# 2023 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** of this test requires that student answers be written in this test booklet in the spaces provided underneath the questions. Part II test booklet and scratch paper should be made available to the student only during the examination period. All testing materials including scratch paper should be collected from students after the examination. Only test booklets should be shipped to the USNCO office immediately after the national exam and no later than **April 24, 2023**.

When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in **Part II** of the testing materials and all scratch paper. Be sure that the student has supplied 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 use the same identification number you used for **Part I and write it on top of each page in the indicated fields**. 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 and scratch paper.

**Do not forget to turn in your U.S. citizenship/Green Card Holder statement before leaving the testing site today.**

**STUDENT USNCO ID:**

## ABBREVIATIONS AND SYMBOLS

| | | | | | |
|---|---|---|---|---|---|
| amount of substance | $n$ | Faraday constant | $F$ | molar mass | $M$ |
| ampere | A | free energy | $G$ | mole | mol |
| atmosphere | atm | frequency | $\nu$ | 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 | year | y |

## CONSTANTS

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

$R = 0.08314 \ \text{L bar mol}^{-1}\,\text{K}^{-1}$

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

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

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

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

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

$0 \ °\text{C} = 273.15 \ \text{K}$

$1 \ \text{atm} = 1.013 \ \text{bar} = 760 \ \text{mm Hg}$

Specific heat capacity of $H_2O$ = $4.184 \ \text{J g}^{-1}\,\text{K}^{-1}$

## EQUATIONS

$$E = E° - \frac{RT}{nF}\ln Q$$

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

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

# 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 78.97 | 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%] **A** is an ionic compound that contains only the elements hydrogen, nitrogen, and oxygen.

    a.  A 1.000-g sample of **A** is dissolved in 20 mL water and titrated with 0.5000 M NaOH solution, giving the data shown below.  What is the molar mass of **A**?

Write your answer here:



mL 0.5000 M NaOH added
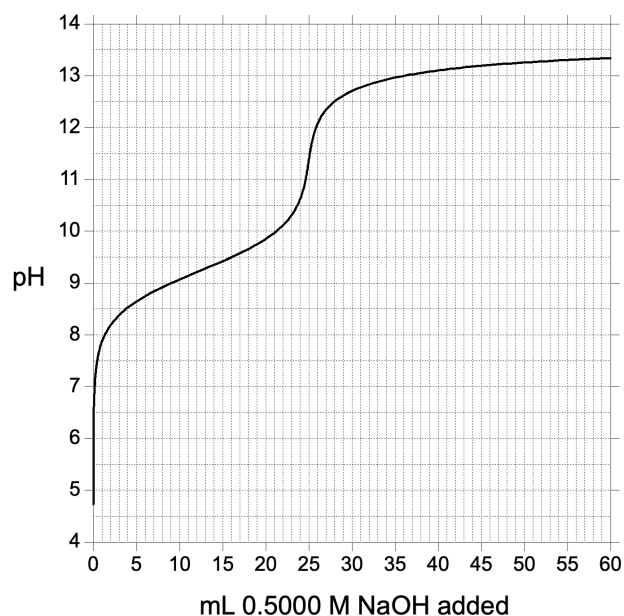
    b.  When a 1.000-g sample of **A** is heated at 230 °C in an evacuated 1.50 L vessel, it decomposes into gaseous products, giving a final pressure of 784 mm Hg.  How many moles of gas are formed in this reaction?

c.   If the gases produced from the decomposition of 1.000 g of **A** are instead first passed through a column packed with magnesium perchlorate (which strongly absorbs water vapor) and then collected at 25 °C and a pressure of 755 mm Hg, the total volume of gas is 308 mL.  How many moles of gas are collected in this experiment?

d.   What is the formula of **A**?  Explain your reasoning.

e.   Write Lewis structures for the cation and the anion present in **A** and for the product(s) of its decomposition at 230 °C.  Your Lewis structures should include all bonds, lone pairs, and nonzero formal charges.  You should show all significant resonance structures for each species.

**2.** [14%] When water is bound to a metal ion, its acidity increases. For example, the $pK_a$ of $Zn^{2+}(aq)$ is 8.96.

   a.   Calculate the pH of a 0.010 M solution of zinc nitrate, $Zn(NO_3)_2$.

   b.   Calculate the pH of a 0.010 M solution of zinc acetate, $Zn(CH_3COO)_2$. The $pK_a$ of $CH_3COOH$ is 4.75.

   c.   Zinc hydroxide is sparingly soluble, with $K_{sp} = 4.5 \times 10^{-17}$. Calculate the pH of a solution of water saturated with solid $Zn(OH)_2$.

d.  Under what circumstances, if any, will a solution of zinc acetate spontaneously form a precipitate of $Zn(OH)_2$? If precipitation is possible, specify the circumstances under which it is spontaneous. If it is not possible, justify why not.

e.  Zinc also forms a complex ion, $Zn(OH)_4^{2-}$, with $K_f = 5.0 \times 10^{14}$. Calculate the solubility of $Zn(OH)_2$ in a solution with pH = 12.00.

