2019 U. S. NATIONAL CHEMISTRY OLYMPIAD
NATIONAL EXAM - PART II

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

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 with 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 29, 2019**, 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 required information on the "Blue Book". When the student has completed **Part II**, or after one hour and forty-five minutes have 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 questions**	**laboratory practical**	**1 hour, 30 minutes**

A periodic table and other useful information are provided on page two 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

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 you were assigned for **Part I**.) Answer all of the questions in order, and use both sides of the paper. 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 signed U.S. citizenship/Green Card Holder statement before leaving the testing site today.**

EQUATIONS

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

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

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

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	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	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	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 78.97	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 (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)

1. **[12%]** Studtite is a mineral that contains only hydrogen, oxygen, and a metal M. Its empirical formula is $MO_x(H_2O)_y$, where x and y are integers.

   A 1.0000 g sample of studtite is heated at 520 ºC, which causes it to decompose to molecular oxygen, water vapor, and the solid metal trioxide MO_3. The gases from this reaction are collected in a rigid container with a volume of 1.000 L. When this container is maintained at 200.0 ºC, the pressure is 355.0 mm Hg. When the container is cooled to 25.0 ºC, some of the water vapor condenses to the liquid, and the pressure in the container falls to 48.65 mm Hg. The vapor pressure of water at 25.0 ºC is 23.80 mm Hg.

   a. Calculate the number of moles of O_2 produced in this reaction.

   b. Calculate the number of moles of H_2O produced in this reaction.

   c. Calculate the mass of solid MO_3 produced in this reaction.

   d. What is the identity of the metal M? Support your answer.

   e. What is the oxidation state of the metal M in the mineral studtite? Explain your answer.

2. **[14%]** Group 2 iodates such as $Ca(IO_3)_2$ and $Ba(IO_3)_2$ are sparingly soluble compounds.

   The K_{sp} of $Ba(IO_3)_2$ is measured by the following experiment: An aqueous solution is saturated with $Ba(IO_3)_2$ at 298 K and a 10.00 mL aliquot of this solution (free of any solid) is added to a solution containing an excess of KI in 1 M aqueous HCl, causing the solution to turn yellow. This yellow solution is then titrated with 0.0150 M $Na_2S_2O_3$ solution until the color disappears; 8.00 mL of the thiosulfate solution is required to reach this endpoint.

   a. Write balanced net ionic equations for

      i. the reaction of the saturated $Ba(IO_3)_2$ solution with the acidified KI solution; and

      ii. the reaction of the yellow solution with the sodium thiosulfate solution.

   b. Calculate the K_{sp} of $Ba(IO_3)_2$ at 298 K.

   The K_{sp} of $Ca(IO_3)_2$ can be measured by similar experiments. Below is shown a plot of $\ln(K_{sp})$ of $Ca(IO_3)_2$ as a function of $1/T$.
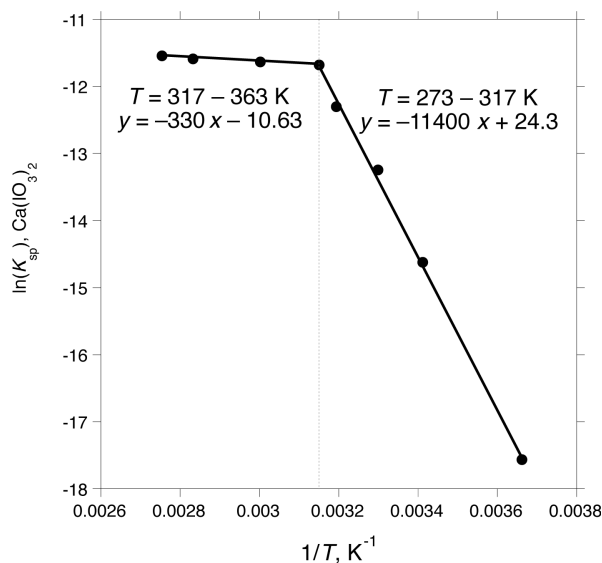
   c. Calculate $\Delta H°$ and $\Delta S°$ for the dissolution of $Ca(IO_3)_2$ in the range of $T = 273$ to 317 K.

   d. The $\ln(K_{sp})$ vs. $1/T$ plot has a break in the curve because the stable crystalline form of calcium iodate changes in the temperature range shown. At some temperatures, the stable form is anhydrous $Ca(IO_3)_2$, while at other temperatures the hexahydrate $Ca(IO_3)_2 \cdot 6\ H_2O$ is the stable form. Assign which form is stable at which temperatures, and justify your assignment.

