# 2009 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 April 29, 2009, 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 45 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. $(12 \%)$ Butanoic (butyric) acid, $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOH}$, is a monoprotic acid with $\mathrm{K}_{\mathrm{a}}=1.51 \times 10^{-5}$. A 35.00 mL sample of butanoic acid is titrated with 0.200 M KOH .
a. Calculate the $\left[\mathrm{H}^{+}\right]$in the original butanoic acid solution.
b. Calculate the pH after 10.00 mL of KOH have been added.
c. Determine the pH at the half-equivalence point of the titration.
d. Find the volume of KOH solution needed to reach the equivalence point for the titration.
e. Calculate the pH at the equivalence point.
(a.) Let $\mathrm{HA}=\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOH}$, and $\mathrm{A}^{-}=\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COO}^{-}$
$K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$ Let $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{A}^{-}\right]=\mathrm{x}$. Plugging in we get, $1.51 \times 10^{-5}=\frac{x^{2}}{(0.500-x)}$. Solving for x gives, $\left[\mathrm{H}^{+}\right]=2.73 \times 10^{-3}$
(b.) Determine the initial number of moles of acid: $0.03500 \mathrm{~L} \times 0.500 \mathrm{M}=0.0175 \mathrm{~mol} \mathrm{HA}$

Determine the number of moles of NaOH added: $0.0100 \mathrm{~L} \times 0.200 \mathrm{M}=0.0020 \mathrm{~mol} \mathrm{OH}^{-}$added
Determine the molarity of $\mathrm{H}^{+}: 0.0175-0.0020=0.0155 \mathrm{~mol} \mathrm{HA}$ remain, in 0.045 L , so the molarity is $\frac{0.0155 \mathrm{~mol} \mathrm{HA}}{0.045 \mathrm{~L}}=0.344 \mathrm{M}$
The $\left[\mathrm{A}^{-}\right]$is changed only through dilution, $\left[\mathrm{A}^{-}\right]=\frac{0.0020 \mathrm{~mol} \mathrm{~A}^{-}}{0.045 \mathrm{~L}}=0.0444 \mathrm{M}$
Plug these values into the equilibrium constant expression and solve for $\left[\mathrm{H}^{+}\right]$.
$1.51 \times 10^{-5}=\frac{\left[\mathrm{H}^{+}\right](0.0444)}{(0.344)}$, and $\left[\mathrm{H}^{+}\right]=1.16 \times 10^{-4}$, so $\mathrm{pH}=\log \left(1.16 \times 10^{-4}\right)=3.93$
(c.) At the half equivalence point: $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$and $\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{a}}=1.51 \times 10^{-5}$. So, $\mathrm{pH}=\log \left(1.51 \times 10^{-5}\right)=4.82$
(d.) The initial moles HA (from part b.) $=0.0175 \mathrm{~mol} \mathrm{HA}$, so the equivalence point is reached when we have $0.0175 \mathrm{~mol} \mathrm{OH}^{-}$added.

$$
0.0175 \mathrm{~mol} \mathrm{OH}^{-} \times \frac{1 \mathrm{~L}}{0.200 \mathrm{~mol} \mathrm{OH}^{-}}=0.0875 \mathrm{~L}
$$

(e.) Total volume at the equivalence point is $0.0875 \mathrm{~L}+0.0350 \mathrm{~L}=0.1225 \mathrm{~L}$

