1999 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM—PART II

Prepared by the American Chemical Society Olympiad Examinations Task Force

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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 26, 1999, 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**	**1 hour, 30 minutes**
Part II	**8 questions**	**problem-solving, explanations**	**1 hour, 45 minutes**
Part III	**2 questions**	**laboratory practical**	**1 hour, 15 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 you 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® 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.

Not valid for use as an USNCO National Examination after April 26, 1999.

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1. (14%) A certain compound contains only C, H, and N. Combustion of 0.125 g of this compound produces 0.172 g of H_2O and 0.279 g of CO_2.

a. Calculate the number of moles of CO_2 and H_2O.

b. Find the mass percentages of C, H, and N and the empirical formula of this compound.

c. Assume the empirical formula is also the molecular formula. Draw structural formulas for the four different isomers that are possible for a compound with this formula.

d. The four compounds have boiling points that range from 3 °C to 48 °C. Identify the isomers that you would expect to exhibit the lowest and highest boiling points. Explain your reasoning in terms of the intermolecular forces involved.

2. (14%) A 0.495 M solution of nitrous acid, HNO_2, has a pH of 1.83.

a. Find the $[H^+]$ and the percent ionization of nitrous acid in this solution.

b. Write the equilibrium expression and calculate the value of K_a for nitrous acid.

c. Calculate the pH of the solution formed by adding 1.0 g of $NaNO_2$ (molar mass = 69.0 g·mol^{-1}) to 750 mL of 0.0125 M solution of nitrous acid.

d. Determine the pH of a solution formed by adding 1.0 g of $NaNO_2$ to 750 mL of water, H_2O.

e. Sketch the pH curve that results when 20.0 mL of a 0.0125 M nitrous acid solution is titrated with 0.0125 M NaOH solution. Label the axes, the equivalence point, and the buffer region clearly.

3. (11%) The first step in the production of high purity silicon for semiconductors is represented by this equation.

$$SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g) \qquad \Delta H^o = +689.9 \text{ kJ}$$

a. Calculate ΔH_f^o for SiO_2. Given: ΔH_f^o for CO = –110.5 kJ·mol^{-1}

b. Find ΔS_{rxn} for the production of pure silicon. Given: S^o for C = 5.7 J·K^{-1}·mol^{-1}, for CO is 197.6 J·K^{-1}·mol^{-1}, for Si = 18.8 J·K^{-1}·mol^{-1}, and for SiO_2 = 41.8 J·K^{-1}·mol^{-1}

c. Determine ΔG^o for the reaction at 25 °C.

d. Find the minimum temperature in °C at which this reaction is spontaneous. Assume that ΔH^o and ΔS^o do not vary with temperature.

4. (11%) Water is electrolyzed by passing a current of 0.500 amps through 1.00 L of 1.00 M Na_2SO_4 solution for 120 minutes. One gas is collected at the anode and a different gas is collected at the cathode.

a. Write the balanced equation for the cathode half-reaction.

b. Find the number of moles of gas produced at the cathode and calculate the volume in liters it occupies as a dry gas at a pressure of 745 mmHg and 25.0 °C.

c. Determine the pH of the solution in the cathode chamber after the electrolysis was stopped. Assume that the volume of the cathode chamber is 500 mL.

d. Give the formula for the gas produced at the anode and predict the volume of this gas produced during the electrolysis. Outline your reasoning.

5. (14%) Write net equations for each of these reactions. Use ionic and molecular formulas, as appropriate, for the reactants and products. Omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the reactions. All reactions occur in aqueous solution unless otherwise indicated.

a. Excess sulfuric acid is added to solid sodium sulfite.

b. Solid calcium carbonate is heated strongly.

c. Lithium nitride is added to water.

d. Concentrated hydrochloric acid is added to a solution of sodium hypochlorite.

e. Solutions of lead(II) acetate and hydrobromic acid are mixed.

f. Excess concentrated ammonia is added to a solution of zinc chloride.

g. A mixture of acidified potassium dichromate and ethanol is heated.

(**Note:** Some of these reactions are extremely hazardous. Do not attempt to verify your predictions by experimentation when you return to your high school.)

6. (12%) Consider the reaction **A** → **B**. The initial [**A**] is 0.10 M. After 1.0 hour, 50% of **A** has reacted.

a. Draw a a graph of concentration vs. time for each of the cases below. Use these graphs to predict how much **A** will be left after 2.0 hours for each case.

i. The reaction is zero order in **A**.

ii. The reaction is first order in **A**.

b. Predict what the concentration of **A** will be after 2.0 hours for each case in part a if the initial [**A**] were 0.050 M. Explain your reasoning.

7. (14%) Consider the molecules BF_3, NF_3, and IF_3. Answer these questions for ***each*** molecule.

a. Write a Lewis electron dot structure, showing all valence electrons.

b. Predict the geometry, including all bond angles.

c. State whether the molecule is polar or nonpolar, outlining your reasoning.

d. Discuss the possible Lewis acid-base behavior.

