



ACS USNCO  
U.S. National Chemistry Olympiad

# 2020 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 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 27, 2020**, 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.

<b>Part I</b>	<b>60 questions</b>	<b>single-answer multiple-choice</b>	<b>1 hour, 30 minutes</b>
<b>Part II</b>	<b>8 questions</b>	<b>problem-solving, explanations</b>	<b>1 hour, 45 minutes</b>
<b>Part III</b>	<b>2 lab questions</b>	<b>laboratory practical</b>	<b>1 hour, 30 minutes</b>

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 used 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 U.S. citizenship/Green Card Holder statement before leaving the testing site today.**

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

CONSTANTS
$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$
$F = 96,500 \text{ C mol}^{-1}$
$F = 96,500 \text{ J V}^{-1} \text{ mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J s}$
$c = 2.998 \times 10^8 \text{ m s}^{-1}$
$0 \text{ }^\circ\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 1.013 \text{ bar} = 760 \text{ mm Hg}$
Specific heat capacity of $\text{H}_2\text{O} = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$

### 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

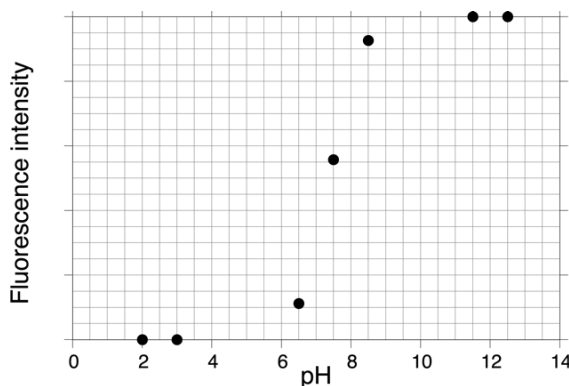
1	PERIODIC TABLE OF THE ELEMENTS																18																	
1A																	8A																	
1 <b>H</b> 1.008	2 <b>He</b> 4.003																																	
3 <b>Li</b> 6.941	4 <b>Be</b> 9.012															10 <b>Ne</b> 20.18																		
11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95	19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.88	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.97	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80									
37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.95	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3	55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57 <b>La</b> 138.9	58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.0	71 <b>Lu</b> 175.0
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89 <b>Ac</b> (227)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>Ds</b> (281)	111 <b>Rg</b> (272)	112 <b>Cn</b> (285)	113 <b>Nh</b> (286)	114 <b>Fl</b> (289)	115 <b>Mc</b> (289)	116 <b>Lv</b> (293)	117 <b>Ts</b> (294)	118 <b>Og</b> (294)																	

58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.0	71 <b>Lu</b> 175.0
90 <b>Th</b> 232.0	91 <b>Pa</b> 231.0	92 <b>U</b> 238.0	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)

1. [14%] A substance **X** is 18.93% C, 25.21% O, and 55.86% a halogen by mass. **X** is a gas at 70 °C and 1.00 bar pressure, with a vapor density of 4.45 g/L.
- What is the molar mass of **X**?
  - What is the molecular formula of **X**?
  - Draw the Lewis structure of **X**.

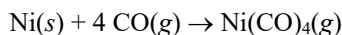
A 1.00 g sample of **X** is added to an excess of aqueous sodium hydroxide, which causes evolution of a colorless gas. The gas is collected over water at an ambient pressure of 1.00 bar and a temperature of 21 °C, and the volume of the gas is found to be 197 mL. Addition of a dilute solution of barium nitrate to the aqueous solution results in the formation of a white precipitate.

- How many moles of gas are evolved in this reaction? (The vapor pressure of water at 21 °C is 18.7 mm Hg.)
  - Write a balanced net ionic equation for the reaction of **X** with aqueous sodium hydroxide, and explain how this reaction is consistent with the number of moles of gas calculated in part (d), and with the observation of a precipitate upon addition of barium nitrate.
2. [12%] 1-Hydroxypyrene-3,6,8-trisulfonate (HPTS) is a monoprotic acid that can be used as a fluorescent acid-base indicator because its conjugate acid form does not emit light (on excitation at  $\lambda = 454$  nm), while its conjugate base form does. The fluorescence intensity (at 520 nm) of an HPTS solution was measured in seven different phosphate buffers of differing pH, giving the relative fluorescence intensities shown below.



