

# 2008 U. S. NATIONAL CHEMISTRY OLYMPIAD NATIONAL EXAM-PART II 

Prepared by the American Chemical Society Olympiad Examinations Task Force

# OLYMPIAD EXAMINATIONS TASK FORCE 

Arden P. Zipp, State University of New York, Cortland Chair

Sherry Berman-Robinson, Consolidated HS, Orland Park, IL (retired)<br>Paul Groves, South Pasadena HS, Pasadena, CA William Bond, Snohomish HS, Snohomish, WA

David Hostage, Taft School, Watertown, CT
Peter Demmin, Amherst HS, Amherst, NY (retired)
Marian Dewane, Centennial HS, Boise, ID
Jane Nagurney, Scranton Preparatory School, Scranton, PA
Valerie Ferguson, Moore HS, Moore, OK
Ronald Ragsdale, University of Utah, Salt Lake City, UT
Kimberly Gardner, US Air Force Academy, Colorado Springs, CO

## 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 23, 2008, 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 | 60 questions | single-answer multiple-choice | $\mathbf{1}$ hour, 30 minutes |
| :--- | :--- | :--- | :--- |
| Part II | 8 questions | problem-solving, explanations | 1 hour, 45 minutes |
| Part III | 2 lab problems | laboratory practical | 1 hour, 30 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 ${ }^{\circledR}$ 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.

## Key for 2008 National Olympiad (part 2)

1. ( $14 \%$ ) Benzene, $\mathrm{C}_{6} \mathrm{H}_{6}$, reacts with $\mathrm{Br}_{2}$ in the presence of $\mathrm{FeBr}_{3}$ as a catalyst to give an organic compound with composition by mass; $\mathrm{C} 30.55 \%, \mathrm{H} 1.71 \%, \mathrm{Br} 67.74 \%$ and hydrogen bromide.
a. Determine the empirical formula of the compound.
b. When 0.115 g of this compound are dissolved in 4.36 g of naphthalene the solution freezes at $79.51^{\circ} \mathrm{C}$. Pure nap freezes at $80.29{ }^{\circ} \mathrm{C}$ and has a $k_{\mathrm{f}}=6.94{ }^{\circ} \mathrm{C} \cdot \mathrm{m}^{-1}$. Determine the molar mass and molecular formula of the compound.
c. Write a balanced equation for the reaction.
d. Calculate the theoretical yield for the organic compound when 4.33 g of of benzene is reacted with an excess of bromine.
e. If the actual yield of the reaction is 5.67 g , what is the percentage yield?
f.
i. Write structures for the possible isomers that could be formed in this reaction.
ii. Identify the major isomer(s) formed in this reaction and explain your reasoning.
a) convert masses to moles:
$1.71 \mathrm{~g} \mathrm{H} \times\left(\frac{1 \mathrm{~mol}}{1.008 \mathrm{~g}}\right)=1.70 \mathrm{~mol}(\div 0.848)=2.00$
$30.55 \mathrm{~g} \mathrm{C} \times\left(\frac{1 \mathrm{~mol}}{12.011 \mathrm{~g}}\right)=2.54 \mathrm{~mol}(\div 0.848)=3.00$
$67.74 \mathrm{~g} \mathrm{Br} \times\left(\frac{1 \mathrm{~mol}}{79.90 \mathrm{~g}}\right)=0.848 \mathrm{~mol}(\div 0.848)=1.0$
These numbers are whole numbers, so the empirical formula must be $\mathrm{C}_{3} \mathrm{H}_{2} \mathrm{Br}$
b) $\Delta \mathrm{T}=80.29-79.51=0.78^{\circ} \mathrm{C}$. Plugging this value into the formula for freezing point depression gives,
$\Delta \mathrm{T}=k_{\mathrm{f}} \bullet m$ and $m=0.78{ }^{\circ} \mathrm{C} / 6.94{ }^{\circ} \mathrm{C} / m=0.11 m$
$0.11 \frac{\mathrm{~mol}}{\mathrm{~kg}} \times 0.00436 \mathrm{~kg}=0.00048 \mathrm{~mol}$ so, $\mathrm{MM}=\frac{0.115 \mathrm{~g}}{0.00048 \mathrm{~mol}}=240 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$
$240 / 117.9=2.03$ which is approximately 2 , so the molecular formula must be $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2}$
c) $\mathrm{C}_{6} \mathrm{H}_{6}+2 \mathrm{Br}_{2} \rightarrow \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2}+2 \mathrm{HBr}$
d) The theoretical yield is:
$4.33 \mathrm{~g} \mathrm{C}_{6} \mathrm{H}_{6} \times\left(\frac{1 \mathrm{~mol} \mathrm{C}_{6} \mathrm{H}_{6}}{78.11 \mathrm{~g} \mathrm{C}_{6} \mathrm{H}_{6}}\right) \times\left(\frac{1 \mathrm{~mol} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2}}{1 \mathrm{~mol} \mathrm{C}_{6} \mathrm{H}_{6}}\right) \times\left(\frac{235.89 \mathrm{~g} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2}}{1 \mathrm{~mol} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2}}\right)=13.1 \mathrm{~g} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Br}_{2}$
e) Percent yield is: $\left(\frac{5.67 \mathrm{~g}}{13.07 \mathrm{~g}}\right) \times 100 \%=43.4 \%$