At the equivalence point all HA is converted to $\mathrm{A}^{-}$, so: $\left[\mathrm{A}^{-}\right]=\frac{0.0175 \mathrm{~mol}}{0.1225 \mathrm{~L}}=0.143 \mathrm{M}$
The A- is a base according to the equation, $\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \Leftrightarrow \mathrm{HA}^{\mathrm{O}}+\mathrm{OH}^{-}$, and $K_{b}=\frac{K_{\mathrm{w}}}{K_{a}}=\frac{1.0 \times 10^{-14}}{1.51 \times 10^{-5}}=6.63 \times 10^{-10}$
Let $\left[\mathrm{OH}^{-}\right]$and $[\mathrm{HA}]=x$. Plugging in we get, $6.63 \times 10^{-10}=\frac{x^{2}}{(0.143)}$. Solving for $\mathrm{x}=[\mathrm{OH}-]=9.73 \times 10^{-6}$.
So, $\mathrm{pOH}=-\log \left(9.73 \times 10^{-6}\right)=5.01$ and $\mathrm{pH}=14.00-5.01=8.99$
2. $(12 \%)$ Chromium metal reacts with acid to produce $\mathrm{Cr}^{3+}$ ions and hydrogen gas.
a. Write a balanced equation for this reaction.
b. When a sample of chromium metal is reacted with excess acid, 94.7 mL of gas is collected over water at 745 mm Hg and $20^{\circ} \mathrm{C}$. Assuming ideal gas behavior determine the mass of metal reacted. (The vapor pressure of water at $20^{\circ} \mathrm{C}$ is 24 mmHg .)
c. State and explain how the volume of gas would change if $\mathrm{Cr}^{2+}$ (rather than $\mathrm{Cr}^{3+}$ ) ions were formed in this reaction.
d. Determine the number of molecules of water vapor that would be present in the volume of gas produced assuming ideal behavior.
e. Calculate the ratio of the average molecular velocity of hydrogen to the average molecular velocity of water vapor at the same temperature.
f. The van der Waals equation for real gases is $\left[P+a\left(\frac{n}{V}\right)^{2}\right] \times[V-n b]=n R T$.

The coefficients, $a$ and $b$, for the hydrogen gas are $a=0.242 \mathrm{~atm} \cdot \mathrm{~L}^{2} \cdot \mathrm{~mol}^{-2}$ and $\mathrm{b}=0.0266 \mathrm{~L} \cdot \mathrm{~mol}^{-1}$. The c of $a$ and $b$ for sulfur dioxide are 6.714 and 0.05636 , respectively.
i. Identify the molecular property that corresponds to the a coefficient and account qualitatively for the differ its values for these two gases.
ii. Identify the molecular property that corresponds to the b coefficient and account qualitatively for the difference its values for these two gases.
a. $2 \mathrm{Cr}+6 \mathrm{H}^{+} \rightarrow 2 \mathrm{Cr}^{3+}+3 \mathrm{H}_{2}$
b. The pressure of $\mathrm{H}_{2}(\mathrm{~g})$ produced is: $745 \mathrm{mmHg}-24 \mathrm{mmHg}=721 \mathrm{mmHg}$

Determine number of moles of hydrogen: $n=\frac{p V}{R T}=\frac{\left(\frac{721}{760} \mathrm{~atm}\right)(0.0947 \mathrm{~L})}{(0.0821 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{K})(293 \mathrm{~K})}=0.00373 \mathrm{~mol} \mathrm{H}_{2}$
Now get mass of chromium: $0.00373 \mathrm{~mol} \mathrm{H}_{2} \times \frac{2 \mathrm{~mol} \mathrm{Cr}}{3 \mathrm{~mol} \mathrm{H}_{2}} \times \frac{52.00 \mathrm{~g} \mathrm{Cr}}{1 \mathrm{~mol} \mathrm{Cr}}=0.129 \mathrm{~g} \mathrm{Cr}$
c. The volume of gas would be only $2 / 3$ as much $(63.1 \mathrm{~mL})$ becase each Cr atom would release only two electrons to reduce the $\mathrm{H}^{+}$ions (rather than 3.)
 and $1.24 \times 10^{-4} \mathrm{~mol} \mathrm{H}_{2} \times \frac{6.02 \times 10^{23} \text { molecules } \mathrm{H}_{2}}{1 \mathrm{~mol} \mathrm{H}_{2}}=7.49 \times 10^{19}$ molecules $\mathrm{H}_{2}$
e. $\frac{\mathrm{v}_{\mathrm{H}_{2}}}{\mathrm{v}_{\mathrm{H}_{2} \mathrm{O}}}=\sqrt{\frac{M M_{\mathrm{H}_{2} \mathrm{O}}}{M M_{\mathrm{H}_{2}}}}=\sqrt{\frac{18}{2}}=3$ so the ratio of velocities is 3:1
f. (i.) The "a" coefficient is part of the term that is a correction factor for the attractive forces between molecules. $\mathrm{SO}_{2}$ has a larger value for "a" because $\mathrm{SO}_{2}$ molecules have stronger forces (due to it being both larger than $\mathrm{H}_{2}$, and polar.)
(ii.) The " $b$ " coefficient is part of the term that is a correction factor for the molecular volume. Because $\mathrm{SO}_{2}$ is a larger molecule, (more volume) the value for " b " is larger.
3. $(14 \%)$ The reaction of bromate and bromide ions in acid solution is represented by the equation,
$5 \mathrm{Br}^{-}(\mathrm{aq})+\mathrm{BrO}_{3}^{-}(\mathrm{aq})+6 \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightarrow 3 \mathrm{Br}_{2}(\mathrm{aq})+9 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
In order to measure the rate of the reaction, stock solutions

