2015 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART III

Prepared by the American Chemical Society 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 may carry out the two tasks in any order they wish and move directly from one to the other within the allotted time. Each procedure must be approved for safety by the examiner before the student begins that procedure.

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

A periodic table and other useful information are provided on page 7 for student reference.

Students should be permitted to use non-programmable calculators. The use of a programmable calculator, cell phone, or any other device that can access the internet or make copies or photographs during the exam is grounds for disqualification.

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 examination site.

2015 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 and disposable, non-latex rubber gloves 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

Devise and carry out an experimental procedure to determine the concentration (in mass %) of the hydrogen peroxide solution with which you have been provided.

Lab Problem 2

Consider the reaction:

$$[Cu(H_2O)_4]^{2+}(aq) + 4\ Cl^{-}(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 4\ H_2O(l) \quad \Delta H = \_\_\_\_$$

Prepare an initial $[Cu(H_2O)_4]^{2+}$ / $[CuCl_4]^{2-}$ equilibrium mixture by dissolving sodium chloride in 0.3 *M* copper(II) nitrate solution until you observe a color change.

Devise and carry out experimental procedures to
1) ***determine the sign of ΔH for this reaction, and***
2) ***identify Solution A and Solution B as containing either KCl or $AgNO_3$ based on their effect on this equilibrium system.***

Answer Sheet for Laboratory Practical **Problem 1**

Student's Name: ____ ________

Student's School:______________________________**Date:** ____________________

Proctor's Name: ____

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

1. Give a brief description of your experimental plan.

2. Record your data/observations.

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

3. Show all calculations

4. The concentration of the hydrogen peroxide solution provided = _______mass %.

5. List as many sources of error as you can think of for your procedure and indicate whether each would yield a result lower than or higher than the actual concentration of the hydrogen peroxide solution.

Answer Sheet for Laboratory Practical **Problem 2**

Student's Name: ____

Student's School:______________________________**Date:** ____________________

Proctor's Name: ____

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

1. Give a brief description of your experimental plan.

2. Record your data and observations. Explain each change in color that you observed, in terms of a shift in the equilibrium position of this system.

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

3. What is the color of each species in this equilibrium system?

4. The sign of ΔH for this reaction is _____.

5. a) Solution A contains ___________________________.

   b) Solution B contains ___________________________.

ABBREVIATIONS AND SYMBOLS					
amount of substance	*n*	Faraday constant	*F*	molar mass	*M*
ampere	A	free energy	*G*	mole	mol
atmosphere	atm	frequency	ν	Planck's constant	*h*
atomic mass unit	u	gas constant	*R*	pressure	*P*
Avogadro constant	N_A	gram	g	rate constant	*k*
Celsius temperature	°C	hour	h	reaction quotient	*Q*
centi– prefix	c	joule	J	second	s
coulomb	C	kelvin	K	speed of light	*c*
density	d	kilo– prefix	k	temperature, K	*T*
electromotive force	*E*	liter	L	time	*t*
energy of activation	E_a	measure of pressure	mm Hg	vapor pressure	VP
enthalpy	*H*	milli– prefix	m	volt	V
entropy	*S*	molal	*m*	volume	*V*
equilibrium constant	*K*	molar	M		

CONSTANTS

$R = 8.314\ \text{J•mol}^{-1}\text{•K}^{-1}$

$R = 0.0821\ \text{L•atm•mol}^{-1}\text{•K}^{-1}$

$1\ F = 96{,}500\ \text{C•mol}^{-1}$

$1\ F = 96{,}500\ \text{J•V}^{-1}\text{•mol}^{-1}$

$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$

$h = 6.626 \times 10^{-34}\ \text{J•s}$

$c = 2.998 \times 10^{8}\ \text{m•s}^{-1}$

0 °C = 273.15 K

1 atm = 760 mm Hg

Specific heat capacity of H_2O = $4.184\ \text{J•g}^{-1}\text{•K}^{-1}$

EQUATIONS

$$E = E^{o} - \frac{RT}{nF}\ln Q \qquad \ln K = \left(\frac{-\Delta H^{o}}{R}\right)\left(\frac{1}{T}\right) + \text{constant} \qquad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

PERIODIC TABLE OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 (Uut) (284)	114 **Fl** (289)	115 (Uup) (288)	116 **Lv** (293)	117 (Uus) (294)	118 (Uuo) (294)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

AMERICAN CHEMICAL SOCIETY

U.S. National Chemistry Olympiad

2015 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART III — EXAMINER'S INSTRUCTIONS

Prepared by the American Chemical Society Chemistry Olympiad Laboratory Practical Task Force

Directions to the Examiner:

Thank you for administering the 2015 USNCO laboratory practical on behalf of your Local Section. It is essential that you follow the instructions provided, in order to ensure 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 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.

