2000 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM—PART III

Prepared by the American Chemical Society Olympiad Laboratory Practical Task Force

OLYMPIAD LABORATORY PRACTICAL TASK FORCE

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DIRECTIONS TO THE EXAMINER–PART III

The laboratory practical part of the National Olympiad Examination is designed to test skills related to the laboratory. Because the format of this part of the test is quite different from the first two parts, there is a separate, detailed set of instructions for the examiner. This gives explicit directions for setting up and administering the laboratory practical.

There are two laboratory tasks to be completed during the 90 minutes allotted to this part of the test. Students do not need to stop between tasks, but are responsible for using the time in the best way possible. Each procedure must be approved for safety by the examiner before the student begins that procedure.

Part III	**2 lab problems**	**laboratory practical**	**1 hour, 30 minutes**

Students should be permitted to use non-programmable calculators.

DIRECTIONS TO THE EXAMINEE–PART III

DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO. WHEN DIRECTED, TURN TO PAGE 2 AND READ THE INTRODUCTION AND SAFETY CONSIDERATIONS CAREFULLY BEFORE YOU PROCEED.

There are two laboratory-related tasks for you to complete during the next 90 minutes. There is no need to stop between tasks or to do them in the given order. Simply proceed at your own pace from one to the other, using your time productively. You are required to have a procedure for each problem approved for safety by an examiner before you carry out any experimentation on that problem. You are permitted to use a non-programmable calculator. At the end of the 90 minutes, all answer sheets should be turned in. Be sure that you have filled in all the required information at the top of each answer sheet. Carefully follow all directions from your examiner for safety procedures and the proper disposal of chemicals at your examining site.

Not valid for use as an USNCO National Examination after April 16, 2000.
Distributed by the ACS DivCHED Examinations Institute, Clemson University, Clemson, SC

2000 UNITED STATES NATIONAL CHEMISTRY OLYMPIAD
PART III — LABORATORY PRACTICAL

Student Instructions

Introduction

These problems test your ability to design and carry out laboratory experiments and to draw conclusions from your experimental work. You will be graded on your experimental design, on your skills in data collection, and on the accuracy and precision of your results. Clarity of thinking and communication are also components of successful solutions to these problems, so make your written responses as clear and concise as possible.

Safety Considerations

You are required to wear approved eye protection at all times during this laboratory practical. You also must follow all directions given by your examiner for dealing with spills and with disposal of wastes.

Lab Problem 1

If anhydrous ammonium nitrate is added to water at room temperature, the temperature of the solution decreases. However, if anhydrous calcium chloride is added to water at room temperature, the temperature of the solution increases. Design and carry out an experiment to determine what mass of ammonium nitrate must be added along with 10.0 g of $CaCl_2$ to 100. mL of water so that the final temperature of the solution is the same as the initial room temperature of the water. You will be asked to describe the method you developed to solve this problem.

Lab Problem 2

Although bromocresol green is often used as an acid-base indicator, in this problem it is being used as a reactant. When mixed with a dilute solution of household bleach, bromocresol green is gradually oxidized and changes to a different color, a color that happens to match that of bromocresol green at a pH of 4. Design and carry out an experiment to determine the kinetic order of this redox reaction with respect to bleach. You will be asked to describe the method you developed to solve this problem.

Answer Sheet for Laboratory Practical **Problem 1**

Student's Name: ______________________________

Student's School: ______________________ **Date:** ______________

Proctor's Name: ______________________________

ACS Section Name : ____________________ **Student's USNCO test #:** __________

1. Give a brief description of your experimental plan. Include a sketch of the equipment you will use and the steps you plan to take to solve this problem.

Before beginning your experiment, you must get approval (for safety reasons) from the examiner.	Examiner's Initials:

2. Record your data and other observations.

3. What is the mass of ammonium nitrate that must be added along with 10.0 g of calcium chloride to 100 mL of water and so that the temperature of the resulting solution is the same as that of the water? Show your methods clearly.

