2017 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM - PART II

Prepared by the American Chemical Society Olympiad Examinations Task Force

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DIRECTIONS TO THE EXAMINER – PART II

Part II of this test requires that student answers be written in a response booklet with blank pages. Only this "Blue Book" is graded for a score on **Part II**. Testing materials, scratch paper, and the "Blue Book" should be made available to the student only during the examination period. All testing materials including scratch paper should be turned in and kept secure until **April 24, 2017**, after which tests can be returned to students and their teachers for further study.

Allow time for the student to read the directions, ask questions, and fill in the required information on the "Blue Book". When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in the "Blue Book", **Part II** of the testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested on the front of the "Blue Book," and that the same identification number used for **Part I** has been used again for **Part II**.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest breaks between parts.

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

A periodic table and other useful information are provided on page two for student reference.

Students should be permitted to use non-programmable calculators. The use of a programmable calculator, cell phone, or any other device that can access the internet or make copies or photographs during the exam is grounds for disqualification.

DIRECTIONS TO THE EXAMINEE

DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO. Part II requires complete responses to questions involving problem-solving and explanations. **One hour and forty-five minutes** are allowed to complete this part. Be sure to print your name, the name of your school, and your identification number in the spaces provided on the "Blue Book" cover. (Be sure to use the same identification number that was coded onto your Scantron sheet 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.**

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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		

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 °C = 273.15 K

1 atm = 1.013 bar = 760 mm Hg

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

EQUATIONS

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

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

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

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A
1 **H** 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

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

1. [12%] A compound used as a fertilizer contains only the elements C, H, N, and O.
   a. Combustion of 1.000 g of the fertilizer in an oxygen atmosphere produces 0.5637 g CO_2, 0.6924 g H_2O, and 0.3589 g N_2. What are the mass percentages of C, H, and N in the fertilizer?
   b. Give the empirical formula of the fertilizer.
   c. A solution of 1.000 g of the fertilizer dissolved in 20.00 g water has a freezing point of –2.38 ºC. What is the apparent molar mass of the fertilizer? Combined with the result in (b), what is the implication of this molar mass? (For water, the freezing point depression constant $K_f = 1.86$ ºC/*m*.)
   d. Propose a structure for the fertilizer compound.

2. [12%] Consider these reactions among copper and iodine compounds (all reactions at 298 K):

$$\begin{array}{cl}
\mathrm{CuI}(s) \rightleftharpoons \mathrm{Cu^+}(aq) + \mathrm{I^-}(aq) & K_{sp} = 1.2 \times 10^{-12} \\
\mathrm{Cu^+}(aq) + 2\,\mathrm{I^-}(aq) \rightleftharpoons \mathrm{CuI_2^-}(aq) & K_f = 7.1 \times 10^{8} \\
\mathrm{Cu^{2+}}(aq) + 2\,e^- \rightarrow \mathrm{Cu}(s) & E^\circ = +0.337\ \mathrm{V} \\
\mathrm{Cu^{2+}}(aq) + e^- \rightarrow \mathrm{Cu^+}(aq) & E^\circ = +0.159\ \mathrm{V} \\
\mathrm{I_2}(s) + 2\,e^- \rightarrow 2\,\mathrm{I^-}(aq) & E^\circ = +0.540\ \mathrm{V}
\end{array}$$

   a. Calculate the number of moles of copper that dissolve if 1.00×10^{-3} mol CuI(*s*) is suspended in 1.00 L of solution.
   b. Calculate the minimum number of moles of NaI that would need to be added to the mixture in (a) to fully dissolve the CuI. You may assume that the volume remains 1.00 L.
   c. Calculate K_{eq} for the (favorable) disproportionation of aqueous Cu^+ ion in neutral solution:
   $$2\,\mathrm{Cu^+}(aq) \rightleftharpoons \mathrm{Cu^{2+}}(aq) + \mathrm{Cu}(s)$$
   d. Copper(II) iodide, CuI_2, is not stable. Write a reasonable chemical reaction that describes the decomposition of CuI_2 in aqueous solution, and show that this is a spontaneous reaction under standard conditions.

