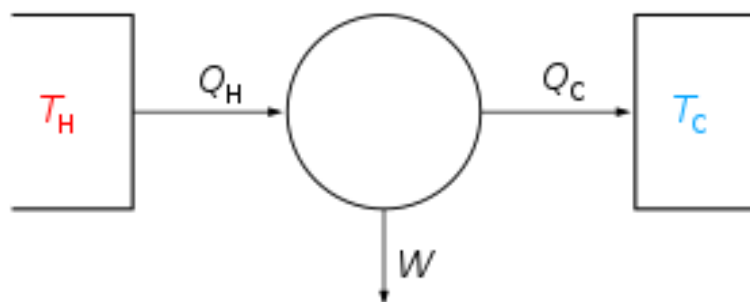
i. Step 1: a reversible isothermal expansion. In the engine, there is 1 mole of monatomic ideal gas that has an initial temperauture of T_H, initial volume of V_1, the end volume is V_2. Calculate the work and heat exchange in this process in terms of the variables given and R. *(2 points)*

$$w = -nRTln(\frac{V_2}{V_1}) = -RT_H ln(\frac{V_2}{V_1})$$

(+1 point) (Note: $< 0 \rightarrow$ word done by the engine on surroundings)

$$q = Q_H = -w = RT_H ln(\frac{V_2}{V_1})$$

(+1 point) (Note: $> 0 \rightarrow$ heat transferred from the hot reservoir to the engine)

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)*

$$w = C_V ln(\frac{T_C}{T_H}) = \frac{3}{2}Rln(\frac{T_C}{T_H}) = -Rln(\frac{V_3}{V_2}) = Rln(\frac{V_2}{V_3})$$ **(+1 point)**

(Note: $< 0 \rightarrow$ work done by the engine on surroundings)

$$q = 0 J$$ **(+1 point)**

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)*

$$w = -RT_C ln(\frac{V_4}{V_3})$$ (Note: $> 0 \rightarrow$ work done by the surroundings on the engine) **(+1 point)**

$$q = -Q_C = -w = RT_C ln(\frac{V_4}{V_3})$$

(+1 point) (Note: $< 0 \rightarrow$ heat transferred from the engine to the cold reservoir)

      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)***

$$w = C_V ln(\frac{T_H}{T_C}) = \frac{3}{2}Rln(\frac{T_H}{T_C}) = -Rln(\frac{V_1}{V_4}) = Rln(\frac{V_4}{V_1}) \text{ (+1 point)}$$

(Note: $> 0 \rightarrow$ work done by the surroundings on the engine)

$q = 0\,J$ **(+1 point)**

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)***

$$W = \left| -RT_H ln(\frac{V_2}{V_1}) + \frac{3}{2}Rln(\frac{T_C}{T_H}) + (-RT_C ln(\frac{V_4}{V_3})) + \frac{3}{2}Rln(\frac{T_H}{T_C}) \right|$$

$$= \left| -RT_H ln(\frac{V_2}{V_1}) - RT_C ln(\frac{V_4}{V_3}) \right| = RT_H ln(\frac{V_2}{V_1}) + RT_C ln(\frac{V_4}{V_3}) \text{ (+1 point)}$$

$$Q_H = RT_H ln(\frac{V_2}{V_1})$$

$$\frac{W}{Q_H} = \frac{RT_H ln(\frac{V_2}{V_1}) + RT_C ln(\frac{V_4}{V_3})}{RT_H ln(\frac{V_2}{V_1})} = 1 + \frac{T_C ln(\frac{V_4}{V_3})}{T_H ln(\frac{V_2}{V_1})} \text{ (+1 point)}$$

$$\frac{W}{Q_H} = 1 + \frac{T_C ln(\frac{V_4}{V_3})}{T_H ln(\frac{V_2}{V_1})} = 1 + \frac{T_C ln(\frac{V_1}{V_2})}{T_H ln(\frac{V_2}{V_1})} = 1 + \frac{-T_C ln(\frac{V_2}{V_1})}{T_H ln(\frac{V_2}{V_1})} = 1 - \frac{T_C}{T_H} \text{ (+1 point)}$$