8. (10%) Account for each of these observations about metals in terms of the properties of atoms and ions.

a. Metals conduct electricity well but nonmetals do not. Semiconductors conduct to an intermediate degree.

b. The electrical conductivity of a metal (such as iron) decreases with increasing temperature, but the electrical conductivity of a semiconductor (such as silicon) increases with increasing temperature.

c. Iron objects corrode when exposed to water and oxygen, but not when they are kept dry. Aluminum objects do not appear to corrode under either of these conditions.

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

CONSTANTS

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

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

$1\ F = 96{,}500\ C{\cdot}mol^{-1}$

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

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

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

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

PERIODIC TABLE OF THE ELEMENTS

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** 181.0	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** 226.0	89 **Ac** 227.0	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 (269)	111 (272)	112 (277)		114 (289)				

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** 237.0	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** (260)

USNCO PART II – 1999
Answers to Part II

1.a. Moles H_2O = 0.172g x $\frac{1\,mol}{18.0\,g}$ = 9.56×10^{-3} mol H_2O

Moles CO_2 = 0.279g x $\frac{1\,mol}{44.0\,g}$ = 6.34×10^{-3} mol CO_2

b. Grams CO_2= 6.34×10^{-3} mol CO_2 = 6.34×10^{-3} mol C x $\frac{12.01\,g}{mol}$ = 0.0761g

Grams H_2O = 9.56×10^{-3} mol H_2O = 0.191 mol H x $\frac{1.008\,g}{mol}$ = 0.0193g

Sum of hydrogen and carbon in the compound = 0.0761g + 0.0193g = 0.0954g, the remainder must be nitrogen.

Grams N = 0.125g – 0.0954g = 0.0296g N

% C = $\frac{0.0761\,g}{0.125\,g} x100$ = 60.9%   60.9g x $\frac{1 mol}{12.01\,g}$ = $\frac{5.07\,g}{1.69\,g} \approx 3$

% H = $\frac{0.0193\,g}{0.125\,g} x100$ = 15.4%   15.4g x $\frac{1 mol}{1.008\,g}$ = $\frac{15.28\,g}{1.69\,g} \approx 9$

% N = $\frac{0.0296\,g}{0.125\,g} x100$ = 23.7%   23.7g x $\frac{1 mol}{14.01\,g}$ = $\frac{1.69\,g}{1.69\,g} \approx 1$

Answer = C_3H_9N

c. C-C-C-N   C-C-N-C   C–C–C (N on middle C)   C–N–C (C on N)

d. C–N–C (C on N) Should be the lowest as it has the least amount of hydrogen bonding.

C-C-C-N Should be the highest, as it is a primary amine and has the most hydrogen bonding.

2.a. pH = 1.83 $[H^+] = 1.48 \times 10^{-2}$

Percent ionized = $\frac{0.0148}{0.495}$ x 100 = 3.0%

b. Ka = $\frac{[H^+][NO_2^-]}{[HNO_2]}$ = $\frac{(1.48 \times 10^{-2})^2}{0.495} = 4.43 x10^{-4}$

Answer if ionized acid is subtracted

$\frac{(1.5 \times 10^{-2})^2}{0.48} = 4.7 x10^{-4}$

c. 1.0g $NaNO_2$ x $\frac{1 mol}{69.0\,g}$ = $\frac{0.0145\,mol\ NO_2^-}{0.750\,L} = 0.0193\,M\ NO_2^-$

$4.43 \times 10^{-4} = \frac{[H^+][0.0193]}{0.0125}$ $[H^+] = 2.87 \times 10^{-4}$ pH = 3.54

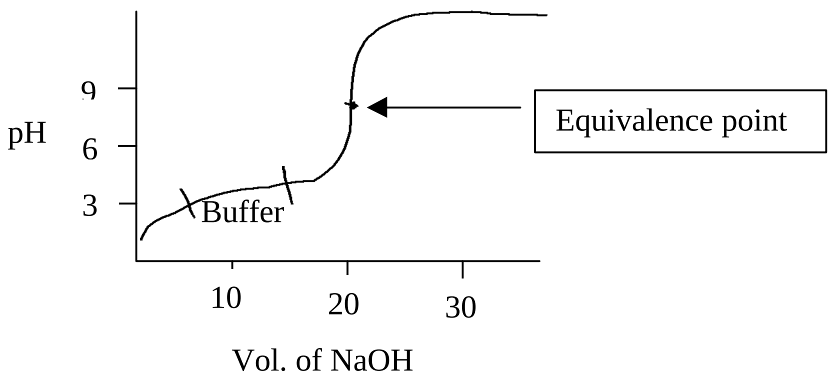
| 4.7×10^{-3} | 3.0×10^{-4} | 3.50 |

USNCO PART II – 1999
Answers to Part II

d. NO_2^- + H_2O $\leftrightarrow$ HNO_2 + OH- K= $\frac{1x10^{-14}}{4.43\,x10^{-4}} = 2.26x10^{-11}$