Mass of ammonium nitrate:	

Answer Sheet for Laboratory Practical Problem 2

Student's Name: ______________________________

Student's School: ______________________ **Date:** ____________

Proctor's Name: ______________________________

ACS Section Name : ______________________ **Student's USNCO test #:** ____________

1. Give a brief description of your experimental plan. List the equipment and materials you plan to use and the steps you plan to take to solve this problem.

Before beginning your experiment, you must get approval (for safety reasons) from the examiner.	**Examiner's Initials:**

2. Record your data and other observations.

3. Determine the order of the reaction with respect to bleach. Show your reasoning clearly.

Order of reaction with respect to bleach:	

2000 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM—PART III

Prepared by the American Chemical Society Olympiad Laboratory Practical Task Force

Examiner's Instructions

Directions to the Examiner:

Thank you for administering the 2000 USNCO laboratory practical on behalf of your Local Section. It is essential that you follow the instructions provided, in order to insure consistency of results nationwide. There may be considerable temptation to assist the students after they begin the lab exercise. It is extremely important that you do not lend any assistance or hints whatsoever to the students once they begin work. As in the international competition, the students are not allowed to speak to anyone until the activity is complete.

The equipment needed for each student for both lab exercises should be available at his/her lab station or table when the students enter the room. The equipment should be initially placed so that the materials used for Lab Problem 1 are separate from those used for Lab Problem 2.

After the students have settled, read the following instructions (in italics) to the students.

Hello, my name is ________. Welcome to the lab practical portion of the U.S. National Chemistry Olympiad Examination. In this part of the exam, we will be assessing your lab skills and your ability to reason through a laboratory problem and communicate its results. Do not touch any of the equipment in front of you until you are instructed to do so.

One of this year's problems requires the use of a Styrofoam® cup calorimeter. These have been assembled for you to preserve maximum time for your experimentation. There are extra cups available for you to use as the inner cup.

Show a Styrofoam® cup calorimeter. (See picture of the set-up on page 3 of these instructions.)

This problem also requires you to use a balance, which is located ______________________________.

Another of this year's problems uses small-scale chemistry equipment. Small-scale chemistry techniques help to minimize the amount of materials you use, thereby increasing safety and minimizing waste. Specialized equipment for small-scale chemistry that you will use today include Beral-type pipets and reaction plates.

Show a 1-mL, 3-mL, or a 5-mL Beral-type pipet, and show a 6-well or a 12-well reaction plate.

You will be asked to complete two laboratory problems. All the materials and equipment you may want to use to solve each problem has been set out for you and is grouped by the number of the problem. You must limit yourself to this equipment for each problem. You will have ***one hour and thirty minutes*** *to complete the* ***two problems****. You may choose to start with either problem. You are required to have a procedure for each problem approved for safety by an examiner. (Remember that approval does not mean that your procedure will be successful–it is a safety approval.) When you are ready for an examiner to come to your station for each safety approval, please raise your hand.*

Safety is an important consideration during the lab practical. ***You must wear goggles at al*** [illegible]*h off any chemicals spilled on your skin or clothing with large amounts of tap water. The approp*[illegible] *procedures for disposing of solutions at the end of this lab practical are:*

We are about to begin the lab practical. Please do not turn the page until directed to do so, but read the directions on the front page. Are there any questions before we begin?

Distribute **Part III** booklets and again remind students not to turn the page until the instruction is given. **Part III** contains student instructions and answer sheets for both laboratory problems. There is a periodic table on the last page of the booklet. Allow students enough time to read the brief cover directions.

> *Do not turn to page 2 until directed to do so. When you start to work, be sure that you fill out all information at the top of the answer sheets. Are there any additional questions?*

If there are no further questions, the students should be ready to start **Part III**.

> *You may begin.*

After **one hour and thirty minutes**, give the following directions.