The possible isomers for i. are,
ii. the major products are,



because -Br is an ortho-para director. The para isomer should be the most prominent product because of steric hindrance for the ortho product.
2. $(10 \%)$ Photochemical smog is formed through a sequence of reactions, the first three of which are given belo when the $\mathrm{O}(\mathrm{g})$ produced in reaction (3) reacts with organic molecules.

$$
\begin{array}{ll}
(1) & \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}(\mathrm{~g})  \tag{1}\\
(2) & 2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \\
(3) & \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{h} v \rightarrow \mathrm{NO}(\mathrm{~g})+\mathrm{O}(\mathrm{~g})
\end{array}
$$

a. For reaction $(1), \Delta H^{\mathrm{o}}=+180.6 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$. Calculate the bond dissociation energy of $\mathrm{NO}(\mathrm{g})$.
b. Calculate the entropy change for the first reaction.
c. Determine the minimum temperature at which reaction (1) becomes spontaneous.
d. For reaction (3), $\Delta H^{\circ}=+306 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$. If the energy for this reaction were provided by sunlight, estimate the wavelength required and specify the region of the spectrum containing this wavelength.
a) The overall enthalpy change can be estimated from the bond dissociation energies via the equation,
$\Delta \mathrm{H}=\sum$ Energy of bonds broken $-\sum$ Energy of bonds formed
$180.6 \mathrm{~kJ}=941 \mathrm{~kJ}+498 \mathrm{~kJ}-2 \times \mathrm{BDE}_{\mathrm{NO}}$
$s o, \mathrm{BDE}_{\mathrm{NO}}=629 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$
b) Similarly,
$\Delta \mathrm{S}^{\circ}=2 \mathrm{~S}^{\circ}(\mathrm{NO})-\left(\mathrm{S}^{\circ}\left(\mathrm{N}_{2}\right)+\mathrm{S}^{\circ}\left(\mathrm{O}_{2}\right)\right)$
$\Delta S^{\circ}=2(210.6)-((191.5)+(205))=24.7 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}$
c) Utilize the equation, $\Delta \mathrm{G}^{\circ}=\Delta \mathrm{H}^{\circ}-\mathrm{T} \Delta \mathrm{S}^{\circ}$, and set $\Delta \mathrm{G}^{\circ}$ to zero to find the minimum temperature.
$0=180.6 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}-\mathrm{T} \times\left(0.0247 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right)$, so $\mathrm{T}=180.6 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} / 0.0247 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}=7311 \mathrm{~K}$
d) First convert to energy per molecule,
$3.06 \times 10^{3} \frac{\mathrm{~J}}{\mathrm{~mol}} \times\left(\frac{1 \mathrm{~mol}}{6.022 \times 10^{23} \text { molecules }}\right)=5.08 \times 10^{-19} \frac{\mathrm{~J}}{\text { molecule }}$. Now calculate wavelength of light with this energy,
$\lambda=\frac{\mathrm{h} \cdot \mathrm{c}}{\mathrm{E}}=\left(\frac{\left(6.626 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}\right)\left(3.0 \times 10^{8} \mathrm{~m} \cdot \mathrm{~s}^{-1}\right)}{5.08 \times 10^{-19} \mathrm{~J} \cdot \text { molecule }}\right)=3.91 \times 10^{-7} \mathrm{~m} \quad($ per molecule $)=391 \mathrm{~nm}$ (in the ultraviolet).
3. (12\%) Aniline, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$, reacts with water according to the equation: $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

