

# **AP<sup>®</sup> Chemistry** 2002 Scoring Guidelines

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#### **Question 1**

#### **Total Score 10 Points**

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

- 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.

$pH = -log [H^+]$ $[H^+] = 10^{-4.95}$	1 point earned for correct calculation
$[\mathrm{H}^+] = 1.1 \times 10^{-5}  M$	

(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  $1.8 \times 10^{-5}M$ .

$K_a = \frac{[\mathrm{H}^+][\mathrm{OBr}^-]}{[\mathrm{HOBr}]}$	1 point earned for correct expression for $K_a$	
If $[H^+] = 1.8 \times 10^{-5} M$ , then $[OBr^-] = 1.8 \times 10^{-5} M$ . Substituting,	1 point earned for [H <sup>+</sup> ] = [OBr <sup>-</sup> ]	
$2.3 \times 10^{-9} = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]} = \frac{[1.8 \times 10^{-5} M][1.8 \times 10^{-5} M]}{[\text{HOBr}]}$	1 point earned for correct	
$[\text{HOBr}] = \frac{[1.8 \times 10^{-5} M][1.8 \times 10^{-5} M]}{2.3 \times 10^{-9}} = 0.14 M$	[HOBr]	

#### 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).

$$0.0650 \text{ L} \left(\frac{0.146 \text{ mol HOBr}}{1 \text{ L}}\right) \left(\frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HOBr}}\right) \left(\frac{1 \text{ L}}{0.115 \text{ mol Ba(OH)}_2}\right) \qquad 1 \text{ point earned for stoichiometric ratio}$$

$$= 0.0413 \text{ L} \text{ or } 41.3 \text{ mL}$$
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 <sup>-</sup> is a weak base. At the equivalence point, the OBr <sup>-</sup> in solution is the pH-determining species and the hydrolysis reaction produces hydroxide ion:	
$OBr^- + H_2O \rightleftharpoons HOBr + OH^-$	1 point earned for
OR	explanation
$K_b(\text{OBr}^-) = \left(\frac{K_w}{K_a(\text{HOBr})}\right) = \left(\frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}}\right) = 4.3 \times 10^{-6}$	
OR	
the calculated pH = $10.79$	

### 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.

$K_a = \frac{[\mathrm{H}^+][\mathrm{OBr}^-]}{[\mathrm{HOBr}]}$	1 point earned for [OBr <sup>-</sup> ], the set-up, and the substitution
$[OBr^{-}] = \frac{[HOBr] \cdot K_a}{[H^{+}]} = \frac{(0.160 M)(2.3 \times 10^{-9})}{5.00 \times 10^{-9} M}$	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 HBrO<sub>3</sub>. 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
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#### **Question 2**

#### **Total Score 10 points**

2. Answer parts (a) through (e) below, which relate to reactions involving silver ion, Ag<sup>+</sup>.

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 AgNO<sub>3</sub> at 25°C.
  - (i) Identify the limiting reactant. Show calculations to support your answer.

$n_{\text{Zn}} = 1.50 \text{ g Zn} \left(\frac{1 \text{ mol } \text{Zn}}{65.4 \text{ g Zn}}\right) = 2.29 \times 10^{-2} \text{ mol Zn}$	
$n_{\rm Ag}^{\rm +} = 0.250  {\rm L} \left( \frac{0.110  {\rm mol}  {\rm Ag}^{\rm +}}{1  {\rm L}} \right) = 2.75 \times 10^{-2}  {\rm mol}  {\rm Ag}^{\rm +}$	1 point earned for the moles of one reactant <u>and</u> the proper stoichiometry
$n_{\text{Ag}}^{+} = 1.50 \text{ g Zn} \left(\frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}}\right) \left(\frac{2 \text{ mol Ag}^{+}}{1 \text{ mol Zn}}\right) = 4.59 \times 10^{-2} \text{ mol Ag}^{+} \text{ required}$	the proper storemoniety
Since only $2.75 \times 10^{-2}$ mol Ag <sup>+</sup> available, Ag <sup>+</sup> is the limiting reactant.	1 point earned for the limiting reactant <u>and</u> the
OR	supporting calculation or
$n_{\rm Ag}^{\rm +} = 0.250  {\rm L} \left( \frac{0.110  {\rm mol}  {\rm Ag}^{\rm +}}{1  {\rm L}} \right) = 2.75 \times 10^{-2}  {\rm mol}  {\rm Ag}^{\rm +}$	explanation
$n_{Zn} = 2.75 \times 10^{-2} \text{ mol Ag}^+ \left(\frac{1 \text{ mol } \text{Zn}}{2 \text{ mol Ag}^+}\right) = 1.38 \times 10^{-2} \text{ mol Zn required}$	
Since $2.29 \times 10^{-2}$ mol Zn are available, more is available than required, so Zn is in excess and Ag <sup>+</sup> is limiting.	
(Correct solutions other than shown above earn both points.)	