> *This is the end of the lab practical. Please stop and bring me your answer sheets. Thank you for your cooperation during this test.*

Collect all the lab materials. Make sure that the student has filled in his or her name and other required information on the answer sheets. At this point, you may want to take five or ten minutes to discuss the lab practical with the students. They can learn about possible observations and interpretations and you can acquire feedback as to what they actually did and how they reacted to the problems. After this discussion, please take a few minutes to complete the Post-Exam Questionnaire; this information will be extremely useful to the Olympiad subcommittee as they prepare next year's exam.

Please remember to return the post-exam Questionnaire, the answer sheets from **Part III**, the Scantron sheets from **Part I**, and the "Blue Books" from **Part II** to this address:

ACS DivCHED Exams Institute
Clemson University
223 Brackett Hall
Box 340979
Clemson, SC 29634-0979

Monday, April 24, 2000, is the ***absolute*** deadline for ***receipt*** of the exam materials at the Examinations Institute. Materials received after this deadline CANNOT be graded.

THERE WILL BE NO EXCEPTIONS TO THIS DEADLINE DUE TO THE TIGHT SCHEDULE FOR GRADING THIS EXAMINATION.

EXAMINER'S NOTES

Lab Problem #1: Materials and Equipment

Each student will need access to a balance that is capable of weighing an object at least to the nearest 0.01 grams. One balance *can* serve 2-3 students, but one balance per student is highly desirable.

Each student will need:

One calorimeter such as shown in this diagram. These should be *preassembled* for the students to preserve maximum time for their experimentation.

1 ring stand
2 clamps
1 thermometer, –10 to 110°C
6 370-mL (12 oz) foam cups
1 370-mL foam cup to serve as cover. Trim off about top one-third of cup, punch two holes of appropriate sizes for the thermometer and stirring rod.
1 5-10 cm piece of wire or string to hold up thermometer
1 30-35 cm piece of 20 gauge copper wire. Bend in a circle on the bottom to serve as a stirrer, hook on top for handle.

Notes: The inner cup can be replaced as needed, which is why there are extra foam cups. 250 mL (8 oz) foam cups may also be used but 190 mL (6 oz) cups are not recommended. You may choose to supply a ring clamp to stabilize the base of the cup assembly. Another option is to place the cup assembly in an appropriately sized beaker that serves to support the cups and to provide extra insulation.

2 plastic or metal scoops; can use cut Beral-style pipets
1 500-mL or larger wash bottle, labeled "distilled water" or "deionized water"
1 100-mL graduated cylinder
1 small glass or plastic vial with top, labeled 25.0 g ammonium nitrate
1 small glass or plastic vial with top, labeled 25.0 g calcium chloride
6 small plastic weighing boats, weighing papers, or small dry paper cups
4 Beral-style plastic pipets, 3 mL or 5 mL; eye droppers may be substituted.
1 plastic tub for disposal of liquid wastes (or easy access to sinks)
supply of paper towels
1 pair safety goggles
1 lab coat or apron (optional)
1 pair plastic gloves (optional)

Lab Problem #1: Chemicals

Each student will need:

25.0 g anhydrous ammonium nitrate *Note*: Be sure particles are not clumped.
25.0 g anhydrous calcium chloride *Note*: Do ***not*** use the dihydrate.
500 mL distilled or deionized water

Lab Problem #1: Notes

1. Note that the examiner will need to initial each student's experimental plan. Please do not comment on the plan other than looking for any potentially unsafe practices.

2. Consistent results will depend on starting with anhydrous salts and minimizing exposure to moisture during transfer of the salts to the vials. Be sure the glass or plastic vials are tightly closed after they are filled for each student.

3. The balances can be used as common equipment, although as noted earlier, it will be highly desirable to have one balance per student. Only the first activity requires the use of a balance and this should minimize delays if a number of students must share a balance. Please note any problems on the Examiner's report sheet if balance use negatively impacts the performance of your students.

4. Safety: It is your responsibility to ensure that all students wear safety goggles during the lab practical. A lab coat or apron for each student is desirable but not mandatory. Please know and follow all safety procedures appropriate for your site. You will need to give students explicit directions for handling spills and for disposing of waste materials, following approved safety practices for your examining site.

