

# 2007 U. S. NATIONAL CHEMISTRY OLYMPIAD NATIONAL EXAM—PART II 

Prepared by the American Chemical Society Olympiad Examinations Task Force

# OLYMPIAD EXAMINATIONS TASK FORCE 

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## DIRECTIONS TO THE EXAMINER-PART II

Part II of this test requires that student answers be written in a response booklet of blank pages. Only this "Blue Book" is graded for a score on Part II. Testing materials, scratch paper, and the "Blue Book" should be made available to the student only during the examination period. All testing materials including scratch paper should be turned in and kept secure until May 1, 2007, after which tests can be returned to students and their teachers for further study.
Allow time for the student to read the directions, ask questions, and fill in the requested information on the "Blue Book". When the student has completed Part II, or after one hour and forty-five minutes has elapsed, the student must turn in the "Blue Book", Part II of the testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested on the front of the "Blue Book," and that the same identification number used for Part I has been used again for Part II.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest-breaks between parts.

| Part I | $\mathbf{6 0}$ questions | single-answer multiple-choice <br> problem-solving, explanations | $\mathbf{1}$ hour, $\mathbf{3 0}$ minutes |
| :--- | :--- | :--- | :--- |
| Part II | $\mathbf{8}$ questions | $\mathbf{1 5}$ minutes |  |
| Part III | 2 lab problems | laboratory practical | $\mathbf{1}$ hour, $\mathbf{3 0}$ minutes |

A periodic table and other useful information are provided on the back page for student reference. Students should be permitted to use non-programmable calculators.

## DIRECTIONS TO THE EXAMINEE-PART II

DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO. Part II requires complete responses to questions involving problem-solving and explanations. One hour and forty-five minutes are allowed to complete this part. Be sure to print your name, the name of your school, and your identification number in the spaces provided on the "Blue Book" cover. (Be sure to use the same identification number that was coded onto your Scantron® sheet for Part I.) Answer all of the questions in order, and use both sides of the paper. Do not remove the staple. Use separate sheets for scratch paper and do not attach your scratch paper to this examination. When you complete Part II (or at the end of one hour and forty-five minutes), you must turn in all testing materials, scratch paper, and your "Blue Book." Do not forget to turn in your U.S. citizenship statement before leaving the testing site today.

