

## PRACTICE PAPERS CHEMISTRY OLYMPIADS

### STAGE – 2

#### Paper – 11 Part – C

TIME: 1HR 30MIN

MAX MARKS: 180

- Attempt all the Questions.
- All questions carry +3 for right answer and -1 for wrong answer.
- Use of Calculator is allowed.

### PERIODIC TABLE OF THE ELEMENTS

1 1A													18 8A				
1 H 1.008	2 2A												2 He 4.003				
3 Li 6.941	4 Be 9.012																
11 Na 22.99	12 Mg 24.31	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 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 78.97	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 95.95	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 (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (281)	111 Rg (272)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (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 (240)	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)				

Name: .....

Correct Questions =.....

Wrong Questions = .....

Unattempt Questions = .....

Marks = .....

## **Lab Problem 1**

US one-cent coins after and including 1983 have a thin outer copper layer with a zinc center. Modern nickels have a thin nickel coating with a zinc core. Modern dimes are a nickel-copper alloy. Japanese 1¥ coins are made of aluminum. You have been given four pennies, three nickels, three dimes, two 1¥ coins, a voltage probe, and other materials. Design and carry out an experiment to create a battery with the greatest voltage, justifying your experimental results.

## **Lab Problem 2**

You have been given a sample of solid potassium nitrate,  $\text{KNO}_3(\text{s})$ , some laboratory equipment, and access to a hot water bath and electronic balance. Using the materials and equipment provided, determine the value of  $\Delta H^\circ$  (crystallization) for potassium nitrate.

Solubility of  $\text{KNO}_3(\text{s})$  in 100. g  $\text{H}_2\text{O}$  @ 80 °C = 160. g

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -2.303RT\log K_{\text{eq}}$$

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

## **Examiner's Instructions**

### **Directions to the Examiner:**

Thank you for administering the 2011 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 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.*

*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 at all times.** Please wash off any chemicals spilled on your skin or clothing with large amounts of tap water.*

*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 to fill out all of the 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 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.



## **Lab Problem #1: Materials and Equipment**

Each student should have available the following equipment and materials:

### **Materials**

- 4 US pennies, in good condition, dated after and including the year 1983.
- 3 US nickels, in good condition, dated after and including the year 1946.
- 3 US dimes, in good condition, dated after and including the year 1965.
- 2 Japanese 1¥ coins (provided by the ACS)
- Small (approximately 5cm x 5cm) piece of sandpaper, #220 grit
- 5 circular pieces of 12.5 cm filter paper (slow, medium, or fast is fine)
- 1 voltmeter or multimeter, precise to 0.1V or better (see attached Notes).
- 1 Beral-style pipet, between 2 to 5mL capacity (stem thickness or precise capacity is not important to this experiment).
- Access to paper towels and a sink with running water.

### **Chemicals**

- A 50-mL beaker containing approximately 30 mL aqueous 1M NaCl solution ( $\text{FW} = 58.5 \text{ g}\cdot\text{mol}^{-1}$ ). This beaker should be labeled ‘NaCl(aq)’.

### **Lab Problem #1 Notes**

- Ideally, each student should have a voltmeter or multimeter. These can be found in most high school chemistry or physics stockrooms. For purchase, we recommend the listed models and their vendors. It is ideal for all of the students being tested to use the same model. As coordinator, you will be asked to provide the brand and model for the instruments used. If units are to be shared, we recommend placing the meters in a central location on the day of the exam, having students take one as needed, then return them to the central location when finished using.
- Make sure that the battery power to the unit is sufficient for student use on the day of the exam.
- Sandpaper can be obtained at most hardware stores.
- Coins should be relatively clean, but not cleaned by you – students should figure out to use the sandpaper to remove any oxidation.

**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. 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.

## **Lab Problem #2: Materials and Equipment**

Each student should have available the following equipment and materials:

### ***Materials***

- 1 glass 25-mL Pyrex® graduated cylinder, with the plastic base removed
- 1 10-mL graduated cylinder
- 1 glass stirring rod
- 1 8 oz. Styrofoam cup
- 1 plastic weigh boat
- 1 filled distilled water bottle, labeled ‘Distilled Water’
- 1 250-mL beaker
- 1 Celsius thermometer (glass, alcohol, at least 0 – 100°C range)
- Access to a hot water bath with constant temperature of 65-70°C, not higher
- Access to a digital electronic balance with 0.01 g precision or better

### ***Chemicals***

- Approximately 30 g KNO<sub>3</sub>(s) placed in the 50-mL beaker and labeled ‘KNO<sub>3</sub>(s)’.

### **Lab Problem #2 Notes:**

- **Do not provide the plastic base** to the 25-mL graduated cylinder for student use in this experiment – only the base-less graduated cylinder should be available.
- When setting up for each student, place the base-less graduated cylinder inside the 250-mL beaker, but the other smaller 10-mL graduated cylinder should remain separate.
- Share Hot Plates. We recognize that individual hot plates would be impractical for larger sections. Therefore, it is suggested to set up 3-4 250-mL beakers each with a 65-70°C hot bath on each hotplate and **label each beaker with the student’s USNCO I.D. #** for personal use. You will have to make clear to on the day of the exam that students have individual hot water baths.