3. [13%] There is considerable interest in producing ammonia by electrolyzing nitrogen/water mixtures (in the presence of suitable catalysts) as shown below.

$$N_2(g) + 3\ H_2O(l) \rightarrow 2\ NH_3(g) + 1.5\ O_2(g)$$
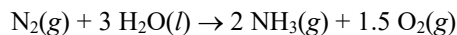
a. Would ammonia be evolved at the cathode or the anode of this electrolytic cell?

b. Calculate the standard cell potential E° for this reaction at 298 K given the thermodynamic data shown.

| Compound	$H_2O(l)$	$NH_3(g)$
ΔG°_f, kJ mol^{-1}	−237.1	−16.4

c. Would E° for this reaction be larger or smaller in magnitude at higher temperatures? Justify your answer.

d. The standard reduction potential of O_2 *in acidic solution* is 1.23 V.

$$O_2(g) + 4\ H^+(aq) + 4e^- \rightarrow 2\ H_2O \qquad\qquad E^\circ = 1.23\ V$$
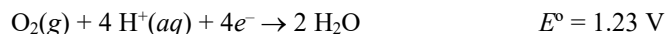
Write the half-reaction corresponding to the reduction of $O_2(g)$ to water in *basic solution* and calculate the standard reduction potential.

e. Write the half-reaction corresponding to the reduction of $N_2(g)$ to $NH_3(g)$ in basic solution and calculate the standard reduction potential.

f. A cell for forming NH_3 by electrolysis of nitrogen as described above runs for 3000 s with a current of 1.20 A and produces 1.05×10^{-3} mol NH_3. What is the faradaic yield of ammonia (that is, the yield of ammonia as a percentage of the maximum amount that could be formed by passage of this amount of electricity)?

4. [11%] Ascorbic acid (Vitamin C, abbreviated HAsc) is a weak acid with $pK_a = 4.10$. It is readily oxidized to form dehydroascorbic acid. One reagent that can carry out this oxidation is the ferricyanide ion, $Fe(CN)_6^{3-}$.
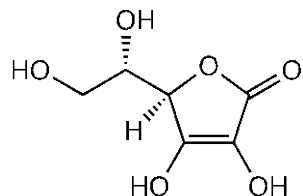
Ascorbic acid, HAsc
$C_6H_8O_6$
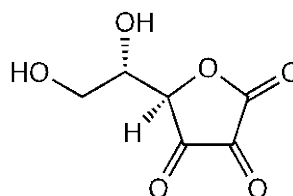
Dehydroascorbic acid
$C_6H_6O_6$

a. Write a balanced net ionic equation for the reaction of $Fe(CN)_6^{3-}$ with HAsc in acidic solution.

The rate of this reaction can be followed by measuring $[Fe(CN)_6^{3-}]$ through its absorbance at 416 nm, where bright yellow $Fe(CN)_6^{3-}$ absorbs light strongly and all the other colorless components of the reaction do not. Two runs were conducted with $[H^+] = 0.06$ M and an initial $[Fe(CN)_6^{3-}] = 5.22 \times 10^{-4}$ M, but with different HAsc concentrations. Plots of $\ln([Fe(CN)_6^{3-}])$ as a function of time for the two runs are shown below.