3. [13%] The initial rate of decomposition of ozone to molecular oxygen has been examined under a variety of conditions by measuring the change in pressure as the reaction takes place.

$$2\,\mathrm{O_3}(g) \rightarrow 3\,\mathrm{O_2}(g)$$

At 90 ºC, in the presence of relatively small amounts of O_3 compared to O_2 (present in constant amount), the following data were obtained:

$p(O_3)$, mm Hg	$\Delta P/\Delta t$, (mm Hg) s^{-1}
7.9	1.21×10^{-3}
17.7	5.8×10^{-3}

   a. If the pressure changes at a rate of 1.21×10^{-3} (mm Hg) s^{-1} at 90 ºC, what is the rate of disappearance of O_3 in mol L^{-1} s^{-1}?
   b. What is the order in O_3 under these conditions?

   Under slightly different conditions, with the initial pressures of O_3 held constant, the initial rates were measured as a function of O_2 pressure at 90 ºC and at 100 ºC:

$p(O_2)$, mm Hg	$\Delta P/\Delta t$, (mm Hg) s^{-1}, at 90 °C	$\Delta P/\Delta t$, (mm Hg) s^{-1}, at 100 °C
200	3.30×10^{-3}	7.4×10^{-3}
400	1.45×10^{-3}	3.64×10^{-3}

   c. What is the order in O_2?
   d. What is the activation energy for the reaction?
   e. The following mechanism has been proposed for the reaction:

$$\mathrm{O_3}(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{O_2}(g) + \mathrm{O}(g)$$

$$\mathrm{O}(g) + \mathrm{O_3}(g) \xrightarrow{k_2} 2\,\mathrm{O_2}(g)$$

   Using the steady-state approximation, derive the rate law predicted by this mechanism. Under what circumstances, if any, is this consistent with the experimental data?

4. [13%] Consider the dimerization of nitrogen dioxide:

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

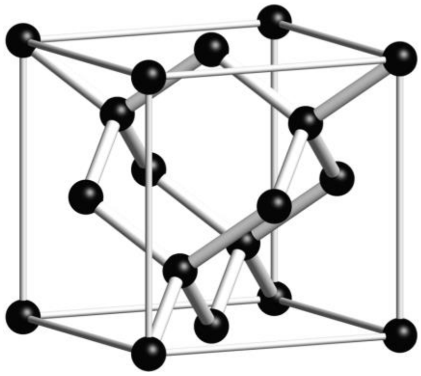
Thermodynamic data are given below for the gaseous species at 298 K, except for the heats of vaporization, which are for the liquids:

	NO_2	N_2O_4
ΔH^o_f, kJ mol^{-1}	33.2	11.1
S^o, J mol^{-1} K^{-1}	240.1	304.4
C_p, J mol^{-1} K^{-1}	37.2	79.2
ΔH^o_{vap}, kJ mol^{-1}	27.7	38.1

a. Calculate ΔH^o_{rxn}, ΔS^o_{rxn}, and ΔG^o_{rxn} for the dimerization of $NO_2(g)$ at 298 K.
b. Calculate K_{eq} for the dimerization of $NO_2(g)$ at 298 K.
c. Would K_{eq} for the dimerization at 308 K be greater than, less than, or equal to K_{eq} at 298 K? Justify your answer based on the above data.
d. Would ΔH^o_{rxn} at 308 K be greater than, less than, or equal to ΔH^o_{rxn} at 298 K? Justify your answer based on the above data.
e. Would ΔH^o_{rxn} in the liquid phase be greater than, less than, or equal to ΔH^o_{rxn} in the gas phase? Justify your answer based on the above data.

5. [12%] Write net equations for each of the reactions below. Use appropriate ionic and molecular formulas but 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. Solutions of sodium sulfate and lead(II) nitrate are mixed.
b. Aluminum foil is added to concentrated sodium hydroxide solution.
c. Mercury(II) oxide is heated.
d. Sodium is added to 2-butanol.
e. Nitrosyl fluoride and boron trifluoride vapors are co-condensed.
f. Fluorine-18 emits a positron.

6. [12%] Silicon is an industrially important semiconductor with the cubic unit cell shown below (Si atoms represented as black spheres):



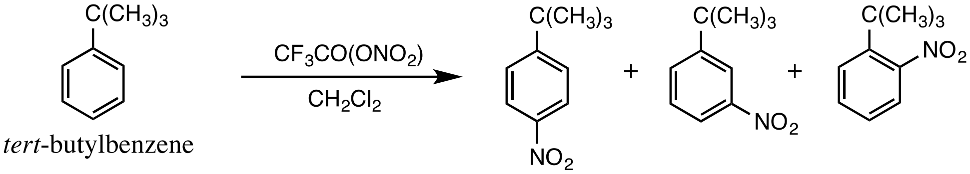
a. How many Si atoms are contained in this unit cell?
b. The length of the edge of the unit cell is 0.543 nm. Calculate the density of silicon in g cm^{-3}.