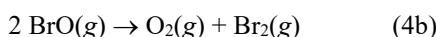
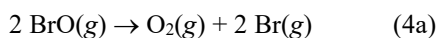
- How much energy is lost as heat when a photon with  $\lambda = 454$  nm is absorbed by HPTS and a photon with  $\lambda = 520$  nm is emitted?
- What is the  $pK_a$  of HPTS? Explain your answer.
- The phosphate buffers used in this experiment were prepared by adding solid NaOH to 100 mL of a 0.100 M solution of  $H_3PO_4$ . How many moles of NaOH would be required to make buffers with each of the following pH values? You may assume that the volume remains 100 mL.  $H_3PO_4$  has  $pK_1 = 2.12$ ,  $pK_2 = 7.21$ , and  $pK_3 = 12.32$ .
  - pH = 6.50
  - pH = 13.00
- Explain why one cannot prepare an effective buffer solution at pH = 10.0 using only 0.100 M  $H_3PO_4$  and solid NaOH.

3. [13%] The Mond process was used in the late 19th and early 20th centuries to purify nickel metal away from impurities such as iron and cobalt. The process relies on the facile reaction of nickel with carbon monoxide to form volatile nickel tetracarbonyl, which can be separated from the solid impurities:



	Ni(s)	Ni(g)	CO(g)	Ni(CO) <sub>4</sub> (g)
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	0	430.1	-110.5	-607
$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	30	182.2	198	417

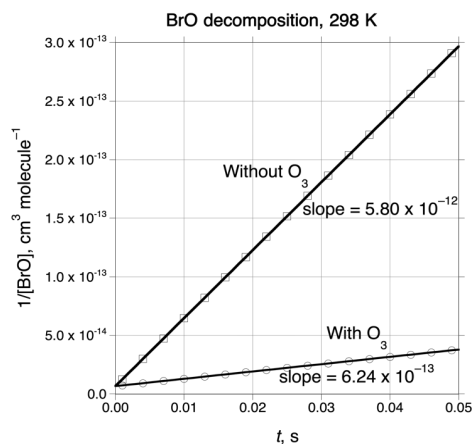
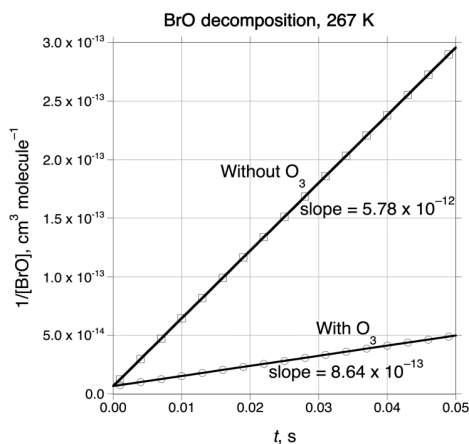
- Draw or clearly describe the three-dimensional arrangement of the atoms in Ni(CO)<sub>4</sub>.
  - Calculate the average bond dissociation enthalpy for the nickel-carbon bonds in Ni(CO)<sub>4</sub>(g).
  - Calculate  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  for the production of Ni(CO)<sub>4</sub>(g) by the Mond process.
  - The boiling point of Ni(CO)<sub>4</sub> at 1 bar pressure is 42 °C and its heat of vaporization is 29.0 kJ mol<sup>-1</sup>. Calculate  $\Delta H_f^\circ$  and  $S^\circ$  for Ni(CO)<sub>4</sub>(l).
  - After the Ni(CO)<sub>4</sub> vapor has been separated from the solid impurities, Ni metal is recovered by heating the Ni(CO)<sub>4</sub> to high temperature, causing it to re-form nickel metal and carbon monoxide. At 230 °C, what is the equilibrium pressure of Ni(CO)<sub>4</sub>(g) in the presence of nickel metal, assuming that the carbon monoxide pressure is maintained at 0.10 bar?
4. [12%] Gas-phase bromine monoxide, BrO, decomposes according to two possible pathways:



The reaction can be studied by generating BrO(g) by using a laser. If this is carried out in the presence of excess ozone, then any Br(g) that is present reacts with ozone to produce bromine monoxide much more rapidly than either reaction 4a or 4b.