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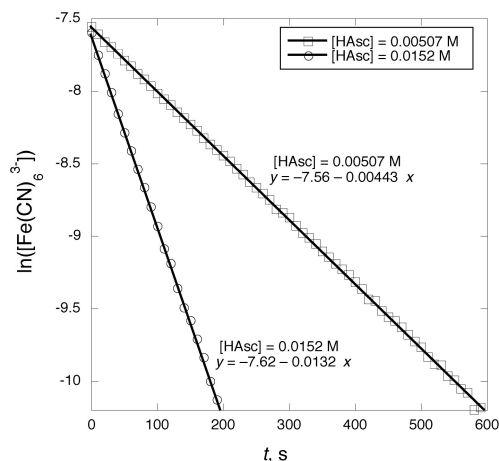
b. What is the rate law for this reaction at $[H^+] = 0.06$ M? Explain your reasoning.

c. What is the rate constant for this reaction at $[H^+] = 0.06$ M? Make sure to include units.

The behavior of the reaction varies with the acidity of the solution. Five runs were conducted at $[HAsc] = 0.00507$ M and an initial $[Fe(CN)_6^{3-}] = 5.22 \times 10^{-4}$ M, but at varying $[H^+]$. For each run, $\ln([Fe(CN)_6^{3-}])$ was plotted as a function of time and the slope of the plot was measured. The slope was multiplied by -1 and its variation as a function of $[H^+]$ is graphed below.
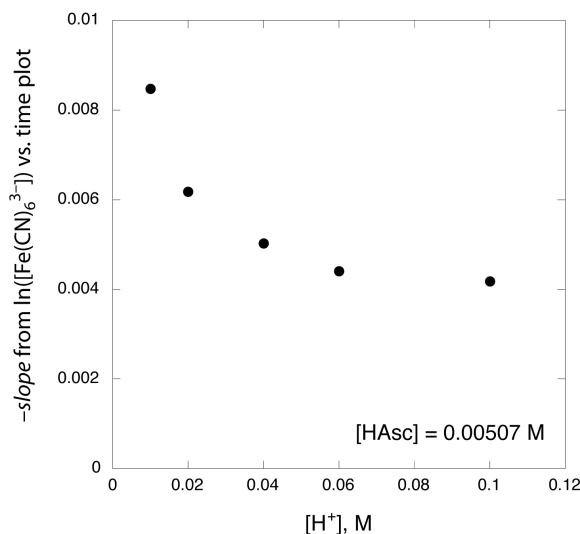
d. Propose a mechanistic explanation for the effect of $[H^+]$ on the reaction kinetics. Be sure to explain how your mechanistic explanation qualitatively predicts the appearance of the plot.

5. [12%] Write net equations for each of the reactions below. Use appropriate ionic and molecular formulas 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 equations.

a. Aqueous solutions of propanoic acid and potassium cyanide are combined.

b. Solid silver chloride is treated with concentrated aqueous ammonia.

c. Aqueous sodium sulfite is heated with elemental sulfur.

d. Solid copper(II) sulfate is added to a potassium iodide solution.

e. Aniline is added to a cold acidified solution of sodium nitrite.

f. Uranium-235 undergoes nuclear fission to form barium-141 and krypton-92.

6. [13%] The chemistry of beryllium (Be) has a number of interesting features.

a. Explain the differences between Be and its heavier congener, barium (Ba), with regard to the following properties.

i. Be has a higher ionization energy (900 kJ mol^{-1}) than Ba (563 kJ mol^{-1}).

ii. Adding an electron to a gas-phase Be atom requires energy, while adding an electron to a gas-phase Ba atom releases a small amount of energy (14 kJ mol^{-1}).

iii. $BeCl_2(s)$ has a more positive ΔH°_f (-496.2 kJ mol^{-1}) than $BaCl_2(s)$ (-858.6 kJ mol^{-1})

iv. Solid $BeCl_2$ adopts the structure shown on the left, while solid $BaCl_2$ adopts the structure shown on the right (metal = black spheres, chlorine = gray spheres).
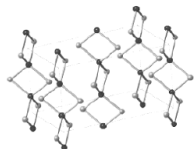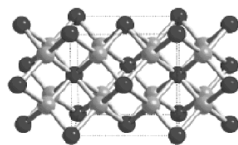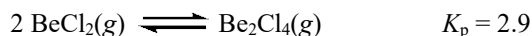

BeCl₂   BaCl₂

b. In the vapor phase, $BeCl_2$ exists as a mixture of $BeCl_2$ monomers and Be_2Cl_4 dimers. Draw or clearly describe the geometries of these two gas-phase species.

c. At 800 K, K_p for dimerization of $BeCl_2(g)$ is 2.9.

$$2\ BeCl_2(g) \rightleftharpoons Be_2Cl_4(g) \qquad K_p = 2.9$$

Calculate the mole fraction of dimeric Be_2Cl_4 in $BeCl_2$ vapor at a total pressure of 0.100 bar at 800 K.