| Stock Solution Concentrations |  |
| :--- | :--- |
| Stock $\mathrm{Br}^{-}$solution | 1.37 M |
| Stock $\mathrm{BrO}_{3}^{-}$solution | $7.10 \times 10^{-3} \mathrm{M}$ |
| Stock $\mathrm{H}_{3} \mathrm{O}^{+}$solution | 0.573 M |

were prepared as shown in the table:
Reaction mixtures were prepared by mixing the volumes of solutions listed below, and the initial rate of disappearance of bromate ion was measured.

| Expt. | Vol. Br $^{-}$stock (mL) | Vol. $\mathrm{BrO}_{3}$ - stock (mL) | Vol $\mathrm{H}_{3} \mathrm{O}^{+}$stock (mL) | $\begin{array}{\|l} \begin{array}{l} \text { Vol } \mathrm{H}_{2} \mathrm{O} \\ (\mathbf{m L}) \end{array} \\ \hline \end{array}$ | Initial rate of $\mathrm{BrO}_{3}^{-}$ disappearance $\left(\mathbf{m o l} \cdot \mathrm{L}^{-1} \cdot \mathrm{~s}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 0.100 | 0.500 | 1.000 | 1.400 | $5.63 \times 10^{-6}$ |
| 2 | 0.200 | 0.500 | 1.000 | 1.300 | $1.09 \times 10^{-5}$ |
| 3 | 0.100 | 1.000 | 1.000 | 0.900 | $1.13 \times 10^{-5}$ |
| 4 | 0.200 | 0.500 | 0.700 | 1.600 | $5.50 \times 10^{-6}$ |

a. Calculate the rate of appearance of $\mathrm{Br}_{2}(\mathrm{aq})$ in experiment one.
b. Write the rate law for this reaction and give the value of the specific rate constant, $k$.
c. The following mechanism is proposed for the reaction:
(I) $\quad \mathrm{BrO}_{3}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightarrow \mathrm{HBrO}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
(II) $\quad \mathrm{HBrO}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{BrO}_{3}{ }^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
(III) $\quad \mathrm{H}_{2} \mathrm{BrO}_{3}{ }^{+}(\mathrm{aq}) \rightarrow \mathrm{BrO}_{2}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
(IV) $\quad \mathrm{BrO}_{2}^{+}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq}) \rightarrow \mathrm{BrOBrO}(\mathrm{aq})$
(V) $\quad \mathrm{BrOBrO}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq}) \rightarrow \mathrm{Br}_{2}(\mathrm{aq})+\mathrm{BrO}_{2}^{-}(\mathrm{aq})$

Subsequent reactions of $\mathrm{BrO}_{2}^{-}(\mathrm{aq})$ are fast.
i. Draw a Lewis structure of $\mathrm{BrO}_{2}{ }^{+}$and predict its geometry.
ii. Given the rate law you determined in b , which of the steps (I)-(V) could potentially be rate-limiting?