3. [12%] Hydrogen gas reacts with oxygen gas to give water vapor with $\Delta H°_{rxn} = -241.8$ kJ mol$^{-1}$ and $\Delta S°_{rxn} = -44.5$ J mol$^{-1}$ K$^{-1}$.

$$H_2(g) + 0.5\ O_2(g) \rightarrow H_2O(g)$$
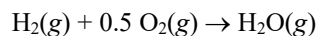
| Species | $S°$, J mol$^{-1}$ K$^{-1}$ | $C_p$, J g$^{-1}$ K$^{-1}$ |
|---|---|---|
| $H_2O(g)$ | ??? | 4.18 |
| $H_2(g)$ | 130.7 | 14.4 |
| $O_2(g)$ | 205.2 | 0.92 |

a. Calculate $S°$ of $H_2O(g)$.

b. The bond dissociation enthalpy (BDE) of an average O–H bond in water is 463 kJ mol$^{-1}$ and the BDE of the H–H bond in $H_2$ is 436 kJ mol$^{-1}$. What is the BDE of the O=O bond in $O_2$?

c. 0.100 mol $H_2(g)$ and 0.100 mol $O_2(g)$, both initially at 100 °C, react completely in a sealed vessel that is maintained at 1 bar pressure. The vessel is machined as part of a 1.00-kg block of aluminum ($C_p = 0.89$ J g$^{-1}$ K$^{-1}$), which efficiently absorbs the heat generated in the reaction but which is well insulated from its surroundings. What is the final temperature of the aluminum block and the contents of the reaction vessel? Assume that $C_p$ and $\Delta H°_{rxn}$ are independent of temperature.

    d.   Humid air at 298 K has an overall pressure of 1.0 bar and is 20. vol% $O_2$ and 3.1 vol% $H_2O$.  What is the minimum volume percentage of $H_2(g)$ in humid air necessary for its combustion to be spontaneous?

    e.   The lower flammability limit (LFL) of a substance is its minimum volumetric concentration needed to propagate a flame under a given set of conditions.  The LFL of hydrogen gas in humid air is approximately 4%. Account for the difference between your answer in part d and the experimental value for the LFL.

4. [13%] The vapor pressure of pure water at its melting point, 0.0 °C, is 611 Pa ($6.11 \times 10^{-3}$ bar).

   a. 0.880 mol $MgCl_2$ is added to 1.00 kg liquid water at 0.0 °C. Calculate the vapor pressure of this solution.

   b. The enthalpy of sublimation of ice is 51.1 kJ $mol^{-1}$ at 0.0 °C and the enthalpy of vaporization of liquid water is 45.1 kJ $mol^{-1}$ at 0.0 °C. Assuming these enthalpies are independent of temperature, calculate the temperature at which pure ice has the same vapor pressure as the magnesium chloride solution at 0.0 °C calculated in part a.

c.  At the freezing point temperature of the aqueous magnesium chloride solution, the vapor pressure of the solution is equal to the vapor pressure of pure ice.  Explain why this statement is true.

d.  Using the principle enunciated in part c, calculate the freezing point temperature of the solution of 0.880 mol $MgCl_2$ dissolved in 1.00 kg water.

e.  The temperature calculated in part d is the temperature of the system when the first solid appears at equilibrium as the system is cooled.  As more solid is formed, do you expect the temperature to increase, decrease, or remain constant?  Briefly justify your choice.

**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, and clearly show stereochemistry where relevant.  You need not balance the equations or show the phase of the species.

    a.    Aqueous hydrochloric acid is added to a solution of sodium hypochlorite.

    b.    Aluminum foil is added to concentrated aqueous potassium hydroxide solution.

    c.    Metallic sodium is added to liquid ammonia in the presence of a trace amount of iron(III) nitrate.

    d.   Potassium tetrachloroplatinate is heated with two equivalents of aqueous ammonia.

    e.   Sodium *tert*-butoxide is added to 3-bromo-3-ethylpentane in *N,N*-dimethylformamide (DMF) solution.

    f.   Cobalt-57 undergoes radioactive decay by electron capture.