7. **[13%]** Borazine, $B_3N_3H_6$, has a structure consisting of a six-membered ring with alternating BH and NH groups.

a. Draw a Lewis structure for borazine, including nonzero formal charges if needed. Show all major resonance structures of borazine.

b. Two other compounds containing boron, nitrogen, and hydrogen are BH_3NH_3 and BH_2NH_2. Draw Lewis structures for these two compounds, again including any formal charges and major resonance structures.

c. The B–N distances in $B_3N_3H_6$, BH_3NH_3, and BH_2NH_2 are 139.1, 142.9, and 156.4 pm (not necessarily in that order). Assign each B–N distances to the proper compound and explain your reasoning.

d. Typically, when one replaces a hydrogen attached to N with a CH_3 group, the boiling point of the compound decreases. For example, piperazine has a normal boiling point of 146 ºC while *N*-methylpiperazine has a normal boiling point of 138 ºC. Explain this observation.

piperazine
bp = 146 °C

N-methylpiperazine
bp = 138 °C
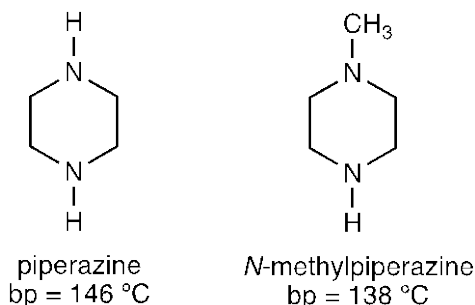
e. In contrast to the situation in (d), when one N-H group in borazine (bp = 55 ºC) is changed to an N-CH_3 group, the normal boiling point of *N*-methylborazine increases significantly, to 84 ºC. Explain why the usual trend in boiling points is not observed for borazine and *N*-methylborazine.

8. **[12%]** Consider the following sequence of reactions:
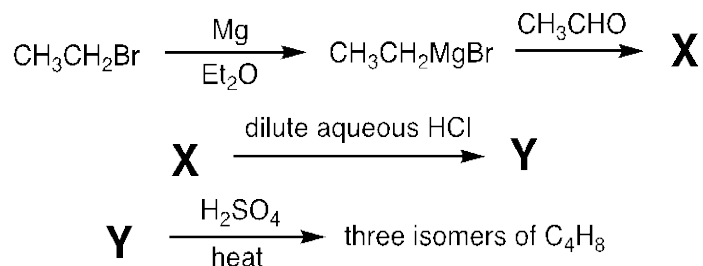
a. If the diethyl ether used in the reaction of ethyl bromide with magnesium metal is not scrupulously dry, CH_3CH_2MgBr is not formed in good yield. What organic product is formed if wet diethyl ether is used?

b. Give the structures of compounds **X** and **Y**.

c. Give the structures of the three isomers of C_4H_8 formed in the final reaction.

d. State which isomer of C_4H_8 is formed in the greatest quantity in this reaction, and explain why.

