AP ${ }^{\circledR}$ Chemistry 2002 Scoring Guidelines

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# AP ${ }^{\circledR}$ CHEMISTRY <br> 2002 SCORING GUIDELINES 

## Question 1

## Total Score 10 Points

$$
\operatorname{HOBr}(a q) \rightleftarrows \mathrm{H}^{+}(a q)+\operatorname{OBr}^{-}(a q) \quad K_{a}=2.3 \times 10^{-9}
$$

1. Hypobromous acid, HOBr , is a weak acid that dissociates in water, as represented by the equation above.
(a) Calculate the value of $\left[\mathrm{H}^{+}\right]$in an HOBr solution that has a pH of 4.95 .

$$
\begin{aligned}
& \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right] \\
& {\left[\mathrm{H}^{+}\right]=10^{-4.95}} \\
& {\left[\mathrm{H}^{+}\right]=1.1 \times 10^{-5} \mathrm{M}}
\end{aligned}
$$

$$
\left[\begin{array}{l|l}
{\left[\mathrm{H}^{+}\right]=10^{-4.95}} & 1 \text { point earned for correct calculation }
\end{array}\right.
$$

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

| $K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{OBr}^{-}\right]}{[\mathrm{HOBr}]}$ | 1 point earned for correct <br> expression for $K_{a}$ |
| :--- | :--- |
| If $\left[\mathrm{H}^{+}\right]=1.8 \times 10^{-5} M$, then $\left[\mathrm{OBr}^{-}\right]=1.8 \times 10^{-5} \mathrm{M}$. <br> Substituting, | 1 point earned for <br> $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OBr}^{-}\right]$ |
| $2.3 \times 10^{-9}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{OBr}^{-}\right]}{[\mathrm{HOBr}]}=\frac{\left[1.8 \times 10^{-5} \mathrm{M}\right]\left[1.8 \times 10^{-5} \mathrm{M}\right]}{[\mathrm{HOBr}]}$ |  |
| $[\mathrm{HOBr}]=\frac{\left[1.8 \times 10^{-5} \mathrm{M}\right]\left[1.8 \times 10^{-5} \mathrm{M}\right]}{2.3 \times 10^{-9}}=0.14 M$ | 1 point earned for correct <br> $[\mathrm{HOBr}]$ |

# AP ${ }^{\circledR}$ CHEMISTRY <br> 2002 SCORING GUIDELINES 

## Question 1 (cont'd.)

(c) A solution of $\mathrm{Ba}(\mathrm{OH})_{2}$ is titrated into a solution of HOBr .
(i) Calculate the volume of $0.115 \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}(a q)$ needed to reach the equivalence point when titrated into a 65.0 mL sample of $0.146 \mathrm{M} \operatorname{HOBr}(a q)$.
$0.0650 \mathrm{~L}\left(\frac{0.146 \mathrm{~mol} \mathrm{HOBr}}{1 \mathrm{~L}}\right)\left(\frac{1 \mathrm{~mol} \mathrm{Ba}(\mathrm{OH})_{2}}{2 \mathrm{~mol} \mathrm{HOBr}}\right)\left(\frac{1 \mathrm{~L}}{0.115 \mathrm{~mol} \mathrm{Ba}(\mathrm{OH})_{2}}\right)$
$=0.0413 \mathrm{~L}$ or 41.3 mL
Another possible correct method for calculating the volume starts with
the expression $\frac{V_{b} M_{b}}{V_{a} M_{a}}=\frac{1}{2}$.

