A sample of solid $\text{U}_3\text{O}_8$ is placed in a rigid 1.500 L flask. Chlorine gas, $\text{Cl}_2(g)$, is added, and the flask is heated to 862°C. The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.

$$\text{U}_3\text{O}_8(s) + 3 \text{Cl}_2(g) \rightleftharpoons 3 \text{UO}_2\text{Cl}_2(g) + \text{O}_2(g) \quad K_p = \frac{(p_{\text{UO}_2\text{Cl}_2})^3(p_{\text{O}_2})}{(p_{\text{Cl}_2})^3}$$

When the system is at equilibrium, the partial pressure of $\text{Cl}_2(g)$ is 1.007 atm and the partial pressure of $\text{UO}_2\text{Cl}_2(g)$ is $9.734 \times 10^{-4}$ atm.

(a) Calculate the partial pressure of $\text{O}_2(g)$ at equilibrium at 862°C.

$$9.734 \times 10^{-4} \text{ atm} \times \frac{1 \text{ mol O}_2}{3 \text{ mol UO}_2\text{Cl}_2} = 3.245 \times 10^{-4} \text{ atm O}_2(g)$$

(b) Calculate the value of the equilibrium constant, $K_p$, for the system at 862°C.

$$K_p = \frac{(p_{\text{UO}_2\text{Cl}_2})^3(p_{\text{O}_2})}{(p_{\text{Cl}_2})^3} = \frac{(9.734 \times 10^{-4})^3(3.245 \times 10^{-4})}{(1.007)^3} = 2.931 \times 10^{-13}$$

(c) Calculate the Gibbs free-energy change, $\Delta G^\circ$, for the reaction at 862°C.

$$\Delta G^\circ = -RT \ln K_p$$

$$= (-8.31 \text{ J mol}^{-1} \text{ K}^{-1})(862+273) \text{ K}(\ln (2.931 \times 10^{-13}))$$

$$= 272,000 \text{ J mol}^{-1} = 272 \text{ kJ mol}^{-1}$$
(d) State whether the entropy change, $\Delta S^\circ$, for the reaction at 862°C is positive, negative, or zero. Justify your answer.

$\Delta S^\circ$ is positive because four moles of gaseous products are produced from three moles of gaseous reactants.

One point is earned for the correct explanation.

(e) State whether the enthalpy change, $\Delta H^\circ$, for the reaction at 862°C is positive, negative, or zero. Justify your answer.

Both $\Delta G^\circ$ and $\Delta S^\circ$ are positive, as determined in parts (c) and (d). Thus, $\Delta H^\circ$ must be positive because $\Delta H^\circ$ is the sum of two positive terms in the equation $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$.

One point is earned for the correct sign.

One point is earned for a correct explanation.

(f) After a certain period of time, 1.000 mol of $O_2(g)$ is added to the mixture in the flask. Does the mass of $U_3O_8(s)$ in the flask increase, decrease, or remain the same? Justify your answer.

The mass of $U_3O_8(s)$ will increase because the reaction is at equilibrium, and the addition of a product creates a “stress” on the product (right) side of the reaction. The reaction will then proceed from right to left to reestablish equilibrium so that some $O_2(g)$ is consumed (tending to relieve the stress) as more $U_3O_8(s)$ is produced.

One point is earned for a correct explanation.
Question 2

Answer the following problems about gases.

(a) The average atomic mass of naturally occurring neon is 20.18 amu. There are two common isotopes of naturally occurring neon as indicated in the table below.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne-20</td>
<td>19.99</td>
</tr>
<tr>
<td>Ne-22</td>
<td>21.99</td>
</tr>
</tbody>
</table>

(i) Using the information above, calculate the percent abundance of each isotope.

