2022 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

All testing materials including scratch paper should be turned in and kept secure until **May 14, 2022**, after which tests can be returned to students and their teachers for further study.

When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in the **Part II** testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested 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. (Be sure to use the same identification number you used for **Part I**.). 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.

ABBREVIATIONS AND SYMBOLS

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

CONSTANTS

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

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

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

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

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

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

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

$0\,°C = 273.15$ K

1 atm $= 1.013$ bar $= 760$ mm Hg

Specific heat capacity of $H_2O =$
4.184 J g^{-1} 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. [11%] Compound **A** contains only carbon, fluorine, and chlorine.

    a. The vapor density of **A** at 1.00 bar and 25.0 °C is 6.895 g L^{-1}. What is the molar mass of **A**?

    b. Chlorofluorocarbons such as **A** react with sodium metal to convert all the chlorine present into sodium chloride. The products from the reaction of sodium with 100.0 mL of gaseous **A** (at 1.00 bar and 25.0 °C) are dissolved in water and a few drops of sodium chromate solution are added. This solution is then titrated with 0.3540 M AgNO$_3$ solution until a bright red precipitate appears, which requires 22.79 mL of the titrant. How many chlorine atoms are there in a molecule of **A**?

    c. What is the molecular formula of **A**? Justify your answer.

    d. There is only one known isomer of **A**, compound **B**. The two compounds have nearly identical boiling points, but can be distinguished by ^{19}F NMR spectroscopy, a technique that is sensitive to small differences in the chemical environments of fluorine atoms in compounds. When analyzed by this method, compound **A** exhibits only a single type of chemical environment for fluorine, while compound **B** shows two distinct environments for its fluorine atoms. Draw structural formulas for compounds **A** and **B** that are consistent with these observations.

2. [13%] A chemist prepares an ammonia/ammonium chloride buffer from solid ammonium chloride, 0.80 M NH_3, and distilled water.

    a. What is the pH of the 0.80 M NH_3 solution? (The K_a of NH_4^+ is 5.6×10^{-10}.)

    b. What mole ratio of ammonia to ammonium chloride is required for the buffer to have pH = 9.20?

    c. Calculate the volume of ammonia solution and mass of ammonium chloride needed to make up 500 mL of the pH = 9.20 buffer with a total concentration of nitrogen-containing species (NH_3 or NH_4^+) of 0.50 mol L^{-1}.

d. To the solution described in (c) is added 10.0 mL of 0.10 M AgNO$_3$.

    i. Some AgCl precipitates from this mixture. Justify that this is the case. The K_{sp} of AgCl is 1.8×10^{-10} and the K_f of Ag(NH$_3$)$_2^+$ is 1.6×10^7.

    ii. What is the final concentration of free Ag$^+$ in solution after this mixture achieves equilibrium?

    iii. What is the mass of AgCl that precipitates from solution?

3. [14%] Gaseous molecular and atomic bromine have the following thermodynamic properties:

Species	$\Delta H°_f$ (kJ mol⁻¹)	$S°$ (J mol⁻¹ K⁻¹)
$Br_2(g)$	30.9	245.4
$Br(g)$	111.9	175.0

a. What is the bond dissociation enthalpy (BDE) of the bromine-bromine bond in $Br_2(g)$?

b. How many atoms of $Br(g)$ will be present at equilibrium in a 1.00-L container with 0.100 bar of $Br_2(g)$ at 298 K?

c. The ionization energy of $Br(g)$ is 1145.9 kJ mol⁻¹, while the ionization energy of $Br_2(g)$ is 1025.1 kJ mol⁻¹. What is the bond dissociation enthalpy of $Br_2^+(g)$ (defined as the enthalpy of reaction of $Br_2^+(g)$ to form $Br^+(g)$ and $Br(g)$)?

d. Propose an explanation for the difference in BDE between $Br_2(g)$ and $Br_2^+(g)$ in terms of the bonding in these two species.

e. The vapor pressure of liquid bromine at 298 K is 0.283 bar. What is the absolute entropy $S°$ of $Br_2(l)$?

f. The absolute entropies of the gas-phase atoms of the fourth period given in the table exhibit a non-monotonic pattern. Explain why the absolute entropies of $Se(g)$ and $Br(g)$ are larger than the absolute entropies of either $As(g)$ or $Kr(g)$.

