AP® Chemistry
2002 Scoring Guidelines

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Question 1

Total Score 10 Points

\[ \text{HOBr}(aq) \rightleftharpoons \text{H}^+(aq) + \text{OBr}^-(aq) \quad K_a = 2.3 \times 10^{-9} \]

1. Hypobromous acid, \( \text{HOBr} \), is a weak acid that dissociates in water, as represented by the equation above.

(a) Calculate the value of \([\text{H}^+]\) in an \( \text{HOBr} \) solution that has a pH of 4.95.

\[
\begin{align*}
\text{pH} & = -\log [\text{H}^+] \\
[\text{H}^+] & = 10^{-4.95} \\
[\text{H}^+] & = 1.1 \times 10^{-5} \text{ M} \\
\end{align*}
\]

1 point earned for correct calculation

(b) Write the equilibrium constant expression for the ionization of \( \text{HOBr} \) in water, then calculate the concentration of \( \text{HOBr}(aq) \) in an \( \text{HOBr} \) solution that has \([\text{H}^+]\) equal to \( 1.8 \times 10^{-5} \text{ M} \).

\[
K_a = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]} 
\]

If \([\text{H}^+] = 1.8 \times 10^{-5} \text{ M} \), then \([\text{OBr}^-] = 1.8 \times 10^{-5} \text{ M}\).

Substituting,

\[
\begin{align*}
2.3 \times 10^{-9} & = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]} = \frac{[1.8 \times 10^{-5} \text{ M}][1.8 \times 10^{-5} \text{ M}]}{[\text{HOBr}]} \\
[\text{HOBr}] & = \frac{[1.8 \times 10^{-5} \text{ M}][1.8 \times 10^{-5} \text{ M}]}{2.3 \times 10^{-9}} = 0.14 \text{ M} \\
\end{align*}
\]

1 point earned for correct expression for \( K_a \)

1 point earned for \([\text{H}^+] = [\text{OBr}^-]\)

1 point earned for correct \([\text{HOBr}]\)
(c) A solution of $\text{Ba(OH}_2$ is titrated into a solution of $\text{HOBr}$.

(i) Calculate the volume of $0.115 \, M \, \text{Ba(OH}_2(aq)$ needed to reach the equivalence point when titrated into a 65.0 mL sample of $0.146 \, M \, \text{HOBr}(aq)$.

\[
\begin{aligned}
0.0650 \, L \cdot \left( \frac{0.146 \, \text{mol \, HOBr}}{1 \, \text{L}} \right) &\cdot \left( \frac{1 \, \text{mol \, Ba(OH}_2}{2 \, \text{mol \, HOBr}} \right) \cdot \left( \frac{1 \, \text{L}}{0.115 \, \text{mol \, Ba(OH}_2} \right) \\
&= 0.0413 \, L \text{ or } 41.3 \, \text{mL}
\end{aligned}
\]

Another possible correct method for calculating the volume starts with the expression $\frac{V_bM_b}{V_aM_a} = \frac{1}{2}$.

(ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

The pH is greater than 7. $\text{HOBr}$ is a weak acid and $\text{OBr}^-$ is a weak base.

At the equivalence point, the $\text{OBr}^-$ in solution is the pH-determining species and the hydrolysis reaction produces hydroxide ion:

$\text{OBr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOBr} + \text{OH}^-$

OR

$K_b(\text{OBr}^-) = \left( \frac{K_w}{K_a(\text{HOBr})} \right) = \left( \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}} \right) = 4.3 \times 10^{-6}$

OR

the calculated pH = 10.79
(d) Calculate the number of moles of NaOBr(s) that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[H^+] = 5.00 \times 10^{-9} M$. Assume that volume change is negligible.

$$K_a = \frac{[H^+][OBr^-]}{[HOBr]}$$

$$[OBr^-] = \frac{[HOBr] \cdot K_a}{[H^+]} = \frac{(0.160 \, M)(2.3 \times 10^{-9})}{5.00 \times 10^{-9} \, M} = 0.074 \, M$$

$$n_{NaOBr} = 0.125 \, L \left( \frac{0.074 \, mol \, OBr^-}{1 \, L} \right) = 9.2 \times 10^{-3} \, mol$$

1 point earned for $[OBr^-]$, the set-up, and the substitution

1 point earned for mol NaOBr

(e) HOBr is a weaker acid than HBrO$_3$. Account for this fact in terms of molecular structure.