**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. 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.

## Voltage/Multimeters

We prefer digital for more precise readings in this experiment. Meters should have at least 0.1V precision or better. Meters should have two wire leads and give a numerical reading. Most have settings for V and 200mV range which is sufficient for this experiment.

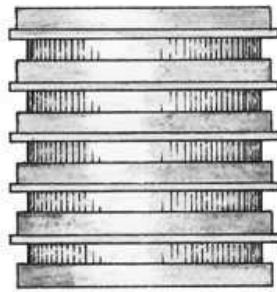
Smaller units (handheld) are better and preferred for this experiment.

Below is a list of vendors and models suggested for this experiment if you do not have access to a set for your students.

1. NASCO	(800) 585-9595	<a href="http://www.eNasco.com/science">www.eNasco.com/science</a>
Digital multimeter	S1343432M	\$9.95
Analog multimeter	SB26384M	\$9.16/5 or more
2. Flinn	(800) 452-1261	<a href="http://www.flinnsci.com">www.flinnsci.com</a>
Voltage Probe	TC1506	\$13.35
3. RadioShack	(800) 843-7422	<a href="http://www.RadioShack.com">www.RadioShack.com</a>
15-Range Digital multimeter	SS-182/Cat # 22-182	\$19.95
4. SK Science Kit & Boreal Labs	(800) 828-7777	<a href="http://www.sciencekit.com">www.sciencekit.com</a>
Digital multimeter	67310M64	\$18.50
5. Sargent Welch	(800) 727-4368	<a href="http://www.sargentwelch.com">www.sargentwelch.com</a>
Digital multimeter	WLS-3071L-53	\$17.75
6. Fisher Science Education	(800) 995-1177	<a href="http://www.fisheredu.com">www.fisheredu.com</a>
Analog voltmeters	S77819	\$18.95
7. Digital Amp Ohm Voltmeter, sold by CenTech, Palm-Size Handheld multimeter, Kaito Electronics, DT830B		<a href="http://www.amazon.com">www.amazon.com</a> \$10.98 <a href="http://www.amazon.com">www.amazon.com</a> \$6.59

## Lab Problem 1

Students had to figure out that stacking coins would lead to creating cells (a cell consisting of two differing coins in physical contact). Testing cells in stacks (known as voltaic piles, historically the first batteries) using the voltage meters gives a measure of the relative voltage of each battery.



### Sample Data:

pennies	nickels	dimes	yen	voltage (V)
4	3			0.178
3	2			0.007
2	1			0.003
	2	3		0.007
	1	2		0.007
4	3			0.012
4		3		0.261
3		2		0.055
2		1		0.002
3			2	0.398
2			1	0.339

The metal combination affects the voltage. The combination of pennies and yen make the best battery; the combination of nickels and dimes the worst. The number of coins also has an influence (for the pennies and nickels, pennies and dimes, and the pennies and yen) with the voltage increasing with the number of coins used.

## Lab Problem 2

Two general approaches are possible for this problem. Students may treat the problem as a calorimetry problem, which would involve dissolving a known mass of KNO<sub>3</sub> in a known mass of water in the Styrofoam cup and measuring the change in temperature. This is a direct approach, but is unlikely to give accurate data with the equipment provided.

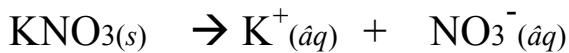
A second approach is to measure the solubility of KNO<sub>3</sub> as a function of temperature. From the variation of K<sub>sp</sub> with temperature, the  $\Delta H^\circ$  for dissolution (and hence for crystallization) can be determined. While indirect, the solubility can be measured more accurately than the heat of reaction given the equipment provided. This second approach will be described in more detail below.

### Possible Procedure

Using the 50-mL graduated cylinder, accurately weigh out about 20 g of KNO<sub>3</sub> and transfer it to the graduated cylinder. Add 15 mL of water and heat the test tube in a hot water bath, with stirring until all of the KNO<sub>3</sub> has dissolved. This volume of water is approximated from the given solubility of KNO<sub>3</sub> in 100 g water at 80°C. Remove the grad. cylinder from the water bath and record the solution volume as accurately as possible. Allow the tube to cool slowly, with gentle stirring. Record the temperature when crystals first appear in the solution. It will be assumed that at this temperature we have a saturated solution in equilibrium with solid. Add about 5 mL of water from the graduated cylinder to the test tube and warm the mixture until the solid has all dissolved. Record the new volume of the solution and allow it to cool to obtain the temperature at which the crystals appear. Repeat this cycle of adding measurements until a crystallization temperature near room temperature is reached. It should be possible to record at least three different descending temperatures at which crystallization occurs.