1. $(12 \%)$ Compound $X$ contains $2.239 \%$ hydrogen, $26.681 \%$ carbon and $71.080 \%$ oxygen by mass. The titration of 0.154 g of this compound with 0.3351 M KOH produces the curve shown.
a. Determine the empirical formula of the compound.
b. Calculate its molar mass and give its molecular formula.
c. When $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ is reacted with X in acidic solution the products are chromium(III) ions and carbon dioxide. Describe the color change that accompanies this reaction.
d. Write a balanced ionic equation for this reaction.
e. Find the volume of dry carbon dioxide that could be collected at $22{ }^{\circ} \mathrm{C}$ and 738 mm Hg when 0.839 g of
 compound X is reacted with an excess of $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$.
a) convert masses to moles:
$2.239 \mathrm{~g} \mathrm{H} \times\left(\frac{1 \mathrm{~mol}}{1.008 \mathrm{~g}}\right)=2.221 \mathrm{~mol}(\div 2.157)=1.03$
$26.681 \mathrm{~g} \mathrm{C} \times\left(\frac{1 \mathrm{~mol}}{12.011 \mathrm{~g}}\right)=2.157 \mathrm{~mol}(\div 2.157)=1$
$71.08 \mathrm{~g} \mathrm{O} \times\left(\frac{1 \mathrm{~mol}}{16.00 \mathrm{~g}}\right)=4.443 \mathrm{~mol}(\div 2.15)=2.06$
These numbers are close enough to whole numbers that the empirical formula must be $\mathrm{CHO}_{2}$
b) Obtain molar mass from titration (estimate endpoint at 10.4 mL )
$\mathrm{Mol} \mathrm{NaOH}=0.3351 \mathrm{~mol} / \mathrm{L} \times 0.0104 \mathrm{~L}=0.00348 \mathrm{~mol}$
molar mass $=0.154 \mathrm{~g} \div 0.00348 \mathrm{~mol}=44.2 \mathrm{~g} / \mathrm{mol}(\times 2$ because titration curve is diprotic $)=88.4 \mathrm{~g} / \mathrm{mol}$
The molar mass is $88.4 \mathrm{~g} / \mathrm{mol}$, the empirical formula molar mass is 45.02 . This value is close to half the value of the experimentally determined molar mass, so the molecular formula must be $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{4}$.
c) The color change will be from orange for $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ to green for $\mathrm{Cr}^{3+}$.
d) The balanced ionic equation is: $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+3 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}+8 \mathrm{H}^{+} \rightarrow 2 \mathrm{Cr}^{3+}+6 \mathrm{CO}_{2}+7 \mathrm{H}_{2} \mathrm{O}$
e) Do the stoichiometry for oxalic acid to carbon dioxide, then calculate volume using ideal gas law.
$0.839 \mathrm{~g} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \times\left(\frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}}{90.04 \mathrm{~g} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}}\right) \times\left(\frac{6 \mathrm{~mol} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}}{3 \mathrm{~mol} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}}\right)=0.0186 \mathrm{~mol} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$
$V=\frac{n R T}{P}=\frac{(0.0186 \mathrm{~mol})\left(0.0821 \mathrm{~L} \cdot \mathrm{~atm} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right)(295 \mathrm{~K})}{\left(738 \mathrm{mmHg} \times\left(\frac{1 \mathrm{~atm}}{760 \mathrm{mmHg}}\right)\right)}=0.464 \mathrm{~L}$
2. $(15 \%)$ Coffee cup calorimetry experiments can be used to obtain $\Delta H_{\mathrm{f}}{ }^{\circ}$ for magnesium oxide.
a. Write a balanced equation for the formation of magnesium oxide, whose enthalpy change is $\Delta H_{\mathrm{f}}{ }^{\circ}$.
b. To determine the heat capacity of the calorimeter, 49.6 mL of 1.01 M HCl are reacted with 50.1 mL of 0.998 M NaOH . The solution's temperature increases by $6.40^{\circ} \mathrm{C}$. Determine the heat capacity of the calorimeter. You may assume the solution's specific heat capacity is $4.025 \mathrm{~J} \cdot \mathrm{~g}^{-1} \cdot{ }^{\circ} \mathrm{C}^{-1}$ and the enthalpy of neutralization is -55.9 kJ per mole of $\mathrm{H}_{2} \mathrm{O}$.
c. When 0.221 g of magnesium turnings are added to 49.9 mL of 1.01 M HCl and 49.7 mL of $\mathrm{H}_{2} \mathrm{O}$ in the same calorimeter, the temperature increases by $9.67^{\circ} \mathrm{C}$. Write a balanced equation for the reaction that occurs and calculate the $\Delta \mathrm{H}$ per mole of
magnesium. (Assume the solution's specific heat capacity is $3.862 \mathrm{~J} \cdot \mathrm{~g}^{-1} \cdot{ }^{\circ} \mathrm{C}^{-1}$ and the calorimeter constant obtained in b.)
d. When 0.576 g of MgO react with 51.0 mL of 1.01 M HCl and 50.1 mL of $\mathrm{H}_{2} \mathrm{O}$ in the same calorimeter the tem $4.72^{\circ} \mathrm{C}$. Write a balanced equation for this reaction and calculate its $\Delta H$ per mole of MgO using the same assumpt part c.
e. Use the above results and $\Delta H_{\mathrm{f}}{ }^{\circ}$ of $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})\left(-285.8 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\right)$ to calculate $\Delta H_{\mathrm{f}}{ }^{\circ}$ of magnesium oxide.
a) $\mathrm{Mg}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{MgO}(\mathrm{s})$
b) First, determine the limiting reactant:
$\mathrm{MolHCl}=1.01 \mathrm{~mol} / \mathrm{L} \times 0.0496 \mathrm{~L}=0.00501 \mathrm{~mol} \mathrm{HCl}$
$\mathrm{Mol} \mathrm{NaOH}=0.998 \mathrm{~mol} / \mathrm{L} \times 0.0501 \mathrm{~L}=0.0500 \mathrm{~mol} \mathrm{NaOH}$, so because it is a $1: 1$ stoichiometry, NaOH is limiting.
Via the enthalpy from the neutralization reaction, $\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \Delta \mathrm{H}=-55.9 \mathrm{~kJ} / \mathrm{mol}$ we can calculate, $0.0500 \mathrm{~mol} \mathrm{NaOH} \times\left(\frac{-55.9 \mathrm{~kJ}}{1 \mathrm{~mol} \mathrm{NaOH}}\right)=-2.795 \mathrm{~kJ}$
Account for heat taken up by the solution, so the rest is taken up by the calorimeter:
Total volume of solution is $49.6 \mathrm{~mL}+50.1 \mathrm{~mL}=99.7 \mathrm{~mL}$ (no information is provided about density, so the simplest assumption is to use 1.00 g ) so we have 99.7 g solution. Using the given specific heat capacity the heat absorbed by the solution is, heat $=99.7 \mathrm{~g} \times 4.025 \mathrm{~J} \cdot \mathrm{~g}^{-1} \cdot{ }^{\circ} \mathrm{C}^{-1} \times 6.40{ }^{\circ} \mathrm{C}=2568 \mathrm{~J}$ (heat absorbed by the solution)
Now we can calculate the heat absorbed by the calorimeter: $2795 \mathrm{~J}-2568 \mathrm{~J}=227 \mathrm{~J}$ absorbed by the calorimeter.
So the heat capacity of the calorimeter is $227 \mathrm{~J} / 6.40^{\circ} \mathrm{C}=35.5 \mathrm{~J} \cdot{ }^{\circ} \mathrm{C}^{-1}$
c) The reaction of magnesium with an acid is: $\mathrm{Mg}+2 \mathrm{H}^{+} \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_{2}$