Let \( x \) represent the natural abundance of Ne-20.

\[
19.99x + 21.99(1-x) = 20.18
\]

\[
\]

\[
\]

\[
-2x = -1.81
\]

\[
x = 0.905
\]

\[\Rightarrow\] percent abundances are: Ne-20 = 90.5%

Ne-22 = 9.5%

(ii) Calculate the number of Ne-22 atoms in a 12.55 g sample of naturally occurring neon.

\[
12.55 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} \times \frac{0.095 \text{ mol Ne-22}}{1 \text{ mol Ne}} \times \frac{6.022 \times 10^{23} \text{ Ne-22 atoms}}{1 \text{ mol Ne-22}}
\]

\[
= 3.6 \times 10^{22} \text{ Ne-22 atoms}
\]
Question 2 (continued)

(b) A major line in the emission spectrum of neon corresponds to a frequency of $4.34 \times 10^{-14}$ s$^{-1}$. Calculate the wavelength, in nanometers, of light that corresponds to this line.

\[
c = \lambda \nu \quad \Rightarrow \quad \lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{4.34 \times 10^{14} \text{ s}^{-1}} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 690 \text{ nm}
\]

One point is earned for the correct setup. One point is earned for the answer.

(c) In the upper atmosphere, ozone molecules decompose as they absorb ultraviolet (UV) radiation, as shown by the equation below. Ozone serves to block harmful ultraviolet radiation that comes from the Sun.

\[O_3(g) \xrightarrow{\text{UV}} O_2(g) + O(g)\]

A molecule of $O_3(g)$ absorbs a photon with a frequency of $1.00 \times 10^{15}$ s$^{-1}$.

(i) How much energy, in joules, does the $O_3(g)$ molecule absorb per photon?

\[
E = h \nu = 6.63 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{15} \text{ s}^{-1} = 6.63 \times 10^{-19} \text{ J per photon}
\]

One point is earned for the correct answer.

(ii) The minimum energy needed to break an oxygen-oxygen bond in ozone is $387 \text{ kJ mol}^{-1}$. Does a photon with a frequency of $1.00 \times 10^{15}$ s$^{-1}$ have enough energy to break this bond? Support your answer with a calculation.

\[
\frac{6.63 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 399 \text{ kJ mol}^{-1}
\]

$399 \text{ kJ mol}^{-1} > 387 \text{ kJ mol}^{-1}$, therefore the bond can be broken.

One point is earned for calculating the energy. One point is earned for the comparison of bond energies.
Question 3

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l) \]

In a hydrogen-oxygen fuel cell, energy is produced by the overall reaction represented above.

(a) When the fuel cell operates at 25°C and 1.00 atm for 78.0 minutes, 0.0746 mol of \( \text{O}_2(g) \) is consumed. Calculate the volume of \( \text{H}_2(g) \) consumed during the same time period. Express your answer in liters measured at 25°C and 1.00 atm.

\[
(0.0746 \text{ mol O}_2) \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 0.149 \text{ mol H}_2
\]

\[
V = \frac{n_{\text{H}_2}RT}{P} = \frac{(0.149 \text{ mol H}_2)(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.00 \text{ atm}}
\]

\[= 3.65 \text{ L H}_2\]

(b) Given that the fuel cell reaction takes place in an acidic medium,

(i) write the two half reactions that occur as the cell operates,

\[
\text{O}_2 + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O}
\]

\[
\text{H}_2 \rightarrow 2 \text{H}^+ + 2 e^-
\]

(ii) identify the half reaction that takes place at the cathode, and

\[
\text{O}_2 + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O}
\]

(iii) determine the value of the standard potential, \( E^\circ \), of the cell.

\[ E^\circ = 1.23 \text{V} + 0.00 \text{V} = 1.23 \text{V} \]
(c) Calculate the charge, in coulombs, that passes through the cell during the 78.0 minutes of operation as described in part (a).

\[
(0.0746 \text{ mol } O_2) \times \frac{4 \text{ mol } e^-}{1 \text{ mol } O_2} \times \frac{96,500 \text{ C}}{1 \text{ mol } e^-} = 2.88 \times 10^4 \text{ C}
\]

One point is earned for the stoichiometry.