	As(*g*)	Se(*g*)	Br(*g*)	Kr(*g*)
$S°$, J mol^{-1} K^{-1}	163.2	176.7	175.0	164.1

4. [14%] Iodide ion reacts with hydrogen peroxide in acidic solution according to the following equation:

$$2\ I^-(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow I_2(aq) + 2\ H_2O(l) \qquad (4)$$
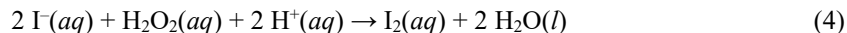
The reaction is carried out at 18.8 °C in the presence of a mixture of CH_3COOH and NaOH to regulate the pH, sodium thiosulfate (which reacts very rapidly with I_2 to form tetrathionate ions), and starch. All the components except the hydrogen peroxide are premixed, and then the hydrogen peroxide solution is added and a stopwatch is started. The solution remains colorless until it suddenly turns blue, at which point the time t is recorded. The following data are obtained:

Run	1.0 M CH₃COOH, mL	1.0 M NaOH, mL	0.20 M KI, mL	0.20 M H₂O₂, mL	0.020 M Na₂S₂O₃, mL	Distilled H₂O, mL	t, s
A	2.0	1.0	2.0	2.0	1.0	2.0	68.2
B	4.0	1.0	2.0	2.0	1.0	0.0	68.9
C	2.0	1.0	4.0	2.0	1.0	0.0	33.2
D	2.0	1.0	2.0	4.0	1.0	0.0	32.9

a. Give a qualitative explanation for why the solution suddenly turns blue after a certain amount of time has elapsed.

b. Calculate the initial $[H^+]$ in runs A and B and explain why $[H^+]$ will not change significantly over the course of the respective reactions. (The K_a of CH_3COOH is 1.8×10^{-5}.)

c. The rate law for reaction (4) has the form Rate = $k_4[I^-]^m[H_2O_2]^n[H^+]^p$, where m, n, and p are integers. What are the values of m, n, and p under these experimental conditions? Briefly explain your reasoning.

d. What is the value of the rate constant k_4 for this reaction?

e. The following mechanism for reaction (4) has been proposed:

$$H_2O_2(aq) + H^+(aq) \rightleftarrows H_3O_2^+(aq) \qquad\qquad \textit{(fast, unfavorable)}$$

$$H_3O_2^+(aq) + I^-(aq) \rightarrow HOI(aq) + H_2O(l) \qquad\qquad \textit{(slow)}$$

$$HOI(aq) + H^+(aq) \rightleftarrows H_2OI^+(aq) \qquad\qquad \textit{(fast, unfavorable)}$$

$$H_2OI^+(aq) + I^-(aq) \rightarrow I_2(aq) + H_2O(l) \qquad\qquad \textit{(fast)}$$
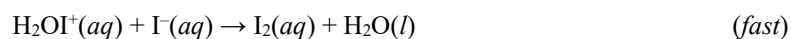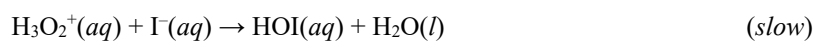
Is this mechanism consistent with the given data? Justify your answer.

f. The experiments are repeated under the same conditions as Runs A and B above, except that phosphoric acid (H_3PO_4, $K_a = 7.6 \times 10^{-3}$) is substituted for acetic acid. The observed times for the solutions to turn blue with this substitution are 46.7 s and 31.5 s, respectively. Propose an interpretation for these observations.

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.   Diiodine pentoxide is added to a barium hydroxide solution.

     b.   Sulfur dioxide is bubbled through an acidified solution of potassium permanganate.

     c.   Iron(III) oxide is heated with carbon monoxide gas at 1200 °C.

     d.   Aqueous hydrobromic acid is electrolyzed at platinum electrodes.

     e.   1-Butanol reacts with an acidified solution of potassium dichromate.

     f.   Oganesson-294 undergoes alpha decay.

6. [12%] A galvanic cell is constructed at 298 K with one half-cell consisting of a 10.00 g silver wire immersed in 1.00 L of a 0.100 M solution of silver nitrate and the second half-cell consisting of a 20.00 g copper plate immersed in 1.00 L of a 0.200 M solution of copper(II) sulfate.

Half-reaction	$E°$, V
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.800
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.337

   a. What voltage is measured for this galvanic cell?

   b. The cell is discharged at a constant current of 0.150 A until the mass of the silver electrode is equal to the mass of the copper electrode. How much time does this take?

   c. A chemist wishes to add sodium oxalate to one of the half-cells in the original cell to decrease the measured voltage. To which cell should the sodium oxalate be added, and why?

d. What mass of sodium oxalate would need to be added to the appropriate half-cell to cause the voltage in the original cell to become 0.200 V? You may assume that there is no change in the volume of the solution. The K_{sp} of $Ag_2C_2O_4$ is 3.5×10^{-11} and the K_{sp} of CuC_2O_4 is 3.0×10^{-8}.