NOTES

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1. a.   At 25 ºC, some liquid water is present, so the pressure of water is equal to the vapor pressure, 23.80 mm Hg. Thus the partial pressure of O_2 is 48.65 mm Hg – 23.80 mm Hg = 24.85 mm Hg. From the ideal gas law,
$$n = PV/RT$$
$$n = (24.85 \text{ mm Hg})(1.000 \text{ L})/(62.36 \text{ L [mm Hg] mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})$$
$$n = 1.337 \times 10^{-3} \text{ mol}$$

   b.   At 200 ºC, the total moles of gas are given by
$$n = (355.0 \text{ mm Hg})(1.000 \text{ L})/(62.36 \text{ L [mm Hg] mol}^{-1} \text{ K}^{-1})(473.15 \text{ K})$$
$$n = 0.01203 \text{ mol}$$
   The number of moles of water vapor = (0.01203 mol total gases) – (1.337×10^{-3} mol O_2) = 0.01069 mol.

   c.   The total mass of gaseous products = $(18.032 \text{ g mol}^{-1})(0.01069 \text{ mol } H_2O) + (32.00 \text{ g mol}^{-1})(1.337 \times 10^{-3} \text{ mol } O_2) = 0.2355$ g. Thus 0.7645 g MO_3 remains.

   d.   The balanced equation for this reaction is:
$$MO_x(H_2O)_y \rightarrow y \, H_2O + (x-3)/2 \, O_2 + MO_3$$
   Since x is an integer, the smallest amount of O_2 that can be produced per mol MO_3 is 0.5, or any integer multiple of this could be produced.
   If $x = 4$, then $2(1.337 \times 10^{-3}$ mol) mol MO_3 is present, and the molar mass of MO_3 is $(0.7645 \text{ g})/(2.674 \times 10^{-3} \text{ mol } MO_3) = 285.9 \text{ g mol}^{-1}$. This would imply that the atomic mass of M is $285.9 – 3(16.00) = 237.9 \text{ g mol}^{-1}$. This is the atomic mass of U.
   If $x = 5$, then only 1.337×10^{-3} mol of MO_3 would be present, and the molar mass of MO_3 would be twice as high, and the atomic mass of M would be over twice that of uranium. This is impossible. (Higher values of x would give even higher values of the atomic mass of M.) Therefore M = U. Since $x = 4$, the 8:1 mol ratio of H_2O to O_2 produced implies that $y = 4$ as well.

   e.   Naively, one would expect that $UO_4(H_2O)_4$ would have U(VIII). But this is impossible: since U has only 6 valence electrons, it cannot possibly have an oxidation state greater than +6! The only reasonable formulation is that some of the oxygens in studtite are in the form of *peroxide*, O_2^{2-}, with an oxidation state of –1 for oxygen (not the –2 of oxide). Since it is unlikely that a strongly oxidizing species such as peroxide would coexist with a reduced oxidation state of uranium, uranium must be in its highest oxidation state, +6. Studtite should then be formulated as $UO_2(O_2)(H_2O)_4$. This mineral and its partially dehydrated form metastudtite, $UO_2(O_2)(H_2O)_2$, are the only known peroxide-containing minerals.

2. a. i. $IO_3^-(aq) + 8\ I^-(aq) + 6\ H^+(aq) \rightarrow 3\ I_3^-(aq) + 3\ H_2O(l)$

   ii. $I_3^-(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 3\ I^-(aq) + S_4O_6^{2-}(aq)$

b. $(8.00 \times 10^{-3}\ \text{L titrant}) \times (0.0150\ \text{mol L}^{-1}) = 1.20 \times 10^{-4}\ \text{mol}\ S_2O_3^{2-}$
       $(1.20 \times 10^{-4}\ \text{mol}\ S_2O_3^{2-}) \times (1\ \text{mol}\ IO_3^-/6\ \text{mol}\ S_2O_3^{2-}) = 2.00 \times 10^{-5}\ \text{mol}\ IO_3^-$
       So the concentration of IO_3^- in the saturated $Ba(IO_3)_2$ solution is $(2.00 \times 10^{-5}$
       mol$)/(0.01000\ \text{L}) = 2.00 \times 10^{-3}\ \text{M}$
       $[Ba^{2+}] = 0.5[IO_3^-] = 1.00 \times 10^{-3}\ \text{M}$
       $K_{sp} = [Ba^{2+}][IO_3^-]^2 = (1.00 \times 10^{-3})(2.00 \times 10^{-3})^2 = 4.00 \times 10^{-9}$

