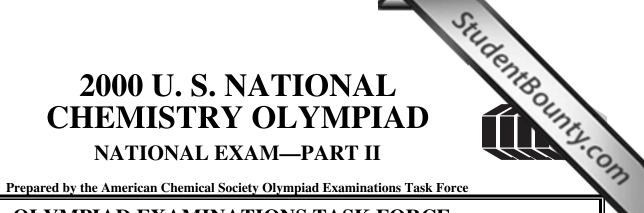


2000 U.S. NATIONAL **CHEMISTRY OLYMPIAD**

NATIONAL EXAM—PART II



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 16, 2000, 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 lab problems	laboratory practical	1 hour, 30 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 your 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.

- 1. (12%) An unknown metal, **M**, reacts with excess chlorine to give the metal chloride, **MCl**_x. When 0. chloride is dissolved in water and passed through an anion exchange column charged with hydroxide is solution requires 23.55 mL of 0.195 M HCl for neutralization.
 - a. Calculate the number of moles of HCl used in the titration.
 - **b.** Determine the mass of chlorine and the mass of metal in this sample of MCl_x .
 - **c.** Assuming that x in MCl_x is 1, 2 or 3, calculate possible atomic masses for M.
 - **d.** Use your knowledge of the Periodic Table to write formulas for the possible compounds between chlorine and metals and identify those expected to be stable.
- 2. (11%) The ionization constant for water is 1.14×10^{-15} at 0 °C and 9.6×10^{-14} at 60 °C.
 - a. Write the equation for the ionization of water and determine the pH of water at 60 °C.
 - **b.** Calculate each value.
 - i. $\Delta H_{\text{ionization}}$ over this temperature range
 - ii. ΔG at 60 °C
 - iii. ΔS at 60 °C
 - **c.** State the significance of the sign of the sign of ΔS obtained in part **2b.iii**, and explain how the process indicated in **2a** could lead to this sign.
- **3.** (15%) These are the reaction steps in a certain polymerization process, which may occur by either an uncatalyzed or an acid-catalyzed pathway.

- **a.** Write a balanced equation for the overall reaction.
- **b.** Name the functional groups labeled [1], [2], and [3].
- **c.** Given these data for the acid-catalyzed reaction, find the rate law and the value of k, specifying its units.

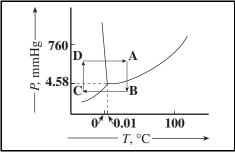
[RCOOH], M	[R′OH], M	[HA], M	Initial Rate, M·min ⁻¹	
0.35	0.35	0.50	4.60	
0.62	0.35	0.50	8.14	
0.35	0.81	0.50	10.6	
0.35	0.50	0.75	9.84	

- **d.** Identify the rate-determining step based on the rate law found in question 3c. Explain your answer.
- e. The initial reaction rate can be followed spectrophotometrically by quenching the reaction and determining the amount of ROH left by its reaction with dichromate ion, $Cr_2O_7^{2-}$.
 - **i.** Write a balanced equation for the reaction of $Cr_2O_7^{2-}$ with R'OH in acid solution. Assume R' is CH_3CH_2 and the products of the reaction are Cr^{3+} and CH_3COOH .
 - ii. Describe the color change expected for the reaction written in question 3e, part i.

Student Bounty.com (12%) 25.00 mL of a solution of a weak monoprotic acid, HX, was titrated with a 0.0640 M solution of requiring 18.22 mL. The pH of the solution varied as a function of the percentage of HX titrated. These were collected.

