

AP[®] Chemistry 2002 Scoring Guidelines

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Question 1

Total Score 10 Points

$$HOBr(aq) \rightleftharpoons H^{+}(aq) + OBr^{-}(aq)$$
 $K_a = 2.3 \times 10^{-9}$

- 1. Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.
 - (a) Calculate the value of [H⁺] in an HOBr solution that has a pH of 4.95.

$$pH = -log [H^+]$$

$$[H^+] = 10^{-4.95}$$

$$[H^+] = 1.1 \times 10^{-5} M$$
1 point earned for correct calculation

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

$$K_{a} = \frac{[H^{+}][OBr^{-}]}{[HOBr]}$$
1 point earned for correct expression for K_{a}
1 point earned for K_{a}
1 point earned for K_{a}
1 point earned for K_{a}
2.3 × 10⁻⁹ = $\frac{[H^{+}][OBr^{-}]}{[HOBr]} = \frac{[1.8 \times 10^{-5} M][1.8 \times 10^{-5} M]}{[HOBr]}$
1 point earned for K_{a}
2 point earned for K_{a}
3 point earned for K_{a}
3 point earned for K_{a}
3 point earned for K_{a}
4 point earned for K_{a}
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Question 1 (cont'd.)

- (c) A solution of Ba(OH)₂ is titrated into a solution of HOBr.
 - (i) Calculate the volume of $0.115 M \text{ Ba}(\text{OH})_2(aq)$ needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M HOBr(aq).

$$0.0650 \text{ L} \left(\frac{0.146 \text{ mol HOBr}}{1 \text{ L}} \right) \left(\frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HOBr}} \right) \left(\frac{1 \text{ L}}{0.115 \text{ mol Ba(OH)}_2} \right)$$

1 point earned for stoichiometric ratio

= 0.0413 L or 41.3 mL

1 point earned for correct substitution and calculation

Another possible correct method for calculating the volume starts with

the expression
$$\frac{V_b M_b}{V_a M_a} = \frac{1}{2}$$

(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.

HOBr is a weak acid and OBr is a weak base.

At the equivalence point, the OBr⁻ in solution is the pH-determining species and the hydrolysis reaction produces hydroxide ion:

$$OBr^- + H_2O \rightleftharpoons HOBr + OH^-$$

1 point earned for explanation

OR

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

OR

the calculated pH = 10.79

Question 1 (cont'd.)

(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.

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

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

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

1 point earned for mol NaOBr

$$[OBr^-] = 0.074 M$$

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

(e) HOBr is a weaker acid than HBrO₃. 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 ${\rm HBrO_3}$.

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, Ag⁺.

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

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

- (a) A 1.50 g sample of Zn is combined with 250. mL of 0.110 M AgNO₃ at 25°C.
 - (i) Identify the limiting reactant. Show calculations to support your answer.

$$n_{\rm Zn} = 1.50 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} \right) = 2.29 \times 10^{-2} \text{ mol Zn}$$

$$n_{\text{Ag}}^{+} = 0.250 \text{ L} \left(\frac{0.110 \text{ mol Ag}^{+}}{1 \text{ L}} \right) = 2.75 \times 10^{-2} \text{ mol Ag}^{+}$$

$$n_{\text{Ag}}^{+} = 1.50 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} \right) \left(\frac{2 \text{ mol Ag}^{+}}{1 \text{ mol Zn}} \right) = 4.59 \times 10^{-2} \text{ mol Ag}^{+} \text{ required}$$

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

OR

$$n_{\text{Ag}}^{+} = 0.250 \text{ L} \left(\frac{0.110 \text{ mol Ag}^{+}}{1 \text{ L}} \right) = 2.75 \times 10^{-2} \text{ mol Ag}^{+}$$

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

Since 2.29×10^{-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.)

1 point earned for the moles of one reactant <u>and</u> the proper stoichiometry

1 point earned for the limiting reactant <u>and</u> the supporting calculation or explanation

Question 2 (cont'd.)