c.   The figure given is a van't Hoff plot for the dissolution reaction of $Ca(IO_3)_2$, since $K_{sp} = K_{eq}$ for the dissolution reaction. Since $\ln(K_{eq}) = -(\Delta G^\circ/RT) = (-\Delta H^\circ/R)(1/T) + (\Delta S^\circ/R)$, the slope of the plot is $-\Delta H^\circ/R$ and the intercept is $\Delta S^\circ/R$.
       $$\Delta H^\circ = -(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(-11400\ \text{K}) = 94.8\ \text{kJ mol}^{-1}$$
       $$\Delta S^\circ = (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(24.3) = 202\ \text{J mol}^{-1}\ \text{K}^{-1}$$

d.   Dissolution of calcium iodate in the 317-363 K range takes place with a much smaller ΔH° (2.7 kJ mol^{-1}) and much smaller (more negative) ΔS° (–88.38 J mol^{-1} K^{-1}) than in the 273-317 K range discussed in (c). The hexahydrate will certainly dissolve with a more positive ΔS°, since the six lattice waters will have many more degrees of freedom in bulk water than they do in the crystal lattice. Thus $Ca(IO_3)_2 \cdot 6\ H_2O$ must correspond to the stable phase at low temperature (273-317 K) and the anhydrous $Ca(IO_3)_2$ must be stable in the 317-363 K range.

3. a. Nitrogen is reduced to ammonia in this cell, so ammonia is produced at the cathode.

b. $\Delta G^\circ = 2(-16.4\ \text{kJ mol}^{-1}) - 3(-237.1\ \text{kJ mol}^{-1}) = 678.5\ \text{kJ mol}^{-1}$
 $$\Delta G^\circ = -nFE^\circ$$
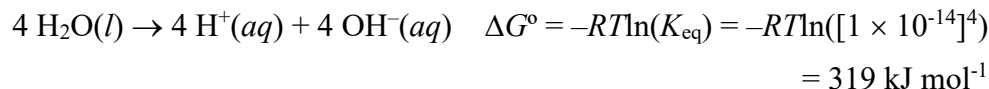 $$678500\ \text{J mol}^{-1} = -(6)(96500\ \text{C mol}^{-1})E^\circ$$
       $$E^\circ = -1.17\ \text{V}$$

c.   In the reaction, 3.5 mol of gaseous products are produced from 2 mol gaseous reagents, so ΔS° is positive (it turns out to be 100.2 J mol^{-1} K^{-1}). Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, if ΔS° is positive, ΔG° will become algebraically smaller as temperature increases. Since ΔG° is positive, this means that its magnitude will become smaller as T increases, and hence E° will become smaller in magnitude (less negative) as T increases.
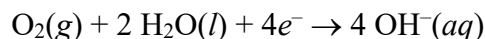
d.   In basic solution,
$$O_2(g) + 2\ H_2O(l) + 4e^- \rightarrow 4\ OH^-(aq)$$
To calculate E^o, one can combine the ΔG^o values for the reduction reaction in acid solution with the ΔG^o for the autoprotolysis of water:

$$O_2(g) + 4\ H^+(aq) + 4e^- \rightarrow 2\ H_2O(l) \qquad\qquad \Delta G^o = -nFE^o = -475\ kJ\ mol^{-1}$$

$$4\ H_2O(l) \rightarrow 4\ H^+(aq) + 4\ OH^-(aq) \quad \Delta G^o = -RT\ln(K_{eq}) = -RT\ln([1 \times 10^{-14}]^4)$$

$$= 319\ kJ\ mol^{-1}$$

$$O_2(g) + 2\ H_2O(l) + 4e^- \rightarrow 4\ OH^-(aq) \qquad\qquad \Delta G^o = -156\ kJ\ mol^{-1}$$

$$E^o = \Delta G^o/(-nF) = (-156000\ J\ mol^{-1})/(-4F) = 0.40\ V$$

e. $N_2(g) + 6\ H_2O(l) + 6e^- \rightarrow 2\ NH_3(g) + 6\ OH^-(aq)$
        Since the difference in standard reduction potentials for the two half-reactions is equal to the overall E^o, then $E^o - 0.40\ V = -1.17\ V$, and $E^o = -0.77\ V$.

f.   Theoretical yield of NH_3 = $(3000\ s)(1.2\ A)/(3)(96500\ C\ mol^{-1}) = 0.0124$ mol NH_3. The faradaic yield is thus $\{(1.05 \times 10^{-3}\ mol)/(0.0124\ mol)\}\times100\% = 8.4\%$.

