2011 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

Steve Lantos, **Chair**, *Brookline High School*, Brookline, MA

Linda Weber, *Natick High School*, Natick, MA

John Mauch, *Braintree High School*, Braintree, MA

Mathieu Freeman, *Greens Farms Academy*, Greens Farms, CT

Anthony Erling, *Arrowhead Union High School*, Hartland, WI

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. You may carry out the two tasks in any order you 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 problems**	**laboratory practical**	**1 hour, 30 minutes**

Students should be permitted to use non-programmable scientific calculators.

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.

2011 U.S. 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

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, $KNO_3(s)$, some laboratory equipment, and access to a hot water bath and electronic balance. Using the materials and equipment provided, determine the value of $\Delta H^\circ_{\text{(crystallization)}}$ for potassium nitrate.

Solubility of $KNO_3(s)$ in 100. g H_2O @ 80 °C = 160. g

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

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

Answer Sheet for Laboratory Practical **Problem 1**

Student's Name: ____

Student's School: ______________________________________ **Date:** _________________________

Proctor's Name: ____

ACS Section Name: ______________________________ **Student's USNCO ID #:** _______________

1. Give a brief description of your experimental plan.

2. Data and Observations.

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

3. Analysis and Conclusions. Describe your optimal battery and justify why this battery outp[illegible]her possibilities.

Answer Sheet for Laboratory Practical **Problem 2**

Student's Name: ____

Student's School:_________________________ **Date:** __________________

Proctor's Name: ____

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

1. Give a brief description of your experimental plan.

2. Data and Observations.

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

3. Calculations.

4. Conclusion. The $\Delta H^\circ_{(crystallization)}$ for KNO_3 =

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

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

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

$1\ F = 96{,}500\ \text{C•mol}^{-1}$

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

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

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

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

$0\ °C = 273.15\ K$

EQUATIONS

$$E = E^{\circ} - \frac{RT}{nF}\ln Q$$

$$\ln K = \left(\frac{-\Delta H}{R}\right)\left(\frac{1}{T}\right) + \text{constant}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (277)	113 (Uut)	114 (Uuq)	115 (Uup)	116 (Uuh)	117 (Uus)	118 (Uuo)

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)

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American Chemical Society
U.S. National Chemistry Olympiad
1155 Sixteenth Street N.W.
Washington, DC 20036
Telephone: 1-800-227-5558 ext. 6328
E-mail: USNCO@acs.org
www.acs.org/olympiad

CELEBRATE THE INTERNATIONAL YEAR OF CHEMISTRY!

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2011 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 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.*

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 instru n. **Part III** contains student instructions and answer sheets for both laboratory problems. There table on the last page of the booklet. Allow students enough time to read the brief cover directio

Do not turn to page 2 until directed to do so. When you start to work, be sure to fill out all o 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 form **Part III,** the Scantron sheets from **Part I,** and the 'Blue Books" from **Part II** in the overnight return envelope you were provided to this address:

American Chemical Society
U.S. National Chemistry Olympiad Office
1155 16th Street, NW
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 copy of the tracking number to allow you to track your shipment.

Wednesday, April 20, 2011, 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 ***Tuesday, April 19, 2011*** for it to arrive on time.

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

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 1*M* NaCl solution (FW = 58.5 g•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_3(s) placed in the 50-mL beaker and labeled ‘KNO_3(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 … r better. Meters should have two wire leads and give a numerical reading. Most have settings for V … 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 www.eNasco.com/science
   Digital multimeter S1343432M $9.95
   Analog multimeter SB26384M $9.16/5 or more