$2.26 \text{ x } 10^{-11} = \frac{[HNO_2][OH^-]}{0.0193}$ $[OH\text{-}]^2 = 4.36 \text{ x } 10^{-13}$ $[OH^-]= 6.6 \text{ x } 10^{-7}$

pOH = 6.18 pH = 7.82



3a. $\Delta H°_{rxn} = 2\Delta H_f CO - \Delta H_f SiO_2$

$689.9 = 2(-110.5) - \Delta H_f SiO_2$

$\Delta H_f SiO_2 = -221-689.9 = -910.9$ kJ

b. $\Delta S°_{rxn} = 18.8 + 2(197.6) – [2(5.7) + 41.8] = 360.8$ J/K

c. $\Delta G° = 689.9$ kJ – 298 K (0.3608 kJ) = 582.4 kJ

d. 689.9= 0.3608 T

$T = \frac{689.9}{0.3608} = 1912 K or (1639^o C)$

4.a. $2H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$

b. 0.500 amps x 120 minutes x $\frac{60 \text{ sec}}{1 \text{ min}}$. = 3600 C

3600 C x $\frac{1\,F}{9,500}$ = 0.03737 x $\frac{1\,mol\ H_2}{2\,F}$ = 0.0186 mol H_2

PV=nRT $V= \frac{(0.0186\ mol)(0.0821\ L \bullet atm\ /\ mol \bullet K)298\,K}{(745\ /\ 760\ )\ atm}$ V= 0.464L

c. $\frac{0.0373\ mol\ OH^-}{0.50\ L} = 0.0746\ M$ pOH = 1.13 pH= 12.87

d. O_2 is produced at the anode. Volume will be 0.0232 L

It takes twice as much electricity to produce 1 mole of O_2 as one mole of H_2.

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ therefore volume will be 1/2.

5. a. $2\ H^+ + Na_2SO_3 \rightarrow 2\ Na^+ + SO_2 + H_2O$

b. $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

c. $Li_3N + 3\ H_2O \rightarrow NH_3 + 3\ Li^+ + 3\ OH^-$

d. $2\ H^+ + Cl^- + OCl- \rightarrow Cl_2 + H_2O$ (HOCl)

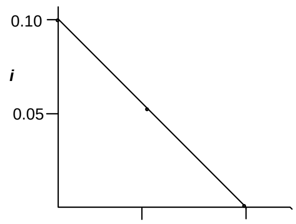
e, $Pb^{2+} + 2\ Br^- \xrightarrow{C_2H_3O_2^-,\,H^+} PbBr_2 + HC_2H_3O_2$

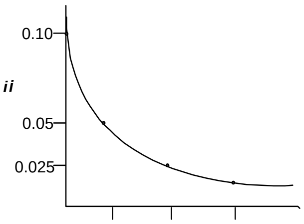
f. $4\ NH_3 + Zn^{2+} \rightarrow Zn(NH_3)_4^{2+}$

g. $Cr_2O_7^{2}- + H^+ + C_2H_5OH \rightarrow 2\ Cr^{3+}\ CH_3COOH + H_2O$

USNCO PART II – 1999
Answers to Part II

6.a.



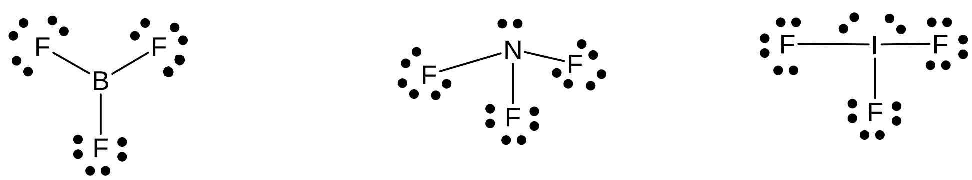


A zero order reaction will have no A left after 2.0 hours. The [A] will be 0.025 M after 2.0 hours. The [A] = 0.025 M after 2.0 hours.

b. The [A] = 0 after 2.0 hours for the zero order reaction because k = 0.05 $\frac{M}{L \ x \ h}$

The [A] = 0.0125 for the first order reaction. Half-life is 1 hr, therefore 2.0 hours represents 2 half-lives. At time zero the conc. is 0.05, after one half-life 0.025 and after two half-lives 0.0125 M.

7. a.



b. Trigonal planar 120° Trigonal pyramidal <107°, T-shaped 90° (or a little less).
c. nonpolar (bond moments cancel), polar (bond dipoles don't cancel), polar (bond dipoles don't cancel.)
d. Lewis acid, Lewis base, Lewis acid.

8.a. Metals consist of cations in a sea of mobile electrons that can carry current. Nonmetal electrons are held in localized covalent bonds. Semiconductors have a few mobile electrons.
b. When a metal is heated, cations vibrate and interfere with the electron movement. When a semiconductor is heated, more electrons are freed to move through the lattice.
c. Iron corrodes because of an electrochemical reaction that requires H_2O and O_2. Aluminum forms a thin oxide coating that prevents further reaction.