The disappearance of BrO(g) was studied spectrophotometrically at both 267 K and 298 K, either in the absence of excess ozone (open squares) or in the presence of excess ozone (open circles). The reciprocal of the concentration of BrO as a function of time is graphed below for the four experiments.



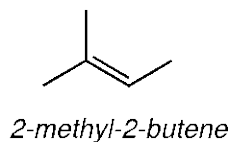
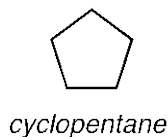
- a. What is the reaction order in BrO for its decomposition in the absence of O<sub>3</sub>? Justify your answer based on the experimental data.
- b. A sample of BrO in N<sub>2</sub> at 298 K with an initial concentration of  $4.0 \times 10^{14}$  molecules cm<sup>-3</sup> is prepared. How much time will it take for the BrO concentration to decay to half its original value?
- c. Is the observed decomposition of BrO faster or slower in the presence of ozone? Justify your answer based on the experimental data and provide a chemical explanation for the observed difference.
- d. Calculate the values of  $k_{4a}$  and  $k_{4b}$  at 298 K.
- e. Calculate the activation energy for the decomposition of BrO in the presence of ozone.
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. Chlorine gas is bubbled through cold aqueous sodium hydroxide.
- b. Solid calcium carbonate is roasted.
- c. Solutions of iron(III) nitrate and potassium thiocyanate are mixed.
- d. Ethyl formate (ethyl methanoate) is heated with aqueous potassium hydroxide.
- e. Nitrous oxide (dinitrogen monoxide) is heated with solid sodium amide.
- f. Boron-10 captures a neutron to produce an alpha particle and another species.
6. [13%] A solution is made by adding some CuSO<sub>4</sub>•5H<sub>2</sub>O to water, followed by enough sulfuric acid to make the pH = 1.00. Two platinum electrodes are then placed in the solution (which has a total volume of 0.500 L) and the solution is electrolyzed at a constant current of 0.120 A, separately capturing any gases that are evolved at the two electrodes.

Initially, gas is evolved at the anode, but no gas is evolved at the cathode. However, after 10.0 min of electrolysis, gas evolution begins at the cathode as well, and eventually the total volume of gas evolved at the cathode is equal to the total volume of gas evolved at the anode.

Half-Reaction	$E^\circ$ , V	Half-Reaction	$E^\circ$ , V
$\text{Cu}^+(aq) + e^- \rightarrow \text{Cu}(s)$	0.518	$\text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu}(s)$	0.337
$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{H}_2\text{O}_2(aq)$	1.780	$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.229
$2 \text{H}^+(aq) + e^- \rightarrow \text{H}_2(g)$	0.000		

- a. Write the balanced reaction that takes place initially in this electrolytic cell.
- b. How many moles of copper(II) sulfate pentahydrate were initially added to the solution?
- c. What is the initial cell potential for this reaction at 298 K? (In air, the partial pressure of O<sub>2</sub>(g) is 0.20 bar and the partial pressure of H<sub>2</sub>(g) may be taken to be 10<sup>-4</sup> bar.)
- d. As the electrolysis proceeds (before  $t = 10.0$  min), will this cell potential become more positive, more negative, or remain unchanged? Explain your answer.

- e. What gas is evolved at the anode? What gas is evolved at the cathode (after  $t = 10.0$  min)?
- f. At what time will the total volumes of evolved gases at the two electrodes be equal?
7. [12%] Silicon and its compounds have a number of interesting features.
- Elemental silicon adopts a structure analogous to diamond. Describe this structure and explain why no form of elemental silicon analogous to graphite is known.
  - Explain why elemental silicon is a much better conductor of electricity than diamond.
  - Silicon tetrafluoride readily reacts with fluoride ion to form species such as  $\text{SiF}_5^-$  and  $\text{SiF}_6^{2-}$ . Sketch or describe the three-dimensional shapes of these fluorosilicate anions, and explain why  $\text{SiF}_4$  readily reacts with fluoride ion while  $\text{Si}(\text{CH}_3)_4$  does not.
  - Explain why the ionization energy of a ground-state gas-phase silicon atom ( $787 \text{ kJ mol}^{-1}$ ) is smaller than that of a phosphorus atom ( $1012 \text{ kJ mol}^{-1}$ ), but the amount of energy released on adding an electron to a gas-phase Si atom ( $144 \text{ kJ mol}^{-1}$ ) is greater than that of a P atom ( $71 \text{ kJ mol}^{-1}$ ).
  - Explain why  $\text{SiH}_2(\text{g})$  in its ground state has no unpaired electrons, while  $\text{CH}_2(\text{g})$  in its ground state has two unpaired electrons.
8. [12%] Two hydrocarbons with the formula  $\text{C}_5\text{H}_{10}$  are cyclopentane and 2-methyl-2-butene.