+1 point for the correct expression for W

+1 point for the correct unsimplified ratio of W to Q$_H$

+1 point for the correct simplified ratio of W to Q$_H$, using the fact that $\frac{V_4}{V_3} = \frac{V_1}{V_2}$

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)*

$$\frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad \textbf{(+1 point)}$$

Since $\Delta S_{net} = S_1 + S_3 = 0 \Rightarrow \frac{Q_H}{T_H} + \frac{-Q_C}{T_C} = 0 \Rightarrow \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$ **(+1 point)**

Therefore, $\frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$ **(+1 point)**

+1 point for the correct ratio of W to Q$_H$ in terms of Q's
+1 point for the implication derived from knowing that $\Delta S = 0$
+1 point for the correct ratio of W to Q$_H$ in terms of T's

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 (HClO2), chloric acid (HClO3), and perchloric acid (HClO4) 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)*
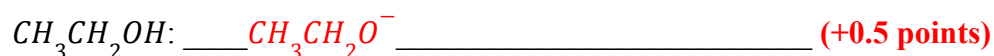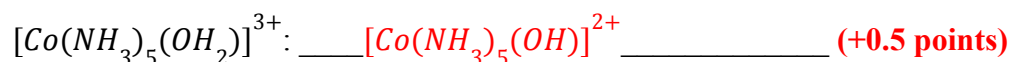
Chlorous acid is a weak acid, therefore it does not completely ionize in aqueous solutions, while **chloric acid and perchloric acid are strong acids** that will completely ionize in aqueous solutions. There will therefore be a **greater H+ concentration** for chloric acid and perchloric acid giving them a **lower pH value**.

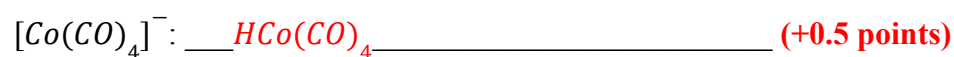**+1 point for identifying that chlorous acid is weak, while chloric and perchloric acids are strong**
+1 point for relating acid strength to concentration of H⁺ to pH

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)*

   $[Co(NH_3)_5(OH_2)]^{3+}$: ____$[Co(NH_3)_5(OH)]^{2+}$_____ **(+0.5 points)**

   H_2O: ____ OH^- _____ **(+0.5 points)**

   CH_3CH_2OH: ____ $CH_3CH_2O^-$ _____ **(+0.5 points)**

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

O^{2-} : ____OH^- _____ **(+0.5 points)**

HCO_3^- : ____H_2CO_3_____ **(+0.5 points)**

$[Co(CO)_4]^-$: ____$HCo(CO)_4$_____ **(+0.5 points)**

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)*

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
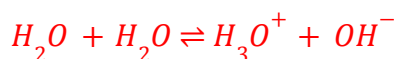
iv.   What is the relationship between the strength of acids and the strengths of their conjugate bases? *(1 point)*

The **stronger the acid**, the **weaker its conjugate base**.

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)*

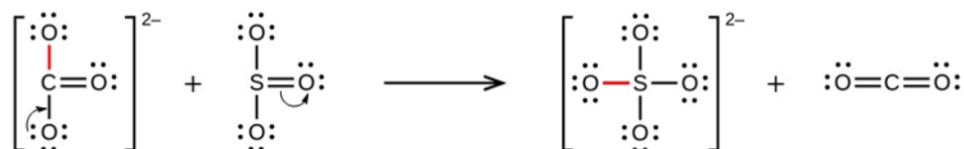____CH_3N^{2-}____ > ____CH_3O^-____ > ____CH_3F____
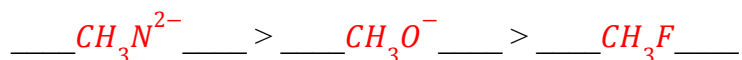
The higher the electronegativity of the electron-donor is, the weaker the lewis base is.