6. [12%] The standard reduction potentials of some compounds of platinum and silver at 298 K are given below.
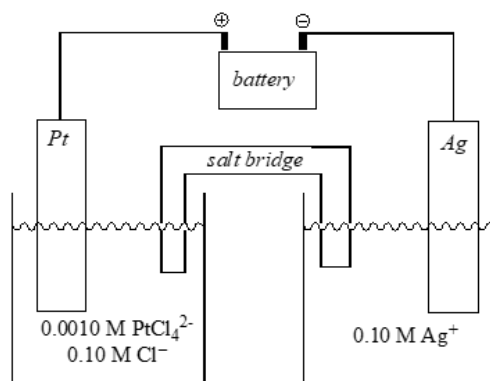
| Half-reaction | $E°$, V |
|---|---|
| $Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$ | +1.188 |
| $PtCl_4^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4\ Cl^-(aq)$ | +0.758 |
| $PtCl_6^{2-}(aq) + 2e^- \rightarrow PtCl_4^{2-}(aq) + 2\ Cl^-(aq)$ | +0.726 |
| $Ag^+(aq) + e^- \rightarrow Ag(s)$ | +0.799 |

a.  What is $K_f$ for the $PtCl_4^{2-}$ ion?

b.  What is $E°$ for the reduction of hexachloroplatinate(IV) to give platinum metal?

$$PtCl_6^{2-}(aq) + 4e^- \rightarrow Pt(s) + 6\ Cl^-(aq)$$
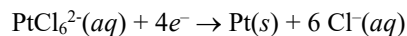
An electrolytic cell is set up as shown below.

c.  What is the minimum potential that would need to be applied in order to cause the platinum electrode to dissolve to form $PtCl_4^{2-}(aq)$ and the $Ag^+(aq)$ to deposit on the Ag electrode?

d.  As electrolysis is carried out, is it thermodynamically possible for a significant amount of hexachloroplatinate(IV) to be produced at the anode? Justify your answer.

7. [13%] Fluorine atoms and methyl groups each form one bond, so there are often analogous compounds with the formulas $AF_n$ and $A(CH_3)_n$. In the graphs below, the normal boiling points and the A–X bond distances of a series of $AX_n$ molecules are compared (A = 2$p$ element; X = F or $CH_3$).

| Boiling point comparison | Bond length comparison |
| --- | --- |
|  |  |
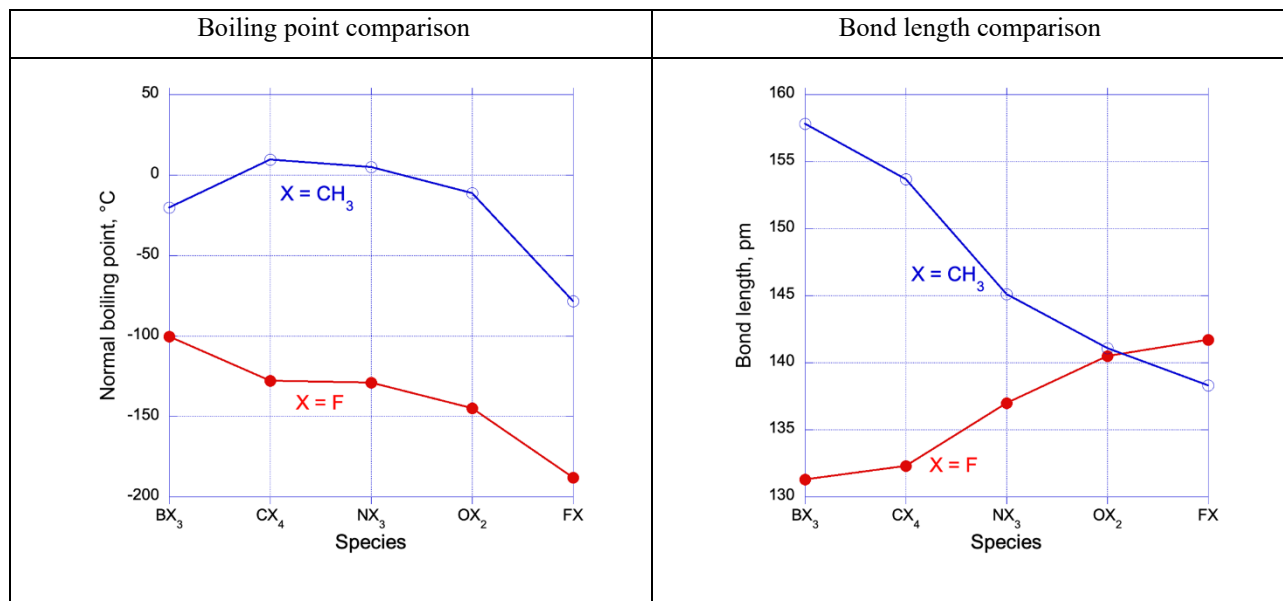
　a.　Draw or clearly describe the shapes of the molecules $BF_3$ and $NF_3$.

　b.　In all cases, the normal boiling points of the $AF_n$ molecules are lower than those of the $A(CH_3)_n$ molecules. Explain this observation.

c. Not counting the boron compounds, the trend in boiling points is that they decrease as the central atom A moves to the right in the periodic table. Explain this trend.

d. Explain why $BF_3$ has a higher boiling point than $CF_4$, while $B(CH_3)_3$ has a lower boiling point than $C(CH_3)_4$.

e. Explain why the A–C bond distances decrease as A moves to the right in the periodic table.

f. Explain why the A–F bond distances increase as A moves to the right in the periodic table.