It is your responsibility to ensure that all students wear safety goggles and non-latex rubber gloves during the lab practical. A lab coat or apron for each student is desirable but not mandatory. You will also need to give students explicit directions for handling spills and for disposing of waste materials, following approved safety practices for your examination site. Please check and follow procedures appropriate for your site.

After the students have settled, read the following *instructions* 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.

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 may use equipment from one problem to work on the other problem, but the suggested ideal equipment and chemicals to be used for each problem has been grouped for you. 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 and non-latex rubber gloves at all times.*** *Please wash off any chemicals spilled on your skin or clothing with large amounts of tap water.*

The appropriate 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 they 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 to fill out all of the information at the top of the answer sheets. Are they 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 portion of the exam.

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 might wish to take a few 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 USNCO subcommittee as they prepare for 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 in the UPS Next Day return envelope you were provided to this address:

American Chemical Society
U.S. National Chemistry Olympiad
1155 16th Street, NW – Room 811
Washington, DC 20036

The label on the UPS Express Pak envelope should have this address and your return address already. The cost of the shipping is billed to ACS USNCO. You can keep a copy of the tracking number to allow you to track your shipment.

Wednesday, April 22, 2015, is the ***absolute*** deadline for ***receipt*** of the exam material. Materials received after this deadline **CANNOT** be graded. Be sure to have your envelope sent no later than ***Monday, April 20, 2015*** for it to arrive on time.

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

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 POTENTIAL UNSAFE PRACTICES.

Lab Problem #1: Materials and Equipment

Each student should have available the following equipment and materials:

Materials:

- **3 – 250 mL** Erlenmeyer flasks (Pyrex, Kimax or equivalent)
- **3** – watch glasses, large enough in diameter to cover the mouths of the Erlenmeyer flasks
- **1** – spatula (a Scoopula® is fine)
- **2** – Beral pipets
- disposable, non-latex rubber gloves
- access to electronic balance, capable of determining mass to at least two decimal places, and with a capacity of at least 250 g
- access to paper towels and a sink with running water

Chemicals:

- **100 mL** – Hydrogen Peroxide Solution - 6 mass % (see Note 1), in a bottle labeled only as "Hydrogen Peroxide Solution" (DO NOT provide the concentration on the label)
- **1 g** – Manganese(IV) Oxide (see Note 2), in a small vial labeled "Manganese(IV) Oxide"

Notes:

1) This solution is best prepared within a few days of the administration of the lab practical. Prepare the 6% by mass hydrogen peroxide solution by appropriate dilution of 30% hydrogen peroxide (e.g., Fisher brand H325-500 Hydrogen Peroxide, 30%, or 27% hydrogen peroxide available at swimming pool stores have been found to be suitable). From the Certificate of Analysis of the lot of hydrogen peroxide used, obtain the actual concentration of the hydrogen peroxide solution, as determined by assay. Use distilled or deionized water (do not use tap water). Store the solution in amber bottles (4 ounce or 125 mL narrow mouth bottles are fine).
2) It was brought to the attention of the USNCO Subcommittee that the MnO_2 should be checked to ensure that it hasn't somehow become deactivated. A small amount of MnO_2 should facilitate a fairly rapid and exothermic decomposition of 25 mL of 6% hydrogen peroxide.
3) Avery Label Template (Template 5160) provided for your convenience.

These materials are in addition to and separate from lab problem #1.

Lab Problem #2: Materials and Equipment

Each student should have available the following equipment and materials:

Materials:

- **3 – 50 mL** beakers (Pyrex, Kimax or equivalent)
- **1** – stirring rod
- **1** pair – beaker tongs
- **1 – 10 mL** graduated cylinder
- **1** – Spatula (a Scoopula® is fine)
- disposable, non-latex rubber gloves
- access to a hotplate (can be shared with up to 3 other students)
- access to an ice bath (shallow, but large enough to accommodate up to four 50 mL beakers; can be shared with up to 3 other students)
- access to paper towels and a sink with running water

Chemicals:

- **5 g –** Sodium Chloride, in a small vial labeled "Sodium Chloride"
- **50 mL** – 0.3 M copper(II) nitrate solution, in a bottle labeled "Copper(II) Nitrate Solution, 0.3 M"
- **Solution A**: 3 mL of 0.1M silver nitrate solution in a Beral pipet labeled only as "Solution A"
- **Solution B**: 3 mL of 2M potassium chloride solution in a Beral pipet labeled only as "Solution B"

Notes:

1) The type of Beral pipets for Solution A and Solution B (5 mL capacity is sufficient):

2) Cut off the excess stem to yield about a 2 cm tip:

3) Avery Label Template (Template 5160) provided for your convenience.

Safety Instructions for Lab Problem #1 and #2:

It is your responsibility to ensure that all students wear safety goggles and non-latex rubber gloves during the lab practical. A lab coat or apron for each student is desirable but not mandatory. You will also need to give students explicit directions for handling spills and for disposing of waste materials, following approved safety practices for your examination site. Please check and follow procedures appropriate for your site.