1 point earned for stoichiometric ratio

1 point earned for correct substitution and calculation
(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 $\mathrm{OBr}^{-}$is a weak base. |  |
| At the equivalence point, the $\mathrm{OBr}^{-}$in solution is the pH -determining |  |
| species and the hydrolysis reaction produces hydroxide ion: |  |
| $\mathrm{OBr}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{HOBr}+\mathrm{OH}^{-}$ |  |
| OR |  |
| $K b\left(\mathrm{OBr}^{-}\right)=\left(\frac{K_{w}}{K_{a}(\mathrm{HOBr})}\right)=\left(\frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}}\right)=4.3 \times 10^{-6}$ | 1 point earned for <br> explanation |
| OR |  |
| the calculated $\mathrm{pH}=10.79$ |  |

## AP ${ }^{\circledR}$ CHEMISTRY <br> 2002 SCORING GUIDELINES

## Question 1 (cont'd.)

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

| $K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{OBr}^{-}\right]}{[\mathrm{HOBr}]}$ | 1 point earned for $\left[\mathrm{OBr}^{-}\right]$, the set-up, <br> and the substitution |
| :--- | :--- |
| $[\mathrm{OBr}-]=\frac{[\mathrm{HOBr}] \cdot K_{a}}{\left[\mathrm{H}^{+}\right]}=\frac{(0.160 M)\left(2.3 \times 10^{-9}\right)}{5.00 \times 10^{-9} M}$ | 1 point earned for mol NaOBr |
| $\left[\mathrm{OBr}^{-}\right]=0.074 M$ |  |
| $n_{\mathrm{NaOBr}}=0.125 \mathrm{~L}\left(\frac{0.074 \mathrm{~mol} \mathrm{OBr}^{-}}{1 \mathrm{~L}}\right)=9.2 \times 10^{-3} \mathrm{~mol}$ |  |

(e) HOBr is a weaker acid than $\mathrm{HBrO}_{3}$. Account for this fact in terms of molecular structure.

| The $\mathrm{H}-\mathrm{O}$ bond is weakened or increasingly polarized by the additional oxygen <br> atoms bonded to the central bromine atom in $\mathrm{HBrO}_{3}$. | 1 point earned <br> for a correct <br> 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, $\mathrm{Ag}^{+}$.

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

$$
2 \mathrm{Ag}^{+}(a q)+\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(a q)+2 \mathrm{Ag}(s)
$$

(a) A 1.50 g sample of Zn is combined with $250 . \mathrm{mL}$ of $0.110 \mathrm{M} \mathrm{AgNO}_{3}$ at $25^{\circ} \mathrm{C}$.
(i) Identify the limiting reactant. Show calculations to support your answer.
$n_{\mathrm{Zn}}=1.50 \mathrm{~g} \mathrm{Zn}\left(\frac{1 \mathrm{~mol} \mathrm{Zn}}{65.4 \mathrm{~g} \mathrm{Zn}}\right)=2.29 \times 10^{-2} \mathrm{~mol} \mathrm{Zn}$
$n_{\mathrm{Ag}^{+}}=0.250 \mathrm{~L}\left(\frac{0.110 \mathrm{~mol} \mathrm{Ag}^{+}}{1 \mathrm{~L}}\right)=2.75 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}^{+}$
$n_{\mathrm{Ag}^{+}}=1.50 \mathrm{~g} \mathrm{Zn}\left(\frac{1 \mathrm{~mol} \mathrm{Zn}}{65.4 \mathrm{~g} \mathrm{Zn}}\right)\left(\frac{2 \mathrm{~mol} \mathrm{Ag}^{+}}{1 \mathrm{~mol} \mathrm{Zn}}\right)=4.59 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}^{+}$required
Since only $2.75 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}^{+}$available, $\mathrm{Ag}^{+}$is the limiting reactant.
OR
$n_{\mathrm{Ag}^{+}}=0.250 \mathrm{~L}\left(\frac{0.110 \mathrm{~mol} \mathrm{Ag}^{+}}{1 \mathrm{~L}}\right)=2.75 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}^{+}$
$n_{\mathrm{Zn}}=2.75 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}^{+}\left(\frac{1 \mathrm{~mol} \mathrm{Zn}}{2 \mathrm{~mol} \mathrm{Ag}^{+}}\right)=1.38 \times 10^{-2} \mathrm{~mol} \mathrm{Zn}$ required
Since $2.29 \times 10^{-2} \mathrm{~mol} \mathrm{Zn}$ are available, more is available than required, so Zn is in excess and $\mathrm{Ag}^{+}$is limiting.
(Correct solutions other than shown above earn both points.)