7. [12%] Formamide and glyoxal are six-atom molecules with essentially planar structures as depicted below (these are *NOT* Lewis structures).

formamide   glyoxal
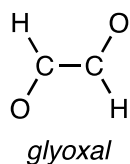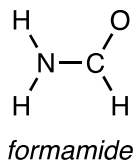
a. Draw complete Lewis structures for these two molecules, including all bonds, lone pairs, and nonzero formal charges.

b. One of these compounds has a normal boiling point of 51 °C, while the other has a normal boiling point of 210 °C. Assign which compound has which boiling point, and propose an explanation for the large difference.

c. The H–N–H bond angle in formamide (122°) is much larger than the H–N–H angle in ammonia (107°). Explain this difference.

d. Rotation of the central bond in the two molecules (the C-N bond in formamide or the C-C bond in glyoxal) occurs at very different rates, with the barrier to rotation in formamide being much larger (74 kJ mol^{-1} vs. 25 kJ mol^{-1}). Explain why rotation is much more difficult in formamide than in glyoxal.

8. [12%] Consider the following isomers with the formula $C_3H_6O_2$.

A   **B**   **C**
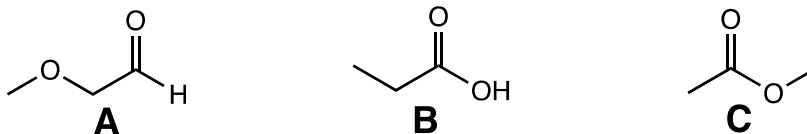
a. Rank the three compounds in order of increasing normal boiling point, and justify your ordering.

b. Compounds **A**–**C** are all optically inactive. Draw the structure of an optically active isomer of $C_3H_6O_2$.

c. Compounds **A** and **B** react reversibly with water in the presence of a suitable catalyst as shown below:
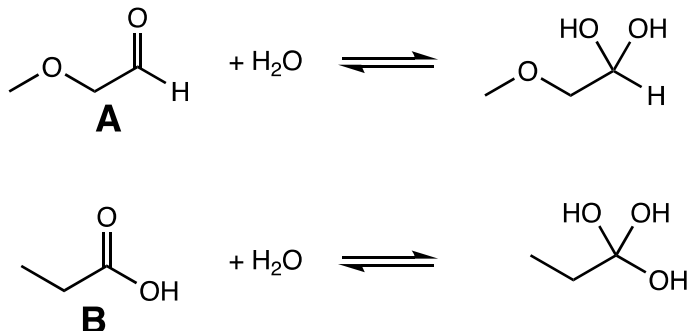
Which reaction has the larger equilibrium constant? Explain your answer in terms of the structure or bonding of the species in the reactions.

d.   Compound **C** reacts with water in the presence of a strong acid to form two new organic compounds. Write a balanced equation for this reaction, including structural formulas for the two organic products.

e.   In the presence of excess strong base, compound **C** reacts with water irreversibly. Explain why this reaction is irreversible while the reaction in the presence of acid is reversible.

1. a. $PV = nRT$, so $n = PV/RT$. 1.000 L of gas will have

$$n = (1.000 \text{ bar})(1.000 \text{ L})/(298.15 \text{ K})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})$$
$$n = 0.04034 \text{ mol}$$
$$\text{molar mass} = (6.895 \text{ g L}^{-1})/(0.04034 \text{ mol L}^{-1}) = 170.9 \text{ g mol}^{-1}$$

   b. $0.02279 \text{ L titrant} \times 0.3540 \text{ mol L}^{-1} = 8.068 \times 10^{-3} \text{ mol chloride}$

100.0 mL gas has $n = (1.000 \text{ bar})(0.1000 \text{ L})/(298.15 \text{ K})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})$
$$= 4.034 \times 10^{-3} \text{ mol } \mathbf{A}$$
$$(8.068 \times 10^{-3} \text{ mol chloride})/(4.034 \times 10^{-3} \text{ mol } \mathbf{A}) = 2.000 \text{ mol Cl/mol } \mathbf{A}$$

   c.   Since the molar mass of **A** is 170.9 and there are 2 mol Cl per mol **A**, the carbons and fluorines in **A** must have a combined mass of $170.9 - 2(35.45) = 100.0$ amu. If **A** has only one carbon, it must have $(100.0 - 12.01)/19.00 = 4.63$ F atoms, which is impossible (it must have an integer number of each type of atom per formula unit, plus over six halogens per carbon atom is not chemically reasonable). Two carbons in **A** would imply $(100.0 - 2 \times 12.01)/19.00 = 4.00$ atoms of F, which *is* possible. Each additional carbon in the formula would result in 0.63 fewer F atoms, which will not be especially close to an integer from 3-7 carbon atoms, at which point there would need to be fewer than one F atom. Thus the only possibility is $C_2F_4Cl_2$.