Semiconductors like Si have an electronic structure characterized by a band of nominally filled orbitals (the “valence band”) separated from a band of nominally empty orbitals (the “conduction band”) by an energy gap called the “band gap” of the semiconductor. Conduction arises in a pure semiconductor when there is thermal promotion of an electron from the valence to the conduction band; both the electron in the conduction band and the vacancy (“hole”) in the valence band are efficient carriers for electrical conduction.

c. Diamond, silicon, and germanium all have the same structure, but the band gap decreases in the order C (diamond) >> Si > Ge. Explain the trend in the size of the band gap.
d. Substituting just a few parts per million of B into Si results in a dramatic increase of electrical conductivity compared to ultrapure Si. Explain why.

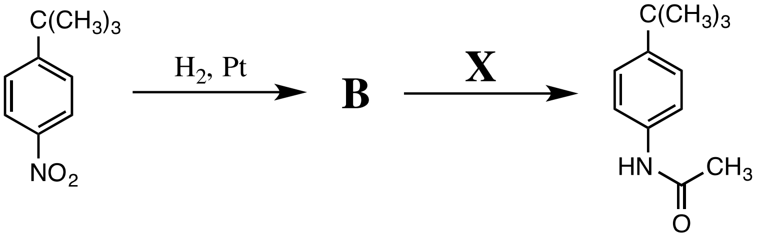
7. [14%] Oxygen and sulfur form a number of binary fluorides.
   a. Draw the Lewis structure of dioxygen difluoride, O_2F_2, and sketch or describe the three-dimensional shape of this polar molecule.
   b. Explain why the O–F bonds in dioxygen difluoride, O_2F_2 (157.5 pm) are much longer than those in oxygen difluoride, OF_2 (140.5 pm).
   c. Disulfur difluoride, S_2F_2, exists as two structural isomers. One isomer is analogous in structure to dioxygen difluoride, O_2F_2, but the second, more thermodynamically stable isomer, has a structure in which the two sulfur atoms are in different chemical environments. Draw a Lewis structure of the more stable isomer of disulfur difluoride, S_2F_2, and sketch or describe its three-dimensional shape.
   d. Sulfur difluoride, SF_2, is very unstable, converting to disulfur tetrafluoride, S_2F_4, in which all four fluorines are in different environments. Clearly show a chemically reasonable three-dimensional structure of disulfur tetrafluoride, S_2F_4, and explain how the structure accounts for the inequivalence of all four fluorine atoms.
   e. Sulfur tetrafluoride, SF_4 (bp –38 ºC), has a higher boiling point than sulfur hexafluoride, SF_6 (bp –64 ºC). Explain why sulfur tetrafluoride, SF_4, is less volatile than sulfur hexafluoride, SF_6.

8. [12%] *tert*-Butylbenzene is nitrated to give predominantly *para*-*tert*-butylnitrobenzene (**A**), with only small amounts of the *meta* (**A'**) and *ortho* (**A''**) isomers.



A *para*, 83% **A'** *meta*, 5% **A''** *ortho*, 12%

   a. Explain why the *meta* isomer (**A'**) is a minor product in this reaction.
   b. Explain why the *ortho* isomer (**A''**) is a minor product in this reaction.
   c. Give a structure for synthetic intermediate **B** and propose a reagent or set of reagents **X** for the transformation of **B** to *para*-*tert*-butylacetanilide (**C**).



A **C**

   d. Propose a synthesis of *tert*-butylbenzene from benzene and any other necessary reagents.