% titrated	0	33.3%	66.7%		
рН	3.39	5.14	5.74		

- a. Calculate the initial concentration of the weak acid in the 25.00 mL of solution.
- **b.** Determine the value of K_a for two of these three conditions.
- c. Calculate the pH at the equivalence point of this titration and write an equation to account for this pH.
- d. Calculate the number of moles of a salt, NaX, that must be added to produce a pH of 6.00 in 150.00 mL of the original solution.
- (14%) Write net equations for each of these reactions. Use appropriate ionic and molecular formulas for the reactants and products and 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. Phosphorus is burned in excess oxygen.
 - **b**. Sulfur dioxide is bubbled into water.
 - **c.** Chlorine gas is bubbled through a sodium bromide solution.
 - **d**. Solutions of magnesium nitrate and potassium hydroxide are mixed.
 - **e.** A sodium thiosulfate solution is added to a suspension of silver chloride.
 - **f.** Bromine is added to a solution of ethylene in hexane.
 - g. Radium-226 emits an alpha particle.
- 6. (12%) Nitrogen dioxide, NO₂, can undergo reactions to form nitrite ion, NO₂⁻, and nitronium ion, NO₂⁺.
 - **a.** Draw Lewis structures for NO₂⁻ and NO₂⁺ including any resonance forms.
 - **b.** Predict the shape of each ion and account for each shape using a modern bonding theory.
 - c. Describe and account for the difference in the N-O bond lengths in NO₂⁻ and NO₂⁺.
 - **d.** Determine the oxidation number and the formal charge of nitrogen in the NO₂ ion. Outline your reasoning and state the difference between formal charge and oxidation number.
- 7. (12%) Use the given phase diagram of water to answer these questions. Note that the axis values are not drawn to scale.
 - a. Identify the physical state at points A, B, C, and D.
 - **b.** Calculate the volume of one mole of water in each of the phases at the triple point, (At the triple point, the density of $H_2O(l)$ is $0.9998 \text{ g} \cdot \text{mL}^{-1}$ and the density of $H_2O(s)$ is $0.917 \text{ g} \cdot \text{mL}^{-1}$.)
 - c. Starting with point A, describe the pressure, temperature, and phase changes that correspond to the rectangle around the triple point.



- (12%) The behavior of elements can often be predicted based on their positions in the Periodic Table. Use your 8. knowledge about trends in the behavior of elements to answer the following questions about the recently isolated elements 114, 116 and 118.
 - a. Give the names and symbols of the elements in the row above 114, 116, and 118 in the Periodic Table.
 - b. Predict the relative ionization energies of elements 114, 116, and 118 and describe how the ionization energy of one of them is expected to compare with the ionization energy of the element above it, giving reasons for your answers.
 - c. Predict the oxidation states expected for element 114 and indicate which oxidation state is expected to be most stable, giving reasons for your answers.
 - d. Suggest a reason that elements 114, 116, and 118 have been made, but elements 113, 115, and 117 have not.

END OF PART II

ABBREVIATIONS AND SYMBOLS amount of substance equilibrium constant milli- prefix m ampere Α Faraday constant F molal matmosphere atm formula molar mass M molar M atomic mass unit u free energy Gmole mol atomic molar mass \boldsymbol{A} frequency Planck's constant h $^{N_{ m A}}$ $^{\circ}{ m C}$ Avogadro constant gas constant R pressure P gram Celsius temperature rate constant kg centi- prefix hour h second S \mathbf{C} coulomb joule J speed of light cTEelectromotive force kelvin K temperature, K $E_{\rm a}$ Henergy of activation kilo- prefix k time enthalpy liter volt V entropy measure of pressure mmHg volume

CONSTANTS $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ $R = 0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ $1 F = 96,500 \text{ C} \cdot \text{mol}^{-1}$ $1 F = 96,500 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1}$ $N_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1}$ $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ $c = 2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}$

USEFUL EQUATIONS
$$E = E^{o} - \frac{RT}{nF} \ln Q \qquad \qquad \ln K = \left(\frac{-\Delta H}{R}\right) \left(\frac{1}{T}\right) + c$$