(ii) On the basis of the limiting reactant that you identified in part (i), determine the value of [Zn²⁺] after the reaction is complete. Assume that volume change is negligible.

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

(b) Determine the value of the standard potential, E° , for a galvanic cell based on the reaction between AgNO₃(aq) and solid Zn at 25°C.

$$E^{\circ}_{cell} = E^{\circ}(reduction) - E^{\circ}(reduction)$$

$$= (0.80 \text{ V}) - (-0.76 \text{ V})$$

$$= 1.56 \text{ V}$$

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

$$OR$$

$$\frac{E^{\circ}}{Ag^{+}(aq) + e^{-} \rightarrow Ag(s)} + 0.80 \text{ V}$$

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

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

Question 2 (cont'd.)

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° , for the cell is 0.46 V.

$$2 \operatorname{Ag}^+(aq) + \operatorname{Cu}(s) \rightarrow \operatorname{Cu}^{2+}(aq) + 2 \operatorname{Ag}(s)$$

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

 $\Delta G^{\circ} = -nFE^{\circ}$ $\Delta G^{\circ} = (-2 \text{ mol } e^{-})(96,500 \frac{\text{J}}{\text{V mol}})(+0.46 \text{ V})$ $\Delta G^{\circ} = -89,000 \text{ J or } -89 \text{ kJ} \quad \text{(units required)}$ 1 point earned for n and E° in the correct equation
1 point earned for correct value and sign of ΔG°

(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° , for the cell.

 $E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{RT}{nF} \ln \frac{[Cu^{2+}]}{[Ag^{+}]^{2}} = E^{\circ} - \frac{.0592}{n} \log \frac{[Cu^{2+}]}{[Ag^{+}]^{2}}$

Note: Q must include only ion concentrations

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

1 point earned for correct substitution

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

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

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

 $E_{\text{cell}} = +0.38 \text{ V}$

1 point earned for correct 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 ΔG (not ΔG°) is acceptable. If no answer to (d) is given, students must make an assumption or a general statement about E_{cell} , not E° .

1 point earned for correct answer <u>and</u> correct explanation

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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.

$$C_5H_{12} + 8 O_2 \rightarrow 5 CO_2 + 6 H_2O$$
1 point earned for showing O_2 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?

$$n_{\text{C}_5\text{H}_{12}} = 2.50 \text{ g C}_5\text{H}_{12} \left(\frac{1 \text{ mol C}_5\text{H}_{12}}{72.15 \text{ g C}_5\text{H}_{12}}\right) = 0.0347 \text{ mol C}_5\text{H}_{12}$$

$$1 \text{ point earned for correct mol of CO}_2$$

$$1 \text{ point earned for correct substitution of } T, P, \text{ and } R \text{ and the calculation of } V$$

$$V = \left(\frac{nRT}{P}\right) = \frac{0.173 \text{ mol} \cdot 0.0821 \frac{\text{L atm}}{\text{mol K}} \cdot 298 \text{ K}}{\frac{785 \text{ mm Hg}}{760 \text{ mm Hg}}} = 4.10 \text{ L}$$

(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 H for the complete combustion of one mole of pentane.

$$(5.00 \text{ g C}_5\text{H}_{12}) \left(\frac{1 \text{ mol } \text{C}_5\text{H}_{12}}{72.15 \text{ g } \text{C}_5\text{H}_{12}}\right) = 0.0693 \text{ mol } \text{C}_5\text{H}_{12}$$

$$1 \text{ point earned for correct value of mol C}_5\text{H}_{12}$$

$$\left(\frac{243 \text{ kJ}}{0.0693 \text{ mol } \text{C}_5\text{H}_{12}}\right) = 3.51 \times 10^3 \text{ kJ mol}^{-1}$$

$$\Delta H = -3.51 \times 10^3 \text{ kJ mol}^{-2}$$

$$1 \text{ point earned for correct substitution and calculation of } \Delta H \text{ (Sign required; if units given, they must be correct)}$$

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.