Justify your answer.
a. $\frac{\Delta\left[\mathrm{Br}_{2}\right]}{\Delta \mathrm{t}}=3 \times \frac{\Delta\left[\mathrm{Br}_{2}\right]}{\Delta \mathrm{t}}=3\left(5.63 \times 10^{-6}\right)=1.69 \times 10^{-5} \mathrm{~mol} / \mathrm{L} \cdot \mathrm{s}$
b.

- Looking at experiments 2 and 1, the volume of $\mathrm{Br}^{-}$is doubled and the rate increases by 1.94 (essentially doubles) so the reaction is first order in $\mathrm{Br}^{-}$.
- Looking at experiments 3 and 1 , the volume of $\mathrm{BrO}_{3}^{-}$is doubled and the rate doubles so the reaction is first order in $\mathrm{BrO}_{3}{ }^{-}$.
- Looking at experiments 2 and 4 , the volume ratio of $\mathrm{H}_{3} \mathrm{O}^{+}$is $(1.00 / 0.700=1.4)$ and the rate ratio is $(1.09 / 0.55=1.98)$ so the reaction is second order in $\mathrm{H}_{3} \mathrm{O}^{+}$because $(1.4)^{2}=1.96$
Thus, the rate law is : rate $=k\left[\mathrm{Br}^{-}\right]\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$ and

$$
k=\frac{\text { rate }}{\left[\mathrm{Br}^{-}\right]\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}}=\frac{5.63 \times 10^{-6} \mathrm{~mol} / \mathrm{L} \cdot \mathrm{~s}}{\left(\frac{0.1}{3} * 1.37 \mathrm{~mol} / \mathrm{L}\right)\left(\frac{0.5}{3} * 7.1 \times 10^{-3} \mathrm{~mol} / \mathrm{L}\right)\left(\frac{1}{3} * 0.573 \mathrm{~mol} / \mathrm{L}\right)^{2}}=2.86 \mathrm{~L}^{3} / \mathrm{mol}^{3} \cdot \mathrm{~s}
$$

c. (i.) One resonance structure is shown below, and the shape determined by VSEPR is bent.

(ii.) To have the rate law determined in part (b), the rate limiting step of the mechanism must depend on the concentrations of $\left[\mathrm{Br}^{-}\right],\left[\mathrm{BrO}_{3}^{-}\right]$, and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$. The only way for this to be true is for Step IV to be the rate limiting step. One way to confirm this is to determine what the rate law would be for each step as the rate limiting step.
If Step I is limiting, the rate would vary with $\left[\mathrm{BrO}_{3}{ }^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
If Step II is limiting, the rate would vary with $\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$
If Step III is limiting, the rate would vary with $\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$
If Step IV is limiting, the rate would vary with $\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{Br}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$
If Step $V$ is limiting, the rate would vary with $\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{Br}^{-}\right]^{2}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{2}$
4. $(12 \%)$ There is great current interest in developing fuel cells based on the reaction,

$$
2 \mathrm{CH}_{3} \mathrm{OH}(\mathrm{l})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