   d.
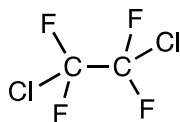
all F atoms in the same environment
(each bonded to a carbon with 2F's and 1 Cl)
Isomer **A**
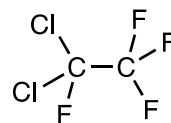
Two different F environments
(one F bonded to a carbon with 2 Cl's,
three F's bonded to a C with no Cl's)
Isomer **B**

2. a.   The major reaction is:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $K_{eq} = (K_w/K_a$ of $NH_4^+)$
$$K_{eq} = (1 \times 10^{-14})/(5.6 \times 10^{-10})$$
$$K_{eq} = 1.8 \times 10^{-5}$$
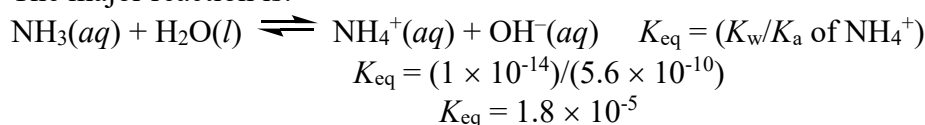
Since this is the major reaction, $[NH_4^+] \approx [OH^-]$, and since it is not very favorable, $[NH_3] \approx 0.80$ M.

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[OH^-]^2}{[0.80]} = 1.8 \times 10^{-5}$$
$$[OH^-]^2 = 1.44 \times 10^{-5}$$
$$[OH^-] = 3.8 \times 10^{-3} \text{ M}$$
$$pH = 14 + \log[OH^-] = 11.60$$

b. $pH = pK_a$ of $NH_4^+ + \log([NH_3]/[NH_4^+])$
$9.20 = 9.25 + \log([NH_3]/[NH_4^+])$
$\log([NH_3]/[NH_4^+]) = -0.05$
$[NH_3]/[NH_4^+] = 0.89$

c.   There are two constraints on the number of moles of NH_3 and of NH_4^+. From the fact that the total concentration of nitrogen species is 0.500 M in 0.500 L,
$$(\text{mol } NH_3) + (\text{mol } NH_4^+) = 0.250 \text{ mol}$$
From the calculation in (b),
$$(\text{mol } NH_3) = 0.89(\text{mol } NH_4^+)$$
Solving the two simultaneous equations gives:
$$0.89(\text{mol } NH_4^+) + (\text{mol } NH_4^+) = 0.250 \text{ mol}$$
$$(\text{mol } NH_4^+) = 0.132 \text{ mol}$$
$$0.132 \text{ mol } NH_4^+ \times (53.49 \text{ g } NH_4Cl/\text{mol}) = 7.06 \text{ g } NH_4Cl$$

$$(\text{mol } NH_3) = 0.89(\text{mol } NH_4^+) = 0.89(0.132 \text{ mol}) = 0.117 \text{ mol } NH_3$$
$$0.117 \text{ mol } NH_3/(0.80 \text{ M } NH_3) = 0.147 \text{ L of the } 0.80 \text{ M } NH_3 \text{ solution}$$

d. i.   mol $Ag^+ = (0.0100$ L$)\times(0.10$ mol/L$) = 0.0010$ mol Ag^+. Since the amounts of both chloride and ammonia are over 100 times this amount, we can neglect the changes of these latter two species as $AgCl(s)$ and $Ag(NH_3)_2^+$ form. So $[Cl^-] = 0.132$ mol/(0.510 L) $= 0.259$ M and $[NH_3] = 0.117$ mol/(0.510 L) $= 0.229$ M.
    There are a number of ways to approach the analysis of whether a precipitate forms. Let us assume that no precipitate forms, so all of the Ag^+ (initial concentration = 0.0010 mol/0.51 L $= 1.96 \times 10^{-3}$ M) remains in solution. Of course, much of it will be in the form of the complex ion:

$$\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][0.229]^2} = K_f = 1.6 \times 10^7$$
$$\frac{[Ag(NH_3)_2^+]}{[Ag^+]} = 8.4 \times 10^5$$

    This means that almost all the silver ion in solution is in the form of the complex ion, so $[Ag^+] = [Ag(NH_3)_2^+]/(8.4 \times 10^5) = (1.96 \times 10^{-3})/(8.4 \times 10^5) = 2.3 \times 10^{-9}$ M.