2017 USNCO Part II Exam Answers

1. a. 0.5637 g CO_2 × (12.01 g C/44.01 g CO_2) = 0.1538 g C, 15.38% C
0.6924 g H_2O × (2.016 g H/18.016 g H_2O) = 0.07748 g H, 7.75% H
0.3589 g N_2 = 35.89% N

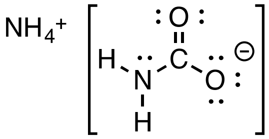
b. %O = 100% – (15.38% + 7.75% + 35.89%) = 40.98% O
So in 100 g fertilizer there would be:
15.38 g C/(12.01 g mol^{-1}) = 1.28 mol C
7.748 g H/(1.008 g mol^{-1}) = 7.69 mol H
35.89 g N/(14.01 g mol^{-1}) = 2.56 mol N
40.98 g O/(16.00 g mol^{-1}) = 2.56 mol O
Dividing by 1.28 mol gives an empirical formula $CH_6N_2O_2$.

c. 2.38 ºC/(1.86 ºC/*m*) = 1.28 *m* solution
(1.28 mol/1000g H_2O)•(20 g H_2O) = 0.0256 mol solute
1.000 g solute/0.0256 mol solute = 39.1 g mol^{-1}.

From the empirical formula, the formula mass is 78.1 g mol^{-1}! This says that the molar mass appears to be half the formula mass; the only way this is possible is if each mol of fertilizer gives rise to *two* moles of particles. Thus, the fertilizer is likely an ionic compound.

d. The most likely cation given the formula is ammonium ion, which leaves an ion with the formula CH_2NO_2. Several chemically plausible structures can be written, but the only one where the anion is not so basic that it would deprotonate the ammonium ion is carbamate, $NH_2CO_2^-$. (The only other chemically reasonable alternative is hydrazinium formate, $(NH_2NH_3^+)(HCOO^-)$.) Ammonium carbamate is a common fertilizer.

Fertilizer =



2. a. $[Cu^+] = [I^-]$ in this solution, and $[Cu^+][I^-] = K_{sp} = 1.2 \times 10^{-12}$
$[Cu^+] = 1.1 \times 10^{-6}$ M, so 1.1×10^{-6} mol Cu dissolve in 1.00 L.
(Because the $[I^-]$ is so low, there is a negligible amount of CuI_2^- present:

$$\frac{[CuI_2^-]}{[Cu^+][I^-]^2} = 7.1 \times 10^8$$, so $[CuI_2^-]/[Cu^+] = 8.6 \times 10^{-4}$ if $[I^-] = 1.1 \times 10^{-6}$ M)

b. The major reaction that takes place is

$$CuI(s) + I^-(aq) \rightleftharpoons CuI_2^-(aq) \qquad K_{eq} = K_{sp} \bullet K_f = 8.5 \times 10^{-4}$$

Since almost all the Cu in solution is complexed, $[CuI_2^-] = 1.00 \times 10^{-3}$ M.

$$\frac{[CuI_2^-]}{[I^-]} = \frac{[1.00 \times 10^{-3}]}{[I^-]} = 8.5 \times 10^{-4}$$

$$[I^-] = 1.18 \text{ M}$$

Only 1.00×10^{-3} mol iodide has bonded to the copper, which is negligible compared to the amount found free in solution. So 1.18 mol NaI needs to be added to dissolve the CuI.

c.

$$\begin{array}{lr} 2\,\mathrm{Cu}^{+}(aq) \rightarrow 2\,\mathrm{Cu}^{2+}(aq) + 2\,e^{-} & E^{\circ} = -0.159\ \mathrm{V} \\ \mathrm{Cu}^{2+}(aq) + 2\,e^{-} \rightarrow \mathrm{Cu}(s) & E^{\circ} = +0.337\ \mathrm{V} \\ \hline 2\,\mathrm{Cu}^{+}(aq) \rightarrow \mathrm{Cu}(s) + \mathrm{Cu}^{2+}(aq) & E^{\circ} = 0.178\ \mathrm{V} \end{array}$$

$\Delta G^{\circ} = -nFE^{\circ} = -(2)(96.485\ \mathrm{kJ\ V^{-1}\ mol^{-1}})(0.178\ \mathrm{V}) = -34.3\ \mathrm{kJ\ mol^{-1}}$

$K_{\mathrm{eq}} = e^{-\Delta G^{\circ}/RT} = e^{(34300\ \mathrm{J\ mol\text{-}1})/(8.314\ \mathrm{J\ mol\text{-}1\ K\text{-}1})(298\ \mathrm{K})} = 1.05 \times 10^{6}$

d. Net reaction: $\mathrm{Cu}^{2+}(aq) + 2\,\mathrm{I}^{-}(aq) \rightarrow \mathrm{CuI}(s) + 0.5\ \mathrm{I}_2(s)$

This can be written as a sum of two reactions:

(I) A redox reaction:

$$\mathrm{Cu}^{2+}(aq) + \mathrm{I}^{-}(aq) \rightarrow \mathrm{Cu}^{+}(aq) + 0.5\ \mathrm{I}_2$$

$$\Delta G^{\circ} = -(1)(96.485\ \mathrm{kJ\ V^{-1}\ mol^{-1}})(0.159\ \mathrm{V} - 0.540\ \mathrm{V}) = +36.8\ \mathrm{kJ\ mol^{-1}}$$

(II) A precipitation reaction:

$$\mathrm{Cu}^{+}(aq) + \mathrm{I}^{-}(aq) \rightarrow \mathrm{CuI}(s)$$

$$\Delta G^{\circ} = -RT\ln(K_{\mathrm{eq}}) = -(0.008314\ \mathrm{kJ\ mol^{-1}\ K^{-1}})(298\ \mathrm{K})\ln(1/K_{\mathrm{sp}}) = -68.0\ \mathrm{kJ\ mol^{-1}}$$

Thus the net reaction has $\Delta G^{\circ} = +36.8\ \mathrm{kJ\ mol^{-1}} + (-68.0\ \mathrm{kJ\ mol^{-1}}) = -31.2\ \mathrm{kJ\ mol^{-1}}$, and is spontaneous (under standard conditions).

3. a. With each mol of O_3 that reacts of the reaction, 0.5 mol of additional total gas is produced. So if the total pressure is increasing by 1.21×10^{-3} (mm Hg) s^{-1}, then the pressure of O_3 is decreasing by twice this, or 2.42×10^{-3} (mm Hg) s^{-1}. To convert to mol $\mathrm{L}^{-1}\ \mathrm{s}^{-1}$, one needs to convert mm Hg to mol L^{-1} at 90 ºC:

$$PV = nRT$$

$$n/V = P/RT$$

$$n/V = (2.42 \times 10^{-3}\ \mathrm{mm\ Hg})/(62.4\ [\mathrm{mm\ Hg}]\ \mathrm{L\ mol^{-1}\ K^{-1}})(363\ \mathrm{K})$$

$$n/V = 1.07 \times 10^{-7}\ \mathrm{mol\ L^{-1}}$$

So the rate of disappearance of O_3 is $1.07 \times 10^{-7}\ \mathrm{mol\ L^{-1}\ s^{-1}}$.

b. When O_3 pressure increases by a factor of 2.24, the rate increases by a factor of 4.79, close to $(2.24)^2 = 5.01$. So the reaction is second order in O_3 under these conditions.

c. Doubling the O_2 pressure results in roughly a factor of two *decrease* in the rate. Thus the order in O_2 is –1.

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

$\ln(3.64 \times 10^{-3}/1.45 \times 10^{-3}) = (E_a/8.314\ \mathrm{J\ mol^{-1}\ K^{-1}})(1/363\ \mathrm{K} - 1/373\ \mathrm{K})$

$E_a = 104\ \mathrm{kJ\ mol^{-1}}$ (using the data from 200 mm Hg O_2 gives 90.9 $\mathrm{kJ\ mol^{-1}}$)

e. Applying the steady-state approximation to [O] gives:

$$k_1[\mathrm{O}_3] = k_{-1}[\mathrm{O}][\mathrm{O}_2] + k_2[\mathrm{O}][\mathrm{O}_3]$$

$$[\mathrm{O}] = \frac{k_1[\mathrm{O}_3]}{k_{-1}[\mathrm{O}_2] + k_2[\mathrm{O}_3]}$$

$$\mathrm{Rate} = k_2[\mathrm{O}_3][\mathrm{O}] = \frac{k_1 k_2[\mathrm{O}_3]^2}{k_{-1}[\mathrm{O}_2] + k_2[\mathrm{O}_3]}$$

This is consistent with the experimental data if $k_{-1}[O_2] >> k_2[O_3]$. This is likely to be fulfilled under these conditions of relatively high O_2 pressure and low O_3 pressure.