a. Write a balanced equation for the half-reaction that occurs in acid solution for such a fuel cell at the;
i. anode.
ii. cathode.
b. If the $E^{\circ}$ value for the cell reaction is 1.21 V , calculate the value of $\Delta G^{\circ}$.
c. The $E^{\circ}$ value for the $\mathrm{O}_{2}(\mathrm{~g})$ half reaction is 1.23 V in $1 \mathrm{M} \mathrm{H}^{+}$, calculate the $E^{\circ}$ value expected in $1 \mathrm{M} \mathrm{OH}^{-}$.
d. State two advantages of carrying out this reaction in a fuel cell rather than burning methanol and converting the heat into electricity.
a. i. anode: $\mathrm{CH}_{3} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{CO}_{2}+6 \mathrm{H}^{+}+6 \mathrm{e}^{-} \quad$ ii.) cathode: $\mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$
b. $\Delta \mathrm{G}^{\mathrm{o}}=-\mathrm{n} F E^{0}=-(12 \mathrm{~mol})(96500 \mathrm{~J} / \mathrm{V} \cdot \mathrm{mol})(1.21 \mathrm{~V})=-1.40 \times 10^{3} \mathrm{~kJ}$
c. Use the Nernst equation: $E=E^{\circ}-\frac{R T}{n F} \ln \left(\frac{1}{\left[\mathrm{H}^{+}\right]^{4}}\right)$
so, $E=1.23-\frac{(8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K})(298 \mathrm{~K})}{(4)(96500)} \ln \left(\frac{1}{\left(10^{-14}\right)^{4}}\right)=1.23-\frac{0.0257}{4} \ln \left(10^{56}\right)=0.40 \mathrm{~V}$
d. 1. No wasted heat. 2. No energy lost during conversion.
5. ( $12 \%$ ) Write net equations for each of the combinations of reactants below. Use appropriate ionic and molecular fort omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic subs You need not balance the equations. All reactions occur in aqueous solution unless otherwise indicated.
a. Solid calcium is heated in nitrogen gas.
b. Solid sodium ethoxide is added to water.
c. Solutions of magnesium sulfate and barium hydroxide are mixed.
d. An acidic potassium permanganate solution is added to a solution of sodium sulfite.
e. Radium- 222 undergoes alpha decay.
f. 2-propanol is heated with concentrated sulfuric acid.
a. $\mathrm{Ca}(\mathrm{s})+\mathrm{N}_{2}(g) \longrightarrow \mathrm{Ca}_{3} \mathrm{~N}_{2}(s)$
b. $\mathrm{NaOCH}_{2} \mathrm{CH}_{3}(s)+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$
c. $\mathrm{Mg}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq})+\mathrm{Ba}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq}) \longrightarrow \mathrm{BaSO}_{4}(\mathrm{~s})+\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{~s})$
d. $\mathrm{MnO}_{4}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{SO}_{3}^{2-}(\mathrm{aq}) \longrightarrow \mathrm{Mn}^{2+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}+\mathrm{SO}_{4}^{2-}(\mathrm{aq})$
e. ${ }_{88}^{222} \mathrm{Ra} \longrightarrow{ }_{2}^{4} \mathrm{He}+{ }_{86}^{218} \mathrm{Rn}$
f. $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3} \xrightarrow{\mathrm{H}_{2} \mathrm{SO}_{4}} \mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH}_{2}+\mathrm{H}_{2} \mathrm{O}$
6. $(12 \%)$
a. Explain why many chemical reactions that are nonspontaneous, with $\Delta G^{\circ}>0$ at room temperature, proceed to a significant extent at that temperature.
b. Account for the fact that standard enthalpies of formation of compounds at $25^{\circ} \mathrm{C}$ may be either positive or negative.
c. Explain why all elements and compounds have positive $S^{\circ}$ values at $25^{\circ} \mathrm{C}$.
d. Give an example of a chemical species that does not have a positive $S^{\circ}$ value at $25^{\circ} \mathrm{C}$ and explain why its standard entropy is not positive.
a. $\Delta \mathrm{G}^{\mathrm{o}}$ values refer to standard conditions including 1 M concentrations. Reactions that are nonspontaneous under these conditions may be caused to occur by increasing the concentration of the reactants and/or decreasing the concentrations of the products.
b. $\Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}$ values of compounds are relative to their elements in standards states (for which $\Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}=0$ ). Depending on the compound, formation may either release energy $\left(\Delta H_{f}{ }^{\circ}<0\right)$ or absorb energy $\left(\Delta H_{f}{ }^{\circ}>0\right)$.
c. The standard for entropy, $S^{\circ}$, is a perfect crystal at 0 K , which by the Third Law of Thermodynamics is zero. As temperature increases, entropy increases, so $S^{\circ}$ is positive at $25^{\circ} \mathrm{C}$.
d. $S^{\circ}$ values of many ions (such as $\mathrm{F}^{-}, \mathrm{Cl}^{-}, \mathrm{PO}_{4}^{3-}$ ) are less than zero, This occurs because the reference for aqueous ions is the standard entropy for $\mathrm{H}^{+}$, which is set to zero. Some ions, like those listed, may organize the solvent molecules more than the hydrogen ions, so their standard entropy will be negative.
7. $(12 \%)$ Account for the following observations in terms of atomic/ionic/molecular properties.
a. Sodium fluoride melts at a higher temperature than potassium chloride.
b. Titanium(III) chloride is a solid at room temperature but titanium(IV) chloride is a liquid at room temperature..
c. $\mathrm{N}_{2} \mathrm{O}_{3}$ is an acidic anhydride but $\mathrm{Bi}_{2} \mathrm{O}_{3}$ is a basic anhydride.
d. Lithium chloride is much more soluble in ethanol than is sodium chloride.
a. The internuclear distance in NaF is less than that in KCl so the lattice energy of NaF is greater. Overcoming larger lattice energy leads to higher melting points.
b. $\mathrm{TiCl}_{3}$ has $\mathrm{Ti}^{3+}$ ions at the center and is an ionic compound whereas for $\mathrm{TiCl}_{4}$, the smaller $\mathrm{Ti}^{4+}$ ion causes the $\mathrm{Ti}-\mathrm{Cl}$ bonds to have more covalent character. Covalent molecules typically melt at lower temperatures than ionic ones.
c. $\mathrm{N}_{2} \mathrm{O}_{3}$ reacts with $\mathrm{H}_{2} \mathrm{O}$ to form HONO , the high electronegativity of N draws electrons from H of $\mathrm{H}-\mathrm{O}$ bond to give $\mathrm{H}^{+}$. $\mathrm{Bi}_{2} \mathrm{O}_{3}$ reacts with $\mathrm{H}_{2} \mathrm{O}$ to form $\mathrm{Bi}(\mathrm{OH})_{3}$. The less electronegative $\mathrm{Bi}^{3+}$ bonds less strongly to O so $\mathrm{OH}^{-}$is released.
d. The smaller $\mathrm{Li}^{+}$ion has a higher charge density than the larger $\mathrm{Na}^{+}$ion. This makes LiCl more covale the same reasons noted in part (a)). Covalent compounds are more soluble in $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ which has lower
8. (14\%) Four compounds with a molar mass of 59 have the formula $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{~N}$ and the structures:
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$