Total mass is: 99.6 g solution $+0.221 \mathrm{~g} \mathrm{Mg}=99.821 \mathrm{~g}$
Total heat is heat absorbed by solution + heat absorbed by calorimeter:
heat solution $=99.821 \mathrm{~g} \times 3.862 \mathrm{~J} \cdot \mathrm{~g}^{-1} .{ }^{\circ} \mathrm{C}^{-1} \times 9.67{ }^{\circ} \mathrm{C}=3728 \mathrm{~J}$
heat calorimeter $=35.5 \mathrm{~J} \cdot{ }^{\circ} \mathrm{C}^{-1} \times 9.67{ }^{\circ} \mathrm{C}=343 \mathrm{~J}$
Total heat $=3728 \mathrm{~J}+343 \mathrm{~J}=4071 \mathrm{~J}$
This is heat given off by 0.221 g Mg (using molar mass): $0.221 \mathrm{~g} \mathrm{Mg} \times(1 \mathrm{~mol} / 24.31 \mathrm{~g})=0.00909 \mathrm{~mol} \mathrm{Mg}$
Thus, $\frac{-4071 \mathrm{~J}}{0.00909 \mathrm{~mol}}=-4.479 \times 10^{5} \mathrm{~J} \cdot \mathrm{~mol}^{-1}=-447.9 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$
d) The reaction is: $\mathrm{MgO}+2 \mathrm{H}^{+} \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_{2} \mathrm{O}$

First determine moles reacted: $0.576 \mathrm{~g} \mathrm{MgO} \times(1 \mathrm{~mol} / 40.31 \mathrm{~g})=0.0143 \mathrm{~mol} \mathrm{MgO}$
Once again, total heat is heat absorbed by solution + heat absorbed by calorimeter: (and solution mass includes MgO )
heat solution $=101.676 \mathrm{~g} \times 3.862 \mathrm{~J} \cdot \mathrm{~g}^{-1} .{ }^{\circ} \mathrm{C}^{-1} \times 4.72{ }^{\circ} \mathrm{C}=1853 \mathrm{~J}$
heat calorimeter $=35.5 \mathrm{~J} \cdot{ }^{\circ} \mathrm{C}^{-1} \times 4.72{ }^{\circ} \mathrm{C}=168 \mathrm{~J}$
Total heat $=1853 \mathrm{~J}+168 \mathrm{~J}=2021 \mathrm{~J}$
Thus, $\frac{-2021 \mathrm{~J}}{0.0143 \mathrm{~mol}}=-1.413 \times 10^{5} \mathrm{~J} \cdot \mathrm{~mol}^{-1}=-141.3 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$
e) Now construct a series of reactions that when summed are the formation reaction for MgO :