4. a. $\Delta H^\circ = 11.1\text{ kJ mol}^{-1} - 2(33.2\text{ kJ mol}^{-1}) = -55.3\text{ kJ mol}^{-1}$
$\Delta S^\circ = 304.4\text{ J mol}^{-1}\text{ K}^{-1} - 2(240.1\text{ J mol}^{-1}\text{ K}^{-1}) = -175.8\text{ J mol}^{-1}\text{ K}^{-1}$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -55.3\text{ kJ mol}^{-1} - (298\text{ K})(-0.1758\text{ kJ mol}^{-1}\text{ K}^{-1}) = -2.9\text{ kJ mol}^{-1}$

b. $\Delta G^\circ = -RT\ln(K_{eq})$
$\ln(K_{eq}) = -(-2900\text{ J mol}^{-1})/(8.314\text{ J mol}^{-1}\text{ K}^{-1})(298\text{ K}) = 1.17$
$K_{eq} = 3.2$

c. The reaction is exothermic, so K_{eq} will decrease as the temperature is increased.

d. From the thermochemical cycle:

$$\begin{tikzcd}
\textbf{298 K} & 2\,NO_2(g) \arrow[r, "\Delta H^\circ_{rxn}\,(298\text{ K})"] & N_2O_4(g) \arrow[d, "\Delta H = C_p(N_2O_4)\bullet(10\text{ K})"] \\
\textbf{308 K} & 2\,NO_2(g) \arrow[u, "\Delta H = -2C_p(NO_2)\bullet(10\text{ K})"] \arrow[r, "\Delta H^\circ_{rxn}\,(308\text{ K})"] & N_2O_4(g)
\end{tikzcd}$$

$\Delta H^\circ_{rxn}\,(308\text{ K}) = \Delta H^\circ_{rxn}\,(298\text{ K}) + 10\text{ K}(C_p[N_2O_4] - 2C_p[NO_2])$
Since $C_p[N_2O_4] - 2C_p[NO_2] = 4.8\text{ J mol}^{-1}\text{ K}^{-1}$ is positive, then ΔH°_{rxn} (308 K) will be greater (more positive) than ΔH°_{rxn} (298 K), although the difference is rather small.

e. An analogous thermochemical cycle . . .

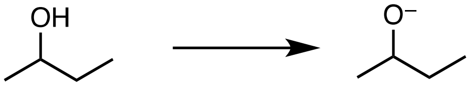
$$\begin{tikzcd}
\textbf{gas} & 2\,NO_2(g) \arrow[r, "\Delta H^\circ_{rxn}\,(g)"] & N_2O_4(g) \arrow[d, "\Delta H = -\Delta H_{vap}(N_2O_4)"] \\
\textbf{liquid} & 2\,NO_2(l) \arrow[u, "\Delta H = 2\Delta H_{vap}(NO_2)"] \arrow[r, "\Delta H^\circ_{rxn}\,(l)"] & N_2O_4(l)
\end{tikzcd}$$

. . . establishes that $\Delta H^\circ_{rxn}\,(l) = \Delta H^\circ_{rxn}\,(g) + 2\Delta H_{vap}(NO_2) - \Delta H_{vap}(N_2O_4)$.
Since $2\Delta H_{vap}(NO_2) - \Delta H_{vap}(N_2O_4) = 17.3\text{ kJ mol}^{-1}$ is positive, then ΔH°_{rxn} (l) will be greater (more positive) than ΔH°_{rxn} (g).

5. a. $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

b. $Al(s) + 3\,H_2O(l) + OH^-(aq) \rightarrow Al(OH)_4^-(aq) + {}^3/_2\,H_2(g)$

c. $HgO(s) \rightarrow Hg(l) + {}^1/_2\,O_2(g)$

d. Na(s) +  + $Na^+ + {}^1/_2\,H_2$

e. $NOF(g) + BF_3(g) \rightarrow [NO][BF_4](s)$

f. $^{18}F \rightarrow {}^{18}O + \beta^+$

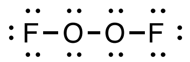
6. a. There are 8 Si atoms in the unit cell.

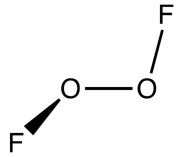
b. $V = (0.543 \times 10^{-7}\ \text{cm})^3 = 1.60 \times 10^{-22}\ \text{cm}^3$
mass = $8 \times (28.09\ \text{g mol}^{-1})/(6.022 \times 10^{23}\ \text{mol}^{-1}) = 3.73 \times 10^{-22}$ g
density = $3.73 \times 10^{-22}\ \text{g}/1.60 \times 10^{-22}\ \text{cm}^3 = 2.33\ \text{g cm}^{-3}$

c. The filled valence band consists of σ-bonding orbitals, while the empty conduction band consists of σ-antibonding orbitals. Thus, the stronger the bonding, the larger the band gap. The smaller elements form shorter, stronger bonds (C–C >> Si–Si > Ge–Ge), so the band gaps also decrease in this order.