PERIODIC TABLE OF THE ELEMENTS

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	4.003 10 Ne
6.941	9.012											10.81	12.01	14.01	16.00	19.00	20.18
11	12											13	14	15	16	17	18
Na 22.99	Mg 24.31											Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45	Ar 39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K 39.10	Ca 40.08	Sc 44.96	Ti 47.88	V 50.94	Cr 52.00	Mn 54.94	Fe 55.85	Co 58.93	Ni 58.69	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.61	As 74.92	S e 78.96	Br 79.90	Kr 83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc (98)	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	Xe 131.3
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs 132.9	Ba 137.3	La 138.9	Hf 178.5	Ta 181.0	W 183.8	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197.0	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po (209)	At (210)	Rn (222)
87	88	89	104	105	106	107	108	109	110	111	112						
Fr (223)	Ra 226.0	Ac 227.0	Rf (261)	Db (262)	Sg (263)	Bh (262)	Hs (265)	Mt (266)	(269)	(272)	(277)						

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce 140.1	Pr 140.9	Nd 144.2	Pm (145)	Sm 150.4	Eu 152.0	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0	Lu 175.0
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th 232.0	Pa 231.0	U 238.0	Np 237.0	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (260)

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2000 U. S. NATIONAL CHEMISTRY OLYMPIAD

KEY for NATIONAL EXAM—PART II

1. a.
$$0.02355 \text{ L HCl} \times \frac{0.195 \text{ mol}}{\text{L}} = 0.00459 \text{ mol H}^+ = 0.00459 \text{ mol Cl}^-$$

b.
$$0.00459 \text{ mol Cl}^- \times \frac{35.45 \text{ g}}{\text{mol}} = 0.163 \text{ g Cl}^-$$

0.396 g MCl - 0.163 g Cl⁻ = 0.233 g ×
$$\frac{1}{0.00459 \text{ mol}}$$
 = $\frac{50.8 \text{ g}}{\text{mol}}$
0.396 g MCl₂ - 0.163 g Cl⁻ = 0.233 g × $\frac{1}{0.00230 \text{ mol}}$ = $\frac{101.3 \text{ g}}{\text{mol}}$
0.396 g MCl₃ - 0.163 g Cl⁻ = 0.233 g × $\frac{1}{0.00153 \text{ mol}}$ = $\frac{152.3.3 \text{ g}}{\text{mol}}$

c.
$$50.8 \text{ g} \cdot \text{mol}^{-1}$$
 most likely V VCl unlikely to be stable $101.3 \text{ g} \cdot \text{mol}^{-1}$ most likely Ru RuCl₂ stable

2. **a.**
$$H_2O \rightarrow H^+ + OH^ [H^+] = \sqrt{9.6 \times 10^{-14}} = 3.1 \times 10^{-7}; \text{ pH} = 6.51$$

b. i.
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$\ln\left(\frac{9.6 \times 10^{-14}}{1.14 \times 10^{-15}}\right) = \frac{\Delta H}{8.314} \left(\frac{1}{273} - \frac{1}{333}\right)$$

$$\ln 84.2 = \frac{\Delta H}{8.314} (0.003663 - 0.003003); \ \frac{4.43 (8.314)}{0.000660} = \Delta H$$

$$\Delta H = 5.58 \times 10^4 \text{ J or } 55.8 \text{ kJ}$$

ii.
$$\Delta G = -RT \ln K = (-8.314)(333) \ln(9.6 \times 10^{-14}) = 8.30 \times 10^4 \text{ J}$$

iii.
$$\Delta G = \Delta H - T\Delta S$$
; $\Delta S = \frac{8.30 \times 10^4 - 5.58 \times 10^4}{-333} = -81.7 \text{ J}$

c. The negative sign corresponds to an increase in order. An increase in order can result from the H^+ and OH^- ions structuring the H_2O molecules around them.

3. a.
$$RCOOH + R'OH \rightarrow RCOOR' + H_2O$$

Functional group II – hydroxyl group (alcohol)

Functional group **III** – ester

c.
$$\frac{8.14}{4.60} = 1.77$$
 $\frac{0.62}{0.35} = 1.77$ RCOOH is first order.

$$\frac{10.6}{4.60} = 2.30$$
 $\frac{0.81}{0.35} = 2.30$ R'OH is first order.