In a 0.180 M aqueous aniline solution the $\left[\mathrm{OH}^{-}\right]=8.80 \times 10^{-6}$.
a. Write the equilibrium constant expression for this reaction.
b. Determine the value of the base ionization constant, $K_{\mathrm{b}}$, for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})$.
c. Calculate the percent ionization of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$ in this solution.
d. Determine the value of the equilibrium constant for the neutralization reaction;

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

e.
i. Find the $\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}(\mathrm{aq})\right] /\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})\right]$ required to produce a pH of 7.75 .
ii. Calculate the volume of 0.050 M HCl that must be added to 250.0 mL of $0.180 \mathrm{M} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}(\mathrm{aq})$ to achieve this ratio.
a) $K_{\mathrm{b}}=\frac{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}\right]}$

## Key for 2008 National Olympiad (part 2)

b) $K_{\mathrm{b}}=\frac{\left(8.80 \times 10^{-6}\right)\left(8.80 \times 10^{-6}\right)}{(0.180)}=4.3 \times 10^{-10}$
c) $\%$ ionization $=\frac{\left(8.80 \times 10^{-6}\right)}{(0.180)} \times 100 \%=4.9 \times 10^{-3} \%$
d) $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}+\mathrm{H}_{2} \mathrm{O}$ so $K=\frac{K_{b}}{K_{w}}=\frac{4.3 \times 10^{-10}}{1.0 \times 10^{-14}}=4.3 \times 10^{4}$
e) (i) For a $\mathrm{pH}=7.75$, the $\mathrm{pOH}=6.25$ so $\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}=5.62 \times 10^{-7} \mathrm{M}$.
$4.3 \times 10^{-10}=\frac{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}\right]}$ so, $\frac{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}^{+}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}\right]}=\frac{4.3 \times 10^{-10}}{5.62 \times 10^{-7}}=7.65 \times 10^{-4}$
(ii) The HCl is a strong acid that will protonate the aniline, so to get the HCl required, we need the amount of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$ required multiplied by the value of the ratio from (i): $7.65 \times 10^{-4} \times 0.250 \mathrm{~L} \times 0.180 \mathrm{M} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}=3.44 \times 10^{-5} \mathrm{~mol} \mathrm{HCl}$
Now determine the volume of reagent: $3.44 \times 10^{-5} \mathrm{~mol} \mathrm{HCl} \times 1 \mathrm{~L} / 0.050 \mathrm{~mol} \mathrm{HCl}=6.88 \times 10^{-4} \mathrm{~L}=0.688 \mathrm{~mL}$
4. ( $10 \%$ ) Gaseous dinitrogen pentoxide, $\mathrm{N}_{2} \mathrm{O}_{5}$, decomposes to form nitrogen dioxide and oxygen gas with the initial rate data at $25^{\circ} \mathrm{C}$ given in the table.

| $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right], \mathrm{M}$ | 0.150 | 0.350 | 0.650 |
| :--- | :--- | :--- | :--- |
| Rate, $\mathrm{mol} \cdot \mathrm{L}^{-1} \cdot \mathrm{~min}^{-1}$ | $3.42 \times 10^{-4}$ | $7.98 \times 10^{-4}$ | $1.48 \times 10^{-3}$ |