$$
\begin{array}{lr}
\mathrm{Mg}^{2+}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{MgO}+2 \mathrm{H}^{+} & \Delta \mathrm{H}=141.3 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \\
\mathrm{Mg}+2 \mathrm{H}^{+} \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_{2} & \Delta \mathrm{H}=-447.9 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}
\end{array}
$$

Summed: These reaction yield:

$$
\mathrm{Mg}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{MgO}+\mathrm{H}_{2} \quad \Delta \mathrm{H}=-306.6 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}
$$

Now combine this reaction with the heat of formation for water to yield the desired result:

$$
\begin{array}{ll}
\mathrm{Mg}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{MgO}+\mathrm{H}_{2} & \Delta \mathrm{H}=-306.6 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \\
\mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O} & \Delta \mathrm{H}=-285.8 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \\
\hline \mathrm{Mg}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{MgO} & \Delta \mathrm{H}=-592.4 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}
\end{array}
$$

3. $(13 \%)$ Hydrogen sulfide, $\mathrm{H}_{2} \mathrm{~S}$, is a weak acid that can be used to precipitate metal ions from solution selectively by controlling the pH .
a. Write equations to represent each of the ionization steps of $\mathrm{H}_{2} \mathrm{~S}$.
b. Write an equation to represent the overall ionization of $\mathrm{H}_{2} \mathrm{~S}$ to form $\mathrm{S}^{2-}$ and $2 \mathrm{H}^{+}$ and calculate the equilibrium constant for this process.
c. For a solution with $\left[\mathrm{H}_{2} \mathrm{~S}\right]=0.10 \mathrm{M}$, with $\left[\mathrm{Bi}^{3+}\right]=\left[\mathrm{Mn}^{2+}\right]=1.5 \mathrm{mM}$ and

| Acid Ionization Constants, $\mathbf{H}_{\mathbf{2}} \mathbf{S}$ |  |
| :---: | :---: |
| $K_{1}$ | $5.7 \times 10^{-8}$ |
| $K_{2}$ | $1.3 \times 10^{-13}$ |
| $\boldsymbol{K}_{\mathrm{sp}}$ |  |
| $\mathrm{Bi}_{2} \mathrm{~S}_{3}$ | $1.6 \times 10^{-72}$ |
| MnS | $3.0 \times 10^{-11}$ | $\left[\mathrm{H}^{+}\right]=10 \mathrm{mM}$, give the formula for the metal sulfide which precipitates first and calculate the percentage of it that will remain in solution at equilibrium.

d. The pH of the solution is raised until the other metal sulfide begins to precipitate. Determine the pH of the solution at which the second metal sulfide begins to precipitate.
a)

$$
\begin{array}{ll}
\mathrm{H}_{2} \mathrm{~S} \leftrightarrow \mathrm{H}^{+}+\mathrm{HS}^{-} & \mathrm{K}_{1}=5.7 \times 10^{-8} \\
\mathrm{HS}^{-} \leftrightarrow \mathrm{H}^{+}+\mathrm{S}^{2-} & \mathrm{K}_{2}=1.3 \times 10^{-13}
\end{array}
$$

b)

$$
\mathrm{H}_{2} \mathrm{~S} \leftrightarrow 2 \mathrm{H}^{+}+\mathrm{S}^{2-} \quad \mathrm{K}=7.4 \times 10^{-21}
$$

c) Calculate sulfide ion concentration:

$$
\mathrm{K}=\frac{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{~S}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]}=\frac{(0.010)^{2}\left[\mathrm{~S}^{2-}\right]}{(0.1)}=7.4 \times 10^{-21} \text { so }\left[\mathrm{S}^{2-}\right]=7.4 \times 10^{-18}
$$