The H-O bond is weakened or increasingly polarized by the additional oxygen atoms bonded to the central bromine atom in HBrO$_3$.

1 point earned for a correct explanation
Question 2

Total Score 10 points

2. Answer parts (a) through (e) below, which relate to reactions involving silver ion, $\text{Ag}^+$. 

The reaction between silver ion and solid zinc is represented by the following equation.

$$2 \text{Ag}^+(aq) + \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 \text{Ag}(s)$$

(a) A 1.50 g sample of $\text{Zn}$ is combined with 250. mL of 0.110 $M$ $\text{AgNO}_3$ at 25ºC.

(i) Identify the limiting reactant. Show calculations to support your answer.

\[
\begin{align*}
n_{\text{Zn}} &= 1.50 \text{ g Zn} \left( \frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} \right) = 2.29 \times 10^{-2} \text{ mol Zn} \\
n_{\text{Ag}^+} &= 0.250 \text{ L} \left( \frac{0.110 \text{ mol Ag}^+}{1 \text{ L}} \right) = 2.75 \times 10^{-2} \text{ mol Ag}^+ \\
n_{\text{Ag}^+} &= 1.50 \text{ g Zn} \left( \frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} \right) \left( \frac{2 \text{ mol Ag}^+}{1 \text{ mol Zn}} \right) = 4.59 \times 10^{-2} \text{ mol Ag}^+ \text{ required} \\
\end{align*}
\]

Since only $2.75 \times 10^{-2}$ mol Ag$^+$ available, Ag$^+$ is the limiting reactant.

OR

\[
\begin{align*}
n_{\text{Ag}^+} &= 0.250 \text{ L} \left( \frac{0.110 \text{ mol Ag}^+}{1 \text{ L}} \right) = 2.75 \times 10^{-2} \text{ mol Ag}^+ \\
n_{\text{Zn}} &= 2.75 \times 10^{-2} \text{ mol Ag}^+ \left( \frac{1 \text{ mol Zn}}{2 \text{ mol Ag}^+} \right) = 1.38 \times 10^{-2} \text{ mol Zn required} \\
\end{align*}
\]

Since $2.29 \times 10^{-2}$ mol Zn are available, more is available than required, so Zn is in excess and Ag$^+$ is limiting.

(Correct solutions other than shown above earn both points.)
(ii) On the basis of the limiting reactant that you identified in part (i), determine the value of \([\text{Zn}^{2+}]\) after the reaction is complete. Assume that volume change is negligible.

\[
n_{\text{Zn}^{2+}} = 2.75 \times 10^{-2} \text{ mol Ag}^+ \left( \frac{1 \text{ mol Zn}^{2+}}{2 \text{ mol Ag}^+} \right) = 1.38 \times 10^{-2} \text{ mol Zn}^{2+}
\]

\[
\frac{1.38 \times 10^{-2} \text{ mol Zn}^{2+}}{0.250 \text{ L}} = 0.0550 \text{ M Zn}^{2+}
\]

**OR**

\[
[\text{Ag}^+]_{\text{initial}} = 0.110 \text{ M}, \text{ therefore } [\text{Zn}^{2+}] = \frac{1}{2} (0.110 \text{ M}) = 0.0550 \text{ M}
\]

If the student concludes Zn is the limiting reactant, then

\[
1.50 \text{ g Zn} \left( \frac{1 \text{ mol Zn}}{65.4 \text{ g}} \right) \left( \frac{1 \text{ mol Zn}^{2+}}{1 \text{ mol Zn}} \right) = 2.29 \times 10^{-2} \text{ mol Zn}^{2+} \text{ formed}
\]

\[
\frac{2.29 \times 10^{-2} \text{ mol Zn}^{2+}}{0.250 \text{ L}} = 0.0916 \text{ M Zn}^{2+}
\]

**Note:** There must be consistency between parts (a) (i) and (a) (ii).

(b) Determine the value of the standard potential, \(E^\circ\), for a galvanic cell based on the reaction between \(\text{AgNO}_3(aq)\) and solid Zn at 25°C.