Lab Problem #2: Materials and Equipment

Each student will need:

2 6-well or 1 12-well reaction plate. If reaction plates cannot be obtained or borrowed, 6 50-mL or 100-mL beakers can be substituted.
1 piece of white paper to place under the reaction plates or beakers
3 Beral-style plastic pipets, 1 mL. Eye droppers may be substituted.
1 100-mL or larger wash bottle, labeled "distilled water" or "deionized water"
4 10-mL narrow-mouth plastic dropping bottles. Small glass bottles fitted with eye droppers may be substituted.
    One labeled "diluted household bleach solution"
    One labeled "bromocresol green solution"
    One labeled "pH 4.0 buffer"
    One labeled "pH 7.0 buffer"
1 timer, stop watch, or access to classroom clock with a second hand
1 plastic tub for disposal of liquid wastes (or easy access to sinks)
supply of paper towels
1 pair safety goggles
1 lab coat or apron (optional)
1 pair plastic gloves (optional)

Lab Problem #2: Chemicals

Each student will need:

10 mL of pH 4.0 buffer
10 mL of pH 7.0 buffer
10 mL of diluted bleach solution.
Preparation: Obtain fresh commercial bleach containing 5.25% sodium hypochlorite solution. Combine 5.0 mL of this solution with 295 mL distilled water to form the diluted bleach solution.
10 mL of diluted bromocresol green solution.
Preparation: Dilute 0.2 g of bromocresol green to form 500 mL of aqueous solution. Do not use existing solutions of bromocresol green, for they may contain alcohol or NaOH commonly used in their preparation.
50 mL of distilled or deionized water

Lab Problem #2: Notes

1. Note that the examiner will need to initial each student's experimental plan. Please do not comment on the plan other than looking for any potentially unsafe practices.

2. Simply combining the two reagents provides enough mixing for the reaction to take place. However, you may wish to provide toothpicks or plastic stirring rods.

3. Premade buffer solutions of pH 4.0 and 7.0 may be used, or purchased from any one of several suppliers. If preparing your own buffer solutions, a useful reference is Silberman, R. G., *The Journal of Chemical Education*, 1992 (Vol 69, No. 2), p. A42. This article describes a system using boric acid, citric acid monohydrate, and trisodium phoshate dodecahydrate. These directions are also given in *ACS Small-Scale Laboratory Assessment Activities*, ACS Examinations Institute, 1996, p. C-14.

4. Safety: It is your responsibility to ensure that all students wear **safety goggles** during the lab practical. A lab coat or apron for each student is desirable but not mandatory. Please know and follow all safety procedures appropriate for your site. You will need to give students explicit directions for handling spills and for disposing of waste materials, following approved safety practices for your examining site.

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KEY for NATIONAL EXAM—PART III

Lab Problem 1

Plan: State:

a. Add mass $CaCl_2$ to recorded amount of H_2O

b. Record initial and final temperatures to obtain ΔT for $CaCl_2$ sample.

c. Add mass NH_4NO_3 to recorded amount of H_2O.

d. Record initial and final temperatures to obtain ΔT for NH_4NO_3 sample

e. Repeat 2-3 times.

Sketch the apparatus as directed in the instructions.

Data: Record:

a. mass $CaCl_2$ and volume of water.

b. T_i and T_f for $CaCl_2$

c. mass NH_4NO_3 and volume of water

d. T_i and T_f for NH_4NO_3 Amounts of solids added should be large enough to get a reasonable value for ΔT

e. results of a "verification" experiment to check prediction.