One point is earned for the answer.
Question 4

For each of the following three reactions, in part (i) write a balanced equation for the reaction and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be graded.

(a) Solid ammonium carbonate decomposes as it is heated.

(i) Balanced equation:
\[(\text{NH}_4\text{)}_2\text{CO}_3 \rightarrow 2 \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}\]

One point is earned for the correct reactant. Two points are earned for correct products. One point is earned for balancing mass and charge.

(ii) Predict the algebraic sign of $\Delta S^\circ$ for the reaction. Explain your reasoning.

The algebraic sign of $\Delta S^\circ$ for the reaction will be positive because one mole of solid (with relatively low entropy) is converted into four moles of gas (with much greater entropy).

One point is earned for the correct answer.

(b) Chlorine gas, an oxidizing agent, is bubbled into a solution of potassium bromide.

(i) Balanced equation:
\[\text{Cl}_2 + 2 \text{Br}^- \rightarrow 2 \text{Cl}^- + \text{Br}_2\]

One point is earned for correct reactants. Two points are earned for correct products. One point is earned for balancing mass and charge.

(ii) What is the oxidation number of chlorine before the reaction occurs? What is the oxidation number of chlorine after the reaction occurs?

The oxidation number of chlorine is 0 before the reaction and −1 after the reaction.

One point is earned for the correct answer.

(c) A small piece of sodium is placed in a beaker of distilled water.

(i) Balanced equation:
\[2 \text{Na} + 2 \text{H}_2\text{O} \rightarrow \text{H}_2 + 2 \text{Na}^+ + 2 \text{OH}^-\]

One point is earned for correct reactants. Two points are earned for correct products. One point is earned for balancing mass and charge.

(ii) The reaction is exothermic, and sometimes small flames are observed as the sodium reacts with the water. Identify the product of the reaction that burns to produce the flames.

It is the $\text{H}_2$ gas that burns.

One point is earned for the correct answer.
Question 5

Answer the following questions about laboratory solutions involving acids, bases, and buffer solutions.

(a) Lactic acid, HC₃H₅O₃, reacts with water to produce an acidic solution. Shown below are the complete Lewis structures of the reactants.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{O} \quad \text{O} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} - \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

In the space provided above, complete the equation by drawing the complete Lewis structures of the reaction products.

(b) Choosing from the chemicals and equipment listed below, describe how to prepare 100.00 mL of a 1.00 M aqueous solution of NH₄Cl (molar mass 53.5 g mol⁻¹). Include specific amounts and equipment where appropriate.

NH₄Cl(s)  50 mL buret  100 mL graduated cylinder  100 mL pipet
Distilled water  100 mL beaker  100 mL volumetric flask  Balance

mass of NH₄Cl = (0.100 L)(1.00 mol L⁻¹)(53.5 g mol⁻¹) = 5.35 g NH₄Cl

1. Measure out 5.35 g NH₄Cl using the balance.
2. Use the 100 mL graduated cylinder to transfer approximately 25 mL of distilled water to the 100 mL volumetric flask.
3. Transfer the 5.35 g NH₄Cl to the 100 mL volumetric flask.
4. Continue to add distilled water to the volumetric flask while swirling the flask to dissolve the NH₄Cl and remove all NH₄Cl particles adhered to the walls.
5. Carefully add distilled water to the 100 mL volumetric flask until the bottom of the meniscus of the solution reaches the etched mark on the flask.

One point is earned for each correct structure.
(c) Two buffer solutions, each containing acetic acid and sodium acetate, are prepared. A student adds 0.10 mol of HCl to 1.0 L of each of these buffer solutions and to 1.0 L of distilled water. The table below shows the pH measurements made before and after the 0.10 mol of HCl is added.