\[
E^\circ_{\text{cell}} = E^\circ(\text{reduction}) - E^\circ(\text{reduction})
\]

\[
= (0.80 \text{ V}) - (-0.76 \text{ V})
\]

\[
= 1.56 \text{ V}
\]

\[
2 \text{ Ag}^+(aq) + \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 \text{ Ag}(s) \quad +1.56 \text{ V}
\]

**OR**

\[
\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \quad +0.80 \text{ V}
\]

\[
\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 e^- \quad +0.76 \text{ V}
\]

\[
2 \text{ Ag}^+(aq) + \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 \text{ Ag}(s) \quad +1.56 \text{ V}
\]
Another galvanic cell is based on the reaction between \( Ag^+ (aq) \) and \( Cu(s) \), represented by the equation below. At 25°C, the standard potential, \( E^\circ \), for the cell is 0.46 V.

\[
2 \text{Ag}^+(aq) + \text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2 \text{Ag}(s)
\]

(c) Determine the value of the standard free-energy change, \( \Delta G^\circ \), for the reaction between \( Ag^+ (aq) \) and \( Cu(s) \) at 25°C.

\[
\Delta G^\circ = -nFE^\circ
\]

\[
\Delta G^\circ = (-2 \text{ mol e}^-)(96,500 \frac{\text{J}}{\text{V mol}})(+0.46 \text{ V})
\]

\[
\Delta G^\circ = -89,000 \text{ J} \quad \text{or} \quad -89 \text{ kJ} \quad \text{(units required)}
\]

1 point earned for \( n \) and \( E^\circ \) in the correct equation

1 point earned for correct value and sign of \( \Delta G^\circ \)

(d) The cell is constructed so that \([Cu^{2+}]\) is 0.045 M and \([Ag^+]\) is 0.010 M. Calculate the value of the potential, \( E^\circ \), for the cell.

\[
E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \frac{[Cu^{2+}]}{[Ag^+]^2}
\]

\[
E_{\text{cell}} = +0.46 \text{ V} - \frac{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 298 \text{ K}}{2 \text{ mol e}^- \cdot 96500 \frac{\text{J}}{\text{V} \cdot \text{mol}}} \ln \frac{0.045}{(0.010)^2}
\]

\[
E_{\text{cell}} = +0.46 \text{ V} - 0.0128 \text{ V} \ln 450
\]

\[
E_{\text{cell}} = +0.46 \text{ V} - 0.0128 \text{ V} \cdot 6.11
\]

\[
E_{\text{cell}} = +0.46 \text{ V} - 0.0782 \text{ V}
\]

\[
E_{\text{cell}} = +0.38 \text{ V}
\]

1 point earned for correct substitution

1 point earned for correct answer

(e) Under the conditions specified in part (d), is the reaction in the cell spontaneous? Justify your answer.

\[
E_{\text{cell}} = +0.38 \text{ V}
\]

The cell potential under the non-standard conditions in part (d) is positive. Therefore the reaction is spontaneous under the conditions stated in part (d).

A correct reference (from answer in part (d)) to a negative \( \Delta G \) (not \( \Delta G^\circ \)) is acceptable. If no answer to (d) is given, students must make an assumption or a general statement about \( E_{\text{cell}} \), not \( E^\circ \).

1 point earned for correct answer and correct explanation
Question 3

Total Score 10 points

3. Consider the hydrocarbon pentane, C₅H₁₂ (molar mass 72.15 g).

(a) Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.

\[ C₅H₁₂ + 8 O₂ \rightarrow 5 CO₂ + 6 H₂O \]

1 point earned for showing O₂ as a reactant and having the equation balanced correctly.

(b) What volume of dry carbon dioxide, measured at 25°C and 785 mm Hg, will result from the complete combustion of 2.50 g of pentane?

\[ n_{C₅H₁₂} = \frac{2.50 \text{ g } C₅H₁₂}{72.15 \text{ g } C₅H₁₂} = 0.0347 \text{ mol } C₅H₁₂ \]
\[ n_{CO₂} = 0.0347 \text{ mol } C₅H₁₂ \left( \frac{5 \text{ mol } CO₂}{1 \text{ mol } C₅H₁₂} \right) = 0.173 \text{ mol } CO₂ \]
\[ V = \frac{nRT}{P} = \frac{0.173 \text{ mol} \times 0.0821 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}}{785 \text{ mm Hg} / 760 \text{ mm Hg}} = 4.10 \text{ L} \]

1 point earned for correct mol of CO₂
1 point earned for correct substitution of T, P, and R and the calculation of V
1 point earned for correct value for V

(c) The complete combustion of 5.00 g of pentane releases 243 kJ of heat. On the basis of this information, calculate the value of \( \Delta H \) for the complete combustion of one mole of pentane.

\[ (5.00 \text{ g } C₅H₁₂) \left( \frac{1 \text{ mol } C₅H₁₂}{72.15 \text{ g } C₅H₁₂} \right) = 0.0693 \text{ mol } C₅H₁₂ \]
\[ \frac{243 \text{ kJ}}{0.0693 \text{ mol } C₅H₁₂} = 3.51 \times 10³ \text{ kJ mol}^{-1} \]
\[ \Delta H = -3.51 \times 10³ \text{ kJ mol}^{-1} \]

1 point earned for correct value of mol C₅H₁₂
1 point earned for correct substitution and calculation of \( \Delta H \) (Sign required; if units given, they must be correct)
Question 3 (cont’d.)

(d) Under identical conditions, a sample of an unknown gas effuses into a vacuum at twice the rate that a sample of pentane gas effuses. Calculate the molar mass of the unknown gas.

\[
\frac{\text{rate}_{\text{unknown}}}{\text{rate}_{\text{C}_5\text{H}_{12}}} = \sqrt{\frac{72.15 \text{ g mol}^{-1}}{\text{MM}_{\text{unknown}}}}
\]

\[
2 \times \frac{\text{rate}_{\text{C}_5\text{H}_{12}}}{\text{rate}_{\text{C}_5\text{H}_{12}}} = 2 = \sqrt{\frac{72.15 \text{ g mol}^{-1}}{\text{MM}_{\text{unknown}}}}
\]

\[
2^2 = \frac{72.15 \text{ g mol}^{-1}}{\text{MM}_{\text{unknown}}} = 4
\]

\[
\text{MM}_{\text{unknown}} = \frac{72.15 \text{ g mol}^{-1}}{4} = 18.04 \text{ g mol}^{-1}
\]

1 point earned for correct substitution

1 point earned for correct value of MM

(e) The structural formula of one isomer of pentane is shown below. Draw the structural formulas for the other two isomers of pentane. Be sure to include all atoms of hydrogen and carbon in your structures.

1 point earned for each correct structural formula
Total Score 15 points

Note: for reactions with three products, 1 product point is earned for one or two of the products

(a) A solution of sodium iodide is added to a solution of lead(II) acetate.

\[ I^- + Pb^{2+} \rightarrow PbI_2 \]
3 points

(b) Pure solid phosphorus (white form) is burned in air.

\[ P_4 + O_2 \rightarrow P_{4}O_{10} \]
3 points

Note: products other than P_{4}O_{10} showing correct oxidation states are acceptable

(c) Solid cesium oxide is added to water.

\[ Cs_2O + H_2O \rightarrow Cs^+ + OH^- \]
3 points

Note: CsOH earns 1 product point if no additional incorrect species are included in the product

(d) Excess concentrated hydrochloric acid is added to a 1.0 M solution of cobalt(II) chloride.

\[ Cl^- + Co(H_2O)_6^{2+} \rightarrow H_2O + CoCl_4^{2-} \]
\[ OR \]
\[ Cl^- + Co^{2+} \rightarrow CoCl_4^{2-} \]
3 points

Note: Other species, such as Co(H_2O)_4^{2+} as a reactant or CoCl_3^- as a product, are acceptable
Question 4 (cont’d.)

(e) Solid sodium hydrogen carbonate (sodium bicarbonate) is strongly heated.

\[
\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

3 points

(f) An excess of hydrochloric acid is added to solid zinc sulfide.

\[
\text{H}^+ + \text{ZnS} \rightarrow \text{Zn}^{2+} + \text{H}_2\text{S}
\]

3 points

(g) Acidified solutions of potassium permanganate and iron(II) nitrate are mixed together.

\[
\text{MnO}_4^- + \text{H}^+ + \text{Fe}^{2+} \rightarrow \text{H}_2\text{O} + \text{Fe}^{3+} + \text{Mn}^{2+}
\]

3 points

(h) A solution of potassium hydroxide is added to solid ammonium chloride.

\[
\text{NH}_4\text{Cl} + \text{OH}^- \rightarrow \text{NH}_3 + \text{Cl}^- + \text{H}_2\text{O}
\]

3 points

Note: no product points are earned for NH\(_2\)OH
Question 5

Total Score 10 Points

\[ \text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) \]

5. A student is asked to determine the molar enthalpy of neutralization, \( \Delta H_{\text{neut}} \), for the reaction represented above. The student combines equal volumes of 1.0 \( M \) HCl and 1.0 \( M \) NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation \( q = mc\Delta T \).

Assume the following.
- Both solutions are at the same temperature before they are combined.
- The densities of all the solutions are the same as that of water.
- Any heat lost to the calorimeter or to the air is negligible.
- The specific heat capacity of the combined solutions is the same as that of water.

(a) Give appropriate units for each of the terms in the equation \( q = mc\Delta T \).

<table>
<thead>
<tr>
<th>Term</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q )</td>
<td>joules (or kilojoules or calories or kilocalories)</td>
</tr>
<tr>
<td>( m )</td>
<td>grams or kilograms</td>
</tr>
<tr>
<td>( c )</td>
<td>( J , \text{g}^{-1} , \text{C}^{-1} ) or ( J , \text{g}^{-1} , \text{K}^{-1} ) (calories or kilograms acceptable alternatives)</td>
</tr>
<tr>
<td>( T )</td>
<td>°C or K</td>
</tr>
</tbody>
</table>

1 point earned for any two units
2 points earned for all four units

(b) List the measurements that must be made in order to obtain the value of \( q \).

- volume or mass of the HCl or NaOH solutions
- initial temperature of HCl or NaOH before mixing
- final (highest) temperature of solution after mixing

1 point earned for any volume (mass of reactant)
1 point earned for initial and final (highest) temperature
\( \Delta T \) is not a measurement
(c) Explain how to calculate each of the following.

(i) The number of moles of water formed during the experiment

Since there is mixing of equal volumes of the same concentration and the reaction has 1:1 stoichiometry, moles of $\text{H}_2\text{O} = \text{moles of } \text{HCl} = \text{moles NaOH}$. To determine the number of moles of HCl:

$$\text{(volume HCl)} \left( \frac{\text{mol HCl}}{1 \text{ L}} \right) \left( \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}} \right) = \text{mol H}_2\text{O}$$

OR

$$\text{(volume NaOH)} \left( \frac{1.0 \text{ mol NaOH}}{1 \text{ L}} \right) \left( \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol NaOH}} \right) = \text{mol H}_2\text{O}$$

OR

$$n_{\text{H}_2\text{O}} = n_{\text{HCl}} = n_{\text{NaOH}} = V_{\text{HCl}} \times 1 \text{ M} = V_{\text{NaOH}} \times 1 \text{ M}$$

1 point earned for the number of moles of H$_2$O using the stoichiometric relationship between HCl (or NaOH) and H$_2$O

(ii) The value of the molar enthalpy of neutralization, $\Delta H_{\text{neut}}$, for the reaction between HCl($\text{aq}$) and NaOH($\text{aq}$)

Determine the quantity of the heat produced, $q$, from $q = mc\Delta T$, where $m = \text{total mass of solution}$; divide $q$ by mol H$_2$O determined in part (c) (i) to determine $\Delta H_{\text{neut}}$:

$$\Delta H_{\text{neut}} = -\frac{q}{\text{mol H}_2\text{O}} \text{ OR } \frac{q}{\text{mol H}_2\text{O}}$$

(mol reactant can substitute for mol H$_2$O)

1 point earned for $q$

1 point earned for $\Delta H_{\text{neut}}$
(d) The student repeats the experiment with the same equal volumes as before, but this time uses 2.0 M HCl and 2.0 M NaOH.