Now calculate Q and compare to K for each cation (with sulfide):
Bismuth: $\mathrm{K}_{\text {sp }}=\left[\mathrm{Bi}^{3+}\right]^{2}\left[\mathrm{~S}^{2-}\right]^{3}=1.6 \times 10^{-72}$
$\mathrm{Q}=\left(1.5 \times 10^{-3}\right)^{2}\left(7.4 \times 10^{-18}\right)^{3}=9.1 \times 10^{-58}$
$\mathrm{Q}>\mathrm{K}_{\text {sp }}$ so there will be a precipitate formed.

Manganese: $\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Mn}^{2+}\right]\left[\mathrm{S}^{2-}\right]=3.0 \times 10^{-11}$
$\mathrm{Q}=\left(1.5 \times 10^{-3}\right)\left(7.4 \times 10^{-18}\right)=1.1 \times 10^{-20}$
$\mathrm{Q}<\mathrm{K}_{\text {sp }}$ so there will not be a precipitate formed.
Thus - the bismuth is the first metal sulfide to precipitate. Now to calculate what percentage will remain in solution:
$\left[\mathrm{Bi}^{3+}\right]^{2}=\frac{K_{\mathrm{sp}}}{\left[\mathrm{S}^{2-}\right]^{3}}=\frac{\left(1.6 \times 10^{-72}\right)}{\left(7.4 \times 10^{-18}\right)^{3}}=3.95 \times 10^{-21}$ so $\left[\mathrm{Bi}^{3+}\right]=6.3 \times 10^{-11}$
The percentage can be calculated using the ratio of the amount remaining in solution divided by the original amount:
$\%=\frac{\left(6.9 \times 10^{-11}\right)}{\left(1.5 \times 10^{-3}\right)} \times 100=4.2 \times 10^{-6} \%$
d) first determine the concentration of sulfide that will result in precipitation:

$$
\begin{aligned}
& {\left[\mathrm{S}^{2-}\right]=\frac{K_{\mathrm{sp}}}{\left[\mathrm{Mn}^{2+}\right]}=\frac{\left(3.0 \times 10^{-11}\right)}{\left(1.5 \times 10^{-3}\right)}=2.0 \times 10^{-8} \text { Now plug this value into the equation for } \mathrm{K} \text { from Part (c): }} \\
& {\left[\mathrm{H}^{+}\right]^{2}=\frac{K\left[\mathrm{H}_{2} \mathrm{~S}\right]}{\left[\mathrm{S}^{2-}\right]}=\frac{\left(7.4 \times 10^{-21}\right)(0.10)}{\left(2.0 \times 10^{-8}\right)}=3.7 \times 10^{-14} \text { and }[\mathrm{H}+]=1.92 \times 10^{-7} \text { so } \mathrm{pH}=6.7}
\end{aligned}
$$

4. $(10 \%)$ A galvanic cell is based on the half-reactions;

$$
\begin{array}{ll}
\mathrm{Cr}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Cr} & E^{\circ}=-0.744 \mathrm{~V} \\
\mathrm{Ni}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ni} & E^{\circ}=-0.236 \mathrm{~V}
\end{array}
$$