Student Bounty.com Trials 1 and 4 can be used to determine the order with respect to HA. [RCOOH] is held constant; however, both [R'OH] and [HA] vary. The effect of [R'OH] is:

$$\frac{0.50 \text{ M}}{0.35 \text{ M}} = 1.43$$
 and then $(1.43)(4.60) = \frac{6.57 \text{ M}}{\text{min}}$

The effect of [HA] is
$$\frac{9.84}{6.57} = 1.50$$
 $\frac{0.75}{0.50} = 1.50$ HA is first order

Rate =
$$k[RCOOH][R'OH][HA]$$

$$\frac{4.60 \text{ M}}{\text{min}} = k (0.35\text{M}) (0.35\text{M}) (0.50\text{M})$$

$$k = 75 \text{ M}^{-2} \cdot \text{min}^{-1}$$

- d. Rate determining step could be either:
 - Step 2 that involves R'OH and product from the reaction of RCOOH and HA, or
 - Step 3 that involves the breakup of product in step 2.
- $2Cr_2O_7^{2-} + 3CH_3CH_2OH + 16H^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$ e. i.
 - The color will change from orange $(Cr_2O_7^{2-}(aq))$ to green $(Cr^{3+}(aq))$. ii.

4. a.
$$\frac{0.0640 \text{ mol} \cdot \text{L}^{-1} \times 18.22 \text{ mL}}{25.00 \text{ mL}} = 0.0466 \text{ M acid}$$

With zero % titrated, pH = 3.39; $[H^+] = 4.07 \times 10^{-4}$

Assuming negligible dissociation:

Assuming significant dissociation

$$K_a = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{X}^-\right]}{\left[\mathrm{HX}\right]} = \frac{\left(4.07 \times 10^{-4}\right)^2}{\left(0.0466\right)} = 3.56 \times 10^{-6} \qquad K_a = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{X}^-\right]}{\left[\mathrm{HX}\right]} = \frac{\left(4.07 \times 10^{-4}\right)^2}{\left(0.0466 - 4.07 \times 10^{-4}\right)} = 3.59 \times 10^{-6}$$

With 33.3 % titrated, pH = 5.14;
$$[H^+] = 7.24 \times 10^{-6}$$

Assuming negligible dissociation:

Assuming significant dissociation:

$$K_a = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{X}^-\right]}{\left[\mathrm{HX}\right]} = \frac{\left(7.24 \times 10^{-6}\right)\left(0.0155\right)}{\left(0.0311\right)} = 3.62 \times 10^{-6} \quad K_a = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{X}^-\right]}{\left[\mathrm{HX}\right]} = \frac{\left(7.24 \times 10^{-6}\right)\left(0.0155\right)}{\left(0.0311 - 7.24 \times 10^{-6}\right)} = 3.61 \times 10^{-6}$$

With 66.7 % titrated, pH = 5.74;
$$[H^+] = 1.82 \times 10^{-6}$$

Assuming negligible dissociation:

Assuming significant dissociation:

$$K_a = \frac{\left[H^+\right]\left[X^-\right]}{\left[HX\right]} = \frac{\left(1.82 \times 10^{-6}\right)\left(0.0312\right)}{\left(0.0155\right)} = 3.64 \times 10^{-6} \ K_a = \frac{\left[H^+\right]\left[X^-\right]}{\left[HX\right]} = \frac{\left(1.82 \times 10^{-6}\right)\left(0.0312\right)}{\left(0.0155 - 1.82 \times 10^{-6}\right)} = 3.66 \times 10^{-6}$$

c.
$$X^- + H_2O \rightleftharpoons HX + OH^ K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.60 \times 10^{-6}} = 2.78 \times 10^{-9}$$

 $[X^-] = \frac{(0.0466)(25)}{(43.22)} = 0.0270M$

$$(45.22)$$
)
 $2.78 \times 10^{-9} = \frac{\left[OH^{-}\right]^{2}}{0.0270}$; $\left[OH^{-}\right] = 8.66 \times 10^{-6}$; $pOH = 5.06$; $pH = 8.94$

d. pH = 6.0 and [H⁺] = 1.0
$$\times$$
 10⁻⁶

$$3.60 \times 10^{-6} = \frac{(1.0 \times 10^{-6})[X^{-}]}{0.0466}; [X^{-}] = 0.168 \text{ M}$$