a. Write a balanced equation for this reaction.
b. Use the data provided to write the rate law and calculate the value of $k$ for this reaction. Show all calculations.
c. Calculate the time required for the concentration of a 0.150 M sample of $\mathrm{N}_{2} \mathrm{O}_{5}$ to decrease to 0.050 M .
d. The initial rate for the reaction of a 0.150 M sample is $2.37 \times 10^{-3} \mathrm{~mol}^{-} \cdot \mathrm{L}^{-1} \mathrm{~min}^{-1}$ at $40^{\circ} \mathrm{C}$. Determine the activation energy for this reaction.
a) $2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}$
b) The rate will be given by the rate law ( $\mathrm{Rate}=k\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]^{x}$ ) in each case, so by taking the ratio, the rate constant cancels,
$\frac{\text { Rate }_{1}}{\text { Rate }_{2}}=\frac{\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{1}^{x}}{\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]_{2}^{x}}$
$\frac{7.98 \times 10^{-4}}{3.42 \times 10^{-4}}=\left(\frac{0.350}{0.150}\right)^{x}$ means that $2.33^{x}=2.33$ so $\mathrm{x}=1$. Checking with a second set of data, $\frac{1.48 \times 10^{-3}}{3.42 \times 10^{-4}}=\left(\frac{0.650}{0.150}\right)^{x}$ leads to $4.33^{x}=4.33$, confirming that the reaction is first order.
Now calculate the rate constant: $1.48 \times 10^{-3}=k(0.650)^{1}$ so $\mathrm{k}=2.28 \times 10^{-3} \mathrm{~min}^{-1}$ and we have
Rate $=2.28 \times 10^{-3} \mathrm{~min}^{-1}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]$.
c) Use the integrated rate law, $\ln \left(\frac{\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{\text {init }}}{\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]_{t}}\right)=k t$. Plugging in $\ln \left(\frac{0.150}{0.050}\right)=\ln (3)=\left(2.28 \times 10^{-3} \mathrm{~min}^{-1}\right) t$ so $\mathrm{t}=481$ minutes.
d) Use the information from the two temperatures given in the Arrhenus equation:
$\ln \left(\frac{\mathrm{k}_{2}}{\mathrm{k}_{1}}\right)=\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{1}}-\frac{1}{\mathrm{~T}_{2}}\right)$, so, plugging in values gives: $\ln \left(\frac{1.58 \times 10^{-2}}{2.28 \times 10^{-3}}\right)=\frac{\mathrm{E}_{\mathrm{a}}}{8.314 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}} \times\left(\frac{1}{298 \mathrm{~K}}-\frac{1}{313 \mathrm{~K}}\right)$
so $\ln (6.93)=\frac{\mathrm{E}_{\mathrm{a}}}{8.314 \mathrm{~J} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}} \times(0.00335-0.00319)$ and solving for $\mathrm{E}_{\mathrm{a}}$ gives : $\mathrm{E}_{\mathrm{a}}=1.00 \times 10^{5} \mathrm{~J} \cdot \mathrm{~mol}^{-1}=100 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$. (Note that using rates, rather than rate constants in the argument of the natural $\log$ is an alternative, correct method.)
5. (12\%) Write net equations for each of the combinations of reactants below. Use appropriate ionic and molecular it omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic su You need not balance the equations. All reactions occur in aqueous solution unless otherwise indicated.
a. Barium peroxide is added to water.
b. Acidic solutions of potassium iodide and potassium iodate are mixed.
c. A phosphoric acid solution is added to a solution of calcium hydrogencarbonate.
d. Solutions of lead(II) nitrate and potassium chromate are mixed.
e. Concentrated hydrochloric acid is added to an aqueous solution of cobalt(II) nitrate.
f. 2-butanol is heated with concentrated sulfuric acid.
a) $\mathrm{BaO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Ba}^{2+}+\mathrm{HO}_{2}^{-}+\mathrm{OH}^{-}$
b) $\mathrm{I}^{-}+\mathrm{IO}_{3}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{I}_{2}+\mathrm{H}_{2} \mathrm{O}$
c) $\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{Ca}^{2+}+\mathrm{HCO}_{3}^{-} \rightarrow \mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
d) $\mathrm{Pb}^{2+}+\mathrm{CrO}_{4}^{2-} \rightarrow \mathrm{PbCrO}_{4}$
e) $\mathrm{Co}^{2+}+\mathrm{Cl}^{-} \rightarrow \mathrm{CoCl}_{4}^{2-}$
f)