a. Write the balanced equation for the overall cell reaction.
b. State which electrode increases in mass as the cell operates. Explain your answer.
c. Calculate $E_{\text {cell }}^{\circ}$
d. Determine the value of $\Delta G^{\circ}$ for the cell reaction at $25^{\circ} \mathrm{C}$.
e. Calculate the value of $K$ for the cell reaction at $25^{\circ} \mathrm{C}$.
f. Find the voltage of the cell at $25^{\circ} \mathrm{C}$ if $\left[\mathrm{Cr}^{3+}\right]$ and $\left[\mathrm{Ni}^{2+}\right]$ are both changed to 0.010 M .
a) $2 \mathrm{Cr}+3 \mathrm{Ni}^{2+} \rightarrow 2 \mathrm{Cr}^{3+}+3 \mathrm{Ni}$
b) The nickel electrode increases in mass as the cell operates because $\mathrm{Ni}^{2+}$ ions in solution are reduced there (it is the cathode) and are deposited as $\mathrm{Ni}(\mathrm{s})$.
c) $\mathrm{E}_{\text {cell }}^{0}=\mathrm{E}_{\text {red }}^{0}+\mathrm{E}_{\mathrm{ox}}^{0}=-0.236 \mathrm{~V}+0.744 \mathrm{~V}=0.508 \mathrm{~V}$
d) $\Delta \mathrm{G}^{\mathrm{o}}=-\mathrm{n} F \mathrm{E}=-(6 \mathrm{~mol})\left(96500 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~V}^{-1}\right)(0.508 \mathrm{~V})=-294000 \mathrm{~J}=-294 \mathrm{~kJ}$
$\Delta \mathrm{G}^{\mathrm{o}}=-\mathrm{RT} \ln K$
e) $-294100 \mathrm{~J}=-\left(8.314 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right)(298 \mathrm{~K}) \ln K \quad$ or $\quad \mathrm{K}=10^{\mathrm{nE}^{\mathrm{o}} / 0.592}=10^{3.048 / 0.592}=3.1 \times 10^{51}$
$\ln K=118.7$ and $K=3.62 \times 10^{51}$
f) $\mathrm{E}=\mathrm{E}^{\mathrm{o}}-\frac{0.0257}{6} \ln \left(\frac{[.01]^{2}}{[.01]^{3}}\right)=0.508 \mathrm{~V}-\frac{0.0257}{6} \ln (100) \mathrm{V}=0.508-0.0197 \mathrm{~V}=0.488 \mathrm{~V}$
5. ( $12 \%$ ) Write net equations for each of the combinations of reactants below. Use appropriate ionic and molecular formulas and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations. All reactions occur in aqueous solution unless otherwise indicated.
a. Solid ammonium chloride and solid calcium hydroxide are mixed.
b. Excess carbon dioxide gas is bubbled into a sodium hydroxide solution.
c. Sodium sulfite is added to a neutral potassium permanganate solution.
d. Aqueous hydrofluoric acid is placed on a piece of silica.
e. Chlorobenzene is heated with a mixture of concentrated nitric and sulfuric acids.
f. Iodine-131 undergoes radioactive decay.
a) $\mathrm{NH}_{4} \mathrm{Cl}+\mathrm{Ca}(\mathrm{OH})_{2} \rightarrow \mathrm{CaCl}_{2}+\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O}$
b) $\mathrm{CO}_{2}+\mathrm{OH}^{-} \rightarrow \mathrm{HCO}_{3}^{-}$
c) $\mathrm{SO}_{3}^{2-}+\mathrm{MnO}_{4}^{-} \rightarrow \mathrm{SO}_{4}^{2-}+\mathrm{MnO}_{2}$
d) $\mathrm{HF}+\mathrm{SiO}_{2} \rightarrow \mathrm{SiF}_{4}+\mathrm{H}_{2} \mathrm{O}$
e) $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Cl}+\mathrm{H}^{+}+\mathrm{NO}_{3}^{-} \rightarrow$

or

f) ${ }_{53}^{131} \mathrm{I} \rightarrow{ }_{-1}^{0} \beta+{ }_{54}^{131} \mathrm{Xe}$ or ${ }_{53}^{131} \mathrm{I} \rightarrow{ }_{2}^{4} \mathrm{He}+{ }_{51}^{127} \mathrm{Sb}$ (for half credit)
6. (12\%) The reaction of NO with $\mathrm{O}_{2}$ to give $\mathrm{NO}_{2}$ is an important step in the commercial production of $\mathrm{HNO}_{3}$.
a. Describe an experiment to measure the rate of this reaction.
b. If the rate equation is found to be Rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$, give the effect on the rate of tripling the concentration of.
i. NO
ii. $\mathrm{O}_{2}$
c. These two mechanisms have been proposed for this reaction,