8. [12%] Consider the two cyclic compounds cyclopentanone and 1-methylcyclopentene.



cyclopentanone     1-methylcyclopentene
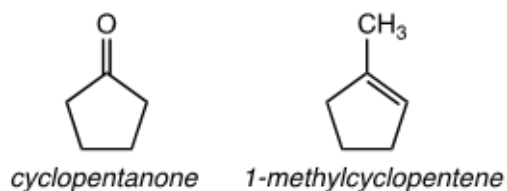
    a. Which compound has the higher normal boiling point? Justify your choice.

    b. One of the two compounds will rapidly decolorize bromine in carbon tetrachloride solvent. Which one? Draw the structure of the major product formed in the reaction, clearly showing stereochemistry if relevant.

    c. One of the two compounds will react rapidly with the Grignard reagent methylmagnesium bromide. Which one? Draw the structure of the major organic product formed in the reaction (as isolated after workup with dilute aqueous acid), clearly showing stereochemistry if relevant.

d.  The product of the reaction in part c can be transformed into either cyclopentanone or 1-methylcyclopentene in good yield in a single reaction. Specify which compound is the product and the reagent(s) needed to accomplish this transformation.

e.  Both cyclopentanone and 1-methylcyclopentene are achiral. Draw the structure of an acyclic isomer of 1-methylcyclopentene that is chiral.

1. a. The endpoint is at 25.0 mL added NaOH, and from the shape of the titration curve the compound is a monoprotic acid. So $n = (0.0250 \text{ L})(0.5000 \text{ mol L}^{-1}) = 0.0125$ mol. 1.000 g/0.0125 mol = 80.0 g mol$^{-1}$.

b.
$$PV = nRT$$
$$(784 \text{ torr})(1.50 \text{ L}) = n(62.4 \text{ L torr mol}^{-1} \text{ K}^{-1})(503.15 \text{ K})$$
$$n = 0.0375 \text{ mol}$$
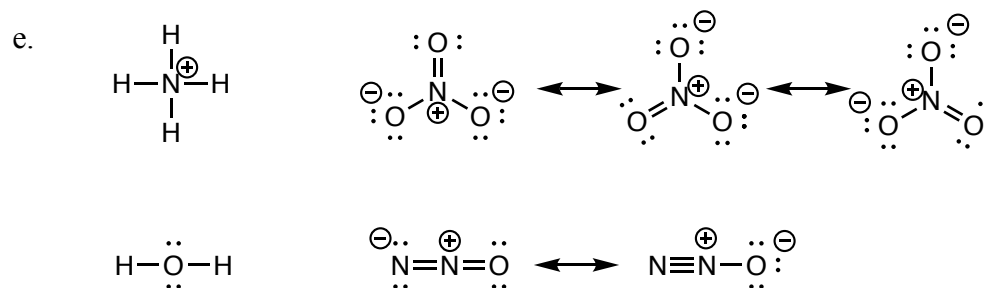This is 3 mol gas per mol **A**, given the answer to part a.

c.
$$PV = nRT$$
$$(755 \text{ torr})(0.308 \text{ L}) = n(62.4 \text{ L torr mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})$$
$$n = 0.0125 \text{ mol}$$
This is 1 mol gas per mol **A**, so the decomposition must have produced 2 mol $H_2O$ per mol **A**.
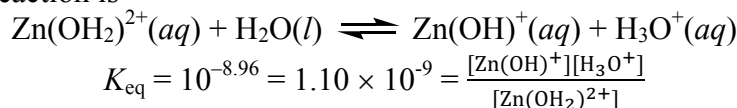
d. Each mol of **A** produces two mol $H_2O$ when it decomposes, so the formula unit must contain at least four H's and two O's. The molar mass of the gas produced in part c. is thus $80 - 2(18) = 44$. The titration in part a indicates that the acid has a p$K_a$ of 9.25; the only reasonable possibility is ammonium ion, $NH_4^+$. This means that the gas observed in part c. must contain at least one N. The only possible formulas of the gas in c. ($M = 44$, at least one N, only possible elements H, N, O) are $NH_{30}$, $H_{14}NO$, $N_2H_{16}$, $N_2O$, and $N_3H_2$. The only chemically reasonable option in this list is $N_2O$, nitrous oxide.