1 point earned for the moles of one reactant and the proper stoichiometry

1 point earned for the limiting reactant and the supporting calculation or explanation

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## Question 2 (cont'd.)

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

| $n \mathrm{Zn}^{2+}=2.75 \times 10^{-2} \mathrm{~mol} \mathrm{Ag}^{+}\left(\frac{1 \mathrm{~mol} \mathrm{Zn}^{2+}}{2 \mathrm{~mol} \mathrm{Ag}^{+}}\right)=1.38 \times 10^{-2} \mathrm{~mol} \mathrm{Zn}^{2+}$ | 1 point earned for $\mathrm{mol} \mathrm{Zn}^{2+}$ <br> 1 point earned for $\left[\mathrm{Zn}^{2+}\right]$ |
| :---: | :---: |
| $\frac{1.38 \times 10^{-2} \mathrm{~mol} \mathrm{Zn}^{2+}}{0.250 \mathrm{~L}}=0.0550 \mathrm{M} \mathrm{Zn}^{2+}$ |  |
| OR | OR |
| $\left[\mathrm{Ag}^{+}\right]_{\text {initial }}=0.110 \mathrm{M}$, therefore $\left[\mathrm{Zn}^{2+}\right]=\frac{1}{2}(0.110 \mathrm{M})=0.0550 \mathrm{M}$ | 2 points earned for [ $\mathrm{Zn}^{2+}$ ] |
| *********************************************************** | ********************** |
| If the student concludes Zn is the limiting reactant, then | 1 point earned for mol $\mathrm{Zn}^{2+}$ |
| $1.50 \mathrm{~g} \mathrm{Zn}\left(\frac{1 \mathrm{~mol} \mathrm{Zn}}{65.4 \mathrm{~g}}\right)\left(\frac{1 \mathrm{~mol} \mathrm{Zn}^{2+}}{1 \mathrm{~mol} \mathrm{Zn}}\right)=2.29 \times 10^{-2} \mathrm{~mol} \mathrm{Zn}^{2+} \text { formed }$ | 1 point earned for $\left[\mathrm{Zn}^{2+}\right]$ |
| $\frac{2.29 \times 10-\mathrm{mol} \mathrm{Zn}}{0.250 \mathrm{~L}}=0.0916 \mathrm{M} \mathrm{Zn}^{2+}$ |  |

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 $\mathrm{AgNO}_{3}(a q)$ and solid Zn at $25^{\circ} \mathrm{C}$.


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## Question 2 (cont'd.)

Another galvanic cell is based on the reaction between $\mathrm{Ag}^{+}(a q)$ and $\mathrm{Cu}(s)$, represented by the equation below. At $25^{\circ} \mathrm{C}$, the standard potential, $E^{\circ}$, for the cell is 0.46 V .

$$
2 \mathrm{Ag}^{+}(a q)+\mathrm{Cu}(s) \rightarrow \mathrm{Cu}^{2+}(a q)+2 \mathrm{Ag}(s)
$$

(c) Determine the value of the standard free-energy change, $\Delta G^{\circ}$, for the reaction between $\mathrm{Ag}^{+}(a q)$ and $\mathrm{Cu}(s)$ at $25^{\circ} \mathrm{C}$.

$$
\begin{aligned}
& \Delta G^{\circ}=-n F E^{\circ} \\
& \Delta G^{\circ}=\left(-2 \mathrm{~mol} e^{-}\right)\left(96,500 \frac{\mathrm{~J}}{\mathrm{~V} \mathrm{~mol}}\right)(+0.46 \mathrm{~V}) \\
& \Delta G^{\circ}=-89,000 \mathrm{~J} \text { or }-89 \mathrm{~kJ} \quad \text { (units required) }
\end{aligned}
$$

1 point earned for $n$ and $E^{\circ}$ in the correct equation

1 point earned for correct value and $\operatorname{sign}$ of $\Delta G^{\circ}$
(d) The cell is constructed so that $\left[\mathrm{Cu}^{2+}\right]$ is 0.045 M and $\left[\mathrm{Ag}^{+}\right]$is 0.010 M . Calculate the value of the potential, $E^{\circ}$, for the cell.