$Q_{sp} = [Ag^+][Cl^-] = [2.3 \times 10^{-9}][0.259] = 6.0 \times 10^{-10} > K_{sp}$. This means that there will be a precipitate of AgCl.
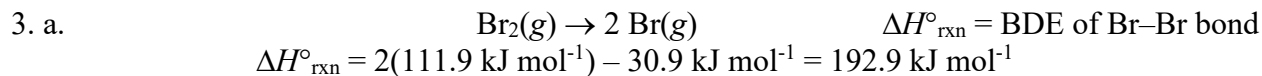
ii.   Since there is a precipitate, $[Ag^+][Cl^-] = K_{sp}$

$$[Ag^+][0.259] = 1.8 \times 10^{-10}$$
$$[Ag^+] = 6.95 \times 10^{-10} \text{ M}$$

iii. From the complexation equilibrium,

$$\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{[Ag(NH_3)_2^+]}{[6.95 \times 10^{-10}][0.229]^2} = K_f = 1.6 \times 10^7$$
$$[Ag(NH_3)_2^+] = 5.8 \times 10^{-4} \text{ M}$$

This accounts for $(5.8 \times 10^{-4}$ mol/L$)\times(0.510$ L$) = 3.0 \times 10^{-4}$ mol of silver. The amount of free Ag^+ is negligible, so the amount of silver that must have precipitated as AgCl is $(1.00 \times 10^{-3}$ mol total Ag$) - (3.0 \times 10^{-4}$ mol complexed Ag$) = 7.0 \times 10^{-4}$ mol AgCl.

$$(7.0 \times 10^{-4} \text{ mol AgCl}) \times (143.4 \text{ g mol}^{-1}) = 0.100 \text{ g AgCl}$$

3. a. $$Br_2(g) \rightarrow 2\ Br(g) \qquad \Delta H°_{rxn} = \text{BDE of Br–Br bond}$$
$$\Delta H°_{rxn} = 2(111.9\ kJ\ mol^{-1}) - 30.9\ kJ\ mol^{-1} = 192.9\ kJ\ mol^{-1}$$

b. For $Br_2(g) \rightarrow 2\ Br(g)$, $\Delta S° = 2(175.0\ J\ mol^{-1}\ K^{-1}) - 245.4\ J\ mol^{-1}\ K^{-1} = 104.6\ J\ mol^{-1}\ K^{-1}$
$$\Delta G° = \Delta H° - T\Delta S° = (192.9\ kJ\ mol^{-1}) - (298\ K)(0.1046\ kJ\ mol^{-1}\ K^{-1}) = 161.7\ kJ\ mol^{-1}$$
$$\Delta G° = -RT\ln(K_{eq})$$
$$161700\ J\ mol^{-1} = -(8.314\ J\ mol^{-1}\ K^{-1})(298\ K)\ln(K_{eq})$$
$$K_{eq} = 4.5 \times 10^{-29}$$

At equilibrium:
$$\frac{p_{Br}^{\ 2}}{p_{Br_2}} = \frac{p_{Br}^{\ 2}}{0.100} = 4.5 \times 10^{-29}$$
$$p_{Br} = 2.1 \times 10^{-15}\ bar$$

In a 1.00 L container, $PV = nRT$:
$$(2.1 \times 10^{-15}\ bar)(1.00\ L) = n(0.08314\ L\ bar\ mol^{-1}\ K^{-1})(298\ K)$$
$$n = 8.6 \times 10^{-17}\ mol$$
$$(8.6 \times 10^{-17}\ mol) \times (6.022 \times 10^{23}\ mol^{-1}) = 5.2 \times 10^{7}\ Br\ atoms$$

c. Using Hess's Law (all species are gas-phase):

$Br_2 \rightarrow 2\ Br$	$\Delta H° = 192.9\ kJ\ mol^{-1}$
$Br \rightarrow Br^+ + e^-$	$\Delta H° = 1145.9\ kJ\ mol^{-1}$
$Br_2^+ + e^- \rightarrow Br_2$	$\Delta H° = -1025.1\ kJ\ mol^{-1}$
$Br_2^+ \rightarrow Br + Br^+$	$\Delta H° = \text{BDE} = 313.7\ kJ\ mol^{-1}$
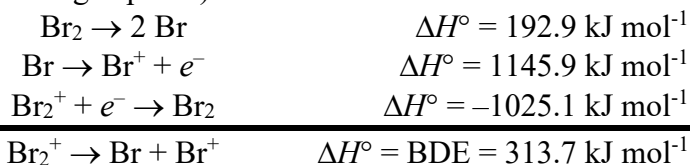
d. The electron that is removed from Br_2 is π^* in character, so the bond order of Br_2^+ is 1.5 compared to 1.0 for Br_2. The higher bond order results in a greater bond strength.