   The overall formula of **A** is thus $N_2O + 2(H_2O) = H_4N_2O_3$. Given the presence of ammonium ion, this translates to $(NH_4)NO_3$, ammonium nitrate.

e.

2. a.    The major reaction is
$$Zn(OH_2)^{2+}(aq) + H_2O(l) \rightleftharpoons Zn(OH)^+(aq) + H_3O^+(aq)$$
$$K_{eq} = 10^{-8.96} = 1.10 \times 10^{-9} = \frac{[Zn(OH)^+][H_3O^+]}{[Zn(OH_2)^{2+}]}$$

Since $[Zn(OH)^+]$ and $[H_3O^+]$ are approximately equal, and $[Zn(OH_2)^{2+}] \approx 0.010$ (since the reaction is quite unfavorable), then
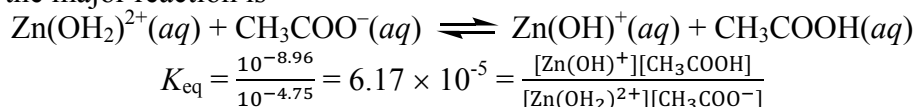$$[H_3O^+]^2 = 1.10 \times 10^{-11}$$
$$[H_3O^+] = 3.31 \times 10^{-6} \text{ M}$$
$$pH = -\log_{10}[H_3O^+] = 5.48$$

This pH is much lower than that of pure water, so the assumption of $[Zn(OH)^+] \approx [H_3O^+]$ is justified.

b.    Now the major reaction is
$$Zn(OH_2)^{2+}(aq) + CH_3COO^-(aq) \rightleftharpoons Zn(OH)^+(aq) + CH_3COOH(aq)$$
$$K_{eq} = \frac{10^{-8.96}}{10^{-4.75}} = 6.17 \times 10^{-5} = \frac{[Zn(OH)^+][CH_3COOH]}{[Zn(OH_2)^{2+}][CH_3COO^-]}$$

Similarly to above, $[Zn(OH)^+] \approx [CH_3COOH]$. Because the reaction is again rather unfavorable, $[Zn(OH_2)^{2+}]$ and $[CH_3COO^-]$ will be little changed from the initial solution, so $[Zn(OH_2)^{2+}] = 0.5[CH_3COO^-]$. Thus:
$$6.17 \times 10^{-5} = \frac{[CH_3COOH]^2}{0.5[CH_3COO^-]^2}$$
$$3.08 \times 10^{-5} = [CH_3COOH]^2/[CH_3COO^-]^2$$
$$5.55 \times 10^{-3} = [CH_3COOH]/[CH_3COO^-]$$

The ratio of acetate ion to acetic acid determines the pH:
$$pH = pK_a + \log([CH_3COO^-]/[CH_3COOH])$$
$$pH = 4.75 + \log(180)$$
$$pH = 7.01$$

Note that the initial concentration of zinc acetate was never used in this calculation! So as long as it is high enough to justify the assumptions made, the pH is the same.

c.    $[Zn^{2+}] \approx 0.5[OH^-]$ in this solution, so:
$$K_{sp} = 4.5 \times 10^{-17} = [Zn^{2+}][OH^-]^2 = 0.5[OH^-]^3$$
$$[OH^-] = 4.48 \times 10^{-6} \text{ M}$$
$$pOH = -\log[OH^-] = 5.35$$
$$pH = 14 - pOH = 8.65$$

d.    From part b, the pH of the solution is 7.01 (independent of the amount of zinc acetate), so $[OH^-] = 1.02 \times 10^{-7}$. Precipitation of $Zn(OH)_2$ is spontaneous if $Q_{sp} > K_{sp}$, so:
$$[Zn^{2+}][OH^-]^2 > 4.5 \times 10^{-17}$$
$$[Zn^{2+}][1.02 \times 10^{-7}]^2 > 4.5 \times 10^{-17}$$
$$[Zn^{2+}] > 4.3 \times 10^{-3} \text{ M}$$

Thus precipitation is spontaneous if the concentration of zinc acetate is greater than 0.0043 M.

e.       At pH = 12.00, $[OH^-] = 0.010$ M. From the solubility equilibrium:
$$[Zn^{2+}][OH^-]^2 = [Zn^{2+}][0.010]^2 = 4.5 \times 10^{-17}$$
$$[Zn^{2+}] = 4.5 \times 10^{-13}$$
From the complex ion equilibrium:
$$K_f = 5.0 \times 10^{14} = \frac{[Zn(OH)_4{}^{2-}]}{[Zn^{2+}][OH^-]^4}$$
$$[Zn(OH)_4{}^{2-}] = (5.0 \times 10^{14})[\ 4.5 \times 10^{-13}][0.010]^4$$
$$[Zn(OH)_4{}^{2-}] = 2.25 \times 10^{-6}$$
Obviously, almost all the zinc in solution is in the form of the complex ion, so $2.3 \times 10^{-6}$ moles of $Zn(OH)_2$ will dissolve per liter of pH 12 solution.