4. a. $C_6H_8O_6(aq) + 2\ Fe(CN)_6{}^{3-}(aq) \rightarrow C_6H_6O_6(aq) + 2\ Fe(CN)_6{}^{4-}(aq) + 2\ H^+(aq)$

b.   The limiting reagent is $Fe(CN)_6{}^{3-}$, with a large excess of both H^+ and HAsc present (pseudo-first-order conditions). Since the natural logarithm of its concentration decays linearly with time, the reaction is first order in $Fe(CN)_6{}^{3-}$. When the concentration of HAsc is increased by a factor of $(0.0152\ M/0.00507\ M) = 3.00$, the observed rate constant $(= -$slope$)$ increases by a factor of $(0.0132/0.00443) = 2.98$. Thus the rate is linearly dependent on [HAsc].
        $\therefore$ Rate $= k$[HAsc]$[Fe(CN)_6{}^{3-}]$

c.   Rate $= k$[HAsc] $[Fe(CN)_6{}^{3-}] = k_{obs}[Fe(CN)_6{}^{3-}]$, where $k_{obs} = -$slope of the $\ln([Fe(CN)_6{}^{3-}])$ vs. time plot. So k[HAsc] $= k_{obs}$, $k = k_{obs}/$[HAsc]. From the first run, $k = (0.00443$ $s^{-1})/(0.00507\ M) = 0.874\ M^{-1}\ s^{-1}$.

d.   Evidently the reaction goes faster at low $[H^+]$, but even at high $[H^+]$, the rate levels off at a finite value rather than approaching zero. This is not consistent with a simple inverse order in H^+, but rather a two-term rate law:
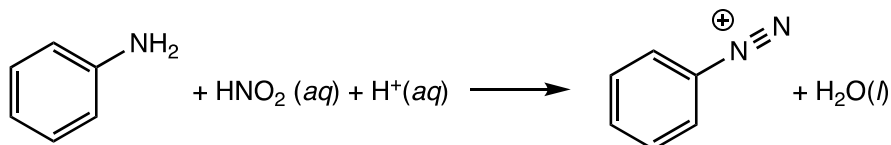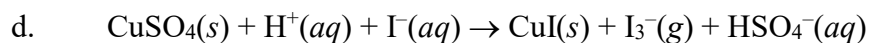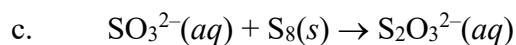$$k_{obs} = k_1 + k_2/[H^+]$$
A plausible explanation is that either HAsc or its conjugate base can react with $Fe(CN)_6{}^{3-}$, with Asc^- reacting much more rapidly than HAsc. As $[H^+]$ decreases, the amount of Asc^- increases and hence the rate increases. Even the highest pH studied, pH $\ll pK_a$, so only a small fraction of the HAsc is in its conjugate base form, and $[Asc^-]$ is proportional to $1/[H^+]$ under these conditions.
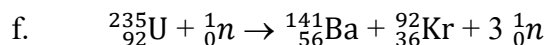
5. a. $CH_3CH_2COOH(aq) + CN^-(aq) \rightarrow CH_3CH_2COO^-(aq) + HCN(aq)$

b. $AgCl(s) + NH_3(aq) \rightarrow Ag(NH_3)_2{}^+(aq) + Cl^-(aq)$

c.　　$SO_3{}^{2-}(aq) + S_8(s) \rightarrow S_2O_3{}^{2-}(aq)$

d.　　$CuSO_4(s) + H^+(aq) + I^-(aq) \rightarrow CuI(s) + I_3{}^-(g) + HSO_4{}^-(aq)$

e.

f.　　$^{235}_{92}U + {}^1_0n \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^1_0n$