2. Flinn (800) 452-1261 www.flinnsci.com
   Voltage Probe TC1506 $13.35

3. RadioShack (800) 843-7422 www.RadioShack.com
   15-Range Digital multimeter SS-182/Cat # 22-182 $19.95

4. SK Science Kit & Boreal Labs (800) 828-7777 www.sciencekit.com
   Digital multimeter 67310M64 $18.50

5. Sargent Welch (800) 727-4368 www.sargentwelch.com
   Digital multimeter WLS-3071L-53 $17.75

6. Fisher Science Education (800) 995-1177 www.fisheredu.com
   Analog voltmeters S77819 $18.95

7. Digital Amp Ohm Voltmeter, sold by CenTech, www.amazon.com $10.98
   Palm-Size Handheld multimeter, Kaito Electronics, DT830B www.amazon.com $6.59

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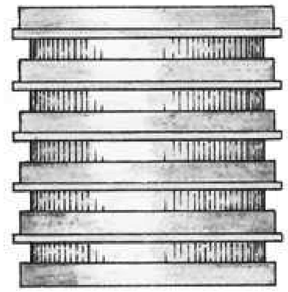
2011 USNCO Part III Answers

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 relativel 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 KNO3 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 KNO3 as a function of temperature. From the variation of Ksp with temperature, the ΔH^o 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_3 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_3 has dissolved. This volume of water is approximated from the given solubility of KNO_3 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_3 is a strong electrolyte its solution reaction will be:

$KNO_{3(s)} \rightarrow K^{+}_{(\hat{a}q)} + NO_3^{-}{}_{(\hat{a}q)}$

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_{eq}, for the reaction will be:

$K_{eq} = [K^{+}]\ [NO_3^{-}] = (s)\ (s) = s^2$

The equilibrium constant, K_{eq}, may be used to calculate the ΔG° for the reaction at each temperature using the following relationship,
$\Delta G^{\circ} = -2.303RT\log K_{eq}$, where T is the absolute temperature in Kelvin and R is the gas constant (8.314 J/K mol). The variation of K_{eq} with temperature is such that if a plot of $\ln K_{eq}$ (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 ΔH° for the reaction.

Calculations include the following:

a. Using the mass of KNO_3 and the volume calculate the molar solubility at each temperature where crystallization was observed.
b. Find the K_{eq} at each temperature.
c. Find a single value of ΔH^{o} from the graph (the ΔH° is nearly constant over a small range of temperatures).

Sample Data:

Trial 1: 10 g KNO_3 in 12.5 mL H_2O, 15 mL total volume, crystallized at 60°C
Solubility equivalent to 67 g KNO_3 in 100 mL solution at this temperature

Trial 2: added 5 mL H_2O = 17.5 mL H_2O, 20 mL total, crystallized at 55°C
Solubility equivalent to 50 g KNO_3 in 100 mL solution at this temperature

Trial 3: added 5 mL H_2O = 22.5 mL H_2O, 25 mL total, crystallized at 50°C

Solubility equivalent to g KNO_3 in 100 mL solution at this temperat

1) At this temperature, 67 g KNO_3 = 0.66 mol/0.100L = 6.6M
2) At this temperature, 50 g KNO_3 = 0.50 mol/0.100L = 5.0 M
3) At this temperature, 38 g KNO_3 = 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
   ΔG^o = -(8.314J/K mol)(333K)(3.77) = -10,400 J/mol = -10.4 -10.4 kJ/mol

2) K_{eq} = 25; ln(25) = 3.22; 1/T = 0.00305
   ΔG^o = (8.314J/K mol)(328K)(3.22) = -8800 J/mol = -8.8 kJ/mol

3) K_{eq} = 14.4; ln(14.4) = 2.67; 1/T = 0.00309
   ΔG^o = -(8.314J/K mol)(318K)(2.67) = -7200 = -7.2 kJ/mol

To determine ΔH^o 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, 3.32)
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 K = -11800 K^{-1}
ΔH° = -(8.314 J/mol·K)(-11800 K^{-1}) = +98000 J/mol = = +98 kJ/mol

Thus, ΔH^o (*crystallization*) for KNO_3 from these data = -98 kJ/mol

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