Replication: multiple trials

Calculations:

Calculate: **a.** $\frac{\Delta T}{\text{g } CaCl_2}$ and $\frac{\Delta T}{\text{g } NH_4NO_3}$ for the same amount of H_2O **or**

$\frac{q}{\text{g } CaCl_2}$ and $\frac{q}{\text{g } NH_4NO_3}$ for the same amount of H_2O

b. ratio of grams of NH_4NO_3 to $CaCl_2$

c. amount of NH_4NO_3 needed for 100 grams of H_2O

Sample Data:

	Trial 1	**Trial 2**
Mass NH_4NO_3	5.005 g	5.073 g
Volume H_2O	50.0 mL	51.9 mL
Initial temperature	21.5 °C	21.5 °C
Final temperature	14.8 °C	15.0 °C
ΔT (NH_4NO_3)	–6.7 °C	–6.5 °C
mass $CaCl_2$	5.064 g	5.187 g
volume H_2O	50.0 mL	52.0 mL
Initial temperature	21.4 °C	21.0 °C
Final temperature	33.7 °C	34.0 °C
ΔT ($CaCl_2$)	12.3 °C`	13.0 °C

Sample Calculations:

For NH_4NO_3, note that the solution became ***cooler*** as the NH_4NO_3 dissolved. This means the dissolution process is ***absorbing heat*** from the water. $q_{NH_4NO_3} = -q_{H_2O}$

Trial 1

$$q_{NH_4NO_3} = -\frac{mc\Delta T}{g}$$

Trial 2

$$q_{NH_4NO_3} = -\frac{mc\Delta T}{g}$$

$$q_{NH_4NO_3} = -\frac{(50.0\text{g})\ (4.184\ \text{J}\cdot\text{g}^{-1}\cdot{}^\circ\text{C}^{-1})\ (-6.7\ ^\circ\text{C})}{5.005\ \text{g}}$$

$$q_{NH_4NO_3} = \frac{1.40\ \times\ 10^3\ \text{J}}{5.005\ \text{g}} = \frac{2.79\ \times\ 10^2\ \text{J}}{\text{g}}$$

$$q_{NH_4NO_3} = -\frac{(51.9\ \text{g})\ (4.184\ \text{J}\cdot\text{g}^{-1}\cdot{}^\circ\text{C}}{5.073\ \text{g}}$$

$$q_{NH_4NO_3} = \frac{1.41\ \times\ 10^3\ \text{J}}{5.073\ \text{g}} = \frac{2.78\ \times\ 10^2\ \text{J}}{\text{g}}$$

$$q_{average}\ \text{for}\ NH_4NO_3 = \frac{2.79\times 10^2\ \text{J}}{\text{g}}\ \text{ or }\ 279\ \text{J / g}$$

This is the heat ***absorbed from the water*** as the NH_4NO_3 dissolves.

For $CaCl_2$, note that the solution became ***warmer*** as the $CaCl_2$ dissolved. This means the dissolution process is ***releasing heat*** to the water. $q_{CaCl_2} = -q_{H_2O}$

Trial 1

$$q = \frac{mc\Delta T}{g}$$

$$q_{CaCl_2} = -\frac{(50.0\text{g})\ (4.184\ \text{J}\cdot\text{g}^{-1}\cdot{}^\circ\text{C}^{-1})\ (12.3\ ^\circ\text{C})}{5.064\ \text{g}}$$

$$q_{CaCl_2} = -\frac{2.57\ \times\ 103\ \text{J}}{5.064\ \text{g}} = -\frac{5.08\ \times\ 10^2\ \text{J}}{\text{g}}$$

Trial 2

$$q = \frac{mc\Delta T}{g}$$

$$q_{CaCl_2} = -\frac{(52.0\text{g})\ (4.184\ \text{J}\cdot\text{g}^{-1}\cdot{}^\circ\text{C}^{-1})\ (13.0\ ^\circ\text{C})}{5.187\ \text{g}}$$

$$q_{CaCl_2} = -\frac{2.83\ \times\ 10^3\ \text{J}}{5.187\ \text{g}} = -\frac{5.45\ \times\ 10^2\ \text{J}}{\text{g}}$$

$$q_{average}\ \text{for}\ CaCl_2 = -\frac{5.27\times 10^2\ \text{J}}{\text{g}}\ \text{ or }\ -527\ \text{J / g}$$

This is the heat ***released to the water*** as the $CaCl_2$ dissolves.