$$
\begin{array}{ll}
\text { I } 2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2} & \text { II } \\
2 \mathrm{NO} \rightarrow \mathrm{~N}_{2} \mathrm{O}_{2} \\
& \mathrm{~N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}
\end{array}
$$

i. State and explain which of the two mechanisms is more likely.
ii. State and explain which of the two steps in mechanism II must be the slow step if this mechanism is to be consistent with the rate law in $b$.
a) The stoichiometry of the reaction is: $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$ so there is a change in the number of moles of gas as the reaction goes forward. This reaction can be monitored by measuring the total pressure of the system as a function of time. Alternatively, the appearance of the red color of $\mathrm{NO}_{2}$ can be measured (e.g. with a spectropohotometer.)
b) Because the rate law is Rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$, tripling the concentration of NO will cause the rate to increase by a factor of 9 . Tripling the concentration of $\mathrm{O}_{2}$ will cause the rate to increase by a factor of 3 .
c) i. Mechanism is II more likely because mechanism one involves a trimolecular collision. Such a collision is uncommon. By contrast, II has a pair of bimolecular reactions which are considerably more likely to occur.
ii. Step 2 must be the slow step because it would have a rate law of Rate $=k\left[\mathrm{~N}_{2} \mathrm{O}_{2}\right]\left[\mathrm{O}_{2}\right]$, but $\mathrm{N}_{2} \mathrm{O}_{2}$ is an intermediate whose concentration arises from the first step. With a slow second step, the first step achieves equilibrium, so $\left[\mathrm{N}_{2} \mathrm{O}_{2}\right]=\mathrm{K}[\mathrm{NO}]^{2}$ and the overall rate law would be, Rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$.
7. $(16 \%)$ Account for the following observations,
a. The bond angle in $\mathrm{H}_{2} \mathrm{O}\left(104.5^{\circ}\right)$ is greater than that of $\mathrm{H}_{2} \mathrm{~S}\left(92^{\circ}\right)$ but less than that in $\mathrm{Cl}_{2} \mathrm{O}\left(110.8^{\circ}\right)$.
b. The bond dissociation energy of $\mathrm{Cl}_{2}\left(240 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\right)$ is greater than that of $\mathrm{F}_{2}\left(154 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\right)$ or $\mathrm{Br}_{2}\left(190 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}\right)$.
c. The boiling point of $\mathrm{NH}_{3}$ is higher $\left(-33^{\circ} \mathrm{C}\right)$ than that of $\mathrm{NF}_{3}\left(-129^{\circ} \mathrm{C}\right)$ but lower than that of $\mathrm{NCl}_{3}\left(71^{\circ} \mathrm{C}\right)$.
d. $\mathrm{SiF}_{4}$ is tetrahedral while $\mathrm{SF}_{4}$ has a see-saw shape and $\mathrm{XeF}_{4}$ is square planar.
a) The angle in $\mathrm{H}-\mathrm{O}-\mathrm{H}$ is greater than $\mathrm{H}-\mathrm{S}-\mathrm{H}$ because the bonding pairs in $\mathrm{H}-\mathrm{S}-\mathrm{H}$ are further from the S atom (the atomic orbitals used in S have electron density that is further from the nucleus) so they can be forced closer together by the lone pair electrons on the S . The $\mathrm{Cl}-\mathrm{O}-\mathrm{Cl}$ bond angle is larger than either of the because the Cl atoms are large which gives rise to steric interference that forces them apart.
b) The bond in $\mathrm{Cl}_{2}$ is stronger than that in $\mathrm{F}_{2}$ because the F atoms are sufficiently small that the lone pairs on the F atoms repel one another weakening the bond. The bond in $\mathrm{Br}_{2}$ is weaker than that of $\mathrm{Cl}_{2}$ because the obritals in the larger atom ( Br ) do not overlap as efficiently.
c) The boiling point of $\mathrm{NH}_{3}$ is higher than that of $\mathrm{NF}_{3}$ because $\mathrm{NH}_{3}$ molecules can form hydrogen bonds with each other increasing the attractive forces relative to the dispersion and dipole forces between the $\mathrm{NF}_{3}$ molecules. For $\mathrm{NCl}_{3}$, the dispersion forces are sufficiently large (because of the large, polarizable Cl atoms) that they are stronger than the hydrogen bonding in $\mathrm{NH}_{3}$.
d) $\mathrm{SiF}_{4}$ is tetrahedral, with four bonding pairs about the central Si atom. $\mathrm{SF}_{4}$ has 5 pairs of electrons (4 bonding and 1 lone pair) so it has a see-saw shape. $\mathrm{XeF}_{4}$ has 6 pairs of electrons (4 bonding and 2 lone pairs) so it has a square planar shape.
8. $(10 \%)$ There are six different isomers with the formula $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}_{2}$ containing a $-\mathrm{CO}_{2}$ group. When added to water two of the six are substantially more soluble than the other four.
a. Write structural formulas for the two water-soluble compounds and outline how their structures lead to their greater solubility.
b. State the name of the class of compounds represented by the other four isomers.
c. Draw structural formulas for any three of the four less soluble isomers.
d. Write an equation for the laboratory synthesis of one of these four isomers and name each of the reactants.
a) The two more soluble forms have -COOH groups that make them more soluble because that group allow bonding with water.