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

Note: $Q$ must include only ion concentrations

$$
\begin{aligned}
& E_{\text {cell }}=+0.46 \mathrm{~V}-\frac{8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}} \cdot 298 \mathrm{~K}}{2 \mathrm{~mol} \mathrm{e}^{-} \cdot 96500 \frac{\mathrm{~J}}{\mathrm{~V} \cdot \mathrm{~mol}}} \ln \frac{[0.045]}{[0.010]^{2}} \\
& E_{\text {cell }}=+0.46 \mathrm{~V}-0.0128 \mathrm{~V} \ln 450 \\
& E_{\text {cell }}=+0.46 \mathrm{~V}-0.0128 \mathrm{~V} \cdot 6.11 \\
& E_{\text {cell }}=+0.46 \mathrm{~V}-0.0782 \mathrm{~V} \\
& E_{\text {cell }}=+0.38 \mathrm{~V}
\end{aligned}
$$

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.

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

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 $\Delta G\left(\operatorname{not} \Delta G^{\circ}\right)$ 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

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## Question 3

## Total Score 10 points

3. Consider the hydrocarbon pentane, $\mathrm{C}_{5} \mathrm{H}_{12}$ (molar mass 72.15 g ).
(a) Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.

$$
\mathrm{C}_{5} \mathrm{H}_{12}+8 \mathrm{O}_{2} \rightarrow 5 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}
$$

1 point earned for showing $\mathrm{O}_{2}$ as a reactant and having the equation balanced correctly.
(b) What volume of dry carbon dioxide, measured at $25^{\circ} \mathrm{C}$ and 785 mm Hg , will result from the complete combustion of 2.50 g of pentane?

$$
\begin{aligned}
& { }^{n} \mathrm{C}_{5} \mathrm{H}_{12}=2.50 \mathrm{~g} \mathrm{C}_{5} \mathrm{H}_{12}\left(\frac{1 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12}}{72.15 \mathrm{~g} \mathrm{C}_{5} \mathrm{H}_{12}}\right)=0.0347 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12} \\
& { }^{n} \mathrm{CO}_{2}=0.0347 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12}\left(\frac{5 \mathrm{~mol} \mathrm{CO}_{2}}{1 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12}}\right)=0.173 \mathrm{~mol} \mathrm{CO}_{2} \\
& V=\left(\frac{n R T}{P}\right)=\frac{0.173 \mathrm{~mol} \cdot 0.0821 \frac{\mathrm{~L} \mathrm{~atm}}{\mathrm{~mol} \mathrm{~K}} \cdot 298 \mathrm{~K}}{\frac{785 \mathrm{~mm} \mathrm{Hg}}{760 \mathrm{~mm} \mathrm{Hg}}}=4.10 \mathrm{~L}
\end{aligned}
$$

1 point earned for correct mol of $\mathrm{CO}_{2}$

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

| $\left(5.00 \mathrm{~g} \mathrm{C}_{5} \mathrm{H}_{12}\right)\left(\frac{1 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12}}{72.15 \mathrm{~g} \mathrm{C}_{5} \mathrm{H}_{12}}\right)=0.0693 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12}$ | 1 point earned for correct value <br> of $\mathrm{mol} \mathrm{C}_{5} \mathrm{H}_{12}$ |
| :--- | :--- |
| $\left(\frac{243 \mathrm{~kJ}}{0.0693 \mathrm{~mol} \mathrm{C}_{5} \mathrm{H}_{12}}\right)=3.51 \times 10^{3} \mathrm{~kJ} \mathrm{~mol}^{-1}$ | 1 point earned for correct <br> substitution and calculation of $\Delta H$ <br> (Sign required; if units given, they <br> must be correct) |
| $\Delta H=-3.51 \times 10^{3} \mathrm{~kJ} \mathrm{~mol}^{-2}$ |  |