### Calculations

Because KNO<sub>3</sub> is a strong electrolyte its solution reaction will be:



The reaction may be considered to be at equilibrium when the solid is in contact with a saturated solution, just the condition we have when crystallization begins. The solubility, s, of the salt in moles per liter may be calculated from the amount of salt, weighed out and the volume of the solution. The equilibrium constant,  $K_{\text{eq}}$ , for the reaction will be:

$$K_{\text{eq}} = [\text{K}^+] [\text{NO}_3^-] = (s)(s) = s^2$$

The equilibrium constant,  $K_{\text{eq}}$ , may be used to calculate the  $\Delta G^\circ$  for the reaction at each temperature using the following relationship,

$\Delta G^\circ = -2.303RT\log K_{\text{eq}}$ , where T is the absolute temperature in Kelvin and R is the gas constant (8.314 J/K mol). The variation of  $K_{\text{eq}}$  with temperature is such that if a plot of  $\ln K_{\text{eq}}$  (y-axis) vs.  $1/T$  (x-axis) is made, the result is a nearly straight line with the slope =  $-\Delta H^\circ/R$ . Construct this graph, measure the slope of the line and determine the value of  $\Delta H^\circ$  for the reaction.

Calculations include the following:

- a. Using the mass of  $\text{KNO}_3$  and the volume calculate the molar solubility at each temperature where crystallization was observed.
- b. Find the  $K_{\text{eq}}$  at each temperature.
- c. Find a single value of  $\Delta H^\circ$  from the graph (the  $\Delta H^\circ$  is nearly constant over a small range of temperatures).

#### Sample Data:

Trial 1: 10 g  $\text{KNO}_3$  in 12.5 mL  $\text{H}_2\text{O}$ , 15 mL total volume, crystallized at  $60^\circ\text{C}$   
Solubility equivalent to 67 g  $\text{KNO}_3$  in 100 mL solution at this temperature

Trial 2: added 5 mL  $\text{H}_2\text{O}$  = 17.5 mL  $\text{H}_2\text{O}$ , 20 mL total, crystallized at  $55^\circ\text{C}$   
Solubility equivalent to 50 g  $\text{KNO}_3$  in 100 mL solution at this temperature

Trial 3: added 5 mL  $\text{H}_2\text{O}$  = 22.5 mL  $\text{H}_2\text{O}$ , 25 mL total, crystallized at  $50^\circ\text{C}$

Solubility equivalent to g KNO<sub>3</sub> in 100 mL solution at this temperature

- 1) At this temperature, 67 g KNO<sub>3</sub> = 0.66 mol/0.100L = 6.6M
- 2) At this temperature, 50 g KNO<sub>3</sub> = 0.50 mol/0.100L = 5.0 M
- 3) At this temperature, 38 g KNO<sub>3</sub> = 0.38 mol/0.100L = 3.8M

$$K_{eq} = (s)(s) = s^2;$$

- 1)  $K_{eq} = 43.6; \ln(43.6) = 3.77; 1/T = 0.00300$   
 $\Delta G^\circ = -(8.314 \text{ J/K mol})(333 \text{ K})(3.77) = -10,400 \text{ J/mol} = -10.4 \text{ kJ/mol}$
- 2)  $K_{eq} = 25; \ln(25) = 3.22; 1/T = 0.00305$   
 $\Delta G^\circ = -(8.314 \text{ J/K mol})(328 \text{ K})(3.22) = -8800 \text{ J/mol} = -8.8 \text{ kJ/mol}$
- 3)  $K_{eq} = 14.4; \ln(14.4) = 2.67; 1/T = 0.00309$   
 $\Delta G^\circ = -(8.314 \text{ J/K mol})(318 \text{ K})(2.67) = -7200 = -7.2 \text{ kJ/mol}$

To determine  $\Delta H^\circ$  the points  $\ln K_{eq}$  (y-axis) and  $1/T$  (x-axis) can be plotted where  $-\Delta H^\circ/R$  represents the slope:

- 1)  $\ln K_{eq} = 3.77, 1/T = 0.00300 ; (0.00300, 3.77)$
- 2)  $\ln K_{eq} = 3.22, 1/T = 0.00305 ; (0.00305, 3.22)$
- 3)  $\ln K_{eq} = 2.67, 1/T = 0.00309 ; (0.00309, 2.67)$

$$\Delta y/\Delta x = -\Delta H^\circ/R = -1.10/0.000093 \text{ K} = -11800 \text{ K}^{-1}$$
$$\Delta H^\circ = -(8.314 \text{ J/mol}\cdot\text{K})(-11800 \text{ K}^{-1}) = +98000 \text{ J/mol} = +98 \text{ kJ/mol}$$

Thus,  $\Delta H^\circ$  (*crystallization*) for KNO<sub>3</sub> from these data = -98 kJ/mol

**Accepted value for the heat of solution =  $-\Delta H^\circ_{\text{crystallization}} = 34.9 \text{ kJ/mol}$**