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

Al^{3+}, K^+, Ca^{2+}, Na^+ *(1 point)*

____Al^{3+}____ > ____Ca^{2+}____ > ____Na^+____ > ____K^+____
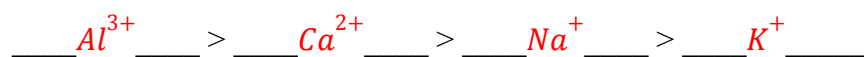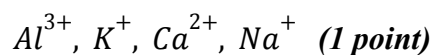
iii.   Label the Lewis acid and base from the reactants of this reaction. *(1 point)*

Lewis Acid: SO_3 **(+0.5 points)**

Lewis Base: CO_3^{2-} **(+0.5 points)**

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: ___Arrhenius_____ **(+0.5 points)**

CH_4: ___None_____ **(+0.5 points)**

BF_3: ____Lewis_____ **(+0.5 points)**

$Mg(OH)_2$: ___Arrhenius_____ **(+0.5 points)**

NH_3 (Reaction: $NH_3 + H_2O \rightleftharpoons NH_4 + OH^-$): ___Brønsted-Lowry__ **(+0.5 points)**

CO_2: _____Lewis_____ **(+0.5 points)**

e. Formic acid ($HCOOH$) is a naturally-occuring monoprotic acid. At 25°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°C. **(3 points)**

Mass of HCOOH $= 300 \ mg = 0.3 \ g$

MW of HCOOH $= 12.011 \ g/mol + 1.0079 \ g/mol \times 2 + 15.999 \ g/mol \times 2$
$= 46.0248 \ g/mol$

Moles of HCOOH $= \frac{0.3 \ g}{46.0248 \ g/mol} \approx 0.006518 \ mol$

Molarity of HCOOH $= \frac{0.006518 \ mol}{0.1 \ L} = 0.06518 \ M$ **(+1 point)**

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$
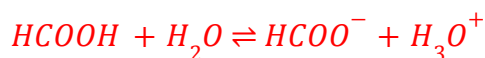
$K_a = 1.77 \times 10^{-4} = \frac{x^2}{0.06518-x}, x = [H_3O^+] \approx 0.003309 \ M$ **(+1 point)**

$pH = -log[H_3O^+] = -log(0.003309) \approx 2.48$ **(+1 point)**

+1 point for correct determining the molarity of HCOOH
+1 point for using the correct expression for K_a to solve for the concentration of H_3O^+
+1 point for correct final pH

f. You have the option to choose one of the following chemicals to make an aqueous buffer at 25°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)*

Formic Acid: $pK_a = 3.75$

Hydrofluoric Acid: $pK_a = 3.18$

Carbonic Acid: $pK_a = 6.37$

Hydrocyanic Acid: $pK_a = 9.21$

Acetic Acid: $pK_a = 4.75$

Since the pH of the buffer is 9, need an acid with a pK_a around that value.

Therefore, hydrocyanic acid is the best choice. **(+1 point)**
Note: no further explanation is necessary for full credit

       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)*

$$pH = pK_a - log(\frac{[HA]_o}{[A^-]_o})$$

$$9 = 9.21 - log(\frac{[HCN]_o}{[CN^-]_o}) \text{ (+1 point)}$$

$$log(\frac{[HCN]_o}{[CN^-]_o}) = -0.21$$

$$\frac{[HCN]_o}{[CN^-]_o} = 10^{-0.21} \approx 0.62$$

Use a ratio of 0.62:1 for $HCN: CN^-$ **(+1 point)**

+1 point for correct substitution into the Henderson-Hasselbach equation
+1 point for correct ratio (note: this point may still be given if the student stops at the second to last line of work shown here)

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)*
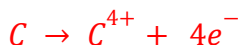
Aluminum: _____+3_____ **(+1 point)**