e. $$\Delta G°_{vap,\ 298K} = -RT\ln(K_{eq}) = -(8.314\ J\ mol^{-1}\ K^{-1})(298\ K)\ln(0.283) = 3.13\ kJ\ mol^{-1}$$
$$\Delta G°_{vap,\ 298K} = \Delta H°_{vap} - T\Delta S°_{vap}$$
$$3.13\ kJ\ mol^{-1} = 30.9\ kJ\ mol^{-1} - (298\ K)(\Delta S°_{vap})$$
$$\Delta S°_{vap} = 93.2\ J\ mol^{-1}\ K^{-1}$$
$$\Delta S°_{vap} = (S°\ of\ Br_2(g)) - (S°\ of\ Br_2(l))$$
$$93.2\ J\ mol^{-1}\ K^{-1} = 245.4\ J\ mol^{-1}\ K^{-1} - (S°\ of\ Br_2(l))$$
$$S°\ of\ Br_2(l) = 152.2\ J\ mol^{-1}\ K^{-1}$$

f. As and Kr have only one way of arranging their valence electrons (for As, each valence p orbital is half-filled, while Kr has each valence p orbital completely filled). In contrast, Se and Br have orbitally degenerate ground states, which gives them more ways of arranging their electrons. This increase in the number of possible arrangements corresponds to a higher entropy ($S = k_B\ln\Omega$).

4. a. I_2 is produced in the reaction between H_2O_2 and I^-. Initially, the I_2 does not accumulate to a significant extent because it immediately reacts with the thiosulfate ion. Once the small amount of thiosulfate is consumed, then I_2 begins to accumulate, and the solution turns blue because of the intensely blue complex formed between starch and iodine.

b. The NaOH will immediately react with the CH_3COOH to form CH_3COO^-. Taking into account the 10-fold dilution, this means that in run A, $[CH_3COOH] = [CH_3COO^-] = 0.1$ M. Since
$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$
$$[H^+] = 1.8 \times 10^{-5} \text{ M}$$
In run B, with $[CH_3COOH] = 0.3$ M and $[CH_3COO^-] = 0.1$ M, $[H^+] = 5.4 \times 10^{-5}$ M.

These solutions are buffers, with the H^+ consumed in reaction 4 being replenished by the CH_3COOH. Thus, at the point where the initially 0.0020 M $S_2O_3^{2-}$ is consumed, the concentration of CH_3COOH will fall to 0.098 M while $[CH_3COO^-]$ rises to 0.102 M, and $[H^+] = 1.73 \times 10^{-5}$ M, a change of only 4%.

c. In each case, $[S_2O_3^{2-}]_0 = 0.0020$ M, so at the point where the blue color appears, $\Delta[H_2O_2]$ $= -0.0010$ M (since two moles of thiosulfate react per mole of I_2 produced). Since rate = $-\Delta[H_2O_2]/\Delta t$, the time recorded is inversely proportional to the initial rate of the reaction.
    Comparing run B to run A, $[H^+]$ increases by a factor of 3 while all other concentrations are the same. The rate is essentially unchanged, so $p = 0$.
    Comparing run C to run A, $[I^-]$ increases by a factor of 2 while all other concentrations are the same. The rate roughly doubles, so $m = 1$.
    Comparing run D to run A, $[H_2O_2]$ increases by a factor of 2 while all other concentrations are the same. The rate roughly doubles, so $n = 1$.
$$\text{Rate} = k_4[I^-][H_2O_2]$$

d. $k_4 = (-\Delta[H_2O_2]/\Delta t)/([I^-][H_2O_2])$. So:
    Run A, $k_4 = (0.0010 \text{ M}/68.2 \text{ s})/([0.040 \text{ M}][0.040 \text{ M}]) = 9.1 \times 10^{-3} \text{ M}^{-1}\text{ s}^{-1}$
    Run B, $k_4 = (0.0010 \text{ M}/68.9 \text{ s})/([0.040 \text{ M}][0.040 \text{ M}]) = 9.2 \times 10^{-3} \text{ M}^{-1}\text{ s}^{-1}$
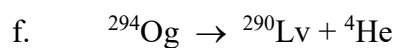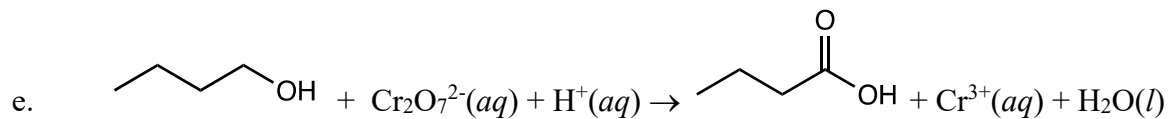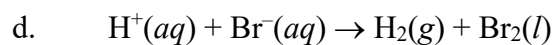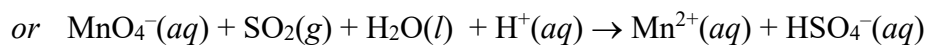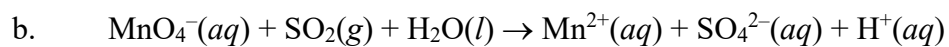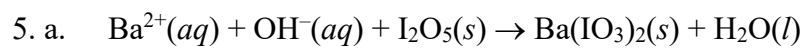   Run C, $k_4 = (0.0010 \text{ M}/33.2 \text{ s})/([0.080 \text{ M}][0.040 \text{ M}]) = 9.4 \times 10^{-3} \text{ M}^{-1}\text{ s}^{-1}$
    Run D, $k_4 = (0.0010 \text{ M}/32.9 \text{ s})/([0.040 \text{ M}][0.080 \text{ M}]) = 9.5 \times 10^{-3} \text{ M}^{-1}\text{ s}^{-1}$
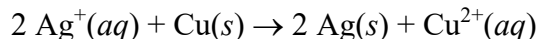$$\textit{Average} = 9.3 \times 10^{-3} \text{ M}^{-1}\text{ s}^{-1}$$