#### Question 2 (cont'd.)

(ii) On the basis of the limiting reactant that you identified in part (i), determine the value of  $[Zn^{2+}]$  after the reaction is complete. Assume that volume change is negligible.

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

$$\frac{1 \text{ point earned for mol } Zn^{2+}}{0.250 \text{ L}} = 0.0550 \text{ } M \text{ Zn}^{2+}$$
OR
$$[Ag^{+}]_{\text{initial}} = 0.110 \text{ } M, \text{ therefore } [Zn^{2+}] = \frac{1}{2}(0.110 \text{ } M) = 0.0550 \text{ } M$$

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

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

$$I \text{ point earned for } [Zn^{2+}]$$

$$I \text{ point earned for } [Zn^{2+}]$$

$$I \text{ point earned for mol } Zn^{2+}$$

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 AgNO<sub>3</sub>(*aq*) and solid Zn at 25°C.

$E^{\circ}_{cell} = E^{\circ}(reduction) - E^{\circ}(reduction)$ = (0.80 V) - (-0.76 V) = 1.56 V		
$2 \operatorname{Ag}^+(aq) + \operatorname{Zn}(s) \to \operatorname{Zn}^{2+}(aq) + 2 \operatorname{Ag}(s)$	+1.56 V	1 point earned for correct $E^{\circ}$
OR	<u> </u>	
$\operatorname{Ag}^+(aq) + e^- \to \operatorname{Ag}(s)$	+0.80 V	
$\operatorname{Zn}(s) \rightarrow \operatorname{Zn}^{2+}(aq) + 2 e^{-}$	+0.76 V	
$2 \operatorname{Ag}^+(aq) + \operatorname{Zn}(s) \to \operatorname{Zn}^{2+}(aq) + 2 \operatorname{Ag}(s)$	+1.56 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,  $E^\circ$ , 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,  $\Delta G^{\circ}$ , for the reaction between Ag<sup>+</sup>(*aq*) and Cu(*s*) at 25°C.

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

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}} = E^{\circ} - \frac{.0592}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$
Note:  $Q$  must include only ion concentrations
$$E_{\text{cell}} = +0.46 \text{ V} - \frac{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 298 \text{ K}}{2 \text{ mol} \text{ e}^{-} \cdot 96500 \frac{\text{J}}{\text{V} \cdot \text{mol}}} \ln \frac{[0.045]}{[0.010]^{2}}$$

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

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

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

$$E_{\text{cell}} = +0.38 \text{ V}$$
1 point earned for correct answer

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

#### **Question 3**

#### **Total Score 10 points**

- 3. Consider the hydrocarbon pentane,  $C_5H_{12}$  (molar mass 72.15 g).
  - (a) Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.

$C_{2}H_{12} + 8\Omega_{2} \rightarrow 5\Omega_{2} + 6H_{2}\Omega_{2}$	1 point earned for showing $O_2$ as	
	a reactant and having the equation balanced correctly	
	balanced confectly.	

(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?

$n_{\text{C}_5\text{H}_{12}} = 2.50 \text{ g } \text{C}_5\text{H}_{12} \left(\frac{1 \text{ mol } \text{C}_5\text{H}_{12}}{72.15 \text{ g } \text{C}_5\text{H}_{12}}\right) = 0.0347 \text{ mol } \text{C}_5\text{H}_{12}$	1 point earned for correct mol of $CO_2$
$n_{\text{CO}_2} = 0.0347 \text{ mol } \text{C}_5 \text{H}_{12} \left( \frac{5 \text{ mol } \text{CO}_2}{1 \text{ mol } \text{C}_5 \text{H}_{12}} \right) = 0.173 \text{ mol } \text{CO}_2$	1 point earned for correct substitution of <i>T</i> , <i>P</i> , and <i>R</i> and the calculation of <i>V</i>
$V = \left(\frac{nRT}{P}\right) = \frac{0.173 \text{ mol} \cdot 0.0821 \frac{\text{L atm}}{\text{mol K}} \cdot 298 \text{ K}}{\frac{785 \text{ mm Hg}}{760 \text{ mm Hg}}} = 4.10 \text{ L}$	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 H for the complete combustion of one mole of pentane.