Oxygen: _____-2_____ **(+1 point)**

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

$$Al_2O_3 + C \rightarrow Al + CO_2$$
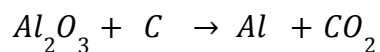
i. Write down the half reaction that occurs at the anode. DO NOT include oxygen atoms in either reactants or products. You do not have to specify physical states (i.e. solid, liquid, etc). *(1 point)*

$$C \rightarrow C^{4+} + 4e^-$$

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)*
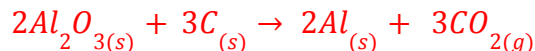
$$Al^{3+} + 3e^- \rightarrow Al$$

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)*

$2Al_2O_{3(s)} + 3C_{(s)} \rightarrow 2Al_{(s)} + 3CO_{2(g)}$

+1 point for correct chemical species and stoichiometric coefficients
+1 point for correct states

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)*

$\varepsilon_{red} + (-\varepsilon_{ox}) = \varepsilon_{overall}$
$-1.677\,V + (-0.207\,V) = -1.884\,V$

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

Electrolytic cell

The overall reaction has a negative voltage, so it requires energy.
Note: no explanation is required to receive full credit

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 Fe_2O_3 H_2O

SiO_2: -0.990V
Fe_2O_3: -0.037V
H_2O: -0.828 V

All of them have a less negative reduction potential than Al_2O_3, so all of these impurities would be reduced before Al_2O_3 is reduced.
**Note: no explanation is required to receive full credit**

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:

$$2A(aq) + 3B(aq) \rightarrow C(aq) + D(aq)$$
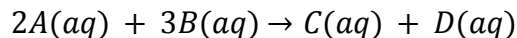
a. The law of mass action was first formulated by Cato Maximilian Guldberg and Peter Waage in 1864, and it states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reacting substances.

   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)*

$Rate = k \cdot [A]^n \cdot [B]^m$

Increasing the concentration of A by two-folds, the reaction rate doubles $\Rightarrow n = 1$

Increasing the concentration of B by 3 times, the reaction rate increases to 9 times of the original $\Rightarrow m = 2$ **(+1 point)**

$Rate = k \cdot [A] \cdot [B]^2$ **(+1 point)**

+1 point for work to support the determination of n and m
+1 for the correct final rate law

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. *(1 point)*

$2.0 \times 10^{-3} M/s = k \cdot 0.2M \cdot (0.1M)^2$ **(+0.5 points)**

$k = \frac{2.0 \times 10^{-3} M/s}{0.2M \cdot (0.1M)^2} = 1\ M^{-2} \cdot s^{-1} = 1\ \frac{1}{M^2 \cdot s}$ **(+0.5 points)**

+0.5 points for substitution into the rate law
+0.5 points for the correct numerical value of k with the correct units

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)*

$$ln(2.5) = \frac{-E_a}{R}\left(\frac{1}{328K} - \frac{1}{298K}\right)$$ **(+0.5 points)**

$$E_a = 24822.1164\ J \cdot mol^{-1} = 24.82211634\ kJ \cdot mol^{-1}$$ **(+0.5 points)**

+0.5 points for correct substitution into the equation
+0.5 points for the correct final answer in either J/mol or kJ/mol

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)*

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\frac{k_{cat}}{k} = e^{\frac{E_a - E_{a,cat}}{RT}}$$

$$E_{a,cat} = E_a - ln2 \cdot R \cdot T$$ **(+1 point)**

$$= 24822.1164\ J \cdot mol^{-1} - ln2 \times 8.31451 J \cdot mol^{-1} \cdot K^{-1} \times 298K$$

$$= 23104.68901\ J \cdot mol^{-1}$$ **(+1 point)**

+1 point for correctly identifying the equation needed to solve for E$_{a,\,cat}$ (doesn't have to be rearranged)
+1 point for the correct final answer

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)*

A catalyst influences a reaction mechanism by providing **an alternative pathway** with a **lower activation energy**. It usually participates in the reaction by forming intermediates or transition states, but it is later **regenerated**. Therefore, while the catalyst is not consumed, it does participate in the reaction.

+1 point for stating that a catalyst provides a lower activation energy pathway
+1 point for stating that the catalyst is used, then regenerated (so not consumed)

<u>Scratch Paper</u>