3. a.　$\Delta S°_{rxn} = S°\,(H_2O(g)) - S°\,(H_2(g)) - 0.5{\cdot}S°\,(O_2(g))$
$-44.5\ \text{J mol}^{-1}\ \text{K}^{-1} = S°\,(H_2O(g)) - (130.7\ \text{J mol}^{-1}\ \text{K}^{-1}) - 0.5{\cdot}(205.2\ \text{J mol}^{-1}\ \text{K}^{-1})$
$S°\,(H_2O(g)) = 188.8\ \text{J mol}^{-1}\ \text{K}^{-1}$

　b.　$\Delta H°_{rxn} = 0.5{\times}BDE(O{=}O) + BDE(H{-}H) - 2{\times}BDE(O{-}H)$
$-242\ \text{kJ mol}^{-1} = 0.5{\times}BDE(O{=}O) + 436\ \text{kJ mol}^{-1} - 2{\times}(463\ \text{kJ mol}^{-1})$
$BDE(O{=}O) = 496\ \text{kJ mol}^{-1}$

　c.　Reacting 0.1 mol $H_2$ (the limiting reagent) will produce 24.18 kJ of heat (at constant pressure). The contents of the vessel after reaction are 0.1 mol $H_2O$ and 0.05 mol $O_2$, so the total heat capacity of the reaction contents plus the Al block is $(1.802\ \text{g } H_2O){\times}(4.18\ \text{J g}^{-1}\ \text{K}^{-1}) + (1.60\ \text{g } O_2){\times}(0.92\ \text{J g}^{-1}\ \text{K}^{-1}) + (1000\ \text{g}){\times}(0.89\ \text{J g}^{-1}\ \text{K}^{-1}) = 899\ \text{J K}^{-1}$.
$\Delta T = q/C_p = (24180\ \text{J})/(899.0\ \text{J K}^{-1}) = 26.9\ \text{K}$
Since the initial temperature is 373 K, the final temperature is 400 K (127 °C).

　d.　$\Delta G = \Delta G° + RT\ln(Q)$. At 298 K, $\Delta G° = \Delta H° - T\Delta S° = -241.8\ \text{kJ mol}^{-1} - (298\ \text{K})(-0.0445\ \text{kJ mol}^{-1}\ \text{K}^{-1}) = -228.5\ \text{kJ mol}^{-1}$.
For the reaction to just be spontaneous, $\Delta G = 0$, so $Q = e^{-\Delta G°/RT} = 1.1 \times 10^{40}$.
$$Q = 1.1 \times 10^{40} = \frac{p(H_2O)}{p(H_2){\cdot}p(O_2)^{1/2}}$$
Substituting in $p(H_2O) = 0.031$ bar and $p(O_2) = 0.20$ bar gives
$$p(H_2) = 6.1 \times 10^{-42}\ \text{bar}$$
This corresponds to $6.1 \times 10^{-40}$ volume% of $H_2$. (This is much, much less than one molecule per liter, so any amount of hydrogen in humid air would react spontaneously to form water vapor.)

　e.　The *thermodynamic* spontaneity of the reaction need not correspond to the *kinetic* conditions required to support a self-sustaining flame. Evidently at concentrations below about 4 vol%, the reaction cannot proceed rapidly enough to produce enough reactive intermediates to support continued rapid reaction.

4. a.   $P_{vap,soln} = (x_{H2O})(P_{vap\ H2O,\ pure})$
$n_{H2O} = 1000\ g \times 1\ mol/18.02\ g = 55.49\ mol$
Because each mol $MgCl_2$ forms 3 moles of ions, the total moles are 55.49 mol $H_2O$ + 3(0.880) mol ions = 58.13 mol.  So $x_{H2O} = 55.49/58.13 = 0.955$.
$P_{vap,soln} = (0.955)(611\ Pa) = 584\ Pa$

b.   $\ln(P_2/P_1) = (-\Delta H^\circ_{subl}/R)(1/T_2 - 1/T_1)$
$\ln(584\ Pa/611\ Pa) = (-51100\ J\ mol^{-1}/8.314\ J\ mol^{-1}\ K^{-1})(1/T_2 - 1/273.15\ K)$
$7.353 \times 10^{-6}\ K^{-1} = 1/T_2 - 1/273.15\ K$
$T_2 = 272.6\ K = -0.5\ °C$

c.   When the solution freezes, the solid formed is pure ice.  Unlike the flexible structure of water in solution, the ice crystal has a rigid structure that cannot accommodate impurities such as magnesium or chloride ions.  If pure ice is in equilibrium with the aqueous solution, then the vapor in equilibrium with ice must be in equilibrium with the vapor in equilibrium with the solution.  This is the same as saying that the vapor pressures are equal.