If you have any questions regarding Part III, please contact USNCO office immediately at USNCO@acs.org.

Lab Problem #1: **[25 points]**

Devise and carry out an experimental procedure to determine the concentration (in mass %) of the hydrogen peroxide solution with which you have been provided.

Answer sheet questions:

1. Give a brief description of your experimental plan. **[3 pts]**

2. Record your data/observations.

a) Data (example; student may tare flask and/or watch glass rather than determine and report their masses, determine the mass of the flask, watch glass and MnO_2,or other:

i) Mass of flask + watch glass = 120.432

ii) Mass of flask + watch glass + MnO_2 = 120.638 g

iii) Mass of flask + watch glass + MnO_2 + H_2O_2 = 140.693 g

iv) Mass of iii above, after reaction = 140.118 g

NOTES: Students should at least have iii and iv above, (or the necessary data to determine them).
Students should have data from at least TWO trials. **[6 pts (3 each)]**

b) Observations – **(Student responses may vary; best response would include at least 3 observations)**

Upon addition of the MnO_2 to the H_2O_2: **[3 pts]**

i) the resulting mixture is black (gray-black) and opaque ("murky")

ii) evolution of a colorless gas is evident

iii) heat is produced

iv) condensation forms on the upper walls of the flask and the bottom of the watch glass

v) gas evolution eventually subsides

3. Show all calculations - Example **(set up and solution may vary)** **[6 pts total]**

a) Balanced equation: $2H_2O_{2(aq)} \rightarrow 2H_2O_{(\ell)} + O_{2(g)}$ **[2 pts]**

b) Mass of H_2O_2 solution used = 140.693 g – 120.638 g = 20.055 g **[1 pt]**

c) Mass of oxygen gas evolved = mass of system before reaction – mass of system after
= 140.693 g – 140.118 g
= 0.575 g **[1 pt]**

d) $0.575 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.0 \text{ g } O_2} \times \frac{2 \text{ mol } H_2O_2}{1 \text{ mol } O_2} \times \frac{34.01 \text{ g } H_2O_2}{1 \text{ mol } H_2O_2} = 1.22 \text{ g } H_2O_2$ **[2 pts]**

e) Mass % H_2O_2 = $\frac{1.22 \text{ g } H_2O_2}{20.055 \text{ g soln}}$ x 100 = 6.08 % (m/m) **[see #4]**

4. The concentration of the hydrogen peroxide solution provided = _6.08_ mass %. **[2 pts; 1 of which is for correct sf]**

5. List as many sources of error as you can think of for your procedure and indicate whether each would yield a result lower than or higher than the actual concentration of the hydrogen peroxide solution. **[5 pts]**

a) Inaccurate mass of unknown hydrogen peroxide solution – if mass greater than actual, then result would be lower; if mass less than actual, then result would be higher

b) Incomplete reaction – lower result

c) Loss of liquid as vapor during the reaction – higher result

d) Student responses may vary; others may be acceptable

Lab Problem #2: **[25 points]**

Consider the reaction:

$$[Cu(H_2O)_4]^{2+}{}_{(aq)} + 4\,Cl^-{}_{(aq)} \leftrightarrows [CuCl_4]^{2-}{}_{(aq)} + 4\,H_2O_{(l)} \qquad \Delta H = \_\_\_\_$$

Prepare an initial $[Cu(H_2O)_4]^{2+}$ / $[CuCl_4]^{2-}$ equilibrium mixture by dissolving sodium chloride in 0.3*M* copper(II) nitrate solution until you observe a color change.

Devise and carry out experimental procedures to

1) **determine the sign of ΔH for this reaction, and**
2) **identify Solution A and Solution B as containing either KCl or $AgNO_3$ based on their effect on this equilibrium system.**

Answer sheet questions:

1. Give a brief description of your experimental plan.
   [3 pts]

2. Record your data and other observations. Explain each change in color that you observed, in terms of a shift in the equilibrium position of this system. **[Each = 2 + 2 pts]**
   a) When heated, the solution becomes greener in color, indicating a shift in the equilibrium position of the system toward the right.
   b) When Solution A is added, the system becomes bluer in color, indicating a shift in equilibrium position toward the left.
   c) When Solution B is added, the system becomes greener in color, indicating a shift in equilibrium position toward the right.

3. What is the color of each species in this equilibrium system? **[4 pts]**

$$[Cu(H_2O)_4]^{2+}{}_{(aq)} + 4\,Cl^-{}_{(aq)} \leftrightarrows [CuCl_4]^{2-}{}_{(aq)} + 4\,H_2O_{(\ell)}$$

blue	colorless	green	colorless

4. The sign of **ΔH** for this reaction is _+ (positive)__. **[2 pts]**

5. a) Solution A contains __$AgNO_3$___. **[2 pts]**
   b) Solution B contains ___KCl_____. **[2 pts]**