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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.

| $\frac{\text { rate }_{\text {unknown }}}{\operatorname{rate}_{\mathrm{C}_{5} \mathrm{H}_{12}}}=\sqrt{\frac{72.15 \mathrm{~g} \mathrm{~mol}^{-1}}{\mathrm{MM}_{\text {unknown }}}}$ | 1 point earned for correct <br> substitution |
| :--- | :--- |
| $\frac{2 \times \text { rate }_{\mathrm{C}_{5} \mathrm{H}_{12}}}{\text { rate }_{\mathrm{C}_{5} \mathrm{H}_{12}}}=2=\sqrt{\frac{72.15 \mathrm{~g} \mathrm{~mol}^{-1}}{\mathrm{MM}_{\text {unknown }}}}$ |  |
| $2^{2}=\frac{72.15 \mathrm{~g} \mathrm{~mol}^{-1}}{\mathrm{MM}_{\text {unknown }}}=4$ | 1 point earned for correct <br> value of MM |
| $M M_{\text {unknown }}=\frac{72.15 \mathrm{~g} \mathrm{~mol}^{-1}}{4}=18.04 \mathrm{~g} \mathrm{~mol}^{-1}$ |  |

(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

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## 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.

| $\mathrm{I}^{-}+\mathrm{Pb}^{2+} \rightarrow \mathrm{PbI}_{2}$ | 3 points |
| :---: | :---: |

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

| $\mathrm{P}_{4}+\mathrm{O}_{2} \rightarrow \mathrm{P}_{4} \mathrm{O}_{10}$ | 3 points |
| :---: | :---: |

Note: products other than $\mathrm{P}_{4} \mathrm{O}_{10}$ showing correct oxidation states are acceptable
(c) Solid cesium oxide is added to water.

$$
\begin{array}{|l|l}
\hline \mathrm{Cs}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Cs}^{+}+\mathrm{OH}^{-} & 3 \text { points } \\
\hline
\end{array}
$$

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.

| $\mathrm{Cl}^{-}+\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }_{6}^{2+} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{CoCl}_{4}{ }^{2-}$ |  |
| :---: | :---: |
| $\mathrm{Cl}^{-}+\mathrm{Co}^{2+} \rightarrow \mathrm{CoCl}_{4}{ }^{2-}$ | 3 points |

Note: Other species, such as $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}^{2+}$ as a reactant or $\mathrm{CoCl}_{3}^{-}$as a product, are acceptable

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## Question 4 (cont'd.)

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

| $\mathrm{NaHCO}_{3} \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$ | 3 points |
| :---: | :---: |

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

| $\mathrm{H}^{+}+\mathrm{ZnS} \rightarrow \mathrm{Zn}^{2+}+\mathrm{H}_{2} \mathrm{~S}$ | 3 points |
| :---: | :---: |

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

$$
\mathrm{MnO}_{4}^{-}+\mathrm{H}^{+}+\mathrm{Fe}^{2+} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{Fe}^{3+}+\mathrm{Mn}^{2+} \quad \text { p points }
$$

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

| $\mathrm{NH}_{4} \mathrm{Cl}+\mathrm{OH}^{-} \rightarrow \mathrm{NH}_{3}+\mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O}$ | 3 points |
| :---: | :---: |

Note: no product points are earned for $\mathrm{NH}_{4} \mathrm{OH}$

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## Question 5

## Total Score 10 Points

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

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 $q=m c \Delta T$.