e. This mechanism predicts Rate $= k_2[I^-][H_3O_2^+] = k_2K_1[I^-][H_2O_2][H^+]$. This is *inconsistent* with the observed data under these conditions, since it predicts first-order dependence on $[H^+]$ while a zero-order dependence is actually observed.

f. H_3PO_4 is a much stronger acid than CH_3COOH, with $[H^+] = 7.6 \times 10^{-3}$ M and 2.3×10^{-2} M in the two new reactions. Even though there was no effect on the rate of reaction in the reactions run with acetic acid, now increasing $[H^+]$ increases the rate! This indicates that there is an acid-catalyzed pathway for the reaction (perhaps by the mechanism proposed in (e)) that has become significant at the lower pH of the reactions run in the presence of phosphoric acid.

5. a. $Ba^{2+}(aq) + OH^-(aq) + I_2O_5(s) \rightarrow Ba(IO_3)_2(s) + H_2O(l)$

b. $MnO_4^-(aq) + SO_2(g) + H_2O(l) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H^+(aq)$

 or $MnO_4^-(aq) + SO_2(g) + H_2O(l) + H^+(aq) \rightarrow Mn^{2+}(aq) + HSO_4^-(aq)$

c. $Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$

d. $H^+(aq) + Br^-(aq) \rightarrow H_2(g) + Br_2(l)$

e. $+ \ Cr_2O_7^{2-}(aq) + H^+(aq) \rightarrow$ $+ Cr^{3+}(aq) + H_2O(l)$

f. $^{294}Og \rightarrow \ ^{290}Lv + \ ^4He$

6. a.   The net cell reaction is
$$2\ Ag^+(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$$
with $E° = 0.800\ V - 0.337\ V = 0.463\ V$. The cell is not under standard conditions, so applying the Nernst equation gives:
$$E = E° - (RT/nF)\ln([Cu^{2+}]/[Ag^+]^2)$$
$$E = (0.463\ V) - ((8.314\ J\ mol^{-1}\ K^{-1})(298\ K)/2(96500\ J\ V^{-1}\ mol^{-1})\ln([0.200]/[0.100]^2)$$
$$E = 0.425\ V$$

b.   Ag deposition will take place with $(107.9\ g\ mol^{-1})/(96500\ C\ mol^{-1}) = 1.118 \times 10^{-3}\ g\ C^{-1}$.
Cu dissolution will require $(63.55\ g\ mol^{-1})/2(96500\ C\ mol^{-1}) = 3.293 \times 10^{-4}\ g\ C^{-1}$.
So if $x =$ the amount of charge passed in the discharge, then
$$10.00\ g + (1.118 \times 10^{-3}\ g\ C^{-1})x = 20.00\ g - (3.293 \times 10^{-4}\ g\ C^{-1})x$$
$$10.00\ g = (1.447 \times 10^{-3}\ g\ C^{-1})x$$
$$x = 6909\ C$$
Since $q = it$,
$$6909\ C = (0.150\ A)t$$
$$t = 46100\ s = 12.8\ h$$

c.   Decreasing the voltage means making the net reaction less favorable, which would involve either decreasing the concentration of the reactants or increasing the concentration of the products. Adding oxalate would cause precipitation of the insoluble oxalate salt, so one would need to do that to the silver-containing half-cell to decrease the voltage.