b) The less soluble isomers are esters.
c) Any 3 of these four structures could be shown.




d) An example reaction would be:


## END OF PART II

| ABBREVIATIONS AND SYMBOLS |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| amount of substance | $n$ | equilibrium constant | K | measure of pressu | mHg |
| ampere | A | Faraday constant | $F$ | milli- prefix | m |
| atmosphere | atm | formula molar mass | M | molal | $m$ |
| atomic mass unit | u | free energy | G | molar | M |
| atomic molar mass | A | frequency | $v$ | mole | mol |
| Avogadro constant | $N_{\text {A }}$ | gas constant | $R$ | Planck's constant | $h$ |
| Celsius temperature | ${ }^{\circ} \mathrm{C}$ | gram | g | pressure | $P$ |
| centi- prefix | c | heat capacity | $C_{\text {p }}$ | rate constant | $k$ |
| coulomb | C | hour | h | retention factor | $R_{\text {f }}$ |
| electromotive force | E | joule | J | second | S |
| energy of activation | $E_{\text {a }}$ | kelvin | K | speed of light | c |
| enthalpy | H | kilo- prefix | k | temperature, K | $T$ |
| entropy | $S$ | liter | L | time | $t$ |
|  |  |  |  | volt | V |


| $R=8.314 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1} \cdot$ |
| :---: |
| $R=0.0821 \mathrm{~L} \cdot \mathrm{~atm} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}$ |
| $1 F=96,500 \mathrm{C} \cdot \mathrm{mol}^{-1}$ |
| $1 \mathrm{~F}=96,500 \mathrm{~J} \cdot \mathrm{~V}^{-1} \cdot \mathrm{~mol}^{-1}$ |
| $N_{\mathrm{A}}=6.022 \times 10^{23} \mathrm{~mol}^{-1}$ |
| $h=6.626 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}$ |
| $c=2.998 \times 10^{8} \mathrm{~m} \cdot \mathrm{~s}^{-1}$ |
|  |

## USEFUL EQUATIONS

$$
E=E^{o}-\frac{R T}{n F} \ln Q \quad \ln K=\left(\frac{-\Delta H}{R}\right)\left(\frac{1}{T}\right)+c \quad \ln \left(\frac{k_{2}}{k_{1}}\right)=\frac{E_{a}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)
$$

## PERIODIC TABLE OF THE ELEMENTS



| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 140.1 | 140.9 | 144.2 | (145) | 150.4 | 152.0 | 157.3 | 158.9 | 162.5 | 164.9 | 167.3 | 168.9 | 173.0 | 175.0 |
| 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| 232.0 | 231.0 | 238.0 | 237.0 | (244) | (243) | (247) | (247) | (251) | (252) | (257) | (258) | (259) | (260) |