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 $q=m c \Delta T$.

| $q$ has units of joules (or kilojoules or calories or kilocalories) | 1 point earned for any two units |
| :--- | :--- |
| $m$ has units of grams or kilograms | 2 points earned for all four units |
| $c$ has units of $\mathrm{J} \mathrm{g}^{-1}{ }^{\circ} \mathrm{C}^{-1}$ or $\mathrm{J} \mathrm{g}^{-1} \mathrm{~K}^{-1}$ (calories or kilograms |  |
| acceptable alternatives) |  |
| $T$ has units of ${ }^{\circ} \mathrm{C}$ 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 $\mathrm{NaOH} \underline{\text { solutions }}$ | 1 point earned for any volume <br> (mass of reactant) |
| :--- | :--- |
| - initial temperature of HCl or NaOH before mixing | 1 point earned for initial and final <br> (highest) temperature <br> - final (highest) temperature of solution after mixing |
|  | $(\Delta T$ is not a measurement) |

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## 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 $\mathrm{H}_{2} \mathrm{O}=$ moles of $\mathrm{HCl}=$ moles NaOH . To determine the number of moles of HCl :
(volume HCl$)\left(\frac{\mathrm{mol} \mathrm{HCl}}{1 \mathrm{~L}}\right)\left(\frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}{1 \mathrm{~mol} \mathrm{HCl}^{2}}\right)=\operatorname{mol~H}_{2} \mathrm{O}$
OR
(volume NaOH$)\left(\frac{1.0 \mathrm{~mol} \mathrm{NaOH}}{1 \mathrm{~L}}\right)\left(\frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}{1 \mathrm{~mol} \mathrm{NaOH}}\right)=\mathrm{mol} \mathrm{H}_{2} \mathrm{O}$
OR
$n_{\mathrm{H}_{2} \mathrm{O}}=n_{\mathrm{HCl}}=n_{\mathrm{NaOH}}=\mathrm{V}_{\mathrm{HCl}} \times 1 \mathrm{M}=\mathrm{V}_{\mathrm{NaOH}} \times 1 \mathrm{M}$
(ii) The value of the molar enthalpy of neutralization, $\Delta H_{\text {neut }}$, for the reaction between $\mathrm{HCl}(a q)$ and $\mathrm{NaOH}(a q)$

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

1 point earned for $q$

1 point earned for $\Delta H_{\text {neut }}$

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## 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 $\Delta T$ 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 $\mathrm{mol} \mathrm{H}_{2} \mathrm{O}$ 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.
(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 $q=m c \Delta T$ a smaller $\Delta T$ will produce a smaller value for $q$ (heat released) than it should. In the equation

$$
\Delta H_{\text {neut }}=\frac{-q}{\mathrm{~mol} \mathrm{H}_{2} \mathrm{O}}
$$

the smaller magnitude of $q$ and the constant $\mathrm{mol} \mathrm{H}_{2} \mathrm{O}$ means that $\Delta H_{\text {neut }}$ will be less negative (more positive).

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

# AP ${ }^{\circledR}$ CHEMISTRY 2002 SCORING GUIDELINES 

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

1 point earned for indicating that $\mathrm{C}_{2} \mathrm{H}_{4}$ has a double bond and $\mathrm{C}_{2} \mathrm{H}_{6}$ has a single bond

1 point earned for indicating that the carbon-carbon double bond in $\mathrm{C}_{2} \mathrm{H}_{4}$ requires more energy to break (is stronger) than the carbon- carbon bond in $\mathrm{C}_{2} \mathrm{H}_{6}$

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

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## Question 6 (cont'd.)

(d) The boiling point of $\mathrm{Cl}_{2}$ is lower than the boiling point of $\mathrm{Br}_{2}$.