Moles
$$X^- = \frac{0.168 \text{ mol}}{L} \times 0.150 \text{ L} = 0.0252 \text{ mol}$$

- **5.** *Note:* Balanced equations were not required.
 - **a.** $P_4 + O_2 \rightarrow P_4 O_{10}$
 - **b.** $SO_2 + H_2O \rightarrow H_2SO_3 \text{ or } H^+ + HSO_3^-$
 - c. $Cl_2 + Br^- \rightarrow Cl^- + Br_2$
 - **d.** $Mg^{2+} + OH^- \rightarrow Mg(OH)_2$
 - e. $AgCl + S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + Cl^{-}$
 - $\mathbf{f.} \qquad \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{C}}{=}}} C \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{H}}{\overset{\mathsf{H}}{=}}}} + \mathrm{Br}_2 \to \mathsf{Br} \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{H}}{=}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{H}}{\overset{\mathsf{H}}{=}}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{H}}{=}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{H}}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}{\overset{\mathsf{H}}{=}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}}} \overset{\mathsf{H}}{\underset{\mathsf{H}}} \overset{\mathsf{H$
 - **g.** $^{226}_{88}$ Ra $\rightarrow {}^{4}_{2}$ He + $^{222}_{86}$ Rn
- 6. a. For $NO_2^ \begin{bmatrix} : O-N=O \end{bmatrix}^- \Rightarrow \begin{bmatrix} : O-N=O \end{bmatrix}^-$ and for NO_2^+ $\begin{bmatrix} : O-N=O \end{bmatrix}^+$
 - **b.** NO_2^- will be bent due to the lone pair of electrons on N. NO_2^+ will be linear.
 - c. Nitrogen-to-oxygen bonds in NO_2^- will be longer than those in NO_2^+ . The average bond order in NO_2^- is $1^1/2$. The bond order in NO_2^+ is 2.
 - **d.** The oxidation number of N in NO_2^- is +3. Formal charge is zero. The oxidation number is obtained by assigning bonding electrons to the more electronegative atom. The formal charge is found by dividing the bonding electrons evenly between atoms. The number of electrons left is compared with the original number.
- 7. **a.** A = liquid; B = gas, C and D = solid
 - **b.** $18.0 \text{ g} \times \frac{1 \text{ mL}}{0.9998 \text{ g}} = 18.0 \text{ mL liquid} \quad 18.0 \text{ g} \times \frac{1 \text{ mL}}{0.917 \text{ g}} = 19.6 \text{ mL solid}$ $PV = nRT; \quad V = \frac{nRT}{P}; \quad V = \frac{1 (0.0821) (273.17) (760)}{4.58}; \quad V = 3.72 \times 10^{3} \text{ L}$
 - c. $A \rightarrow B$ pressure decreases, temperature constant, phase change from liquid to gas
 - $\mathbf{B} \to \mathbf{C}$ pressure constant, temperature decreases, phase change from gas to solid
 - $C \rightarrow D$ pressure increases, temperature constant, no phase change
 - $\mathbf{D} \to \mathbf{A}$ pressure constant, temperature increases, phase change from solid to liquid
- **8. a.** The element above element 114 is lead, Pb; above element 116 is polonium, Po; above element 118 is radon, Rn.
 - **b.** The ionization energy is expected to increase from element 114 to 116 to 118. This is due to increasing nuclear charge density thus resulting in greater attraction for outer electrons. The ionization energy of elements 114, 116, and 118 are expected to be lower than those of the elements directly above them due to the presence of electrons in higher energy levels, those with higher values of n.
 - c. The oxidation states for element 114 are predicted to be +2 (loss of electrons in p orbitals) and +4 (loss of electrons in both s and p orbitals). The oxidation state +2 is likely more stable; lower oxidation states are usually more stable.
 - **d.** Even values of Z are usually more stable due to pairing of protons. Odd values of Z are less stable.