(i) Indicate whether the value of $q$ increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

The $\Delta T$ will be greater, so $q$ increases. There are more moles of HCl and NaOH reacting so the final temperature of the mixture will be higher.

1 point earned for direction and explanation

Note: Arguments about increased mass are not acceptable because the total mass increase is negligible (the solutions have virtually the same density) and is not the driving force for increases in $q$.

(ii) Indicate whether the value of the molar enthalpy of neutralization, $\Delta H_{\text{neut}}$, increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

Both $q$ and mol H$_2$O increase proportionately. However, when the quotient is determined, there is no change in $\Delta H_{\text{neut}}$.

Molar enthalpy is defined as per mole of reaction, therefore it will not change when the number of moles is doubled.

1 point earned for correct direction and explanation

(e) Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization, $\Delta H_{\text{neut}}$? Justify your answer.

Heat lost to the air will produce a smaller $\Delta T$. In the equation $q = mc\Delta T$ a smaller $\Delta T$ will produce a smaller value for $q$ (heat released) than it should. In the equation

$$\Delta H_{\text{neut}} = \frac{-q}{\text{mol H}_2\text{O}}$$

the smaller magnitude of $q$ and the constant mol H$_2$O means that $\Delta H_{\text{neut}}$ will be less negative (more positive).

1 point earned for correct direction and explanation

Notes: $\Delta H$ decreases because $q$ decreases earns 1 point $\Delta T$ decreases because $\Delta H$ decreases earns 1 point No points earned for $\Delta T$ decreases therefore $q$ decreases
Total Score 8 Points

6. Use the principles of atomic structure and/or chemical bonding to explain each of the following. In each part, your answer must include references to both substances.

(a) The atomic radius of Li is larger than that of Be.

Both Li and Be have their outer electrons in the same shell (and/or they have the same number of inner core electrons shielding the valence electrons from the nucleus). However, Be has four protons and Li has only three protons. Therefore, the effective nuclear charge experienced (attraction experienced) by the valence (outer) electrons is greater in Be than in Li, so Be has a smaller atomic radius.

1 point earned for indicating that Be has more protons than Li
1 point earned for indicating that since the electrons are at about the same distance from the nucleus, there is more attraction in Be as a result of the larger number of protons

(b) The second ionization energy of K is greater than the second ionization energy of Ca.

The second electron removed from a potassium atom comes from the third level (inner core). The second electron removed from a calcium atom comes from the fourth level (valence level). The electrons in the third level are closer to the nucleus so the attraction is much greater than for electrons in the fourth level.

1 point earned for saying that electrons are removed from an inner (third) level in potassium but one level higher, (fourth level) in calcium
1 point earned for saying that the distance to the nucleus is less for the third level, so attraction is greater and more energy is needed to remove an electron

(c) The carbon-to-carbon bond energy in C\textsubscript{2}H\textsubscript{4} is greater than it is in C\textsubscript{2}H\textsubscript{6}.

C\textsubscript{2}H\textsubscript{4} has a double bond between the two carbon atoms, whereas C\textsubscript{2}H\textsubscript{6} has a carbon-carbon single bond. More energy is required to break a double bond in C\textsubscript{2}H\textsubscript{4} than to break a single bond in C\textsubscript{2}H\textsubscript{6}; therefore, the carbon-to-carbon bond energy in C\textsubscript{2}H\textsubscript{4} is greater.

1 point earned for indicating that C\textsubscript{2}H\textsubscript{4} has a double bond and C\textsubscript{2}H\textsubscript{6} has a single bond
1 point earned for indicating that the carbon-carbon double bond in C\textsubscript{2}H\textsubscript{4} requires more energy to break (is stronger) than the carbon-carbon bond in C\textsubscript{2}H\textsubscript{6}

Note: Restatement of the prompt does not earn the second point
(d) The boiling point of Cl\(_2\) is lower than the boiling point of Br\(_2\).