> Both $\mathrm{Cl}_{2}$ and $\mathrm{Br}_{2}$ are nonpolar, and the only intermolecular attractive forces are London dispersion forces. Since $\mathrm{Br}_{2}$ has more electrons than $\mathrm{Cl}_{2}$, the valence electrons in $\mathrm{Br}_{2}$ 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 $\mathrm{Cl}_{2}$ and $\mathrm{Br}_{2}$ 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.

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## Question 7

## Total Score 8 points

7. An environmental concern is the depletion of $\mathrm{O}_{3}$ in Earth's upper atmosphere, where $\mathrm{O}_{3}$ is normally in equilibrium with $\mathrm{O}_{2}$ and O . A proposed mechanism for the depletion of $\mathrm{O}_{3}$ in the upper atmosphere is shown below.

$$
\begin{array}{ll}
\text { Step I } & \mathrm{O}_{3}+\mathrm{Cl} \rightarrow \mathrm{O}_{2}+\mathrm{ClO} \\
\text { Step II } & \mathrm{ClO}+\mathrm{O} \rightarrow \mathrm{Cl}+\mathrm{O}_{2}
\end{array}
$$

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

$$
\begin{array}{l|l}
\hline \mathrm{O}_{3}+\mathrm{O} \rightarrow 2 \mathrm{O}_{2} & 1 \text { point earned for correct overall reaction }
\end{array}
$$

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

| Cl is the catalyst in the reaction. It is a reactant <br> in Step I and reappears as a product in Step II. | 1 point earned for identifying Cl as the catalyst <br> 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 |

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## Question 7 (cont'd.)

(d) If the rate law for the overall reaction is found to be rate $=k\left[\mathrm{O}_{3}\right][\mathrm{Cl}]$, 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 $1+1=2$
(ii) $k=\frac{\text { rate }}{\left[\mathrm{O}_{3}\right][\mathrm{Cl}]}=\frac{M \text { time }^{-1}}{M^{2}}=M^{-1}$ time $^{-1}$
(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.

OR
The reaction rate is affected by the concentrations of $\left[\mathrm{O}_{3}\right]$ and [Cl], both appearing only in Step I.

1 point earned for overall order
1 point earned for correct units

1 point earned for the correct
step and justification

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## Question 8

## Total Score 8 Points

$$
\mathrm{C}(s)+\mathrm{CO}_{2}(g) \rightleftarrows 2 \mathrm{CO}(g)
$$

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 |
| :--- | :--- |
| There is more disorder in a gas than in a solid, so the <br> product is more disordered than the reactants. The <br> change in entropy is therefore positive. | $\Delta S$ is positive |
| OR |  |$\quad 1$ point earned for explanation | There is 1 mole of gas in the reactants and 2 moles |
| :--- |
| of gas in the product. |$\quad$.

(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 |
| :---: | :---: |
| $700^{\circ} \mathrm{C}$ | 60 |
| $850^{\circ} \mathrm{C}$ | 94 |


| $\Delta H=+$ | 1 point earned for indicating that <br> $\Delta H$ is positive |
| :--- | :--- |
| More CO at the higher temperature indicates that <br> the reaction shifts to the right with increasing <br> temperature. For this to occur, the reaction must <br> be endothermic. | 1 point earned for explanation |

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(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 $\Delta H_{r x n}$ for the reaction as drawn
(d) If the initial amount of $\mathrm{C}(s)$ 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 $\mathrm{C}(s)$ has no effect.
Solids do not appear in the equilibrium expression, so adding more $\mathrm{C}(s)$ 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 $\mathrm{P}_{\mathrm{CO}}$ and $\mathrm{P}_{\mathrm{CO}_{2}}$ stay the same. The $\% \mathrm{CO}$ then decreases, because now there are more total moles in the system: $\% \mathrm{CO}=n_{\mathrm{CO}} /\left(n_{\mathrm{CO}}+n_{\mathrm{CO}_{2}}+n_{\mathrm{C}}\right)$
As $n_{\mathrm{C}}$ is raised, the denominator increases, and $\% \mathrm{CO}$ decreases.