d.   At the freezing point temperature, the vapor pressure of pure ice is equal to the vapor pressure of the solution, which is 0.955 times the vapor pressure of pure water at this temperature (as in part a).  If we call this vapor pressure $P_f$, then:

From the temperature-dependence of the vapor pressure of ice:
$\ln(P_f/611\ Pa) = (-\Delta H^\circ_{subl}/R)(1/T_f - 1/273.15\ K)$
$\ln(P_f) = (-\Delta H^\circ_{subl}/R)(1/T_f - 1/273.15\ K) + \ln(611\ Pa)$

The vapor pressure of pure water at this temperature is $P_f/0.955$, so:
$\ln(1.047 \bullet P_f/611\ Pa) = (-\Delta H^\circ_{vap}/R)(1/T_f - 1/273.15\ K)$
$\ln(P_f) = (-\Delta H^\circ_{vap}/R)(1/T_f - 1/273.15\ K) + \ln(611\ Pa) - \ln(1.047)$

Equating the two expressions for $\ln(P_f)$ gives:
$\ln(1.047) = ([\Delta H^\circ_{subl} - \Delta H^\circ_{vap}]/R) \bullet (1/T_f - 1/273.15\ K)$
$6.36 \times 10^{-5}\ K^{-1} = (1/T_f - 1/273.15\ K)$
$T_f = 268.5\ K = -4.7\ °C$

Note that this number is slightly different from the value obtained from the molal freezing point depression equation (−4.9 °C), as the derivation of that equation assumes that $\ln(1 - x) \approx -x$ and that $1/T_2 - 1/T_1 \approx (\Delta T)/T_1^2$.  Those assumptions are fine at the limit of dilute concentrations but they introduce small errors as concentration is increased.

e.   As more pure ice crystallizes from the solution, the concentration of ions in solution increases, further depressing the freezing point.  Thus the temperature will decrease as more solid forms.

5. a.  $H^+ + Cl^- + OCl^- \rightarrow Cl_2 + H_2O$

   b.  $Al + OH^- + H_2O \rightarrow Al(OH)_4^- + H_2$

   c.  $Na + NH_3 \rightarrow Na^+ + NH_2^- + H_2$

   d.  $PtCl_4^{2-} + NH_3 \rightarrow$  $+ Cl^-$

   e. 

   f.  $^{57}Co \rightarrow {}^{57}Fe + \gamma$

6. a.
$$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s) \qquad \Delta G° = -2F(1.188 \text{ V})$$
$$\underline{Pt(s) + 4\ Cl^-(aq) \rightarrow PtCl_4^{2-}(aq) + 2e^- \qquad \Delta G° = -2F(-0.758 \text{ V})}$$
$$Pt^{2+}(aq) + 4\ Cl^-(aq) \rightarrow PtCl_4^{2-}(aq) \qquad \Delta G° = -2F(1.188 - 0.758 \text{ V})$$
$$= -83.0 \text{ kJ mol}^{-1}$$

$$K_f = e^{-\Delta G°/RT} = e^{-(-83000 \text{ J mol-1})/(8.314 \text{ J mol-1 K-1})(298 \text{ K})}$$
$$K_f = 3.5 \times 10^{14}$$

b.
$$PtCl_6^{2-}(aq) + 2e^- \rightarrow PtCl_4^{2-}(aq) + 2\ Cl^-(aq) \qquad \Delta G° = -2F(0.726 \text{ V})$$
$$\underline{PtCl_4^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4\ Cl^-(aq) \qquad \Delta G° = -2F(0.758 \text{ V})}$$
$$PtCl_6^{2-}(aq) + 4e^- \rightarrow Pt(s) + 6\ Cl^-(aq) \qquad \Delta G° = -2F(0.726 + 0.758 \text{ V})$$

For the summed half-reaction, $\Delta G° = -4FE°$. So $E° = (0.726 + 0.758 \text{ V})/2 = 0.742 \text{ V}$.