$$(5.00 \text{ g } \text{C}_{5}\text{H}_{12}) \left(\frac{1 \text{ mol } \text{C}_{5}\text{H}_{12}}{72.15 \text{ g } \text{C}_{5}\text{H}_{12}}\right) = 0.0693 \text{ mol } \text{C}_{5}\text{H}_{12}$$

$$1 \text{ point earned for correct value of mol } \text{C}_{5}\text{H}_{12}$$

$$\left(\frac{243 \text{ kJ}}{0.0693 \text{ mol } \text{C}_{5}\text{H}_{12}}\right) = 3.51 \times 10^{3} \text{ kJ mol}^{-1}$$

$$\Delta H = -3.51 \times 10^{3} \text{ kJ mol}^{-1}$$

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

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#### 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.

$$\frac{\operatorname{rate}_{unknown}}{\operatorname{rate}_{C_{5}H_{12}}} = \sqrt{\frac{72.15 \text{ g mol}^{-1}}{\text{MM}_{unknown}}}$$

$$\frac{2 \times \operatorname{rate}_{C_{5}H_{12}}}{\operatorname{rate}_{C_{5}H_{12}}} = 2 = \sqrt{\frac{72.15 \text{ g mol}^{-1}}{\text{MM}_{unknown}}}$$

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

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

$$1 \text{ point earned for correct value of MM}$$

(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.



#### **Question 4**

#### **Total Score 15 points**

- <u>Note:</u> 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.

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<u>Note:</u> products other than  $P_4O_{10}$  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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<u>Note:</u> 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
$\mathrm{Cl}^- + \mathrm{Co}^{2^+} \rightarrow \mathrm{Co}\mathrm{Cl}_4^{2^-}$	

<u>Note:</u> 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

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

$$H^+ + ZnS \rightarrow Zn^{2+} + H_2S$$
 3 points

(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.

$\rm NH_4Cl + OH^- \rightarrow NH_3 + Cl^- + H_2O$	3 points
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Note: no product points are earned for NH<sub>4</sub>OH

### **Question 5**

### **Total Score 10 Points**

 $\mathrm{H}^{+}(aq) + \mathrm{OH}^{-}(aq) \rightarrow \mathrm{H}_{2}\mathrm{O}(l)$ 

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

<i>q</i> has units of joules (or kilojoules or calories or kilocalories) <i>m</i> has units of grams or kilograms <i>c</i> has units of $J g^{-1} \circ C^{-1}$ 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.

<ul> <li>volume or mass of the HCl or NaOH <u>solutions</u></li> <li>initial temperature of HCl or NaOH before mixing</li> <li>final (highest) temperature of solution after mixing</li> </ul>	<ol> <li>point earned for <u>any</u> volume (mass of reactant)</li> <li>point earned for initial and final (highest) temperature</li> </ol>
	$(\Delta T \text{ is } \underline{\text{not}} \text{ a measurement})$

### 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 $H_2O$ = moles of HCl = moles NaOH. To determine the number of moles of HCl:	1 point earned for the number
$(\text{volume HCl})\left(\frac{\text{mol HCl}}{1 \text{ L}}\right)\left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}}\right) = \text{mol H}_2\text{O}$ <b>OR</b>	of moles of $H_2O$ using the stoichiometric relationship between HCl (or NaOH) and $H_2O$
$(\text{volume NaOH})\left(\frac{1.0 \text{ mol NaOH}}{1 \text{ L}}\right)\left(\frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol NaOH}}\right) = \text{ mol H}_2\text{O}$	
OR	
$n_{\text{H}_{2}\text{O}} = n_{\text{HCl}} = n_{\text{NaOH}} = \text{V}_{\text{HCl}} \times 1 M = \text{V}_{\text{NaOH}} \times 1 M$	