6. a. i.　The electron ionized in Be is a $2s$ electron, while Ba loses a $6s$ electron. The higher value of n corresponds to a higher energy, requiring less energy to remove.

　ii.　Since both Be and Ba have an ns^2 configuration, an added electron must enter a new subshell, which is higher in energy. The $2p$ subshell that would be occupied for Be is much higher in energy, but the next available orbital for Ba is a $5d$ orbital, which is closer in energy to the $6s$ subshell.

　iii.　Ba is more electropositive than Be, so it costs much less energy to remove its valence electrons to form the 2+ ion. This difference outweighs the somewhat higher lattice energy of $BeCl_2$ than $BaCl_2$.

　iv.　Be can only form 4 bonds, so it can only adopt the left structure. The larger Ba^{2+} ion can easily achieve the coordination number of 8 required by the right-hand structure.

b.

c.　　Let P_M = partial pressure of monomeric $BeCl_2(g)$
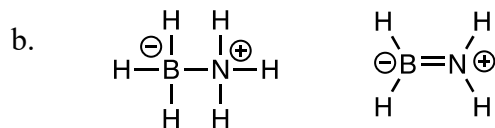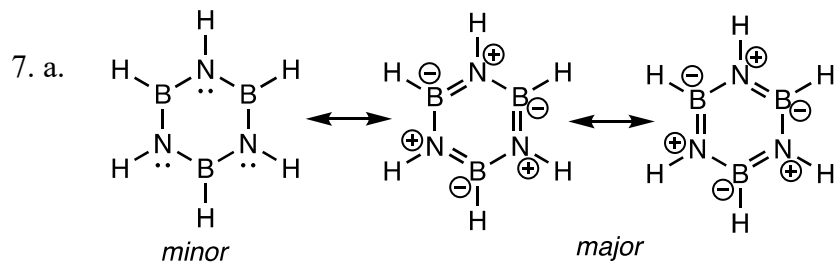　　　　P_D = partial pressure of dimeric $Be_2Cl_4(g)$
$$P_D/P_M{}^2 = 2.9$$
$$0.100 - P_M = 2.9P_M{}^2$$
$$2.9P_M{}^2 + P_M - 0.100 = 0$$
Solving gives $P_M = 0.081$ bar, and therefore $P_D = 0.100$ bar $- 0.081$ bar $= 0.019$ bar.
The mole fraction of the dimer is $P_D/0.100$ bar $= 0.19$.

7. a.

b.

c. BH_3NH_3, 156.4 pm
      $B_3N_3H_6$, 142.9 pm
      BH_2NH_2, 139.1 pm
            From the Lewis structures, the bond order increases (from 1 to 1.5 to 2) in the
      order listed, with the bond lengths decreasing accordingly.

d.   In piperazine, the N–H hydrogen can act as a hydrogen bond donor to another nitrogen
      lone pair. Changing the H to CH_3 thus decreases the amount of hydrogen bonding and
      weakens the intermolecular forces. This effect outweighs the increase in London
      dispersion forces in the $-CH_3$ derivative.

e.   Borazine has no hydrogen bond acceptors! There are not really any lone pairs on
      nitrogen since they are involved in π donation to the boron atoms. So the N–H hydrogens
      do not participate in hydrogen bonding, and converting them to CH_3 groups leads only to
      an increase in London dispersion forces and a corresponding increase in boiling point.

8. a.   Ethane, C_2H_6 (the Grignard reagent is very basic and is easily protonated by water)

b.   **X =**   **Y =**

c.
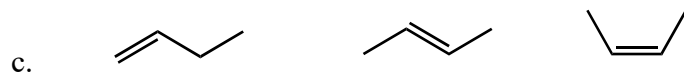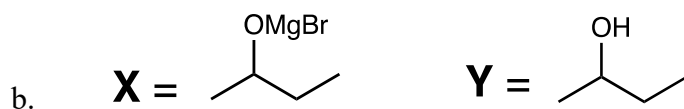
d.   The middle compound, *trans*-2-butene, is formed in the greatest quantity. It is the most
      stable of the three alkenes (most highly substituted, and more stable geometric isomer).