c. The net reaction of the electrolysis is:
$$2\ Ag^+(aq) + Pt(s) + 4\ Cl^-(aq) \rightarrow 2\ Ag(s) + PtCl_4^{2-}(aq)$$
For this reaction, $E° = 0.799 \text{ V} - 0.758 \text{ V} = 0.041 \text{ V}$
Under the nonstandard conditions of the electrolysis setup:
$$E = E° - \frac{RT}{2F}\ln\frac{[PtCl_4^{2-}]}{[Ag^+]^2[Cl^-]^4}$$

$$E = 0.041 \text{ V} - 0.01284 \text{ V} \cdot \ln\frac{[0.001]}{[0.1]^2[0.1]^4}$$
$$E = -0.048 \text{ V}$$
Thus, at least 0.048 V of potential must be applied for electrons to flow spontaneously to oxidize the Pt and reduce the $Ag^+$.

d. There are several ways to analyze this situation. One is to consider the electrolytic oxidation to form $PtCl_6^{2-}$:
$$4\ Ag^+(aq) + Pt(s) + 6\ Cl^-(aq) \rightarrow 4\ Ag(s) + PtCl_4^{2-}(aq)$$
$$E° = 0.799 \text{ V} - 0.742 \text{ V} = 0.057 \text{ V}$$
This reaction is thus even more favorable under standard conditions than formation of $PtCl_4^{2-}$! Under these nonstandard conditions,
$$E = E° - \frac{RT}{4F}\ln\frac{[PtCl_6^{2-}]}{[Ag^+]^4[Cl^-]^6}$$
$$E = 0.057 \text{ V} - (0.00642 \text{ V})\ln\frac{[PtCl_6^{2-}]}{[0.1]^4[0.1]^6}$$
$$E = -0.091 \text{ V} - (0.00642 \text{ V})\ln([PtCl_6^{2-}])$$
Under the conditions of the electrolysis, this will be spontaneous if $E > -0.048$ V, which corresponds to $[PtCl_6^{2-}] < 1.3 \times 10^{-3}$ M. So in fact $PtCl_6^{2-}$ will (thermodynamically) be produced exclusively at the beginning of the electrolysis and will continue to be produced until its concentration is quite similar to that of the initial concentration of $PtCl_4^{2-}$ (there will be some slight effect of the changing $Cl^-$ and $Ag^+$ concentrations). This is definitely significant! (There may be kinetic factors at play that would favor one form over the other, but that is more difficult to predict, and the question specifically asked about the thermodynamic possibilities.)

7. a.    $BF_3$ is trigonal planar, $NF_3$ is trigonal pyramidal.

b.    In all of the molecules, the major type of intermolecular forces at play are London dispersion forces.  F and $CH_3$ have the same number of electrons, but the extremely high electronegativity of F means that it holds its electrons tightly and thus has an unusually low polarizability.  This means that the ability of a spontaneous dipole in one molecule to induce a dipole in a neighboring molecule is low, and hence the LDF are relatively weak, leading to low boiling points.

c.    As one moves to the right, from $CX_4$ to FX, the number of electrons per molecule decreases as the number of X groups decreases.  Since the London dispersion forces increase with increasing numbers of electrons, this leads to a general decline in normal boiling points.

d.    Based on the reasoning in c., the relatively low boiling point of $B(CH_3)_3$ is expected since it has fewer electrons than $C(CH_3)_4$.  $BF_3$'s relatively high boiling point is surprising on these grounds.  The Lewis acidity of $BF_3$ means that there are weak intermolecular attractions based on the weakly Lewis basic lone pairs on F interacting with the empty $p$ orbital on the boron of a neighboring molecule.  This type of interaction is not possible in any of the other molecules.

e.    As one moves to the right in the $2p$ block, the atomic radius of A becomes smaller because the increasing effective nuclear charge (since the added electrons only incompletely shield the added protons).  The contracted orbitals around A thus form bonds at shorter interatomic distances.

f.    The decreasing atomic size of A is offset by increasing lone pair-lone pair repulsions between A and F as one goes to the right in the periodic table.  (At the left, $BF_3$ actually has an attractive interaction between the empty $p$ orbital on B and the filled $p$ orbitals on F.)  This weakens the bonds and pushes the atoms farther apart.

8. a. Cyclopentanone has the higher normal boiling point (131 °C vs. 76 °C). Both compounds have the same number of electrons and roughly the same shape, so London dispersion forces should be very similar in the two compounds. Neither substance forms hydrogen bonds in the pure liquids. 1-Methylcyclopentene contains only nonpolar carbon-carbon and carbon-hydrogen bonds, while cyclopentanone has a very polar C=O bond. So cyclopentanone experiences significant dipole-dipole interactions, which strengthens its intramolecular attractions compared to 1-methylcyclopentene.

b.  + Br$_2$ ⟶  *trans*, racemic

c.  1) CH$_3$MgBr / 2) aqueous workup ⟶ 

d.  H$_2$SO$_4$ / heat ⟶ 

e.  or