$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHCH}_{3}$
$\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$
a. Name the class to which these compounds belong.
b. The boiling points of the four compounds vary from $3^{\circ} \mathrm{C}$ to $46^{\circ} \mathrm{C}$. Identify the lowest and highest boiling compounds and account for the difference in terms of the intermolecular forces in each.
c. Each of the four compounds is basic. For one of the compounds draw a structural formula for the conjugate acid formed with $\mathrm{H}^{+}$. Account for the observation that all of these compounds are more basic than ammonia.
d. There are two amides with the formula $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NO}$ and the same molar mass as the above compounds.
i. Draw structural formulas for these two compounds.
ii. State whether these compounds have boiling points above or below $46^{\circ} \mathrm{C}$. Rationalize your prediction.
iii. State whether these compounds are more or less basic than those with the structures given above. Rationalize your prediction.
a. These molecules are amines.
b. $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$ is the lowest boiling, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ is the highest boiling. $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$ is lowest because it has no hydrogen bonding interactions. The remaining three all have hydrogen bonding, so the highest boiling will have the largest dispersion forces, which the longer chain alkane provides.
c. Any of these four drawings would count...





These compounds are more basic than $\mathrm{NH}_{3}$ because the carbon containing groups are better electron donors than hydrogen. This inductive effect causes the lone pairs on the nitrogen to be donated to $\mathrm{H}^{+}$more readily.
d. i.

or

ii. These compounds have higher boiling points because they will hydrogen bond more strongly.
iii. They will be less basic. The $\mathrm{C}=\mathrm{O}$ functional group will draw electrons from the nitrogen making the lone pairs less available.

END OF PART II

| ABBREVIATIONS AND SYMBOLS |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| amount of substance | $n$ | equilibrium constant | K | measure of pressu | mmHg |
| 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 |


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

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 | ${ }_{\mathbf{L r}}$ |
| 232.0 | 231.0 | 238.0 | 237.0 | (244) | (243) | (247) | (247) | (251) | (252) | (257) | (258) | (259) | (260) |