<table>
<thead>
<tr>
<th></th>
<th>pH Before HCl Added</th>
<th>pH After HCl Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>7.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Buffer 1</td>
<td>4.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Buffer 2</td>
<td>4.7</td>
<td>4.3</td>
</tr>
</tbody>
</table>

(i) Write the balanced net-ionic equation for the reaction that takes place when the HCl is added to buffer 1 or buffer 2.

\[
\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}
\]

One point is earned for the equation.

(ii) Explain why the pH of buffer 1 is different from the pH of buffer 2 after 0.10 mol of HCl is added.

Before the HCl was added, each buffer had the same pH and thus had the same [H\(^+\)]. Because \(K_a\) for acetic acid is a constant, the ratio of \([H^+]\) to \(K_a\) must also be constant; this means that the ratio of \([\text{HC}_2\text{H}_3\text{O}_2^-]\) to \([\text{C}_2\text{H}_3\text{O}_2^-]\) is the same for both buffers, as shown by the following equation, derived from the equilibrium-constant expression for the dissociation of acetic acid.

\[
\frac{[\text{HC}_2\text{H}_3\text{O}_2^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{[H^+]}{K_a}
\]

After the addition of the H\(^+\), the ratio in buffer 1 must have been greater than the corresponding ratio in buffer 2, as evidenced by their respective pH values. Thus a greater proportion of the \(\text{C}_2\text{H}_3\text{O}_2^-\) in buffer 1 must have reacted with the added H\(^+\) compared to the proportion that reacted in buffer 2. The difference between these proportions means that the original concentrations of \(\text{HC}_2\text{H}_3\text{O}_2^-\) and \(\text{C}_2\text{H}_3\text{O}_2^-\) had to be smaller in buffer 1 than in buffer 2.

One point is earned for a correct answer involving better buffering capacity or relative amount of base (acetate ion).
(iii) Explain why the pH of buffer 1 is the same as the pH of buffer 2 before 0.10 mol of HCl is added.

Both buffer solutions have the same acid to conjugate-base mole ratio in the formula below.

$$[H^+] = K_a \left[ \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]} \right]$$

Therefore, the buffers have the same [H⁺] and pH.

One point is earned for the correct answer involving ratio of acid to base in the buffer.
The table above shows the first three ionization energies for atoms of four elements from the third period of the periodic table. The elements are numbered randomly. Use the information in the table to answer the following questions.

(a) Which element is most metallic in character? Explain your reasoning.

<table>
<thead>
<tr>
<th>Element</th>
<th>First Ionization Energy (kJ mol⁻¹)</th>
<th>Second Ionization Energy (kJ mol⁻¹)</th>
<th>Third Ionization Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element 1</td>
<td>1,251</td>
<td>2,300</td>
<td>3,820</td>
</tr>
<tr>
<td>Element 2</td>
<td>496</td>
<td>4,560</td>
<td>6,910</td>
</tr>
<tr>
<td>Element 3</td>
<td>738</td>
<td>1,450</td>
<td>7,730</td>
</tr>
<tr>
<td>Element 4</td>
<td>1,000</td>
<td>2,250</td>
<td>3,360</td>
</tr>
</tbody>
</table>

Element 2. It has the lowest first-ionization energy. Metallic elements lose electron(s) when they become ions, and element 2 requires the least amount of energy to remove an electron.

One point is earned for the identification. One point is earned for the justification.

(b) Identify element 3. Explain your reasoning.

Magnesium. Element 3 has low first and second ionization energies relative to the third ionization energy, indicating that the element has two valence electrons, which is true for magnesium. (The third ionization of element 3 is dramatically higher, indicating the removal of an electron from a noble gas core.)

One point is earned for the identification. One point is earned for the justification.

(c) Write the complete electron configuration for an atom of element 3.

\[ 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \]

One point is earned for the correct electron configuration.

(d) What is the expected oxidation state for the most common ion of element 2?

1+

One point is earned for the correct oxidation state.
(e) What is the chemical symbol for element 2?

| Na         | One point is earned for the correct symbol. |

(f) A neutral atom of which of the four elements has the smallest radius?

| Element 1  | One point is earned for the correct identification of the element. |