Both Cl\(_2\) and Br\(_2\) are nonpolar, and the only intermolecular attractive forces are London dispersion forces. Since Br\(_2\) has more electrons than Cl\(_2\), the valence electrons in Br\(_2\) are more polarizable. The more polarizable the valence electrons, the greater the dispersion forces and the higher the boiling point.

| 1 point earned for indicating that Cl\(_2\) and Br\(_2\) are both nonpolar and/or have only London dispersion forces (or van der Waals). |
| 1 point for indicating that the more electrons, the more polarizable, the greater the dispersion forces, and the higher the boiling point. |

Notes: Stating that the bromine electrons are more loosely bound, and thus lead to stronger London dispersion forces is acceptable. The word “polarizable” is not required. Greater mass is not acceptable. No credit earned if the student implies that covalent bonds break during boiling.
Question 7

Total Score 8 points

7. An environmental concern is the depletion of O₃ in Earth’s upper atmosphere, where O₃ is normally in equilibrium with O₂ and O. A proposed mechanism for the depletion of O₃ in the upper atmosphere is shown below.

Step I  O₃ + Cl → O₂ + ClO
Step II  ClO + O → Cl + O₂

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

O₃ + O → 2 O₂  

1 point earned for correct overall reaction

(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

Cl is the catalyst in the reaction. It is a reactant in Step I and reappears as a product in Step II.  

1 point earned for identifying Cl as the catalyst
1 point earned for justifying Cl as the catalyst

(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

ClO is the intermediate in the reaction. It is a product in Step I and reappears as a reactant in Step II.

1 point earned for identifying ClO as the intermediate
1 point earned for justifying of ClO as the intermediate
(d) If the rate law for the overall reaction is found to be \( \text{rate} = k[O_3][Cl] \), determine the following.

(i) The overall order of the reaction

(ii) Appropriate units for the rate constant, \( k \)

(iii) The rate-determining step of the reaction, along with justification for your answer

| (i) overall order is \( 1 + 1 = 2 \) | 1 point earned for overall order |
| (ii) \( k = \frac{\text{rate}}{[O_3][Cl]} = \frac{M \text{ time}^{-1}}{M^2} = M^{-1} \text{ time}^{-1} \) | 1 point earned for correct units |
| (iii) Step I is the rate-determining step in the mechanism. \nThe coefficients of the reactants in Step I correspond \nto the exponents of the species concentrations in the \nrate law equation. \n**OR** \nThe reaction rate is affected by the concentrations of \([O_3]\) and \n[Cl], both appearing only in Step I. | 1 point earned for the correct step and justification |
8. Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a) Predict the sign for the change in entropy, \( \Delta S \), for the reaction. Justify your prediction.

\[
\Delta S = +
\]

There is more disorder in a gas than in a solid, so the product is more disordered than the reactants. The change in entropy is therefore positive.

**OR**

There is 1 mole of gas in the reactants and 2 moles of gas in the product.

1 point earned for indicating that \( \Delta S \) is positive
1 point earned for explanation

(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, \( \Delta H \), for the reaction. Justify your prediction.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td>60</td>
</tr>
<tr>
<td>850°C</td>
<td>94</td>
</tr>
</tbody>
</table>

\[
\Delta H = +
\]

More CO at the higher temperature indicates that the reaction shifts to the right with increasing temperature. For this to occur, the reaction must be endothermic.

1 point earned for indicating that \( \Delta H \) is positive
1 point earned for explanation
(c) Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate $\Delta H$ for the reaction on the graph.

\[ C(s) + CO_2(g) \]

1 point earned for completing the graph according to the information in part (b)
1 point earned for appropriately labeling $\Delta H_{\text{rxn}}$ for the reaction as drawn

(d) If the initial amount of C(s) were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer.

An increase in the amount of C(s) has no effect.
Solids do not appear in the equilibrium expression, so adding more C(s) will not affect the percent of CO in the equilibrium mixture.

1 point earned for indicating no effect
1 point earned for explanation

Note: Since the question asks about “percent of CO” a student might think of % by mass or % by mole. Adding carbon will not shift the equilibrium, so $P_{CO}$ and $P_{CO_2}$ stay the same. The % CO then decreases, because now there are more total moles in the system:  

$$% \text{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2} + n_C}$$

As $n_C$ is raised, the denominator increases, and % CO decreases.