either isomer counts
6. $(12 \%)$ The apparatus depicted to the right is often used to demonstrate the electrolysis of water. Tubes A and B are initially filled with an aqueous solution of $\mathrm{H}_{2} \mathrm{SO}_{4}$ or $\mathrm{Na}_{2} \mathrm{SO}_{4}$.
a. Describe the purpose of adding the $\mathrm{H}_{2} \mathrm{SO}_{4}$ or $\mathrm{Na}_{2} \mathrm{SO}_{4}$ rather than using pure water.
b. Give the formula of the gas produced in; i. tube A ii. tube B
c. Describe a chemical test that could be used to identify the gas collected in tube A. Include the procedure and expected observation.
d. Calculate the number of moles of gas expected to be collected in tube $B$ when a
 600. milliamp current is applied for 40.0 minutes. (Assume no side reactions occur.)
e. Calculate the volume of the gas produced in part d. for a temperature is $20^{\circ} \mathrm{C}$ and a pressure in the laboratory of 735 mmHg . (The vapor pressure of water is 17.5 mmHg .)
f. If $\mathrm{H}_{2} \mathrm{O}_{2}$ is formed in a side reaction the quantity of only one of the products is affected. Identify the product affected and state how its quantity compares with that produced with no side reaction. Explain your answer.
a) Because pure water is a poor conductor of electricity, the $\mathrm{H}_{2} \mathrm{SO}_{4}$ or $\mathrm{Na}_{2} \mathrm{SO}_{4}$ is added to provide electrolyte (so that the solution will conduct).
b) i) tube A is the cathode, therefore it is the site of reduction where $\mathrm{H}_{2}$ is produced, while (ii) tube $B$ is the anode, where oxidation occurs, therefore $\mathrm{O}_{2}$ is produced.
c) Because $\mathrm{H}_{2}$ is flammable, a burning splint can be inserted into the products from Tube A. If there is a "pop" associated with the reaction, it confirms that the gas is $\mathrm{H}_{2}$.
d) Charge $=$ current $\times$ time: $0.600 \mathrm{C} \cdot \mathrm{s}^{-1} \times 2400 \mathrm{~s}=1440 \mathrm{C}$
and: $1440 \mathrm{C} \times\left(\frac{1 \mathrm{~mol} \mathrm{e}^{-}}{96500 \mathrm{C}}\right) \times\left(\frac{1 \mathrm{~mol} \mathrm{O}_{2}}{4 \mathrm{~mol} \mathrm{e}^{-}}\right)=3.73 \times 10^{-3} \mathrm{~mol} \mathrm{O}_{2}$

## Key for 2008 National Olympiad (part 2)

e) First correct for vapor pressure of water: $\mathrm{P}_{\text {total }}=\mathrm{P}_{\mathrm{O}_{2}}+\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}$ so $\mathrm{P}_{\mathrm{O}_{2}}=735-17.5=717.5 \mathrm{mmHg}$

$$
V=\frac{n R T}{P}=\frac{\left(3.73 \times 10^{-3} \mathrm{~mol}\right)\left(0.821 \mathrm{~L} \cdot \mathrm{~atm} \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~K}^{-1}\right)(293 \mathrm{~K})}{717.5 \mathrm{mmHg} \times \frac{1 \mathrm{~atm}}{760 \mathrm{~mm} \mathrm{Hg}}}=0.095 \mathrm{~L}=95 \mathrm{~mL}
$$

f) The quantity of $\mathrm{O}_{2}$ would be affected, but the quantity of $\mathrm{H}_{2}$ would not. The yield of $\mathrm{O}_{2}$ would be decreased because some of the electricity would oxidize $\mathrm{H}_{2} \mathrm{O}$ into peroxide $\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)$ instead of $\mathrm{O}_{2}$.
7. $(16 \%)$ Explain the following observations in terms of bonding principles.
a. Carbon dioxide is a gas at room temperature and pressure but silicon dioxide is a high-melting solid.
b. The xenon trioxide molecule has a trigonal pyramidal shape while sulfur trioxide is trigonal planar.
c. In many of its ionic compounds oxygen is present as the $\mathrm{O}^{2-}$ ion although the addition of two electrons to an oxygen atom in the gas phase is an endothermic process.
d. $(\mathrm{bmim})^{+} \mathrm{PF}_{6}{ }^{-}$is a liquid at room temperature while $(\mathrm{bmim})^{+} \mathrm{Cl}^{-}$and $\mathrm{Na}^{+} \mathrm{PF}_{6}{ }^{-}$are solids.

Note: (bmim) ${ }^{+}$is an abbreviation for N -butyl-N-methylimadazolium ion, $\mathrm{CH}_{3} \mathrm{~N}_{2} \mathrm{C}_{3} \mathrm{H}_{3} \mathrm{C}_{4} \mathrm{H}_{9}{ }^{+}$.
a) Carbon dioxide is small, non-polar molecule. The intermolecular forces between them are small, so $\mathrm{CO}_{2}$ is a gas. Conversely, silicon dioxide is a network solid. As a network, the connections are covalent bonds, which are quite strong compared to the intermolecular forces between small molecules, and it requires a great deal of energy to break an $\mathrm{SiO}_{2}$ unit away from the rest of the solid. Ultimately the key bonding feature in these molecules that gives rise to this difference is that carbon atoms readily form double bonds, where double bonds to silicon are much less common.
b) Looking at the Lewis structure of the two compounds provides the answer:



There are four charge centers (three bonding, and one lone pair) around Xe in $\mathrm{XeO}_{3}$ leading to a trigonal pyramidal shape, while there are three charge centers (all of them bonding pairs) in $\mathrm{SO}_{3}$ which is trigonal planar.
c) When the oxide ion, $\mathrm{O}^{2-}$, is in ionic compounds, the $2-$ charge is interacting with positively charged cations. Thus, even though the ion formation in the gas phase is endothermic, the oxide ion exists in ionic compounds.
d) Because the (bmim) ${ }^{+}$and $\mathrm{PF}_{6}{ }^{-}$ions are quite large, the lattice energy between the two items will be small. The energy available as heat at room temperature is sufficient to overcome this interaction energy. By contrast (bmim) ${ }^{+}$and $\mathrm{Cl}^{-}$and $\mathrm{Na}^{+}$and $\mathrm{PF}_{6}^{-}$have one large and one small ion, so they can pack more closely and have larger lattice energy. These larger energies mean the compounds are solids at room temperature.
8. $(14 \%)$ This question deals with the bonding in several organic chemicals.
a. Several different compounds have the formula $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}$. Two of these contain $-\mathrm{CO}_{2}$ groups.
i. Give the structures and names of the two compounds with $-\mathrm{CO}_{2}$ groups.
ii. These compounds boil at $31.5^{\circ} \mathrm{C}$ and $118^{\circ} \mathrm{C}$. Assign the two boiling points to the structures in i. and account for the boiling point difference in terms of their structures.
iii. Sketch the structure of one of the other compounds.
b. Fatty acids are important components of a healthy diet. Three fatty acids are stearic, oleic and linoleic which have the formulas $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{32} \mathrm{COOH}, \mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{30} \mathrm{COOH}$, and $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{28} \mathrm{COOH}$, respectively.
i. Describe the differences in bonding suggested by the formulas of these compounds.
ii. The compounds melt at $-5^{\circ} \mathrm{C}, 13{ }^{\circ} \mathrm{C}$ and $69^{\circ} \mathrm{C}$. Assign these melting points to the respective acids and account for this behavior in terms of their structures and bonding.
iii. The salts of fatty acids can be used as soaps or detergents. Describe the chemical basis of this behavior.
a) (i) The two structures are:

ethanoic acid

methylmethanoate
ii) $118^{\circ} \mathrm{C}$ is ethanoic acid and $31.5^{\circ} \mathrm{C}$ is methyl methanoate. The key difference arises from the strength of intermolecular forces present in ethanoic acid, which can participate in hydrogen bonding, while the strongest intermolecular forces present in methylmethanoate are dipole-dipole forces.
iii) Possible correct structures include:




b) (i) $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{32} \mathrm{COOH}$ contains a saturated alkyl chain. $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{30} \mathrm{COOH}$ contains a one carbon-carbon double bond. $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{28} \mathrm{COOH}$ contains two carbon-carbon double bonds.
(ii) $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{32} \mathrm{COOH}$ melts at $69^{\circ} \mathrm{C}$. It is the highest melting point because the saturated alkyl chain tails are capable of being closely packed, thereby maximizing the dispersion forces present. Higher intermolecular forces lead to higher melting points. $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{30} \mathrm{COOH}$ with one double bond has additional geometrical constraints due to the relative rigidity of that double bond, so the tails cannot pack as efficiently, and the melting point is lower, at $13{ }^{\circ} \mathrm{C}$. Finally, for $\mathrm{CH}_{3} \mathrm{C}_{16} \mathrm{H}_{28} \mathrm{COOH}$ with two double bonds, the geometric constraints just noted are even more sizable, so packing is even less efficient. It will, therefore, have the lowest melting point, $-5^{\circ} \mathrm{C}$.
(iii) The key feature is that the molecules have a charged region (often called the head) where the acid group is and an uncharged and not very polar region (called the tail) where the alkyl chains are. The non-polar tail can interact relatively strongly with non-polar dirts, oils and greases, leaving the polar/charged head group "sticking out". This polar/charged group interacts strongly with polar water molecules. Thus, while polar water molecules do not wash away non-polar dirts and oils by themselves, taking advantage of the dual behavior of the long-chain fatty acids, the dirt/oil is encapsulated in a micelle-like structure that can be solvated by water.
Pictorially, showing far too few fatty acids, it would look something like this.


KEY for 2008 National Olympiad (Part 2)

| 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 volt | $t$ V |

## CONSTA

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

## 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) |