$$\frac{\text{rate}_{unknown}}{\text{rate}_{C_{S}H_{12}}} = \sqrt{\frac{72.15 \text{ g mol}^{-1}}{\text{MM}_{unknown}}}$$

1 point earned for correct substitution

$$\frac{2 \times rate_{C_{5}H_{12}}}{rate_{C_{5}H_{12}}} = 2 = \sqrt{\frac{72.15 \text{ g mol}^{-1}}{MM_{unknown}}}$$

$$2^2 = \frac{72.15 \text{ g mol}}{MM_{unknown}}^{-1} = 4$$

$$MM_{unknown} = \frac{72.15 \text{ g mol}^{-1}}{4} = 18.04 \text{ g mol}^{-1}$$

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

Question 4

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

$P_4 + O_2 \rightarrow P_4O_{10}$ 3 points
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Note: products other than P₄O₁₀ showing correct oxidation states are acceptable

(c) Solid cesium oxide is added to water.

$Cs_2O + H_2O \rightarrow Cs^+ + OH^-$	3 points
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Note: CsOH earns 1 product point <u>if</u> 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.

$\text{Cl}^- + \text{Co(H}_2\text{O)}_6^{2+} \rightarrow \text{H}_2\text{O} + \text{CoCl}_4^{2-}$	
OR	3 points
$Cl^- + Co^{2+} \rightarrow CoCl_4^{2-}$	

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.

$NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$	3 points
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(f) An excess of hydrochloric acid is added to solid zinc sulfide.

$H^{+} + ZnS \rightarrow Zn^{2+} + H_{2}S$	3 points
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(g) Acidified solutions of potassium permanganate and iron(II) nitrate are mixed together.

$$MnO_4^- + H^+ + Fe^{2+} \rightarrow H_2O + Fe^{3+} + Mn^{2+}$$
 3 points

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

$NH_4Cl + OH^- \rightarrow NH_3 + Cl^- + H_2O$	3 points
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Note: no product points are earned for NH₄OH

Question 5

Total Score 10 Points

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_2O(l)$$

5. A student is asked to determine the molar enthalpy of neutralization, ΔH_{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 $q = mc\Delta T$.

q has units of joules (or kilojoules or calories or kilocalories) m has units of grams or kilograms c has units of J g ⁻¹ °C ⁻¹ or J g ⁻¹ K ⁻¹ (calories or kilograms acceptable alternatives)	1 point earned for any two units 2 points earned for all four units
T has units of °C or K	

- (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
 (ΔT is not a measurement)

Question 5 (cont'd.)

- (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 $H_2O = \text{moles of HCl} = \text{moles NaOH}$. 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

(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

$$n_{\rm H_2O} = n_{\rm HCl} = n_{\rm NaOH} = V_{\rm HCl} \times 1 M = V_{\rm NaOH} \times 1 M$$

1 point earned for the number of moles of H₂O using the stoichiometric relationship between HCl (or NaOH) and H₂O

(ii) The value of the molar enthalpy of neutralization, ΔH_{neut} , for the reaction between HCl(aq) and NaOH(aq)

Determine the quantity of the heat produced, q, from $q = mc\Delta T$, where $m = \underline{\text{total}}$ mass of solution; divide q by mol H₂O determined in part (c) (i) to determine ΔH_{neut} :

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

(mol reactant can substitute for mol H₂O)

1 point earned for q

1 point earned for ΔH_{neut}

Question 5 (cont'd.)

- (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 ΔT 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

<u>Note:</u> 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, ΔH_{neut} , increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

Both q and mol H₂O increase proportionately. However, when the quotient is determined, there is no change in ΔH_{neut} 1 point earned for correct direction and explanation Molar enthalpy is defined as per mole of reaction, therefore it will not change when the number of moles is doubled.

(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, ΔH_{neut} ? Justify your answer.

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

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

the smaller magnitude of q and the constant mol H_2O means that ΔH_{neut} will be less negative (more positive).

1 point earned for correct direction and explanation

Notes: ΔH decreases because q decreases earns 1 point ΔT decreases because ΔH decreases earns 1 point No points earned for ΔT decreases therefore q decreases

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Question 6

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_2H_4 is greater than it is in C_2H_6 .