d.   Using the Nernst equation,
$$0.200\ V = (0.463\ V) - ((8.314\ J\ mol^{-1}\ K^{-1})(298\ K)/2(96500\ J\ V^{-1}\ mol^{-1})\ln([0.200]/[Ag^+]^2)$$
$$-0.263\ V = 0.021\ V + 0.02567\ln[Ag^+]$$
$$[Ag^+] = 1.567 \times 10^{-5}\ M$$
From the K_{sp} expression, $[Ag^+]^2[C_2O_4^{2-}] = [1.567 \times 10^{-5}]^2[C_2O_4^{2-}] = 3.5 \times 10^{-11}$
$$[C_2O_4^{2-}] = 0.143\ M$$
This requires the addition of $0.143\ mol\ Na_2C_2O_4$ (to achieve this concentration in 1.00 L of solution) + $0.0500\ mol\ Na_2C_2O_4$ (to precipitate $0.0500\ mol\ Ag_2C_2O_4$) = $0.193\ mol$ $Na_2C_2O_4$. The molar mass of $Na_2C_2O_4$ is $134.00\ g\ mol^{-1}$, so this is $0.193\ mol \times 134.00\ g$ $mol^{-1} = 25.9\ g\ Na_2C_2O_4$.

7. a.   (Either resonance structure of formamide would be acceptable.)

*formamide*   *glyoxal*
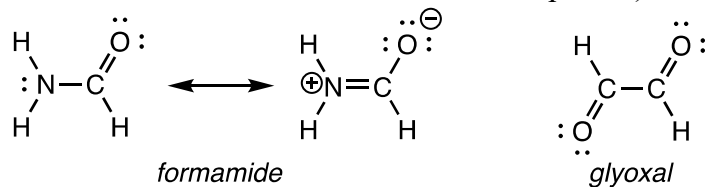
b.   Formamide has the higher normal boiling point because it is capable of forming strong intermolecular N–H•••O hydrogen bonds.

c.   In order to form a partial C–N π bond, as indicated by the minor resonance structure shown above, the nitrogen must have an unhybridized p orbital and thus must be sp^2-hybridized. The bond angles will be close to 120°. In NH_3, the nitrogen is sp^3-hybridized and has bond angles close to 109.5°.

d.   The partial π bond in formamide requires the unhybridized p orbital on nitrogen to be parallel to the p orbital on carbon. Rotating about the carbon-nitrogen bond causes the two p orbitals to lose overlap and thus diminishes the bonding, leading to a large energetic cost. No such cost is incurred in glyoxal, where the carbon-carbon bond is purely σ in character.

8. a.   **C** (bp 57 °C) < **A** (bp 92 °C) < **B** (bp 141 °C)

   Only **B** is capable of forming hydrogen bonds, so it has by far the highest boiling point. **C** has a more compact structure than **A**, which leads to weaker London dispersion forces and a lower boiling point. (The ester is also less polarizable than the ketone + ether.)

   b.   Examples include
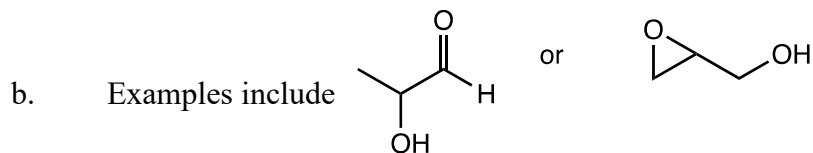
   c.   The equilibrium constant is much larger for compound **A**. Aldehydes are more electrophilic than carboxylic acids, because the carboxylic acid is stabilized by donation from the OH oxygen into the C=O π* orbital, as illustrated by the resonance structures shown below. This resonance stabilization is lost when the carbonyl carbon goes from sp^2 to sp^3 hybridization:

   stabilizing resonance is possible   *no resonance is possible*

   d.
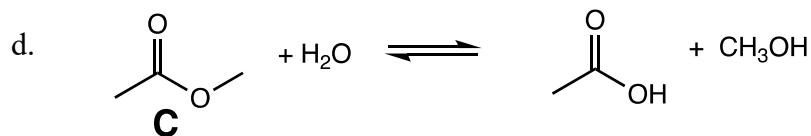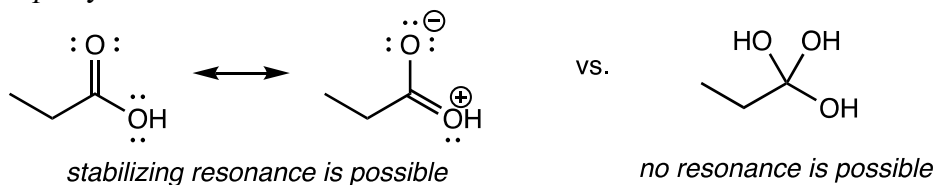
   e. K_{eq} for the reaction in (d) is close to 1. A strong base will react with the carboxylic acid to form the carboxylate anion. This reaction is so favorable ($K_{eq} > 10^9$) that it renders the overall reaction essentially irreversible.