Ratio of heats: $q_{CaCl_2} = -q_{NH_4NO_3}$ so the ratio is: $\dfrac{527\ \text{J / g}\ CaCl_2}{279\ \text{J / g}\ NH_4NO_3} = \dfrac{1.89\ \text{g}\ NH_4NO_3}{1.00\ \text{g}\ CaCl_2}$

Conclusion:

For 10.0 g $CaCl_2$: $10.0\ \text{g}\ CaCl_2 \times \dfrac{1.89\ \text{g}\ NH_4NO_3}{1.00\ \text{g}\ CaCl_2} = 18.9\ \text{g}\ NH_4NO_3$

Lab Problem 2

Plan: State:

a. Add a small amount of bromocresol green to a well of pH 4 buffer and to a well of pH 7 buffer to determine color at each pH.

b. Measure known amounts of bromocresol green to well plates (by counting drops). Add various amounts of bleach (by counting drops) and record time to color change.

c. Ideally, the reactions will be conducted at constant volume by adding either H_2O or pH 7 buffer so that concentration ratios are directly related to volumes of bleach used for each reaction.

Replications should be made for each trial.

Data: Record:

a. color change of bromocresol green from blue at pH = 7 to yellow at pH = 4

b. drops of bromocresol green added to each well

c. drops of buffer or water added to each well, if used in plan

d. drops of bleach added to each well

e. time required for color change

Replication: multiple trials

Calculations:

To determine the order of reaction, use ***one*** of these equations.

$$\frac{time_1}{time_2} = \frac{[bleach_2]^x}{[bleach_1]^x} \quad \text{or} \quad \frac{rate_1}{rate_2} = \frac{[bleach_1]^x}{[bleach_2]^x}$$

Sample Data:

The observed color change for bromocresol green is from blue at pH = 7 to yellow at pH = 4.

Data gathered if reactions are buffered at pH = 7

Trial	Drops of Bromocresol Green	Drops of Buffer	Drops of Bleach	Time for color change to occur	Average time for three trials
1	20	5	20	14	
2	20	5	20	16	15.7
3	20	5	20	17	
4	20	1.5	10	28	
5	20	1.5	10	27	27.7
6	20	1.5	10	28	

Data gathered if reactions are not buffered

Trial	Drops of Bromocresol Green	Drops of Buffer	Drops of Bleach	Time for color change to occur	Average time for three trials
1	20	5	20	50	
2	20	5	20	52	51.7
3	20	5	20	53	
4	20	1.5	10	50	
5	20	1.5	10	51	51.7
6	20	1.5	10	54	

Note: Students do ***not*** need to do both buffered and unbuffered reactions.

Sample Calculation:

Using data from the observations from the pH 7 ***buffered*** reactions:

$\frac{time_1}{time_2} = \frac{[bleach_2]^x}{[bleach_1]^x}$ and the concentration of bleach is directly proportional to the number of drops added.

$\frac{27.7 \text{ seconds}}{15.7 \text{ seconds}} = \frac{(20 \text{ drops})^x}{(10 \text{ drops})^x}$ and x ≈ 1

rate = $k[\text{bleach}]^1$ if the reaction is carried out in the buffer.

Using data from the observations from the ***unbuffered*** reactions:

$\frac{time_1}{time_2} = \frac{[bleach_2]^x}{[bleach_1]^x}$ and the concentration of bleach is directly proportional to the number of drops added.

$\frac{51.7 \text{ seconds}}{51.7 \text{ seconds}} = \frac{(20 \text{ drops})^x}{(10 \text{ drops})^x}$ and x ≈ 0

rate = $k[\text{bleach}]^0$ if the reaction is not carried out in the pH = 7 buffer.

Conclusion:

If buffered at pH = 7, then the reaction is first order with respect to bleach.

If unbuffered, then the reaction is zero order with respect to bleach.