 C_2H_4 has a double bond between the two carbon atoms, whereas C_2H_6 has a carbon-carbon single bond. More energy is required to break a double bond in C_2H_4 than to break a single bond in C_2H_6 ; therefore, the carbon-to-carbon bond energy in C_2H_4 is greater.

1 point earned for indicating that $\rm C_2H_4$ has a double bond and $\rm C_2H_6$ has a single bond

1 point earned for indicating that the carbon-carbon double bond in C_2H_4 requires more energy to break (is stronger) than the carbon- carbon bond in C_2H_6

Note: Restatement of the prompt does not earn the second point

Question 6 (cont'd.)

(d) The boiling point of Cl₂ is lower than the boiling point of Br₂.

Both Cl₂ and Br₂ are nonpolar, and the only intermolecular attractive forces are London dispersion forces. Since Br₂ has more electrons than Cl₂, the valence electrons in Br₂ 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 Cl₂ and Br₂ 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.

<u>Notes</u>: 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. <u>Greater mass</u> 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 O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

$$\begin{array}{lll} \text{Step I} & \text{O}_3 \, + \, \text{Cl} \, \rightarrow \, \text{O}_2 \, + \, \text{ClO} \\ \text{Step II} & \text{ClO} \, + \, \text{O} \, \rightarrow \, \, \text{Cl} \, + \, \text{O}_2 \end{array}$$

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

1 point earned for correct overall reaction	$O_3 + O \rightarrow 2 O_2$
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(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

Cl is the catalyst in the reaction. It is a reactant	1 point earned for identifying Cl as the catalyst
in Step I and reappears as a product in Step II.	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 CIO as the intermediate 1 point earned for justifying of CIO as the intermediate
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Question 7 (cont'd.)

- (d) If the rate law for the overall reaction is found to be $rate = k[O_3][C1]$, 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

(ii) $k = \frac{rate}{[O_3][C1]} = \frac{M \text{ time}^{-1}}{M^2} = M^1 \text{ time}^{-1}$

1 point earned for overall order

1 point earned for correct units

(iii) Step I is the rate-determining step in the mechanism. The coefficients of the reactants in Step I correspond to the exponents of the species concentrations in the rate law equation.

1 point earned for the correct step <u>and</u> justification

OR

The reaction rate is affected by the concentrations of $[O_3]$ and [Cl], both appearing only in Step I.

Question 8

Total Score 8 Points

$$C(s) + CO_2(g) \rightleftharpoons 2 CO(g)$$

- 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, ΔS , for the reaction. Justify your prediction.

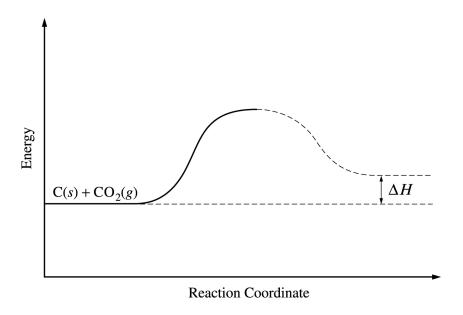
$\Delta S = +$	1 point earned for indicating that ΔS is positive
There is more disorder in a gas than in a solid, so the product is more disordered than the reactants. The change in entropy is therefore positive.	1 point earned for explanation
OR	
There is 1 mole of gas in the reactants and 2 moles of gas in the product.	

(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, ΔH , for the reaction. Justify your prediction.

Temperature	% CO
700°C	60
850°C	94

$\Delta H = +$	1 point earned for indicating that ΔH is positive
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 explanation

(c) Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate ΔH for the reaction on the graph.



1 point earned for completing the graph according to the information in part (b)

1 point earned for appropriately labeling ΔH_{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 <u>decreases</u>, because now there are more total moles in the system: % $CO = n_{CO}/(n_{CO} + n_{CO_2} + n_{CO})$ As n_{C} is raised, the denominator increases, and % CO decreases.