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

Determine the quantity of the heat produced, $q$ , from $q = mc\Delta T$ , where $m = total$ mass of solution; divide $q$ by mol H <sub>2</sub> O determined in part (c) (i) to determine $\Delta H_{neut}$ :	1 point earned for $q$
$\Delta H_{neut} = \frac{-q}{\text{mol H}_2\text{O}} \text{ OR } \frac{q}{\text{mol H}_2\text{O}}$ (mol reactant can substitute for mol H <sub>2</sub> O)	1 point earned for $\Delta H_{_{neut}}$

### 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.

<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,  $\Delta H_{neut}$ , increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

Both $q$ and mol H <sub>2</sub> O increase proportionately. However, when the quotient is determined, there is no change in $\Delta H_{neut}$ Molar enthalpy is defined as <u>per mole</u> of reaction, therefore it will not change when the number of moles is doubled	1 point earned for correct direction <u>and</u> explanation
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,  $\Delta H_{neut}$ ? 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 $\Delta H_{neut} = \frac{-q}{\text{mol H}_2\text{O}}$	1 point earned for correct direction <u>and</u> explanation
the smaller magnitude of $q$ and the constant mol H <sub>2</sub> O means that $\Delta H_{neut}$ will be less negative (more positive).	

<u>Notes:</u>  $\Delta H$  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

### **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 <u>both</u> 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	<ol> <li>point earned for indicating that Be</li></ol>
have the same number of inner core electrons shielding the valence	has more protons than Li <li>point earned for indicating that</li>
electrons from the nucleus). However, Be has four protons and Li has	since the electrons are at about the
only three protons. Therefore, the effective nuclear charge experienced	same distance from the nucleus, there
(attraction experienced) by the valence (outer) electrons is greater in Be	is more attraction in Be as a result of
than in Li, so Be has a smaller atomic radius.	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.	<ol> <li>point earned for indicating that C<sub>2</sub>H<sub>4</sub> has a double bond and C<sub>2</sub>H<sub>6</sub> has a single bond</li> <li>point earned for indicating that the carbon-carbon double bond in C<sub>2</sub>H<sub>4</sub> requires more energy to break (is stronger) than the carbon- carbon bond in C<sub>2</sub>H<sub>6</sub></li> </ol>

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

### Question 6 (cont'd.)

(d) The boiling point of  $\operatorname{Cl}_2$  is lower than the boiling point of  $\operatorname{Br}_2$ .

Both $Cl_2$ and $Br_2$ are nonpolar, and the only intermolecular	re both nonpolar and/or have only London
attractive forces are London dispersion forces. Since $Br_2$ has	(spersion forces (or van der Waals).
more electrons than $Cl_2$ , the valence electrons in $Br_2$ are more	point for indicating that the more electrons,
polarizable. The more polarizable the valence electrons, the	he more polarizable, the greater the dispersion
greater the dispersion forces and the higher the boiling point.	prees, 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.

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

$O_3 + O \rightarrow 2 O_2$	1 point earned for correct overall reaction
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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.

### Question 7 (cont'd.)

- (d) If the rate law for the overall reaction is found to be  $rate = k[O_3][Cl]$ , 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) $k = \frac{rate}{[O_3][Cl]} = \frac{M \text{ time}^{-1}}{M^2} = M^1 \text{ time}^{-1}$	1 point earned for correct units
<ul><li>(iii) Step I is the rate-determining step in the mechanism.</li><li>The coefficients of the reactants in Step I correspond to the exponents of the species concentrations in the rate law equation.</li></ul>	1 point earned for the correct step and 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,  $\Delta S$ , for the reaction. Justify your prediction.

$\Delta S = +$	1 point earned for indicating that $\Delta S$ 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,  $\Delta H$ , for the reaction. Justify your prediction.

Temperature	% CO
700°C	60
850°C	94

$\Delta H = +$	1 point earned for indicating that $\Delta H$ 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  $\Delta H$  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  $\Delta H_{reg}$  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.	<ol> <li>point earned for indicating no effect</li> <li>point earned for explanation</li> </ol>
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<u>Note</u>: 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 =  $n_{CO}/(n_{CO} + n_{CO_2} + n_C)$ As  $n_C$  is raised, the denominator increases, and % CO decreases.