- One can imagine replacing one hydrogen in each of these compounds to form new compounds with the formula  $\text{C}_5\text{H}_9\text{Cl}$ . Draw clear structures of all the possible distinct  $\text{C}_5\text{H}_9\text{Cl}$  isomers that can be formed in this way from
  - cyclopentane
  - 2-methyl-2-butene
- One of the two compounds (cyclopentane or 2-methyl-2-butene) reacts readily with water in the presence of an acid catalyst to give an alcohol. Indicate which compound reacts, and give the structure of the alcohol formed.
- Which is more thermodynamically stable, cyclopentane or 2-methyl-2-butene? Explain your answer.
- Clearly draw the structure of a chiral compound with the formula  $\text{C}_5\text{H}_{10}$ .

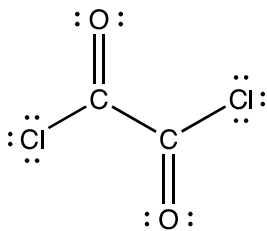
## 2020 USNCO Part 2 Solutions

1. a. At 70 °C and 1.00 bar pressure, a 1-L gas sample would contain:  
 $n = PV/RT = (1.00 \text{ bar})(1.00 \text{ L}) / (0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(343.15 \text{ K})$   
 $n = 0.03505 \text{ mol}$

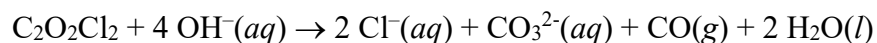
The molar mass is thus  $4.45 \text{ g} / 0.03505 \text{ mol} = 127.0 \text{ g/mol}$

- b. C:  $0.1893 \times 127.0 \text{ g/mol} = 24.0 \text{ g/mol C} = 2 \text{ mol C/mol X}$   
 O:  $0.2521 \times 127.0 \text{ g/mol} = 32.0 \text{ g/mol O} = 2 \text{ mol O/mol X}$   
 Halogen:  $0.5586 \times 127.0 \text{ g/mol} = 70.9 \text{ g halogen/mol X}$

This would correspond to 3.73 mol F, 2.00 mol Cl, 0.887 mol Br, or 0.559 mol I.  
 The halogen must therefore be Cl, and the molecular formula is  $\text{C}_2\text{O}_2\text{Cl}_2$ .



- c.
- d.  $P = 1.000 \text{ bar} - 18.7 \text{ mm Hg} \cdot (1.013 \text{ bar} / 760 \text{ mm Hg}) = 0.975 \text{ bar}$   
 $n = PV/RT = (0.975 \text{ bar})(0.197 \text{ L}) / (0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(294.15 \text{ K}) = 7.85 \times 10^{-3} \text{ mol gas}$
- e. The only reasonable colorless gases that could be produced would be CO and CO<sub>2</sub>; the latter would immediately form carbonate ion, which would explain the white precipitate with Ba<sup>2+</sup> (BaCO<sub>3</sub>). The production of  $7.85 \times 10^{-3} \text{ mol gas}$  per  $(1.00 \text{ g} / 127.0 \text{ g/mol}) = 7.87 \times 10^{-3} \text{ mol X}$  is consistent with production of one mol CO per mol of X, suggesting the other C in C<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> forms carbonate. In the absence of an oxidant and in basic solution, the only reasonable fate of Cl is Cl<sup>-</sup>(aq), giving a net balanced reaction of:



## 2020 USNCO Part 2 Solutions

2. a.  $E = hc/\lambda$ , so

$$E = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})/(454 \times 10^{-9} \text{ m}) = 4.38 \times 10^{-19} \text{ J excitation}$$

$$E = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})/(520 \times 10^{-9} \text{ m}) = 3.82 \times 10^{-19} \text{ J emission}$$

$$\text{Energy lost} = 4.38 \times 10^{-19} \text{ J} - 3.82 \times 10^{-19} \text{ J} = 5.6 \times 10^{-20} \text{ J}$$

$$(5.6 \times 10^{-20} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1}) = 34 \text{ kJ mol}^{-1}$$

b. At  $\text{pH} = \text{p}K_a$ , half of the HPTS will be in the conjugate base form and so the fluorescence will be at half-maximal intensity. Inspection of the curve gives the half-maximal fluorescence at  $\text{pH} = 7.4$ .

c.i. Since  $6.50 \gg 2.12$ , almost all the first proton of  $\text{H}_3\text{PO}_4$  will have been neutralized, requiring 0.0100 mol NaOH. The amount of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  is given by the Henderson-Hasselbalch equation:

$$6.50 = 7.21 + \log([\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]), \text{ so } [\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = 0.195.$$

The total phosphate concentration is 0.100 M, so  $[\text{HPO}_4^{2-}] = (0.195/1.195) \cdot 0.100 \text{ M} = 0.0163 \text{ M}$ , requiring an additional 0.00163 mol NaOH to achieve. Thus a total of 0.0116 mol of NaOH must be added.

ii. As in (i), the first two protons must be neutralized (requiring 0.0200 mol NaOH), then:

$$13.00 = 12.32 + \log([\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}]), \text{ so } [\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] = 4.79$$

$$[\text{PO}_4^{3-}] = 0.100 \text{ M} \cdot (4.79/5.79) = 0.0827 \text{ M}$$

This requires an additional 0.00827 mol NaOH to remove the third proton from  $\text{H}_3\text{PO}_4$ .

BUT WAIT! At  $\text{pH} = 13.00$ ,  $[\text{OH}^-] = 0.100 \text{ M}$ . This must come from yet more NaOH, another 0.0100 mol of it. (This was not an issue at  $\text{pH} = 6.5$ , where the  $\text{OH}^-$  concentration was much smaller than the concentrations of the phosphate ions and so made a negligible difference in the amount of hydroxide one needed to add.) So the total amount of NaOH one must add is  $0.0200 \text{ mol} + 0.00827 \text{ mol} + 0.0100 \text{ mol} = 0.0383 \text{ mol}$  NaOH.

An alternative approach to this problem would involve charge balance considerations.

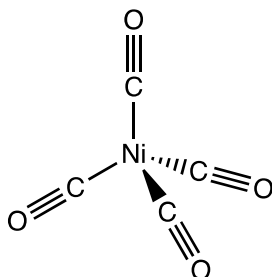
The anions present in significant concentration at  $\text{pH} = 13$  are  $\text{HPO}_4^{2-}$  (0.0173 M),  $\text{PO}_4^{3-}$  (0.0827 M), and  $\text{OH}^-$  (0.100 M). The only cation present in significant concentration is  $\text{Na}^+$ , so  $[\text{Na}^+] = 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] + [\text{OH}^-] = 2[0.0173] + 3[0.0827] + [0.100] = 0.383 \text{ M}$ . It would require adding 0.0383 mol NaOH to 100 mL to achieve this concentration of  $\text{Na}^+$ .

d. At  $\text{pH} = 10.0$ , almost all the phosphate must be in the form of  $\text{HPO}_4^{2-}$ , with less than 1% in the form of either  $\text{H}_2\text{PO}_4^{2-}$  or  $\text{PO}_4^{3-}$ . So any addition of acid will result in a significant increase of  $[\text{H}_2\text{PO}_4^-]$  and hence a significant drop in pH, and addition of base will result in a significant increase in  $[\text{PO}_4^{3-}]$  and a significant rise in pH. Without a significant concentration of *both* an acid *and* its conjugate base, buffering is ineffective.



## 2020 USNCO Part 2 Solutions

3. a. The nickel center is tetrahedral and the Ni–C–O bond is linear:



- b. For the gas-phase reaction

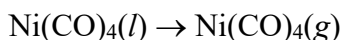


$$\Delta H^\circ = 4 \cdot (-110.5 \text{ kJ mol}^{-1}) + 430 \text{ kJ mol}^{-1} - (-607 \text{ kJ mol}^{-1}) = 595 \text{ kJ mol}^{-1}$$

Since this reaction involves breaking four nickel-CO bonds, the average BDE is  $(595 \text{ kJ mol}^{-1})/4 = 149 \text{ kJ mol}^{-1}$ .

- c.  $\Delta H^\circ_{\text{rxn}} = (-607 \text{ kJ mol}^{-1}) - 4 \cdot (-110.5 \text{ kJ mol}^{-1}) = -165 \text{ kJ mol}^{-1}$   
 $\Delta S^\circ_{\text{rxn}} = (417 \text{ J mol}^{-1} \text{ K}^{-1}) - 4 \cdot (198 \text{ J mol}^{-1} \text{ K}^{-1}) - 30 \text{ J mol}^{-1} \text{ K}^{-1} = -405 \text{ J mol}^{-1} \text{ K}^{-1}$

- d. For:



$\Delta G^\circ_{\text{vap}} = 0$  at the boiling point at 1 bar pressure and  $T = 315 \text{ K}$ .  $\Delta H^\circ_{\text{vap}} = 29.0 \text{ kJ mol}^{-1}$ .

So:

$$0 = 29000 \text{ J mol}^{-1} - (315 \text{ K})(\Delta S^\circ_{\text{vap}})$$

$$\Delta S^\circ_{\text{vap}} = 92.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{Ni(CO)}_4(\text{g})) - \Delta H^\circ_{\text{f}}(\text{Ni(CO)}_4(\text{l})) = \Delta H^\circ_{\text{vap}}$$

$$-607 \text{ kJ mol}^{-1} - \Delta H^\circ_{\text{f}}(\text{Ni(CO)}_4(\text{l})) = 29.0 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{Ni(CO)}_4(\text{l})) = -636 \text{ kJ mol}^{-1}$$

$$S^\circ(\text{Ni(CO)}_4(\text{g})) - S^\circ(\text{Ni(CO)}_4(\text{l})) = \Delta S^\circ_{\text{vap}}$$

$$417 \text{ J mol}^{-1} \text{ K}^{-1} - S^\circ(\text{Ni(CO)}_4(\text{l})) = 92.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ(\text{Ni(CO)}_4(\text{l})) = 325 \text{ J mol}^{-1} \text{ K}^{-1}$$

- e. At  $230^\circ\text{C} = 503 \text{ K}$ ,  $\Delta G^\circ_{\text{rxn}} = -165 \text{ kJ mol}^{-1} - (503 \text{ K})(-405 \text{ J mol}^{-1} \text{ K}^{-1}) = 39 \text{ kJ mol}^{-1}$

$$K_{\text{eq}} = e^{-(39000 \text{ J mol}^{-1})/(503 \text{ K} \cdot 8.314 \text{ J mol}^{-1} \text{ K}^{-1})} = 9.5 \times 10^{-5}$$

$$9.5 \times 10^{-5} = \frac{p(\text{Ni(CO)}_4)}{p(\text{CO})^4} = \frac{p(\text{Ni(CO)}_4)}{(0.1)^4}$$

$$p(\text{Ni(CO)}_4) = 9.5 \times 10^{-9} \text{ bar}$$

## 2020 USNCO Part 2 Solutions

4. a. Since  $1/[\text{BrO}]$  increases linearly with time, the reaction is second-order in BrO.

b.

$$\frac{1}{[\text{BrO}]_t} = \frac{1}{[\text{BrO}]_0} + kt$$

$$\frac{1}{[2.0 \times 10^{14} \text{ molecule cm}^{-3}]} = \frac{1}{[4.0 \times 10^{14} \text{ molecule cm}^{-3}]} + (5.80 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1})t$$

$$t = 4.3 \times 10^{-4} \text{ s}$$

c. The steeper the slope of the plot, the faster BrO is disappearing. Thus the rates are slower in the presence of ozone than in its absence. The reason is that in the presence of ozone, Br(g) reacts rapidly to form equimolar BrO(g), so reaction 4a does not result in the net disappearance of BrO(g)—it is regenerated from the Br(g) and O<sub>3</sub>(g). In the presence of ozone,  $k_{\text{obs}} = 2k_{4b}$ , while in its absence  $k_{\text{obs}} = 2k_{4a} + 2k_{4b}$ , which must be larger.

[The factor of two is because the reaction consumes two moles of BrO(g); this convention will be used in part (d), but students will not be penalized for answers that omit the factor of 2.]

d. The slopes of the second-order plots are equal to the  $k_{\text{obs}}$  for the reaction. From part b, the reaction in the presence of O<sub>3</sub> gives

$$k_{4b} = 0.5(6.24 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 3.12 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

In the absence of O<sub>3</sub>,

$$k_{4a} + k_{4b} = 0.5(5.80 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = 2.90 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{4a} = (2.90 \times 10^{-12} - 3.12 \times 10^{-13}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = 2.59 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

e.

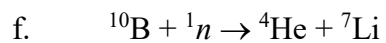
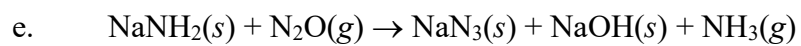
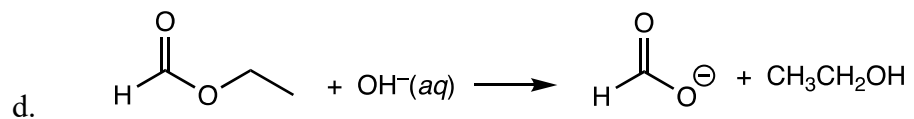
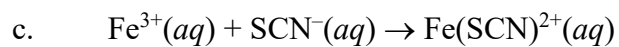
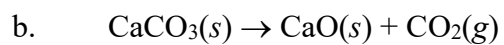
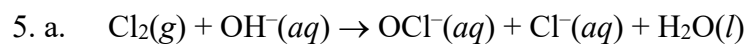
$$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$$

$$\ln(6.24 \times 10^{-13}/8.64 \times 10^{-13}) = (E_a/8.314 \text{ J mol}^{-1} \text{ K}^{-1})(1/267 \text{ K} - 1/298 \text{ K})$$

$$E_a = -6.94 \text{ kJ mol}^{-1}$$

The reaction goes *slower* at higher temperatures, so it has a negative activation energy! This is rare, but sometimes is observed in reactions where there is a lot of bond-forming to make the activated complex. Here, the reaction is hypothesized to involve side-on combination of the two OBr molecules to form an O<sub>2</sub>Br<sub>2</sub> square, which then fragments to give the O<sub>2</sub> + Br<sub>2</sub> products.

## 2020 USNCO Part 2 Solutions

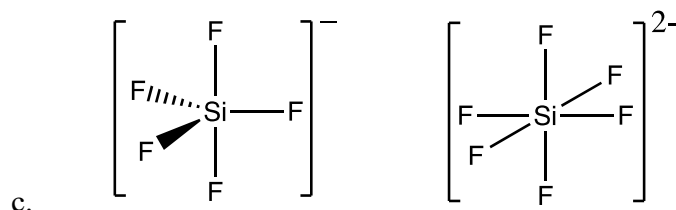


## 2020 USNCO Part 2 Solutions

6. a.  $2 \text{Cu}^{2+}(aq) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Cu}(s) + \text{O}_2(g) + 4 \text{H}^+(aq)$
- b. Gas evolution begins at the cathode when the Cu(II) is exhausted from the solution.  
 $0.120 \text{ A} \times 600. \text{ s} = 72.0 \text{ C}$   
 $72.0 \text{ C} / 96500 \text{ C mol}^{-1} = 7.46 \times 10^{-4} \text{ mol electrons}$   
Since each mol of Cu(s) deposited requires 2 mol electrons, there must have initially been  $(7.46 \times 10^{-4} \text{ mol})/2 = 3.73 \times 10^{-4} \text{ mol CuSO}_4$
- c.  $E^\circ = 0.337 \text{ V} - 1.229 \text{ V} = -0.892 \text{ V}$   
From the Nernst equation,  $E = E^\circ - (RT/nF)\ln([P_{\text{O}_2}][\text{H}^+]^4/[\text{Cu}^{2+}]^2)$   
 $= -0.892 \text{ V} - (0.0591/4)\log([0.20][0.1]^4/[7.46 \times 10^{-4}]^2)$   
 $= -0.915 \text{ V}$
- d. As electrolysis proceeds, the reactants are depleted and the products increase in concentration. These will both contribute to an increasingly negative cell potential.
- e. Oxygen is evolved at the anode and hydrogen at the cathode.
- f. One mole of  $\text{O}_2$  is evolved for every four electrons, while one mole of  $\text{H}_2$  is evolved for every two moles of electrons. Thus, once  $\text{H}_2$  evolution begins, in ten minutes as much volume of  $\text{H}_2$  will be evolved as  $\text{O}_2$  is evolved in twenty minutes. In other words, the two volumes will be equal at  $t = 20.0 \text{ min}$ .

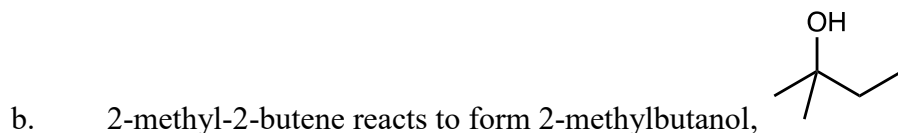
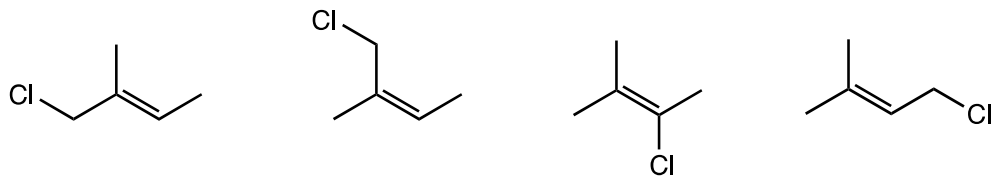
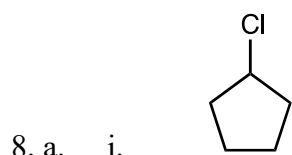
## 2020 USNCO Part 2 Solutions

7. a. In elemental Si, each Si is  $\sigma$ -bonded to four other Si atoms, arranged as a tetrahedron. A graphite-like structure would require Si-Si  $\pi$  bonds, which are very weak compared to carbon-carbon  $\pi$  bonds.
- b. Si-Si  $\sigma$  bonding is weaker than C-C  $\sigma$  bonding. These elements have electrons in nominally filled valence bands separated from nominally empty conduction bands by an energy gap that is larger the stronger the  $\sigma$  bonding (since the valence band is  $\sigma$  bonding in character and the conduction band  $\sigma$  antibonding). In silicon, this gap is small enough in energy that a small number of electrons are promoted from the valence band to the conduction band; these electrons and vacancies in the valence band (“holes”) are mobile charge carriers and allow electrical conductivity. The much larger band gap in diamond gives rise to a negligible number of such carriers.



- The Lewis acidity of  $\text{SiX}_4$  relies on donation of the lone pair from the Lewis base to the  $\sigma^*$  orbital of the Si-X bond. The more electronegative F atom lowers this in energy and thus enhances the Lewis acidity of the silicon.
- d. P has one more proton than Si, and that proton is only incompletely shielded by its additional electron. Thus P has a greater attraction for its highest-energy valence electron than Si and a correspondingly higher ionization energy. Addition of an electron to P requires it to enter an orbital that is already singly occupied, whereas Si can accept an electron into an empty  $3p$  orbital. For phosphorus, the additional electron-electron repulsion outweighs its higher  $Z_{\text{eff}}$ .
- e. In carbon compounds, the  $2s$  orbital and  $2p$  orbital both interact strongly with other atoms. So the two nonbonding electrons in  $\text{CH}_2$  must occupy a  $p$  orbital and what is effectively an  $sp^2$  orbital, which are close enough in energy that it is preferable to occupy each orbital singly than to put both electrons in the lower-energy  $sp^2$  orbital. In Si compounds, the  $s$  orbital is too small to interact strongly with the H atoms, which bond to essentially pure  $p$  orbitals. The  $3s$  orbital is much lower in energy than the  $3p$  orbital, so both nonbonding electrons occupy it.

## 2020 USNCO Part 2 Solutions



- c. Cyclopentane is more stable. Both compounds contain ten C–H bonds, but cyclopentane contains five C–C single bonds, while 2-methyl-2-butene contains three C–C single bonds and one C=C double bond. The bond strength of a C=C double bond is less than that of two C–C single bonds.