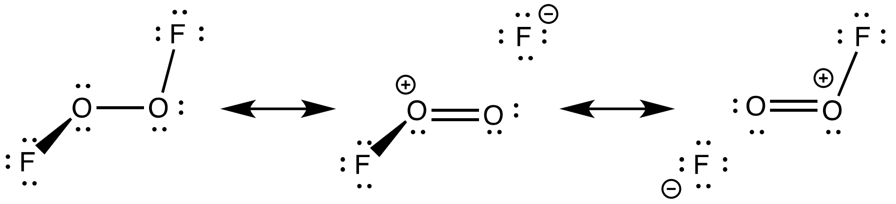
d. Replacing a Si atom (with 4 valence electrons) with a B atom (3 valence electrons) decreases the electron count by one without changing the number or type of orbitals. Thus each B atom leads to a vacancy in the valence band. These "holes" are good charge carriers, and so even a small number of boron atoms lead to a relatively large number of charge carriers (and hence high conductivity) compared to pure Si, where the only charge carriers arise from thermal excitation.

7. a. In FOOF, each oxygen is bent, and the two FOO planes are roughly perpendicular to one another:

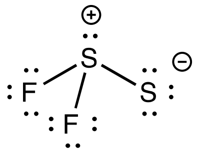




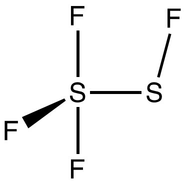
b. Electron donation from the oxygen lone pairs in FOOF into the O–F σ* orbitals ("negative hyperconjugation") lengthens the O–F bond (and shortens the O–O bond, which at 121.7 pm is much shorter than the O–O single bond in H_2O_2, 147.4 pm, and is almost the same length as the double bond in O_2, 121 pm!):



c. The stable isomer of S_2F_2 is pyramidal:

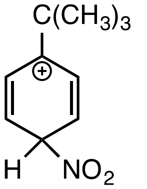


d. The four-coordinated sulfur has a "see-saw" geometry, with the equatorial fluorine distinct from the two axial fluorines. (Obviously the fluorine on the divalent sulfur is distinct from the other three as well!) The two axial fluorines are not equivalent because the S–F bond on the divalent sulfur is pointed toward one of them and away from the other one:

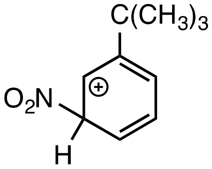


e. SF_4, because of its see-saw geometry, has a dipole moment, while SF_6, which is octahedral, does not. The favorable dipole-dipole interactions increase the boiling point of SF_4 compared to SF_6. (The greater number of electrons in SF_6 would be expected to give it greater London dispersion forces compared to SF_4, but the lower polarizability due to the higher oxidation state in SF_6 may make this effect smaller than one would expect.)

8. a. The *tert*-butyl group is electron-donating compared to H, which stabilizes the key cationic intermediate in the *para* isomer compared to the *meta* isomer:



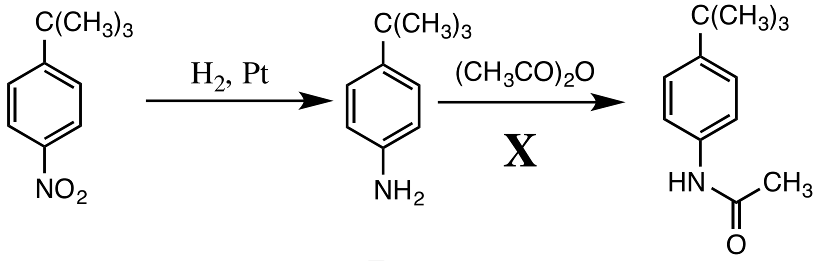
more favorable



less favorable

b. The *ortho* isomer is electronically stabilized in much the same way as the *para* isomer, but the large size of the *tert*-butyl group impedes reactivity adjacent to it.

c. Many acetylating agents will serve the role as **X**; acetic anhydride is shown in the scheme.



A **B** **C**

d. Any source of *tert*-butyl cation ($(CH_3)_3COH/H^+$, $(CH_3)_3CCl/AlCl_3$, etc.) will react with benzene to give *tert*-butylbenzene: